EPA/600/R-14/052
December 2013

Environmental Technology Verification Report

ANDALYZE LEAD 100 TEST KIT AND AND1000 FLUORIMETER

Prepared by

Battelle
The Business of Innovation

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

December 2013

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

ANDALYZE LEAD 100 TEST KIT AND AND1000 FLUORIMETER

by
Brian Yates and Amy Dindal, Battelle
John McKernan and Doug Grosse, U.S. EPA

Notice

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and build the scientific knowledge base needed to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the contribution of the many individuals without whom this verification testing would not have been possible. Quality assurance (QA) oversight was provided by Holly Ferguson, EPA, and Rosanna Buhl and Betsy Cutié, Battelle. We gratefully appreciate the accommodation of DHL Analytical, Inc. Finally, we want to thank Randy Gottler of the City of Phoenix and John Consolvo of the Philadelphia Water Department for their review of the Quality Assurance Project Plan (QAPP) and this verification report.

Contents

Page

Appendices

Tables

Figures

List of Abbreviations

ADQ	Audit of Data Quality
AMS	Advanced Monitoring Systems
BW	bottled water
CFR	Code of Federal Regulations
CV	coefficient of variation
DEI	determination of the effects of interferences
DI	deionized
DLOD	determination of the limit of detection
DLR	determination of linear range
DQO	data quality objective
EPA	Environmental Protection Agency
ETL	Environmental Treatability Laboratory
ETV	Environmental Technology Verification
FCU	failure cause unknown
Fe	iron
FWW	finished well water
HDPE	high density polyethylene

HFe	high iron
HTDS	high total dissolved solid
ICC	Initial Calibration Check
ICP-MS	inductively-coupled plasma mass spectroscopy
IDC	initial demonstration of capability
IFE	instrument failure electrical
IFM	instrument failure mechanical
IOFM	instrument operator failure to follow method
LFM	laboratory-fortified matrix
LFMD	laboratory-fortified matrix duplicate
LOD	limit of detection
LRB	laboratory record book
LTDS	low total dissolved solid
MFWWE	metal finishing wastewater effluent
MGD	million gallons per day
MWWE	municipal wastewater effluent
Pb	lead

PEA	performance evaluation audit
ppb	parts per billion
PT	performance testing
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QCS	quality control standard
QM	Quality Manager
QMP	Quality Management Plan
RB	reagent blank
RCA	root cause analysis
ReW	reservoir water
RiW	river water
RMO	Records Management Office
RPD	relative percent difference
RWW	raw well water
SD	standard deviation

SFC	sensor failure chemical
SFM	sensor failure mechanical
SOP	standard operating procedure
SW	seawater
TDS	total dissolved solid
TPC	three point calibration
TSA	technical systems audit
VTC	Verification Test Coordinator
WF	water fountain

Chapter 1
Background

EPA supports the ETV Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory bench tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous QA protocols to ensure that data of known and adequate quality are generated and that the results are defensible. The definition of ETV is to establish or prove the truth of the performance of a technology under specific, pre-determined criteria or protocols and a strong quality management system. High-quality data are assured through implementation of the ETV Quality Management Plan (QMP). ETV does not endorse, certify, or approve technologies.

EPA's National Risk Management Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the combined ANDalyze lead (Pb) detection technologies: AND1000 handheld fluorimeter and accompanying Lead100 consumable test kit (Lead100/AND1000).

Chapter 2
Technology Description

This report provides results for the verification testing of the Lead100/AND1000. The following is a description of the technology based on information provided by the vendor. The information provided below was not verified in this test.

The ANDalyze Lead100/AND1000 was designed to detect the presence of and measure the concentration of Pb in drinking water and environmental waters. Testing is intended to take place onsite at the source of collection or in a temperature controlled facility without sample preservation. The test makes use of two primary components: a handheld fluorimeter (AND1000) and a consumable test kit (Lead100) specific to each metal or target (in the present case, Pb).

Figure 1. ANDalyze AND1000

Figure 1 presents a picture of the ANDalyze AND1000 fluorimeter. The AND1000 fluorimeter is specifically designed to provide an interactive experience and allow testing, data storage, and signal output without the use of a separate computational device. The fluorimeter has the capability to analyze multiple targets with the appropriate test kit, though the sole target discussed in this method is aqueous Pb in drinking water, wastewater effluent, and environmental waters. The AND1000 fluorimeter enables field testing to be performed in two steps. ANDalyze's catalytic DNA sensors use a metal-specific DNAzyme reaction that leads to an increase in fluorescence in the presence of a target contaminant substance (i.e., aqueous Pb). The fluorescence of the reaction is measured by a fluorimeter to determine the concentration of the target heavy metal and is reported in parts per billion (ppb). The product is a quantitative test that is intended to detect metals in a linear range of 2 to 100 ppb — at and below EPA standards for drinking water. The test is performed by injecting a buffered 1 mL water sample through the sensor and into the AND1000 fluorimeter. This sample is then automatically analyzed and results are reported in less than 2 minutes.

The second component is the Lead100 test kit which is specific to Pb. The test kit provides all necessary materials for in-field instrument calibration and sample testing. This kit contains the DNA sensors specific to the given analyte. The kit is color coded to facilitate use and avoid measurement error. In addition, a product manual is provided with step-by-step instructions including photographs. It should be noted that laboratory evaluation may require additional supplies and standard laboratory glassware. Figure 2 presents a picture of the ANDalyze Lead100 disposable test kit.

The total cost of the ANDalyze AND1000 fluorimeter used for testing was $3,000. The AND1000 fluorimeter package includes the fluorimeter, USB to MINI-B cable, 100 µL fixed volume pipette and tips, and pH test strips. The cost of each Lead100 disposable test kit used for testing was $15. Each kit includes 25 tests and/or calibrations, 25 sensor bags with sensor and cuvette, 25 sample tubes (with buffer), 25 1 mL syringes, 25 disposable transfer pipettes, 8 mL analyte standard solution, instruction manuals, and material safety data sheets.

Figure 2. ANDalyze Lead100

Chapter 3
Test Design and Procedures

3.1 Test Overview

This verification test was conducted according to procedures specified in the QAPP,[1] including deviations as described in Appendix A, and adhered to the quality system defined in the ETV AMS Center QMP[2]. A technical panel of stakeholders was specifically assembled for the preparation of the QAPP. A list of participants in the technical panel is presented in the QAPP. The panel included representatives from industry associations, as well as local and federal governments. The responsibilities of verification test stakeholders and/or peer reviewers included:

- Participate in technical discussions to provide input to the test design;
- Review and provide input to the QAPP; and
- Review and provide input to the verification report/verification statement.

The QAPP and this verification report were reviewed by experts in the fields related to contaminant detection in aqueous media and statistics. The following experts provided peer review:

- Randy Gottler, City of Phoenix, Arizona
- Julius Enriquez, EPA
- Edward Askew, Askew Scientific Consulting

Battelle conducted this verification test with funding support from the technology vendor, and analytical support from DHL Analytical, Inc.

This verification test assessed the performance of the Lead100/AND1000 relative to key verification parameters including accuracy, precision, sample throughput, and ease of use. These performance parameters were evaluated using multiple variables that challenged the Lead100/AND1000's ability to detect Pb in a variety of aqueous matrices. The Lead100/AND1000 technology evaluation was organized as four main tests. Each test evaluated the performance of Lead100/AND1000 operating under different laboratory and field conditions. The four tests were:

1. Initial demonstration of capability (IDC) and performance testing (PT) including determination of the limit of detection (DLOD), determination of linear range (DLR), and determination of the effects of interferences (DEI)
2. Testing accuracy and precision of the instrument for the analysis of finished drinking water samples (bottled water, municipal drinking water, treated groundwater)
3. Testing accuracy and precision of the instrument for the analysis of environmental water samples (surface water, groundwater and seawater)
4. Testing accuracy and precision of the instrument for the analysis of wastewater effluent samples (municipal wastewater effluent, metal finishing wastewater effluent)

ANDalyze, Inc. chose to have its technologies tested as described in the QAPP for Pb detection in aqueous media. The verification testing was conducted in the field and at the Environmental Treatability Laboratory (ETL) at Battelle's Main Campus in Columbus, OH between July 10 and July 27, 2012 (Round 1) and between February 11 and March 13, 2013 (Round 2). The technology was challenged with aqueous samples from a wide range of sources spiked with different Pb concentrations. The resulting observations were used to calculate the accuracy, precision, limit of detection, linear range, and determination of interferences, where appropriate. Operational factors such as maintenance needs, data output, ease of use, and repair requirements were also assessed based on technical staff observations. These performance parameters were evaluated quantitatively using the statistical methods described in Chapter 5 of this document and qualitatively through recorded observations. All tests were performed with the Lead100/AND1000 operating according to the vendor's recommended procedures as described in the user's manuals and during training provided to the operator. Select sections of the user manuals were updated after Round 1 testing to clarify sample preparation procedures for specific samples. All samples analyzed with the Lead100/AND1000 were also collected, stored, transferred, and analyzed in a certified laboratory using industry accepted analytical methods. Select aspects of certain analytical methods were modified after Round 1 testing as per vendor recommendations and requests. Results from the technologies being verified were recorded in laboratory record books (LRBs) and transferred to an appropriate electronic format (i.e., Microsoft® Excel). Table 1 presents a summary of the tests performed as part of this verification, and Section 3.3 presents the experimental design.

Testing was completed according to the QAPP between July 10 and July 27, 2012 as Round 1. Review of the data and methodology revealed the need for deviations from the QAPP for a more appropriate verification. Specifically, concern was raised regarding the effect of the sample preparation methodology on the apparently low recoveries of lead by the certified laboratory compared to both target and detected concentrations by the technology. Round 2 testing was completed between February 11 and March 13, 2013 according to deviations in the QAPP Deviation Report[3] summarized in Appendix A.

The first set of tests (IDC and PT) was performed in a highly-controlled environment within Battelle's ETL. IDC required the detection of a Pb spike (25 ppb) in reagent grade water. DLOD was performed by measuring seven replicates of Pb spiked at 10 ppb, five times the purported limit of detection (2 ppb). The DLR was carried out by measuring the Lead100/AND1000's ability to precisely and accurately measure seven samples with Pb concentrations of 0 ppb, 5 ppb, 15 ppb, 25 ppb, 50 ppb, 75 ppb, and 100 ppb. The samples were analyzed in triplicate and the coefficient of determination was used to assess the linearity of the response of the instrument within this range. Finally, DEI was determined using three synthetic water samples with differing characteristics: low total dissolved solids concentration (LTDS), high total dissolved solids concentration (HTDS), and high iron (Fe) concentration and other dissolved solids (HFe). Each of these synthetic water samples was split into required 100 mL subsamples and received a Pb spike of 25 ppb and 50 ppb before Pb was measured in triplicate from each subsample by Lead100/AND1000. Normal sample preparation procedures were followed for the LTDS and HTDS water, and a special sample preparation procedure for the removal of Fe interference was used to prepare the HFe sample for Pb analysis.

The next set of tests determined the accuracy and precision of the Lead100/AND1000 in recovery of Pb spikes in finished drinking water. Three sets of samples were prepared with Pb spikes of 25 ppb: finished drinking water samples collected from a water fountain (WF), bottled mineral water purchased from a local supermarket (Bottled Water [BW]), and finished drinking water collected from the effluent of a local water treatment facility treating groundwater (Finished Well Water [FWW]). All samples were freshly collected during both Round 1 and Round 2 testing, as agreed upon by the vendor. All waters were analyzed without a Pb spike and in triplicate with a Pb spike of 25 ppb.

The third series of tests aimed at determining the accuracy and precision of the Lead100/AND1000 in recovering Pb spikes in environmental water samples. The environmental water samples for this study included samples collected from both freshwater and saltwater sources. Three freshwater sources were sampled including water collected from the reach of a freshwater river just outside and upstream of Columbus, OH (River Water [RiW]), samples collected from a freshwater reservoir near the same location (Reservoir Water [ReW]), and raw groundwater collected at the source of a drinking water treatment facility just outside Plain City, OH (Raw Well Water [RWW]), which was collected from the source that feeds the facility from which the Finished Well Water was collected. In addition, one seawater sample was collected in West Palm Beach, FL (Seawater [SW]) to determine the accuracy and precision of the Lead100/AND1000 in testing natural waters with high salinity. All samples were collected fresh for both rounds of testing except for Seawater, which was collected during Round 1 testing and retained in proper storage conditions for Round 2 testing as agreed upon by the vendor. All four environmental samples were analyzed with no spike and in triplicate after the addition of a Pb spike to 25 ppb. Performance of tests on Seawater differ from the performance of tests on freshwater in that seawater was diluted tenfold before being subjected to Lead100/AND1000 testing and results are analyzed qualitatively, not quantitatively as with freshwater samples.

The final series of tests aimed at determining the accuracy and precision of the Lead100/AND1000 in recovering Pb spikes in wastewater effluent samples. Three samples were analyzed during this series of tests: two effluent samples collected from two separate traditional activated sludge treatment facilities treating domestic wastewater in Columbus, OH (Municipal Wastewater Effluent [MWWE] #1 and Municipal Wastewater Effluent #2) and a sample collected from the effluent of a metal finishing works (Metal Finishing Wastewater Effluent [MFWWE]). The Metal Finishing Wastewater Effluent was collected from a facility conforming to 40 CFR 433 and/or 40 CFR 413 after all on-site pretreatment. All samples were freshly collected during both Round 1 and Round 2 testing, except for Metal Finishing Wastewater Effluent, which was collected during Round 1 testing and retained in proper storage conditions for Round 2 testing, as agreed upon by the vendor.

Table 1. Summary of Verification Tests and Performance Parameters

Test	Test Description	Performance Parameter	Independent Variables
1a: Initial Demonstration of Capability	Analysis of reagent grade deionized (DI) water spiked with Pb	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration
1b: Three Point Calibration	Analysis of three reagent grade water samples spiked with Pb as part of a three point calibration	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration
1c: Initial Calibration Check	Analysis of reagent grade DI water spiked with Pb	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration
1d: Determination of Limit of Detection	Analysis of reagent grade DI water spiked with Pb concentration 5 times the vendor estimated detection limit repeated 7 times	▪ Limit of Detection ▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration
1e: Determination of Linear Range	Analysis of reagent grade DI water spiked with Pb in 6 concentrations within vendor-estimated detection limits (0-100 ppb), each in triplicate	▪ Linearity of Response ▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration
1f: Determination of Effects of Interferences	Analysis of laboratory prepared samples of LTDS, HTDS, and HFe water, each spiked with Pb at two different concentrations measured in triplicate	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration ▪ Water quality parameters
2: Finished Drinking Water Samples	Analysis of Water Fountain, Bottled, and Finished Well Water spiked with Pb, each in triplicate	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration ▪ Drinking water source
3: Environmental Water Samples	Analysis of Raw Well, River, and Reservoir Water spiked with Pb, and Seawater spiked with two concentrations of Pb, each in triplicate	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration ▪ Environmental water source
4: Wastewater Effluent Samples	Analysis of Wastewater Effluent 1, Wastewater Effluent 2, and Metal Finishing Wastewater Effluent spiked with Pb, each in triplicate	▪ Accuracy ▪ Precision ▪ Operational factors	▪ Pb concentration ▪ Wastewater effluent source

3.2 Test Site Description

PT (including DLOD, DLR, and DEI) was completed at Battelle's ETL according to the QAPP and QAPP Deviation Report. Finished drinking water was collected from three different sources: a WF located within Battelle headquarters in Columbus, OH; bottled water available from a local supermarket, in Columbus, OH; and finished well water from a small water treatment facility located outside in Plain City, OH. Environmental samples were collected from four different sources: river water was collected from the Scioto River in Columbus, OH; reservoir water was collected from Griggs Reservoir in Columbus, OH; raw well water was collected from a well located outside Plain City, OH; and seawater was collected from the Atlantic Ocean off West Palm Beach, FL. Wastewater effluent was collected from three sources: Southerly Wastewater Treatment Plant in Columbus, OH; Jackson Pike Wastewater Treatment Plant in Columbus, OH; and a metal finishing plant. Detailed descriptions of the research test site and equipment items are provided below.

3.2.1 Battelle Headquarters and Environmental Treatability Laboratory

The Battelle ETL is an operational environmental laboratory centrally located on the Battelle Memorial Institute Main Campus in Columbus, OH. Battelle receives its finished drinking water from the Dublin Road Water Purification Plant in Columbus, OH, which treats raw water from the Scioto River within the city limits and select groundwater wells. The Battelle ETL offers highly controlled laboratory conditions for performing testing, storage facilities for samples and reagents, access to calibrated standard laboratory equipment (scales, pipettes, volumetric flasks, etc.), production of DI water, and established laboratory protocols for the acquisition of reagents and disposal of performance testing waste.

3.2.2 Well Water

Raw and finished well water was collected from a small water treatment facility located in Plain City, OH. The treatment system operating is an on-demand coagulation/filtration system treating approximately 10 gallons per minute.

3.2.3 Scioto River

River water was collected from the east bank of the Scioto River in Columbus, OH, no more than 5 miles north of Griggs Reservoir as indicated on Figure 3. The Scioto River is one of the longest rivers in Ohio as it runs over 230 miles from Auglaize County, in the western part of the state, through Columbus to Portsmouth where it empties into the Ohio River. Two dams have been built on the Scioto River, both in Columbus, for drinking water and recreation purposes[4]. River water was collected from the surface of the river no more than 1 ft below the water surface and no more than 20 ft from the eastern shoreline.

3.2.4 Griggs Reservoir

Griggs Dam was the first dam to be built on the Scioto River in Columbus, Ohio in 1908, which forms the Griggs Reservoir. Griggs Reservoir is a long, narrow body of water at almost 6 miles long and 500 feet wide with a 1.2 million gallon capacity. The Reservoir is a major drinking water source for Columbus. Reservoir water was sampled from within the boundaries of Griggs Reservoir, and, identically to River Water, it was sampled from the surface, no more than 1 ft below the water surface and no more than 20 ft from the eastern shore of the reservoir, as indicated on Figure 3.

3.2.5 West Palm Beach, FL

Seawater was collected from the Atlantic Ocean off West Palm Beach, FL as indicated on Figure 4. Seawater was collected from the surface of the ocean no more than 1 ft below the water surface and no more than 20 ft from the shoreline.

3.2.6 Southerly Wastewater Treatment Plant

The Southerly Wastewater Treatment Plant (Southerly), built in 1967, is one of two treatment plants servicing Columbus, OH, located south of the city in Lockbourne, Ohio as indicated on Figure 3. Southerly receives and treats influent from the northeast and eastern half of Franklin County through a series of physical and biological processes. Southerly has the capacity to treat 114 million gallons per day (MGD) and discharges into the Scioto River.

3.2.7 Jackson Pike Wastewater Treatment Plant

The Jackson Pike Wastewater Treatment Plant (Jackson Pike), built in 1935, is the original treatment plant servicing Columbus, OH and is located on the southern limit of the city as indicated on Figure 3. Jackson Pike receives and treats influent from the northwestern and western half of Franklin County through a series of physical and biological processes. Jackson Pike has the capacity to treat 68 MGD and, like Southerly, discharges into the Scioto River.

3.2.8 Metal Finishing Plant

Metal Finishing Wastewater Effluent was collected by the vendor from an undisclosed facility conforming to 40 CFR 433 and/or 40 CFR 413 (electroplating, electroless plating, anodizing, coating [chromating, phospating and coloring], chemical etching and milling, and printed circuit board manufacturing).

3.3 Experimental Design

This verification test was designed to evaluate the accuracy, precision, functionality, and ease-of-use of the Lead100/AND1000 in detecting Pb in laboratory, environmental, waste, and drinking water effluent samples including DI water with and without interfering species. The characteristics of independent variables were selected and established during the runs to determine the response of the dependent variables. Performance parameters were evaluated based on the responses of the dependent variables (i.e., comparison of the Lead100/AND1000 performance to reference method performance) and used to characterize the Lead100/AND1000 performance.

Dependent Variable Responses. The Lead100/AND1000 was evaluated with respect to its ability to accurately and precisely determine aqueous Pb concentrations in a variety of water samples. Detection of aqueous Pb concentration thus represents the only quantitative dependent variable included in the test. In addition, functionality and ease of use were evaluated on a subjective basis.

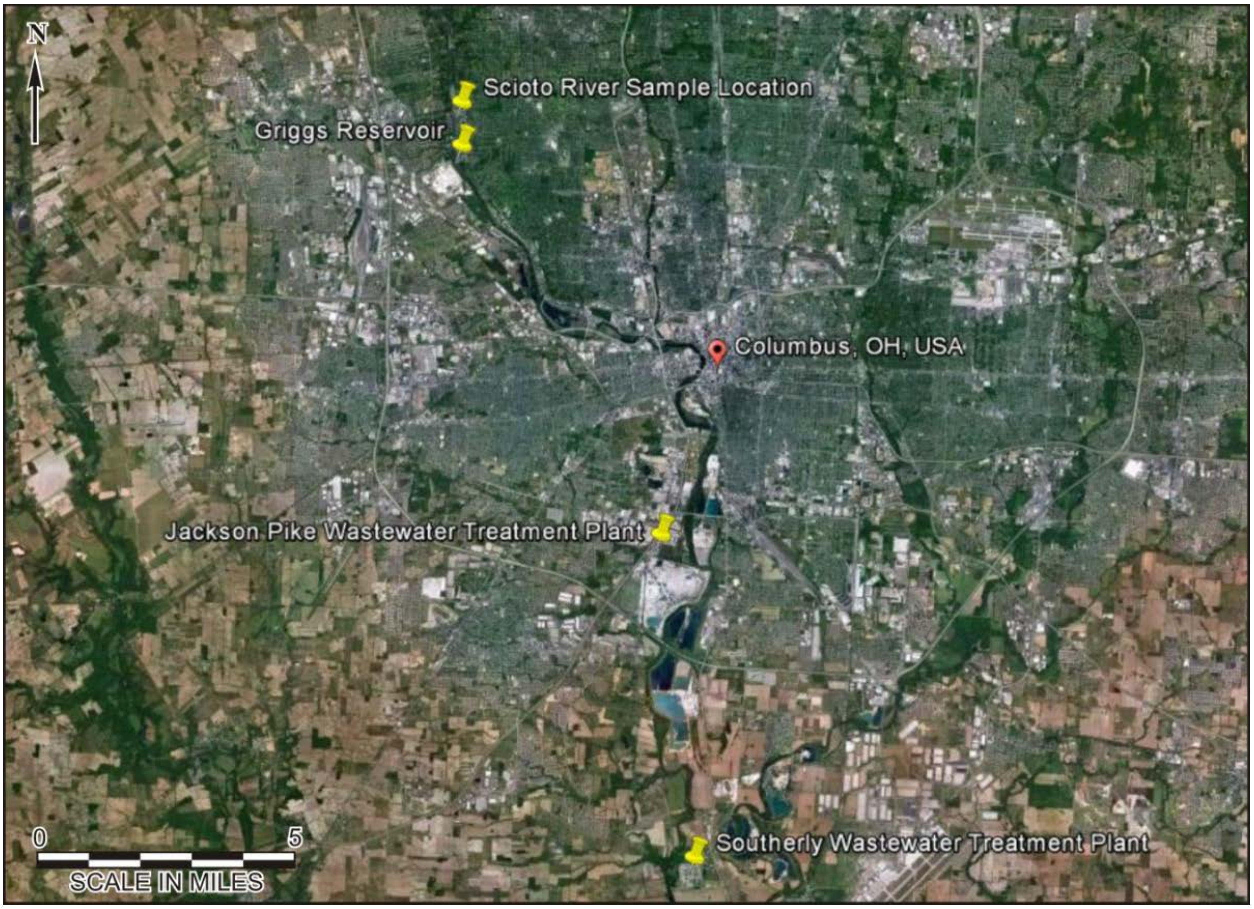


Figure 3. Site Map Showing the Locations of River Water, Reservoir Water, Municipal Wastewater Effluent #1, and Municipal Wastewater Effluent #2

Independent Variable Levels. The levels of the independent variables with respect to water samples that were tested were the following: (1) prevailing water quality characteristics dictated by environmental conditions (e.g., pH, major anions, major cations); and/or (2) water quality characteristics artificially imparted on synthetic environmental or laboratory samples including synthetic matrices and Pb spikes. Additionally, other qualitative independent variables included operator ability and prevailing field conditions.

The verification test consisted of four portions (in addition to QA testing): (1) performance testing (including DLOD, DLR and DEI); (2) finished drinking water sample testing; (3) environmental water sample testing; and (4) wastewater effluent water sample testing. The verification test was conducted in phases as indicated in the QAPP Deviation Report: Phase 1 consisting of performance testing, Phase 2 consisting of finished drinking water and environmental water sample testing, and Phase 3 consisting of wastewater effluent water sample testing.

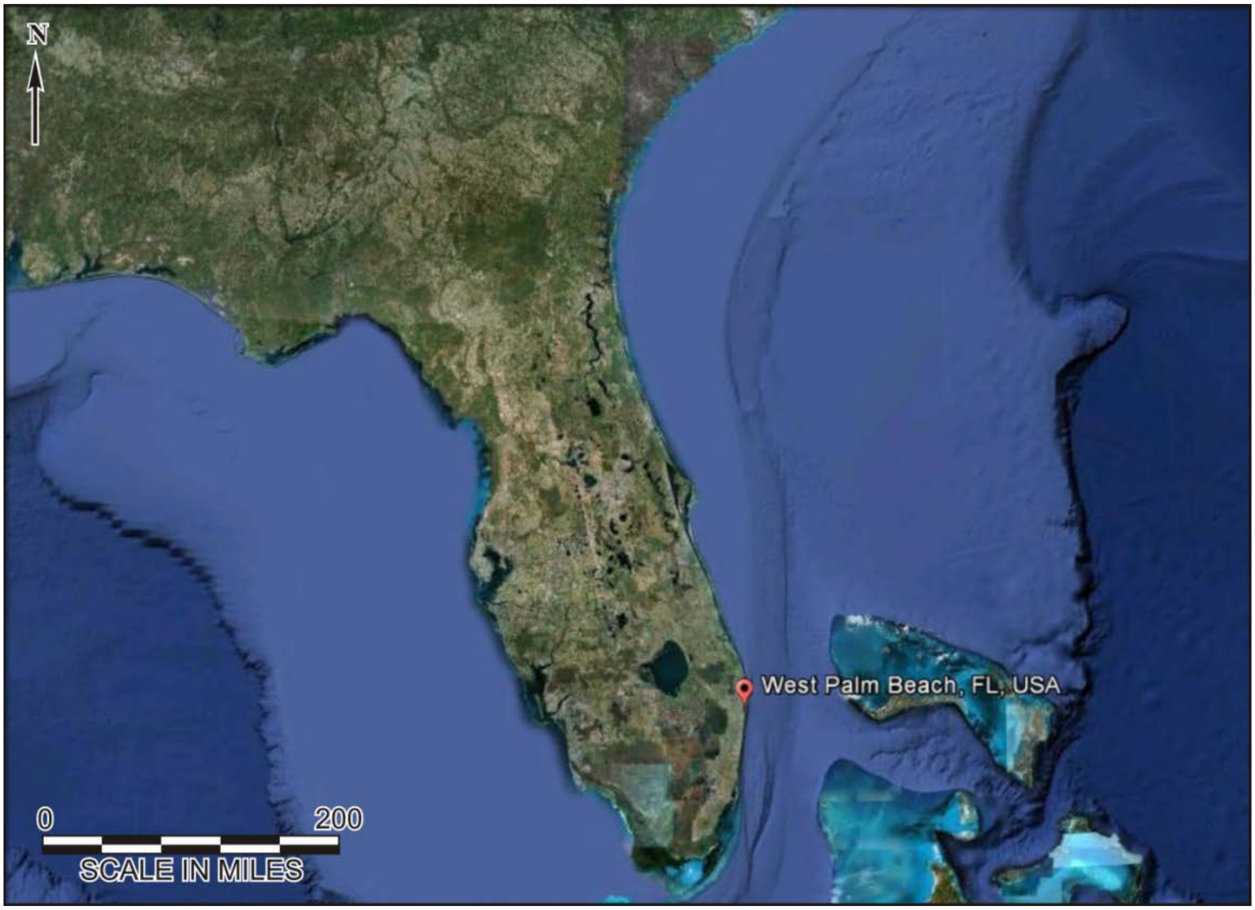


Figure 4. Site Map Showing the Location of the Seawater Sample

The four tests are described in further detail in the following subsections. Table 4 presents an overview of the testing matrix. Table 3 presents a complete list of water samples that were collected for analysis.

3.3.1 Performance Testing

PT was focused on IDC and determination of the inherent features and limitations of Lead100/AND1000. In addition to the IDC and three point calibration (TPC), PT tests also included DLR, DLOD, and DEI. In all cases, the tests were designed to determine the instrument response to a known concentration of aqueous Pb contamination in controlled laboratory samples (both DI and DI with added interferences). Instrument accuracy, precision, and ease of use during aqueous Pb detection in the laboratory samples were determined during these tests. Before a new sample matrix was analyzed, the Lead100/AND1000 was subjected to on-site calibration as outlined in the vendor instrument manuals. An experimental matrix for PT is presented as Table 4.

IDC was aimed at demonstrating the technology with clean samples spiked with a known concentration of Pb. DI was spiked with 25 ppb Pb before being analyzed with the

Lead100/AND1000. Further, these analyses were carried out in triplicate to assess the precision of the Lead100/AND1000.

TPC was carried out to provide a baseline calibration in DI water. Subsequent calibrations (on-site calibrations) augmented this TPC and corrected measurements for matrix effects. The TPC was stored in the Lead100/AND1000 and was augmented each time Pb was measured in a new matrix (on-site calibration). The TPC consisted of analyzing one sample each of DI spiked with Pb at 25 ppb, 50 ppb, and 75 ppb. Initial calibration check (ICC) served to confirm calibration accuracy.

DLR of the instrument was accomplished through a series of triplicate tests on DI spiked with Pb at six different concentrations within the purported linear range of the Lead100/AND1000 (0 to 100 ppb). The six Pb concentrations specified for the DLR experiments were 0 ppb, 5 ppb, 15 ppb, 25 ppb, 50 ppb, 75 ppb, and 100 ppb. The accuracy and precision of the instrument as well as the linearity of the concentration curve were the performance metrics for the DLR tests.

Limit of detection (LOD) of the Lead100/AND1000 has been reported by the vendor as 2 ppb Pb and was confirmed through a series of seven replicate tests of DI samples spiked with one concentration of Pb at five times the purported detection limit (10 ppb) in accordance with 40 Code of Federal Regulations (CFR) Part 136.

The final aspect of PT was the DEI on the instrument's ability to accurately and precisely measure Pb in aqueous samples with added interferences. Triplicate interference tests were carried out each on three samples of DI not only with added interferences (referred to as LTDS, HTDS, and HFe) but also spiked with Pb in the amount of 50 ppb. The ability of the Lead100/AND1000 to accurately and precisely measure Pb at the specified concentration was the performance metric for the interference tests. The first two samples were analyzed after pretreatment with only the vendor-recommended buffer (required for all samples), while the third was pretreated with both the vendor-recommended buffer and a special vendor-provided pretreatment method for the removal of effects of Fe interference. An on-site calibration was performed separately for each of the two samples (i.e., one on-site calibration for the untreated sample and one on-site calibration for the treated sample). A series of three measurements were also made on the HFe with only the vendor-provided buffer to assess the utility of the additional pretreatment method for removal of the effects of Fe interference. The specific water makeup of the three samples is specified in Table 2.

Table 2. DEI Water Sample Composition

Constituent	LTDS (ppm)	HTDS (ppm)	High Iron Water (ppm)
$NaHCO_3$	95	380	NS
$CaSO_4$	50	200	0.142
$MgSO_4$	60	240	NS
KCl	4	16	NS
Glucose	10	100	NS
Fe	NS	NS	1
NaCl	NS	NS	3

NS – Not Spiked

The tests outlined in this section do not explicitly include the QC samples required (see Chapter 4). Data collected during the PT included concentration of Pb reported by the Lead100/AND1000 and the reference method and qualitative data collected regarding ease of operation.

3.3.2 Analysis of Finished Drinking Water Samples

Analyses of finished drinking water samples were aimed at determining the accuracy and precision of the Lead100/AND1000 in measuring soluble Pb in water matrices other than highly controlled, "clean" laboratory samples, but not as complex as environmental samples. Three samples were analyzed with no spike and in triplicate each spiked with 25 ppb Pb: WF, Bottled Water, and Finished Well Water. In addition, Finished Well Water was not only analyzed in triplicate at ETL with a Pb spike of 25 ppb, but also once in the field with no spike. Samples collected from the treatment facility in Plain City, OH were transferred to the ETL and analyzed with Lead100/AND1000 under highly-controlled laboratory conditions to determine the differences between the Lead100/AND1000 performance in the field and in the laboratory. The tests outlined in this section were in addition to QC samples required (see Chapter 4). Data collected during this test included concentration of Pb reported by Lead100/AND1000 and the reference method and qualitative data collected regarding ease of operation, especially differences in ease of use between field and laboratory analyses and difficulties encountered in field analyses.

3.3.3 Analysis of Environmental Water Samples

The analysis of environmental water samples was aimed at determining the accuracy and precision of the Lead100/AND1000 in measuring soluble Pb in water matrices naturally occurring in the environment. Three samples (River Water, Reservoir Water and Raw Well Water) each spiked with 25 ppb Pb were analyzed in triplicate and also analyzed with no spike. River Water was collected from a reach of the Scioto River and Reservoir Water was collected from south of the River Water sampling location in Grigg's Reservoir (see Figure 3 for a map of sampling locations). Both samples were collected from the shore of the water bodies (less than 20 ft from shore). The samples were collected from the surface of the water bodies (less than 1 ft depth). The Raw Well Water was collected from the raw water intake tap at a small water treatment facility at the Plainview Christian School located in Plain City, OH; note that this is the same facility from which the Finished Well Water was collected. All samples were filtered with 0.20 µm nylon syringe filter before analysis. The freshwater environmental samples were analyzed in the field without a Pb spike to determine the ability of the Lead100/AND1000 to detect background Pb levels in the samples. In addition to field analyses, both freshwater environmental samples were transferred to the ETL, subsequently spiked to 25 ppb Pb and analyzed with Lead100/AND1000 identically as in the field under highly-controlled laboratory conditions to determine differences between Lead100/AND1000 performance in the field and in the laboratory. The tests outlined in this section were in addition to QC samples required (see Chapter 4). Data collected during this phase of the test included concentration of Pb reported by Lead100/AND1000 and the reference method and qualitative data collected regarding ease of operation—especially differences in ease of use between field and laboratory analyses and difficulties encountered in field analyses.

In addition to the two freshwater samples, one additional sample (Seawater) was collected from a location off West Palm Beach, FL (see Figure 4 for the Seawater sampling location). The Seawater sample was collected in the same manner as the two freshwater samples (i.e., less than 20 ft from the shoreline and less than 1 ft depth). The Seawater sample was shipped by overnight services to ETL where two samples were separately spiked with 25 ppb Pb and 50 ppb Pb and analyzed by the Lead100/AND1000 in triplicate each to determine the accuracy of the Lead100/AND1000 in recovering the Pb spike as well as the precision of the instrument. All samples were filtered with 0.20 µm nylon syringe filter before analysis. In addition to spiked samples, Seawater was also analyzed without a Pb spike to determine the ability of the Lead100/AND1000 to detect background Pb levels in the samples. Due to the high dissolved solids anticipated in Seawater, the results of the analysis of Seawater (both spiked and unspiked) were qualitative in nature, indicating whether the Seawater samples had low, medium or high concentrations of Pb.

3.3.4 Analysis of Wastewater Effluent Samples

The final series of tests for the verification were the analysis of three effluent water samples collected from wastewater treatment operations. Two samples (Municipal Wastewater Effluent #1 and Municipal Wastewater Effluent #2) were collected from two separate domestic wastewater treatment facilities in Columbus, OH (see Figure 3 for the locations of the treatment facilities). Due to the nature of the Lead100/AND1000 and the high levels of interferences in the municipal wastewater effluent samples, all samples were filtered with 0.20 µm nylon syringe filter and diluted ten-fold with DI water before any sample preparation (i.e., Pb spike) or analysis. Note that dilution of Municipal Wastewater Effluent #1 raised the LOD from 2 ppb Pb to 20 ppb Pb for these samples. After dilution, the samples were analyzed in the field without a Pb spike. Samples were then transferred to the ETL where they were analyzed in triplicate after spiking to 25 ppb Pb.

In addition to the two municipal wastewater effluent samples (i.e., Municipal Wastewater Effluent #1 and Municipal Wastewater Effluent #2), one industrial wastewater effluent sample (Metal Finishing Wastewater Effluent) was supplied by the vendor. The industrial wastewater effluent sample was collected from a metal finishing operation conforming to 40 CFR 433 and/or 40 CFR 413. Due to the nature of the Lead100/AND1000 and the anticipated high levels of interferences in the industrial wastewater effluent samples, Metal Finishing Wastewater Effluent was filtered with 0.20 µm nylon syringe filter and diluted ten-fold with DI water before any sample preparation (i.e., Pb spike) or analysis. Metal Finishing Effluent was collected by the vendor after all on-site pretreatment and shipped to ETL where it was spiked with 25 ppb Pb and analyzed by the Lead100/AND1000 in triplicate to determine the accuracy of the Lead100/AND1000 in recovering the Pb spike as well as the precision of the instrument. One additional aliquot of unspiked effluent from each facility was analyzed to determine the ability of the Lead100/AND1000 to detect potential background Pb levels in each of the samples. Note that dilution of the Metal Finishing Wastewater Effluent raised the limit of detection from 2 ppb Pb to 20 ppb Pb for these samples.

Other Monitoring Data. Other variables may influence the operability of the Lead100/AND1000 and information on these other variables was collected during the tests but not controlled. Monitoring data that were recorded included field and laboratory temperature, field and laboratory barometric pressure, and general field conditions (e.g., inclement weather). There were no adverse field conditions encountered during testing. Appendix G contains barometric pressure and temperature data for Columbus, Ohio obtained from the Battelle Weather Station at Battelle Headquarters.

Table 3. Overview of the Tests Performed for this Verification

Test	Test Sample	Performance Parameter	Independent Variables	# of Analyses
Analysis of Laboratory-Prepared Solutions	DI	Percent recovery of 5, 15, 25, 50, 75, and 100 ppb Pb spikes Standard deviation and coefficient of variation of triplicate analyses Limit of detection Linearity of response	Lead concentration Prevailing field conditions (e.g., temperature)	34 (three 5 ppb spikes; seven 10 ppb spikes; three 15 ppb spikes; ten 25 ppb spikes; four 50 ppb spikes; four 75 ppb spikes; three 100 ppb spikes)
	HTDS	Percent recovery of 25 and 50 ppb Pb spikes Standard deviation and coefficient of variation of triplicate analyses	Lead concentration Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	7 (three 25 ppb spikes; three 50 ppb spikes; 1 unspiked)
	LTDS	Percent recovery of 25 and 50 ppb Pb spikes Standard deviation and coefficient of variation of triplicate analyses	Lead concentration Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	7 (three 25 ppb spikes; three 50 ppb spikes; 1 unspiked)
	HFe	Percent recovery of 25 and 50 ppb Pb spikes Standard deviation and coefficient of variation of triplicate analyses	Lead concentration Water composition (metals and anions) Pretreatment effectiveness Prevailing field conditions (e.g., temperature)	14 (three 25 ppb spikes; three 50 ppb spikes; 1 unspiked; each with and without pretreatment)
Analysis of Finished Drinking Water Samples	WF	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 unspiked)
	Bottled Water	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 unspiked)
	Finished Well Water	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 without a Pb spike)

Table 3. Overview of the Tests Performed for this Verification (Continued)

Test	Test Sample	Performance Parameter	Independent Variables	# of Analyses
Analysis of Environmental Water Samples	River Water	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 without a Pb spike)
	Reservoir Water	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 without a Pb spike)
	Seawater(a)	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	7 (three 25 ppb spikes; three 50 ppb spikes; 1 unspiked at ETL)
Analysis of Wastewater Effluent Samples[a]	Municipal Wastewater Effluent #1	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 without a Pb spike)
	Municipal Wastewater Effluent #2	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 without a Pb spike)
	Metal Finishing Wastewater Effluent	Percent recovery of 25 ppb Pb spike Standard deviation and coefficient of variation of triplicate analyses	Water composition (metals and anions) Prevailing field conditions (e.g., temperature)	4 (three 25 ppb spikes; 1 unspiked at ETL)

(a) Samples were diluted tenfold before any sample preparation or analysis.

Table 4. Experimental Test Matrix(a)

Phase	Test Name	Sample Name	Matrix	Pb Spike (ppb)	AND1000 Analyses	Pb Reference Analyses	Cations, Anions, Alkalinity Reference Analyses
1	IDC	IDC-25	DI	25	3	1	0
	TPC	TPC-25	DI	25	1	1	0
		TPC-50		50	1	1	0
		TPC-75		75	1	1	0
	ICC	ICC-25	DI	25	3	1	0
	DLOD	DLOD-10	DI	10	7	1	0
	DLR	DLR-5	DI	5	3	1	0
		DLR-15		15	3	1	0
		DLR-25		25	3	1	0
		DLR-50		50	3	1	0
		DLR-75		75	3	1	0
		DLR-100		100	3	1	0
	DEI	HTDS-0	HTDS	0	1	1	1
		HTDS-25		25	3	1	0
		HTDS-50		50	3	1	0
		LTDS-0	LTDS	0	1	1	1
		LTDS-25		25	3	1	0
		LTDS-50		50	3	1	0
		HFe-0	HFe	0	2(b)	1	1
		HFe-25		25	6(b)	1	0
		HFe-50		50	6(b)	1	0
2	Finished Drinking Water Samples	WF-0	WF	0	1	1	1
		WF-25		25	3	1	0
		BW-0	Bottled Water	0	1	1	1
		BW-25		25	3	1	0
		FWW-0	Finished Well Water	0	2(c)	1	1
		FWW-25		25	3	1	0
	Environmental Water Samples	RWW-0	Raw Well Water	0	2(c)	1	1
		RWW-25		25	3	1	0
		ReW-0	Reservoir Water	0	2(c)	1	1
		ReW-25		25	3(c)	1	0
		RiW-0	River Water	0	2(c)	1	1
		RiW-25		25	3(c)	1	0
		SW-0	Seawater	0	1	1	1
		SW-25		25	3	1	0
		SW-50		50	3	1	0
3	Wastewater Effluent Water Samples(d)	MWWE#1-0	Municipal Wastewater Effluent #1(e)	0	2(c)	1	1
		MWWE#1-25		25	3	1	0
		MWWE#2-0	Municipal Wastewater Effluent #2(f)	0	2(c)	1	1
		MWWE#2-25		25	3	1	0
		MFWWE-0	Metal Finishing Wastewater Effluent(g)	0	1	1	1
		MFWWE-25		25	3	1	0

(a) Does not include all required QC samples. Required QC samples are discussed in Chapter 4.

(b) Three samples analyzed by Lead100/AND1000 with special pretreatment procedure for the removal of the effects of Fe interference and three additional samples analyzed by Lead100/AND1000 without the special pretreatment procedure.

(c) Two sets of samples analyzed by Lead100/AND1000 each in the field and at ETL.

Table4. Experimental Test Matrix (Continued)

(d) All Wastewater Effluent Samples diluted 1:10 in DI water and filtered through a 0.20 µm nylon filter before addition of Pb spike.
(e) Obtained from Jackson Pike Wastewater Treatment Plant (Columbus, OH).
(f) Obtained from Southerly Wastewater Treatment Plant (Columbus, OH).
(g) Provided by vendor from 40 CFR 433/413 facility after all on-site treatment, properly labeled and preserved sample bottle provided by DHL Analytical and properly stored until are sent for Pb reference analysis.

3.4 Experimental Procedures

3.4.1 General Procedures and Reference analysis

The Lead100/AND1000 were operated exactly as specified in the vendor-provided "AND1000 Fluorimeter for Water Testing User Manual" (AND-prod-1000-2-2012) and the "Lead Testing and On-Site Calibration for Water Testing" (AND-Lead-100-02-2012) (see QAPP for original documentation). In addition, environmental water testing, use of the iron interference pretreatment and TPC was carried out as described in the appropriate solution notes (see QAPP for original documentation).

All Lead100/AND1000 equipment serial numbers and chemical lot numbers were recorded in the LRB, along with any subjective data concerning ease of use in the field compared to ETL and general operations of the Lead100/AND1000 such as calibration or battery replacement. Preparation of stock solutions was undertaken as directed by the QAPP and detailed procedures (such as accurate component weights) were recorded in the LRB.

All samples analyzed by Lead100/AND1000 were also analyzed by a reference method to determine the accuracy of the Lead100/AND1000 in recovering Pb spikes. Pb was measured by inductively-coupled plasma mass spectroscopy (ICP-MS) by EPA Method 200.8 (Pb Reference Method) with supplementary quality control (QC) requirements and procedures indicated in the QAPP Deviation Report, summarized in Appendix A. In addition, each of the finished drinking water, environmental water and wastewater effluent samples was analyzed once for metals and cations by EPA Method 200.8 (Cation Reference Method), major anions by EPA Method 300.1 (Anion Reference Method), and alkalinity (including total, carbonate, bicarbonate and hydroxide alkalinity) by Standard Method 2320B (Alkalinity Reference Method). The Cation Reference Method reports the concentrations of the following species: aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium, vanadium, and zinc. The Anion Reference Method reports the concentrations of the following species: bromide, chloride, fluoride, nitrate, nitrite, ortho-phosphate, and sulfate. All samples except Seawater were preserved in the field as per the methods indicated and sent at 4±2°C to DHL Analytical (Round Rock, TX) for analysis within the hold times specified by the reference methods. The Seawater samples were preserved in the laboratory as per the methods indicated and sent at 4±2°C to DHL Analytical for analysis within the hold times specified by the reference methods.

All tests were conducted in Round 1 testing according to the QAPP; issues encountered in Round 1 testing necessitated the implementation of several changes that were documented in the QAPP Deviation Report summarized in Appendix A. The results and control charts of Round 1 testing are presented in Appendices C and D, respectively. Round 2 testing was conducted according the QAPP Deviation Report and all procedures, analyses, and results discussed in this report reflect Round 2 testing unless otherwise indicated.

3.4.2 IDC Testing

IDC testing was carried out at ETL. IDC-25 was prepared by spiking DI water to 25 ppb Pb before it was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the IDC-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis.

3.4.3 TPC Testing

TPC testing was carried out at ETL. TPC-25 was prepared by spiking DI water to 25 ppb Pb. Similarly, TPC-50 and TPC-75 were prepared by spiking DI water to 50 ppb Pb and 75 ppb Pb, respectively. Each of the TPC samples were analyzed once by the Lead100/AND1000 and results recorded in LRB. If TPC samples had a recovery within 85 to 115 %, then a TPC was stored in the AND1000 and factory calibration was used for ICC, DLOD, DLR tests. If recovery was outside this range, then TPC was not stored in AND1000 as per vendor provided literature. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the TPC samples was filtered through a 0.20 µm nylon syringe filter into a properly labeled and preserved sample bottles provided by DHL Analytical and properly stored until they were sent for Pb Reference analysis.

3.4.4 ICC Testing

ICC testing was carried out at ETL. ICC-25 was prepared by spiking DI water to 25 ppb Pb before it was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the ICC-25 sample was filtered through a 0.20 µm nylon syringe filter into a properly labeled and preserved sample bottle provided by DHL Analytical and properly stored until they were sent for Pb Reference analysis.

3.4.5 DLOD Testing

DLOD testing was carried out at ETL. DLOD-10 was prepared by spiking DI water to 10 ppb Pb before it was analyzed in septuplet by the Lead100/AND1000 per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the DLOD-10 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and properly stored until it was sent for Pb Reference analysis. Note that the reported LOD is applicable only for the matrix under investigation and does not necessarily apply to the other matrices evaluated in this verification.

3.4.6 DLR Testing

DLR testing was carried out at ETL. DLR-5 was prepared by spiking DI water to 5 ppb Pb. Similarly, DLR-15, DLR-25, DLR-50, DLR-75, and DLR-100 were prepared by spiking DI water to 15 ppb Pb, 25 ppb Pb, 50 ppb Pb, 75 ppb, and 100 ppb Pb, respectively. Each of the DLR samples was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainders of the DLR samples were separately filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and properly stored until they were sent for Pb Reference analysis.

3.4.7 DEI Testing

DEI testing included testing the accuracy and precision of Lead100/AND1000 on three different synthetic waters (HTDS, LTDS and HFe). These waters were prepared with compositions indicated in Table 2.

DEI testing on HTDS was carried out at ETL. HTDS-25 and HTDS-50 were prepared by spiking HTDS to 25 ppb Pb and 50 ppb Pb, respectively, before they were analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the HTDS-25 and HTDS-50 samples were filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

DEI testing on LTDS was carried out at ETL. LTDS-25 and LTDS-50 were prepared by spiking LTDS to 25 ppb Pb and 50 ppb Pb, respectively, before they were analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainders of the LTDS-25 and LTDS-50 samples were separately filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

DEI testing on HFe was carried out at ETL. HFe-25 and HFe-50 were prepared by spiking HFe to 25 ppb Pb and 50 ppb, respectively, before they were analyzed in triplicate each by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Two sets of triplicate experiments were carried out: one using a special vendor-recommended pretreatment method for removal of Fe interference and one using the standard pretreatment method. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainders of the HFe-25 and HFe-50 samples were separately filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

3.4.8 Finished Drinking Water Testing

Finished drinking water testing included testing the accuracy and precision of the Lead100/AND1000 on three different finished drinking waters (WF, Bottled Water and Finished Well Water). WF was collected from a WF within Battelle. The WF was activated and water was allowed to flow through the tap for 60 seconds (1-2 L throughput) before samples were collected in a 1 L high-density polyethylene (HDPE) container. WF was collected in a manner to avoid sample agitation and entrainment of air. The 1 L sample collection container was sealed and transported to ETL where it was divided into two 100 mL volumetric flasks. WF-25 was prepared by spiking WF to 25 ppb Pb before it was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the WF- 25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. In addition, the 100 mL sample without the Pb spike (WF-0) was analyzed once by the Lead100/AND1000 and the remainder of the sample was filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

Bottled Water was a 1 gal sample of spring water obtained from a local supermarket in Columbus, OH. The 1 gal Bottled Water sample was transported to ETL where it was divided into two 100 mL volumetric flasks. BW-25 was prepared by spiking one of the 100 mL samples to 25 ppb Pb before it was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the BW-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. In addition, the 100 mL sample without the Pb spike (BW-0) was analyzed once by the Lead100/AND1000 and the remainder of the sample was filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

Finished Well Water was collected from the effluent sample tap at a small water treatment facility located outside Plain City, OH. The effluent sample tap was opened and water was allowed to flow through the tap for 60 seconds (approximately 40 L throughput) before samples were collected in a 1 L HDPE container. Finished Well Water was collected in a manner to avoid sample agitation and entrainment of air. FWW-0 (Finished Well Water with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the FWW-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL where FWW-0 was analyzed once by Lead100/AND1000 and FWW-25 was prepared and analyzed in triplicate. The remainder of the FWW-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

3.4.9 Environmental Water Testing

Environmental water testing included testing the accuracy and precision of Lead100/AND1000 on four different environmental waters (Raw Well Water, Reservoir Water, River Water and Seawater).

Raw Well Water was collected from the raw water intake tap at a small water treatment facility located outside Plain City, OH; note that this is the same facility from which the Finished Well Water was collected. The raw water intake was activated and water was allowed to flow through the tap for 60 seconds (approximately 40 L throughput) before samples were collected in a 1 L HDPE container. Raw Well Water was collected in a manner to avoid sample agitation and entrainment of air. RWW-0 (Raw Well Water with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the RWW-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL and filtered through a 0.20 µm nylon filter before RWW-0 was analyzed once by Lead100/AND1000 and RWW-25 was prepared and analyzed in triplicate. The remainder of the RWW-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

Reservoir Water was collected from the surface of Grigg's Reservoir on the Scioto River in Columbus, OH (see Figure 3 for sampling location). The sample was collected by means of a retractable pole with an attached 1 L HDPE sample collection container. The sample pole was extended to its full length (~20 ft) and a sample was collected from the surface (no more than 1 ft below water surface) of the reservoir. The sample pole was then retracted and brought to the reservoir shore. ReW-0 (Reservoir Water with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the ReW-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL and filtered through a 0.20 µm nylon filter before ReW-0 was analyzed once by Lead100/AND1000 and ReW-25 was prepared and analyzed in triplicate. The remainder of the ReW-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis.

Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

River Water was collected from the surface of the Scioto River in Columbus, OH (see Figure 3). The sample was collected in a manner identical to that for the Reservoir Water sample by means of a retractable pole with an attached 1 L HDPE sample collection container. RiW-0 (River Water with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the RiW-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL and filtered through a 0.20 µm nylon filter before RiW-0 was analyzed once by Lead100/AND1000 and RiW-25 was prepared and analyzed in triplicate. The remainder of the RiW-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

Seawater was collected in two separate 1 L HDPE sample bottles from the shore of West Palm Beach, FL (see Figure 4 for sampling location) no more than 20 ft from the shoreline and no more than 1 ft depth. Two Seawater samples were collected for redundancy; however, only one of the samples was used for testing. The samples were sealed and placed in a cooler with ice and transported to ETL. Upon receipt, the Seawater sample was opened and the temperature measured to ensure that the sample remained at 4±2°C during transit. The sample was then allowed to warm to ambient temperature before further testing. Seawater samples were diluted 1:10 in DI water and filtered through a 0.20 µm nylon filter before analysis.

SW-25 and SW-50 were prepared by spiking Seawater to 25 ppb Pb and 50 ppb Pb, respectively, before they were analyzed in triplicate each by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainders of both the SW-25 and SW-50 samples were separately filtered through a 0.20 µm nylon filter into separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference Analyses. In addition, a 100 mL sample without the Pb spike (SW-0) was analyzed once by the Lead100/AND1000 and the remainder of the sample were filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The Lead100/AND1000 analyses of Seawater samples were considered a qualitative test and were not subjected to the rigorous statistical analysis of the other samples.

3.4.10 Wastewater Effluent Testing

Wastewater effluent testing included testing the accuracy and precision of Lead100/AND1000 on three different wastewater effluent waters (Municipal Wastewater Effluent #1, Municipal

Wastewater Effluent #2, and Metal Finishing Wastewater Effluent). All three of the wastewater effluent water samples were filtered through a 0.20 µm nylon filter before being diluted 1:10 in DI water.

Municipal Wastewater Effluent #1 was collected from the effluent sampling location tap at Jackson Pike (see Figure 3 for facility location) in a 1 L HDPE container. A 1 L volumetric flask was filled halfway with DI water and 100 mL of the filtered Municipal Wastewater Effluent #1 sample was then pipetted to the volumetric flask; the flask was then filled to the line resulting in a 1:10 dilution of Municipal Wastewater Effluent #1. Note that dilution of Municipal Wastewater Effluent #1 raised the limit of detection from 2 ppb Pb to 20 ppb Pb for these samples. MWWE#1-0 (Municipal Wastewater Effluent with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the MWWE#1-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL where MWWE#1-0 was analyzed once by Lead100/AND1000 and MWWE#1-25 was prepared and analyzed in triplicate. The remainder of the MWWE#1-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

Municipal Wastewater Effluent #2 was collected from the effluent sampling location tap at the Southerly Wastewater Treatment Plant in Columbus, OH (see Figure 3) in a 1 L HDPE container. A 1 L volumetric flask was filled halfway with DI water and 100 mL of the filtered Municipal Wastewater Effluent #2 sample was then pipetted to the volumetric flask; the flask was then filled to the line resulting in a 1:10 dilution of the Municipal Wastewater Effluent #2. Note that dilution of Municipal Wastewater Effluent #2 raised the limit of detection from 2 ppb Pb to 20 ppb Pb for these samples. MWWE#2-0 (Municipal Wastewater Effluent with no Pb spike) was analyzed onsite once by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the MWWE#2-0 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis. The remainder of the 1 L sample was transported to ETL where MWWE#2-0 was analyzed once by Lead100/AND1000 and MWWE#2-25 was prepared and analyzed in triplicate. The remainder of the MWWE#2-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. Any differences in results between field and ETL measurements as well as any subjective data concerning ease of use in the field compared to ETL were noted in the LRB.

Metal Finishing Wastewater Effluent was collected by the vendor from a metal finishing facility conforming to 40 CFR 433 and/or 40 CFR413 in a 1 L HDPE sample collection bottle and sent on ice to ETL. The method of sampling was documented by the vendor and provided to Battelle. Upon arrival, the sample bottle was opened and the temperature of the sample was confirmed. The sample was filtered through a 0.20 µm nylon filter before sample preparation. MFWWE-25 was prepared by spiking Metal Finishing Wastewater Effluent to 25 ppb Pb before it was analyzed in triplicate by the Lead100/AND1000 as per vendor-provided manuals and guidance given during training. Results obtained from the Lead100/AND1000 analysis were promptly recorded in the LRB. The remainder of the MFWWE-25 sample was filtered through a 0.20 µm nylon filter into a properly labeled and preserved sample bottle provided by DHL Analytical and stored at 4±2°C until it was sent for Pb Reference analysis. In addition a sample of Metal Finishing Wastewater Effluent without the Pb spike (MFWWE-0) was analyzed twice (once with a pretreatment method for the removal of Fe interference and once without) by the Lead100/AND1000 and the remainder of the sample was filtered through a 0.20 µm nylon filter into two separate properly labeled and preserved sample bottles provided by DHL Analytical and stored at 4±2°C until they were sent for Pb Reference analysis, Cation Reference analysis, Anion Reference analysis, and Alkalinity Reference analysis.

3.5 Operational Factors

Operational factors such as maintenance needs, data output, and sustainability factors such as ease of use and repair requirements were noted when observed. Battelle testing staff documented observations in the LRB and directly into the control charts (MS Excel®). Examples of recorded information included recalibration, replacement of batteries, vendor effort (e.g., time on site for training), the duration and causes of any technology downtime or data acquisition failure and operator observations on many other related items (e.g., ease of use).

Chapter 4
Quality Assurance/Quality Control

QA/ QC procedures were performed in accordance with the QMP for the AMS Center and the QAPP for this verification test. QA/QC procedures and results are described in the following subchapters.

4.1 Data Collection Quality Control

4.1.1 Quality Control Overview

Steps were taken to maintain the quality of data collected during this verification test. QC samples (including quality control standard [QCS], laboratory-fortified matrix [LFM] samples and reagent blank [RB] samples) were incorporated into the sampling and analysis design to assess the quality of the method of assessment.

Prepared QC samples included both RB and LFM. The RB samples were prepared from DI water and exposed to identical handling and analysis procedures as other prepared samples, including the addition of all reagents. These samples were used to help ensure that no sources of contamination were introduced in the sample handling and analysis procedures. Acceptance criteria for RB are discussed in the next section.

The LFM and LFM duplicate [LFMD] samples were prepared as aliquots of environmental samples and spiked in the field to increase the Pb concentration of the samples to 25 ppb. The Pb standard solution used for the LFM was prepared in the laboratory and brought to the field site. These samples were used to help identify whether matrix effects had any influence on the analytical results. At least 10% of all the prepared samples to be analyzed were RBs, and at least two samples taken from each sampling site were LFM and LFMD. The following samples satisfy the LFM requirements for field-collected samples: WF-25, BW-25, FWW-25, RWW-25, ReW-25, RiW-25, SW-25, MWWE#1-25, MWWE#2-25, and MFWWE-25. Acceptance criteria for LFM and LFMD are discussed in the next section.

QCSs were used as a calibration check to verify that Lead100/AND1000 and the reference instruments were properly calibrated and reading within defined control limits. QCS is defined as 30 ppb Pb. These standards were purchased from Fisher Scientific and were subject only to dilution by DI water. The calibration of all instruments was verified using a QCS before and after each testing day, as well as after every tenth sample. In addition, instruments and equipment used for this verification were operated at the expected ranges and calibration records were verified and kept for all monitoring instruments and equipment used during this verification test.

4.1.2 Acceptance Criteria and Root Cause Analysis

Acceptance criteria for QC samples varied depending on the sample(s) being analyzed. For each set of samples a root cause analysis (RCA) might have been required before testing began (see Appendices F, G and H of the original QAPP document for root cause analysis flow-charts).

For IDC, an initial on-site calibration must have been passed before LFM and LFMD samples were analyzed. If on-site calibration was not passed the first time it was repeated and if a second failure occurred, a RCA was performed and the vendor was contacted. If on-site calibration was passed either during the first or (if necessary) the second attempt, LFM and LFMD samples were analyzed. The acceptance criteria for the LFM and LFMD were recovery of the target Pb spike of 75 to 125% and an RPD of less than 30%. If these criteria were not met, on-site calibration was repeated. Analysis of the remaining samples for that specific matrix was initiated only when LFM and LFMD criteria were met.

For ICC and TPC, an initial on-site calibration must have been passed before LFM and LFMD samples were analyzed. If on-site calibration was not passed the first time it was repeated and if a second failure occurred, a RCA was performed and the vendor was contacted. If on-site calibration was passed either during the first or (if necessary) the second attempt, LFM and LFMD samples were analyzed. The acceptance criteria for the LFM and LFMD were recovery of the Pb spike of 85 to 115% and a standard deviation of ±15% of the expected Pb value. If these criteria were not met, on-site calibration was repeated. Analysis of the remaining samples for that specific matrix was initiated only when LFM and LFMD criteria were met.

For DEI, finished drinking water, environmental waters, and wastewater effluents an initial on-site calibration must have been passed before LFM and LFMD samples were analyzed. If on-site calibration was not passed the first time it was repeated and if a second failure occurred, a RCA was performed and the vendor was contacted for collaborative analysis with information regarding the samples (e.g., pH, color, turbidity, conductivity). If on-site calibration was passed either during the first or (if necessary) the second attempt, LFM and LFMD samples were analyzed. The acceptance criteria for the LFM and LFMD were recovery of the Pb spike of 75 to 125% and RPD of less than 30%. If these criteria were not met, on-site calibration was repeated. Analysis of the remaining samples for that specific matrix was initiated only when LFM and LFMD criteria were met.

Acceptance criteria for RB were set at less than the vendor-reported method detection limit of 2 ppb Pb, making the method detection limit and reporting limit identical. If Lead100/AND1000 reported values of Pb equal to or greater than 2 ppb Pb, a second RB was analyzed and if Lead100/AND1000 indicated a value equal to or greater than 2 ppb Pb, on-site calibration was repeated before analysis was continued. A value of less than 2 ppb Pb was indicated by the AND1000 displaying the message "*BELOW LIMIT*" while values measured equal to or greater than 2 ppb Pb were indicated by AND1000 as a quantitative result.

Acceptance criteria for QCS were set at ±25% of the expected Pb concentration (i.e., 30 ppb Pb) in QCS samples for both Lead100/AND1000 and reference methods.

In the cases that a RCA was completed, the laboratory analyst performed a RCA collaboratively with the vendor. The analysis had at a minimum the following areas described in detail:

1. Identification of the problem: the QC failure, including instrument, reagent, sampling, personnel, and any other problems, was identified.
2. Investigation to identify the root cause: it was determined how each identified problem interacted with each other to create the QC problem.
3. Solution: an encompassing solution was developed to address all problems that created the QC failure.
4. Implementation of the solution: an implementation plan was developed which included all components of the developed solution and was implemented by laboratory management.
5. Documentation of the solution: all corrective action steps taken were documented under laboratory management implementation of the corrective action.
6. Communication of the solution: training and management programs were developed to communicate with and evaluate all personnel included in the corrective action solution.
7. Evaluation of the effectiveness of the solution: QC results were documented in trend charts and laboratory staff performances were documented to validate corrective action solution.

The following RCA QC identifiers were used:

- Instrument Failure Mechanical (IFM)
- Instrument Failure Electrical (IFE)
- Instrument Operator Failure to Follow Method (IOFM)
- Sensor Failure Chemical (SFC)
- Sensor Failure Mechanical (SFM)
- Failure Cause Unknown (FCU)

4.1.3 Control Charts

Control charts were maintained throughout the entire verification testing process as per Standard Methods Section 1020[5]. Control limits were calculated after the first five samples and after every 10 samples thereafter. If analysis of the control charts indicated non-conformance as described in Standard Methods Section 1020 B, the sample in question was rerun and in the event of a second non-conformance sample, the vendor was contacted to determine the cause of the problem, which included a RCA.

4.1.4 Equipment Test, Inspection, and Maintenance

The instruments used during the verification test were inspected and maintained according to the instrument manuals or the laboratory standard operating procedures of DHL Analytical. Operation of the Lead100/AND1000 during the verification test was performed by Battelle technical staff as directed by the vendor user manuals and during on-site training.

4.1.5 Calibration and Verification of Test Procedures

The instruments used during the verification test (i.e., Lead100/AND1000 and reference instruments) were calibrated per the instrument manual, the methods being used to make each measurement, or the Standard Operating Procedures (SOPs) of the analysis laboratory. For each measurement, the equipment calibration was verified. Calibration procedures, checks, and results were documented in the project files. Testing did not occur until instrument calibration results met the acceptance criteria as defined in the RCAs.

All calibrations performed were documented by the verification staff in the project LRB. The Lead100/AND1000 technology vendor provided the Battelle verification staff with the necessary training/information to properly calibrate and maintain Lead100/AND1000. Calibration of Lead100/AND1000 was performed as often as indicated in the Lead100/AND1000 user manual and as suggested by the vendors. Vendors were required to describe the necessary calibration procedures specific to Lead100/AND1000.

4.1.6 Inspection and Acceptance of Supplies and Consumables

All materials, supplies, and consumables used to establish the test conditions were ordered by Battelle. Where possible, Battelle relied on sources of materials and consumables that have been used previously without problems as part of past ETV verification testing. Table 4 provides a list of all reagents used in this testing.

Supplies met the following criteria:

- Solvent and reagent grades are based on the intended use. All reagents were of >96% purity (Table 4).
- Equipment used to generate data must provide appropriate sensitivity.
- A certificate of analysis must be provided and retained for reagents and standards.
- The quality and purity of expendable materials must be documented and adequate to meet the data quality objectives (DQOs) of the client.

Table 5. Consumables Used for Verification Testing

Reagent	CAS Number	Description of Use	Purity/ Concentration	Mass/Volume	Vendor	Catalogue Number
NIST-Traceable Lead Solution	10099-74-8	Preparing lead spikes; preparing calibration standards; preparing PEA standards	1,000 ppm	100 mL	Fisher Scientific	SL21-100
Sodium Bicarbonate Anhydrous	144-55-8	Preparing Low TDS and High TDS synthetic Waters	>99.7%	500 g	Fisher Scientific	S233500
Calcium Sulfate Hemihydrate	10034-76-1	Preparing Low TDS and High TDS and High Fe synthetic Waters	97%	100 g	Fisher Scientific	AC38535-1000
Magnesium Sulfate Anhydrous	7487-88-9	Preparing Low TDS and High TDS synthetic Waters	>97%	500 g	Fisher Scientific	AC41348-5000
Potassium Chloride Anhydrous	7447-40-7	Preparing Low TDS and High TDS synthetic Waters	>99%	500 g	Fisher Scientific	P217-500
Sodium Chloride Anhydrous	7647-14-5	Preparing Low TDS, High TDS and High Fe synthetic Waters	>99%	500 g	Fisher Scientific	S271500
Glucose aqueous solution	50-99-7	Preparing Low TDS and High TDS synthetic waters	20% w/v	100 mL	Ricca Chemical	R3254000100
Iron Solution	7437-89-6	Preparing HFe	1,000 ppm	100 mL	Acros Organics	AC19605-1000

4.1.7 Data Management

Various types of data were acquired and recorded electronically or manually by verification staff during this verification test. All data and observations for the operation of the Lead100/AND1000 were documented by the vendor or verification staff in LRBs, data forms or electronically. Results from the laboratory analytical instruments were compiled by laboratory staff in electronic format and submitted to the Verification Test Coordinator (VTC) upon obtaining results. Hand-transcribed data were 100% verified by a second person.

Records received or generated by any of the verification staff during the verification test were reviewed within 2 weeks of receipt of generation before the records were used to calculate, evaluate, or report verification results. The review was documented as the dated initials of the reviewer. If a Battelle staff member generated the record, this review was performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally received or generated the record. The review was documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, at least 10% of data calculations performed by verification staff were checked by Battelle technical staff to ensure that calculations were performed correctly and results were correct. Calculations checked also included any statistical calculations described in the QAPP. The data obtained from this verification test were compiled and reported.

All electronic testing records and documents were stored on a test-specific networked ETV SharePoint site and common drive within Battelle's network. Testing data were uploaded to the SharePoint site within 2 days of receipt. This site is within the protected Battelle network and is backed up regularly. The goal of this data delivery schedule was prompt identification and resolution of any data collection or recording issues.

In addition, once this verification report is complete, all testing records and documents will be sent to Battelle's Records Management Office (RMO) for archival within 2 months of project close-out.

4.2 Audits

Three types of audits were performed during the verification test: a performance evaluation audit (PEA) of the analytical methods, a technical systems audit (TSA) of the verification test procedures, and a data quality audit. Audit procedures are described further below.

4.2.1 Performance Evaluation Audit

PEAs for the Lead100/AND1000 were conducted by having two analysts independently taking triplicate measurements for a 25 ppb Pb standard (in DI water). To be considered acceptable, the average of the two analysts' results should agree within 20% and coefficient of variation (CV) of each analysts triplicate measurements should be no more than 20%. The PEA results were determined to be acceptable.

4.2.2 Technical Systems Audit

The Battelle Quality Manager (QM) performed a TSA during performance evaluation activities. The purpose of the TSA is to ensure that the verification tests are being performed in accordance with the AMS Center QMP[1] and the project QAPP. The Battelle QM compared actual test procedures to those specified or referenced in the QAPP, and reviewed data acquisition and handling procedures. In preparation of the TSA, a project-specific checklist based on the QAPP requirements was prepared to guide the TSA, which included a review of the test locations and general testing conditions; observation of the testing activities; and review test documentation. Data acquisition procedures were also verified. The Battelle QM prepared an initial TSA report. No findings were recorded during the TSA, however, several observations were made. The TSA observations were communicated to technical staff at the time of the audit and documented in the TSA reports. The observations were acknowledged by the VTC and responses were recorded in the final TSA document.

The Battelle AMS Center QA Officer for this verification test performed a TSA during Day 1 testing of Round 1 to ensure that the verification test was performed in accordance with the QMP for the AMS Center and the QAPP. On July 10 and 18, 2012, the QM conducted the TSA to verify that field testing was being conducted according to the QAPP requirements. The TSA on July 10 was conducted at Battelle ETL to observe IDC testing. The TSA included a review of documents available at the test site for reference and records being maintained by the testing staff; observations of the testing equipment; the initiation of IDC testing; and the real-time data recording practices during each run. Verification testing was halted prematurely on July 10 due to the implementation of a RCA. On July 18, 2012, a TSA was again conducted. A debriefing was conducted with the Battelle VTC, Battelle Verification Testing Leader, Battelle AMS Center Manager, and EPA AMS Center Project Officer and QM.

Five observations were noted during the audit: (1) the vendor-supplied lead calibration standard solution was labeled with a different lot number than its outer bag; (2) IDC-25 (replicate 1) percent recovery did not meet the QAPP requirement for the LFM sample; (3) IDC-25 (replicate 2) percent recovery after recalibration did not meet the QAPP requirement for the LFM sample; (4) IDC-25-2 was prepared and percent recovery did not meet the QAPP requirement for the LFM sample, initiating RCA; and (5) Day 1 testing was repeated over two separate days rather than on the same day as stated in the QAPP. Responses to these observations were prepared and recorded by the VTC.

Battelle's assessment was that the noted deviations did not negatively impact the quality of data being generated for Round 2 testing.

4.2.3 Data Quality Audit

The Battelle QM, or designee, audited at least 10% of the sample results data acquired in the verification tests and 100% of the calibration and QC data versus the QAPP requirements. One audits of data quality (ADQ) was conducted for this project. Data were audited at the conclusion of testing using a project-specific checklist and completed within 10 business days of receipt of all test data. During this audit, the Battelle QM, traced the data from initial acquisition (as received from the vendor's technology), through reduction and statistical comparisons, to final reporting. Calculations performed on the data undergoing the ADQ were checked. Data underwent a 100% validation and verification by technical staff (i.e., VTC, or designee) before being assessed as part of the data quality audit. All QC data and all calculations performed on the data undergoing the audit were checked by the Battelle QM. Results of the ADQ were documented using the checklist and reported to the VTC and EPA within 10 business days after completion of the audit. The ADQ which assessed overall data quality, including accuracy and completeness of the technical report, was prepared as a narrative and distributed to the VTC and EPA within 10 business days of completion of the audit.

4.3 Quality Assurance/Quality Control Deviations

Appendix A presents a list of all deviations found during the QA/QC checks performed. Round 1 testing was found to be inadequate for this verification and required deviation. Five causes for deviation were indicated: (1) sample preparation procedures were modified, (2) on-site calibration procedures were modified, (3) additional QA/QC requirements were included for ICP-MS analysis, (4) high iron sample treatment procedures were clarified, and (5) phased sample testing scheme was implemented. These deviations were applied in Round 2 testing. Specific deviations are discussed throughout this verification report where appropriate. The remaining deviations related to QA/QC are discussed below.

Deviation Number 3 stated that the root cause of low recoveries determined by ICP-MS

pertained to the QA/QC procedures employed by the commercial laboratory. Utilizing the requirements for QA/QC samples detailed in Standard Methods for the Examination of Water and Wastewater[5] and 40 CFR Part 136.7, the following QA/QC requirements were added to standard QA/QC requirements of EPA Method 200.8:
QC Failure Requirements:

If the analyst reaches the point where a RCA must be performed, the analyst would contact Battelle. All RCA results must be recorded and submitted for approval by Battelle prior to restarting the ICP-MS analyses.

Understanding between commercial laboratory, Battelle and ANDalyze:

A conference call was held between the lab manager of the commercial lab, Battelle, and ANDalyze to discuss these requirements. A statement of understanding outlining these requirements was developed after the call and circulated to affected parties to ensure all were aware of these specific requirements.

Note that addition of this language to the QAPP did not replace Sections B4 and B5, but were used by the commercial lab as a SOP for this project, supplementing QA/QC requirements specified in EPA Method 200.8. All QA sample preparation and preservation (i.e., RBs, QC samples, and LFM and LFMDs and the PEA) were executed as described in Section B5.1 of the original QAPP. In the event that a RCA was conducted, it was conducted exactly as described in Section B5.2 of the original QAPP. Control charts were maintained and reviewed exactly as described in Section B5.3 of the original QAPP.

Flow charts were prepared for easy interpretation of the additional QA/QC requirements for EPA Method 200.8 (that were included as Appendix F, G and H of the original QAPP document). These flowcharts were not used in isolation but supplemented detailed procedures described in the QAPP deviation.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.3 are presented in this chapter. Qualitative observations were also used to evaluate verification test data. The following subchapters describe each performance parameter evaluated.

5.1 Accuracy

Accuracy of the Lead100/AND1000 was assessed by comparing Pb values obtained from the Lead100/AND1000 (Pb_{AND}) and those reported by the Pb reference analysis (Pb_{REF}) on the same samples. The relative percent difference (RPD) between the two measurements serves as a quantitative measure of the accuracy of the Lead100/AND1000 as detailed in Equation 1.

$$RDP = \frac{|Pb_{AND} - Pb_{REF}|}{Pb_{REF}} * 100$$

Equation 1

RPD is reported for all Lead100/AND1000 and Pb reference measurement pairs of data and are summarized by an average value; however, results from Seawater are reported qualitatively as high, medium or low Pb concentrations.

RPD was also calculated between the LFM and LFMD when determining whether to accept an on-site calibration according to the control charts. RPD as defined by Equation 2 provides a measure of the agreement between the LFM and LFMD.

$$RPD = \frac{|Pb_{LFM} - Pb_{LFMD}|}{(Pb_{LFM} + Pb_{LFMD})/2} * 100$$

Equation 2

Percent recovery was also calculated for the LFM and LFMD when determining whether to accept an on-site calibration according to the control charts. Percent recovery was calculated as shown in Equation 3 for the LFM.

$$Percent\ Recovery\ (LFM) = \frac{(Pb_{LFM} - s * Pb_0)}{25} * 100$$

Equation 3

where s is a dilution correction, Pb_{LFM} is the ANDalyze meter reading for the LFM, and Pb_0 is the ANDalyze meter reading for the unspiked sample (if the reading is “Below Limit” a value of 0 ppb was used). The LFM spike is 25 ppb Pb.

5.2 Precision

Precision of the Lead100/AND1000 was assessed by comparing the spread of Pb concentration data obtained by Lead100/AND1000 on triplicate samples. Precision was expressed quantitatively through the standard deviation (SD) and the CV.

The SD of triplicate samples S_1, S_2 and S_3 were computed as expressed in Equation 4.

$$SD = \sqrt{\frac{1}{3}\sum_{i=1}^{3}(S_i - \mu)^2}$$

Equation 4

where μ is the mean value of the three samples expressed in Equation 5.

$$\mu = \frac{1}{3}\sum_{i=1}^{3} S_i$$

Equation 5

The CV of triplicate samples S_1, S_2, and S_3 was computed as expressed in Equation 6.

$$CV = \frac{SD}{\mu}$$

Equation 6

The mean, SD, and CV was reported for all triplicate samples analyzed by Lead100/AND1000.

5.3 Linearity of Response

During the DLR testing, a series of samples with known concentrations of Pb were analyzed in triplicate by Lead100/AND1000 (0 ppb, 5 ppb, 15 ppb, 25 ppb, 50 ppb, 75 ppb and 100 ppb). In addition to the accuracy and precision of the instrument for these tests, linearity was assessed by linear regression, with the analyte concentration measured by the reference method as the independent variable and the reading from Lead100/AND1000 as the dependent variable. Linearity is expressed in terms of slope, intercept, and the square of the correlation coefficient (r^2) as calculated by Microsoft® Excel standard computation tools.

5.4 Limit of Detection

The LOD for the Lead100/AND1000 was assessed from seven replicate analyses of a fortified sample with an analyte concentration of five times the vendor's estimated detection limit. In the case of the Lead100/AND1000, the vendor's estimated detection limit is 2 ppb. Thus, the LOD tests were carried out on 10 ppb Pb samples. The LOD is calculated from Equation 7.

$$LOD = t * SD$$

Equation 7

where t is the Student's t-test value for a 99% confidence interval (i.e., Student's t-test value for α of 0.01 and 6 degrees of freedom) and SD is the standard deviation of the replicate samples.

5.5 Operational Factors

Operational factors such as maintenance needs, calibration frequency, data output, ease of use, and repair requirements were evaluated and summarized based on technical staff observations for all runs.

Chapter 6
Test Results

This chapter provides results of the quantitative and qualitative evaluations of this verification test for the ANDalyze Lead100/AND1000. Appendix E presents the Round 2 run data that were collected and used to provide these results. Appendix F presents Round 2 control charts which were constructed according to Standard Methods[5]. There are a few important aspects of the control charts which should be noted. Firstly, the observation number on the x-axis refers to the 65 observations of Phase 1 and the 51 observations of Phase 2 in Tables 5 through 10 of Section 6. Upper control limit (UCL), lower control limit (LCL), upper warning limit (UWL), lower warning limit (LWL), positive standard deviation (+SD), negative standard deviation (-SD) and mean were calculated after the first 15 samples and then recalculated after each additional 5 samples. Further details of control charts including equations for the calculation of required variables can be found in Standard Methods[5].

6.1 Accuracy

6.1.1 Percent Recovery

Percent recovery was used for all Lead100/AND1000 observations to verify acceptability of on-site calibration using control charts. Percent recovery was also used for IDC, ICC, DEI, finished drinking water testing, environmental water testing, and wastewater effluent testing as acceptance criteria for observations as described in Section 4.1.2. During testing, reference data were not available, and expected concentration was used as acceptance criteria.

Table 5 presents the expected concentrations, observations, reference concentrations, and percent recovery values for IDC and ICC testing and associated quality control standard (QCS). Control charts for these observations are presented in Appendix F; no QC issues were indicated on control charts for this set of observations. Retesting was performed four times on IDC and ICC related samples. On-site recalibration was performed once during IDC and ICC testing. After on-site recalibration, two IDC samples still did not meet criteria for percent recovery when compared to reference concentrations (IDC-25-2-RR2 and IDC-25-3). Thus on-site recalibration did not seem to improve data quality compared to the reference concentration, although it did appear to improve data quality when compared to the target concentration. Discussion of the precision of triplicate samples for IDC and ICC is presented in Section 6.2.

Table 6. Percent Recovery for IDC and ICC

Phase 1 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
1	QCS-1	QCS	30	31	30	103	103
2	IDC-25-1	IDC	25	20	27	80	**74**
3	IDC-25-2	IDC	25	18		**72**	**67**
4	IDC-25-2-RR1	IDC	25	16		**64**	**59**
5	IDC-25-2-RR2	IDC	25	19		76	**70**
6	IDC-25-3	IDC	25	18		**72**	**67**
7	IDC-25-3-RR1	IDC	25	21		84	78
8	ICC-25-1	ICC	25	20	22	80	91
9	ICC-25-2	ICC	25	25		100	114
10	ICC-25-3	ICC	25	21		84	95
11	QCS-2	QCS	30	20	31	**67**	**65**
12	QCS-2-RR1	QCS	30	25		83	81

Percent recovery values that do not meet criteria are shaded and bold font.

Table 6 presents the expected concentrations, observations, reference concentrations, and percent recovery values for DLOD and DLR testing and associated QCS. Control charts for these observations are presented in Appendix F. Several QC issues were indicated on control charts for observations corresponding to DLR: two consecutive samples were above the upper warning limit, four out of five consecutive samples were outside one standard deviation, and six consecutive samples were above the mean. For each of these QC issues, samples were reanalyzed as described in the original QAPP document and QC issues were resolved. Therefore, the QC issues identified had a minimal impact on data quality. Although on-site recalibration was not required for DLOD and DLR testing, all samples met criteria for percent recovery when compared to reference concentrations. Discussion of limit of detection is presented in Section 6.4. Discussion of the precision of triplicate samples for DLR is presented in Section 6.2. Discussion of linearity of response is presented in Section 6.3.

Table 7. Percent Recovery for DLOD and DLR

Phase 1 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
13	DLOD-10-1	DLOD	10	8	9	80	89
14	DLOD-10-2	DLOD	10	8		80	89
15	DLOD-10-3	DLOD	10	9		90	100
16	DLOD-10-4	DLOD	10	8		80	89
17	DLOD-10-5	DLOD	10	8		80	89
18	DLOD-10-6	DLOD	10	8		80	89
19	DLOD-10-7	DLOD	10	9		90	100
20	DLR-5-1	DLR	5	4	5	80	80
21	DLR-5-2	DLR	5	4		80	80
22	DLR-5-3	DLR	5	5		100	100
23	QCS-3	QCS	30	24	32	80	75
24	DLR-15-1	DLR	15	12	14	80	86
25	DLR-15-2	DLR	15	14		93	100
26	DLR-15-3	DLR	15	12		80	86
27	DLR-25-1	DLR	25	20	29	80	69
28	DLR-25-2	DLR	25	19		76	66
29	DLR-25-3	DLR	25	22		88	76
30	DLR-50-1	DLR	50	51	53	102	96
31	DLR-50-2	DLR	50	46		92	87
32	DLR-50-3	DLR	50	46		92	87
33	QCS-4	QCS	30	28	29	93	97
34	DLR-75-1	DLR	75	77	83	103	93
35	DLR-75-2	DLR	75	78		104	94
36	DLR-75-3	DLR	75	73		97	88
37	DLR-100-1	DLR	100	105	109	105	96
38	DLR-100-2	DLR	100	91		91	83
39	DLR-100-3-RR1	DLR	100	83		83	76
40	QCS-5	QCS	30	34	34	113	100

Percent recovery values that do not meet criteria are shaded and bold font.

Table 7 presents the expected concentrations, observations, reference concentrations, and percent recovery values for DEI consisting of Low TDS (LTDS), High TDS (HTDS), and High Fe (HFe) testing and associated QCS. Control charts for these observations are presented in Appendix F. One QC issue was indicated on control charts for observations corresponding to DEI: seven consecutive observations indicated an increasing trend. Retesting was performed on four samples during DEI. On-site recalibration was not required for DEI as all re-run samples (i.e., LTD-25-2-RR1, HTDS-25-1-RR1 and HFe-25-2-RR1) met criteria for percent recovery when compared to reference concentrations. Discussion of the precision of triplicate samples for DEI is presented in Section 6.2.

Table 8. Percent Recovery for DEI

Phase 1 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
41	QCS-6	Quality Control	30	20	27	**67**	**74**
42	QCS-6-RR1	Quality Control	30	27		90	100
43	LTDS-25-1	Low TDS	25	19	25	76	76
44	LTDS-25-2	Low TDS	25	17		**68**	**68**
45	LTDS-25-2-RR1	Low TDS	25	23		92	92
46	LTDS-25-3	Low TDS	25	25		100	100
47	LTDS-50-1	Low TDS	50	46	47	92	98
48	LTDS-50-2	Low TDS	50	38		76	81
49	LTDS-50-3	Low TDS	50	41		82	87
50	HTDS-25-1	High TDS	25	18	21	**72**	86
51	HTDS-25-1-RR1	High TDS	25	26		104	124
52	HTDS-25-2	High TDS	25	22		88	105
53	HTDS-25-3	High TDS	25	24		96	114
54	QCS-7	Quality Control	30	26	31	87	84
55	HTDS-50-1	High TDS	50	46	49	92	94
56	HTDS-50-2	High TDS	50	41		82	84
57	HTDS-50-3	High TDS	50	47		94	96
58	HFe-25-1	High Fe	25	24	22	96	109
59	HFe-25-2	High Fe	25	18		**72**	82
60	HFe-25-2-RR1	High Fe	25	19		76	86
61	HFe-25-3	High Fe	25	20		80	91
62	HFe-50-1	High Fe	50	42	45	84	93
63	HFe-50-2	High Fe	50	44		88	98
64	HFe-50-3	High Fe	50	45		90	100
65	QCS-8	Quality Control	30	33	31	110	106

Percent recovery values that do not meet criteria are shaded and bold font.

Table 8 presents the expected concentrations, observations, reference concentrations, and percent recovery values for environmental water testing and associated QCS. Observations for Seawater are discussed in Section 6.5. Control charts for these observations are presented in Appendix F. Two QC issues were indicated on control charts for observations corresponding to environmental samples: one observation was below the lower control limit and two consecutive samples (including that observation mentioned) were below the lower warning limit. However, the QCS observation conducted immediately after reaffirmed QC standards and these samples were retested following the iron interference procedure. Retesting was performed on four samples during environmental sample testing. On-site recalibration was required and a RCA was performed for raw well water samples suspected of containing high levels of Fe that interfered with the test. Five observations did not meet criteria for percent recovery when compared to reference concentrations. These observations were for matrices raw well water both without and with Fe removal pretreatment. This indicates that accurate measurement of Pb in this matrix is difficult even with Fe removal pretreatment. This could be because of other interferences which have not been identified. Discussion of the precision of triplicate samples for DEI is presented in Section 6.2.

Table 9. Percent Recovery for Environmental Water

Phase 2 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
1	QCS-9	Quality Control	30	24	29	80	83
2	RiW-25-1	River Water	25	21	20	84	105
3	RiW-25-2	River Water	25	24		96	120
4	RiW-25-3	River Water	25	16		**64**	80
5	RiW-25-3-RR1	River Water	25	23		92	115
6	ReW-25-1	Reservoir Water	25	23	21	92	110
7	ReW-25-2	Reservoir Water	25	20		80	95
8	ReW-25-3	Reservoir Water	25	23		92	110
9	RWW-25-1	Raw Well Water	25	13	18	**52**	**72**
10	RWW-25-1-RR1	Raw Well Water	25	12		**48**	**67**
11	QCS-10	Quality Control	30	24	26	80	92
12	RWW-25-1-RR2	Raw Well Water	25	16	18	**64**	89
13	RWW-25-1-RR3	Raw Well Water	25	21		84	117
14	RWW-25-2	Raw Well Water	25	18		**72**	100
15	RWW-25-2-RR1	Raw Well Water	25	14		**56**	78
16	RWWPT-25-1	Raw Well Water Pretreated	35	43	21	123	**205**
17	RWWPT-25-2	Raw Well Water Pretreated	35	32		91	**152**
18	RWWPT-25-3	Raw Well Water Pretreated	35	26		**74**	124
19	RWWPT-25-3-RR1	Raw Well Water Pretreated	35	31		89	**148**

Percent recovery values that do not meet criteria are shaded and bold font.

Table 9 presents the expected concentrations, observations, reference concentrations, and percent recovery values for finished drinking water testing and associated QCS. Control charts for these observations are presented in Appendix F. Two QC issues were indicated on control charts for observations corresponding to drinking water samples related to QCS testing: one observation was above the upper control limit and two consecutive samples were above the upper warning limit. Furthermore, many of these QCS observations did not meet percent recovery criteria. However, the only finished drinking water sample tested during this time resulted in an average percent recovery. Additionally, the last QCS was retested and resulted in an acceptable percent recovery, and no QC issues were identified in the following control charts. Retesting was performed on three samples during drinking water sample testing. On-site recalibration was required twice during drinking water testing. During testing, Bottled Water did not appear to meet QC criteria and a RCA was performed. It was determined that these observations were in fact within QC criteria once reference data were received. Four observations related to the QCS testing did not meet criteria for percent recovery when compared to reference concentrations. This result was unexpected as QCS samples were prepared in DI water. It is possible that analysis of FWW conducted immediately before the QCS samples had a negative impact on subsequent analysis of QCS samples. Discussion of the precision of triplicate samples for DEI is presented in Section 6.2.

Table 10. Percent Recovery for Finished Drinking Water

Phase 2 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
20	FWW-25-1	Finished Well Water	25	23	24	92	96
21	FWW-25-2	Finished Well Water	25	21		84	88
22	QCS-11	Quality Control	30	43	28	**143**	**154**
23	QCS-11-RR1	Quality Control	30	37		123	**132**
24	FWW-25-3	Finished Well Water	25	19	24	76	79
25	QCS-12	Quality Control	30	40	28	**133**	**143**
26	QCS-12-RR1	Quality Control	30	46		**153**	**164**
27	QCS-12-RR2	Quality Control	30	33		110	118
28	QCS-13	Quality Control	30	27	29	90	93
29	WF-25-1	WF	25	19	21	76	90
30	WF-25-2	WF	25	24		96	114
31	WF-25-3	WF	25	25		100	119
32	BW-25-1	Bottled Water	25	18	20	**72**	90
33	BW-25-1-RR1	Bottled Water	25	17		**68**	85
34	BW-25-1-RR2	Bottled Water	25	16		**64**	80
35	BW-25-1-RR3	Bottled Water	25	17		**68**	85
36	BW-25-1-RR4	Bottled Water	25	18		**72**	90

Percent recovery values that do not meet criteria are shaded and bold font.

Table 10 presents the expected concentrations, observations, reference concentrations, and percent recovery values for wastewater effluent testing and associated QCS. Control charts for these observations are presented in Appendix F. No QC issues were indicated on control charts for observations corresponding to wastewater effluent samples. Retesting was performed on two samples during wastewater effluent testing, and on-site recalibration was required once. Nevertheless, five observations did not meet criteria for percent recovery when compared to reference concentrations which were all associated with MWWE#2. It is unknown why measurement of Pb in MWWE#2 did not meet the percent recovery criterion, however, it is possible that some unidentified interference was present in this matrix. Discussion of the precision of triplicate samples for DEI is presented in Section 6.2.

Table 11. Percent Recovery for Wastewater Effluent

Phase 2 Sample Number	Sample Name	Sample Type	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target	Percent Recovery to ICP-MS
37	MWWE#1-25-1	Wastewater 1	25	20	19	80	105
38	MWWE#1-25-2	Wastewater 1	25	19		76	100
39	MWWE#1-25-3	Wastewater 1	25	17		**68**	89
40	MWWE#1-25-3-RR1	Wastewater 1	25	21		84	111
41	QCS-14	Quality Control	30	23	30	77	77
42	MWWE#2-25-1	Wastewater 2	25	28	20	112	**140**
43	MWWE#2-25-2	Wastewater 2	25	34		**136**	**170**
44	MWWE#2-25-2-RR1	Wastewater 2	25	33		**132**	**165**
45	MWWE#2-25-2-RR2	Wastewater 2	25	26		104	**130**
46	MWWE#2-25-3	Wastewater 2	25	23		92	115
47	MWWE#2-25-4	Wastewater 2	25	26		104	**130**
48	MFWWE-25-1	Metal Finishing	25	22	24	88	92
49	MFWWE-25-2	Metal Finishing	25	21		84	88
50	MFWWE-25-3	Metal Finishing	25	23		92	96
51	QCS-15	Quality Control	30	31	30	103	103

Percent recovery values that do not meet criteria are shaded and bold font.

6.2 Precision

Table 11 presents the mean observation values, SDs, and CVs for all samples analyzed in triplicate. Although Seawater was analyzed in triplicate, quantitative analysis of accuracy and precision is not presented in Table 11 as described in the original QAPP document. Discussion of Seawater results is presented in Section 6.5. The majority of the tested samples had CV values <0.10. The triplicate measurements which had CV values ≥0.10 are IDC-25, DLR-5, DLR-100, LTDS-25, LTDS-50, HFe-25, RWWPT-25, FWW-25, WF-25 and MWWE#2-25 the these are shaded in Table 12. It is unclear why IDC and LTDS samples had CV ≥ 0.10 as these were DI water and relatively simple matrices, respectively. DLR-5 and DLR-100 are at the bottom and top of the limits of detection, respectively and may have spread the data. HFe and RWWPT samples required pretreatment of the samples and may have spread the data. FWW contained Fe, but was not pretreated and this may have spread the data for this sample. It is unclear why WF and MWWE#2 samples have CV ≥ 0.10.

6.3 Linearity of Response

Figure 5 presents observations from DLR sample testing plotted against reference concentrations from ICP-MS analysis. The x-axis of Figure 5 is the ICP-MS reference concentration and the y-axis is the corresponding measured mean concentration. The error bars represent the standard deviation of the measured concentration which are provided in Table 9. Linearity was calculated in terms of slope, intercept, and the the square of the correlation coefficient (r^2) as 0.8841, -0.8418, and 0.9927, respectively.

Table 12. Precision of Samples Analyzed in Triplicate

Sample Name	Sample Type	ICP-MS Concentration (µg/L Pb)	Mean Observation (µg/L Pb)	Standard Deviation	CV
IDC-25	IDC	27	20	1.00	0.05
ICC-25	ICC	22	22	2.65	0.12
DLR-5	DLR	5	4	0.58	0.13
DLR-15	DLR	14	13	1.15	0.09
DLR-25	DLR	29	20	1.53	0.08
DLR-50	DLR	53	48	2.89	0.06
DLR-75	DLR	83	76	2.65	0.03
DLR-100	DLR	109	93	11.14	0.12
LTDS-25	Low TDS	25	22	3.06	0.14
LTDS-50	Low TDS	47	42	4.04	0.10
HTDS-25	High TDS	21	24	2.00	0.08
HTDS-50	High TDS	49	45	3.21	0.07
HFe-25	High Fe	22	21	2.65	0.13
HFe-50	High Fe	45	44	1.53	0.03
RiW-25	River Water	20	23	1.53	0.07
ReW-25	Reservoir Water	21	22	1.73	0.08
RWWPT-25	Raw Well Water Pretreated	21	35	6.66	0.19
FWW-25	Finished Well Water	24	21	2.00	0.10
WF-25	WF	21	23	3.21	0.14
BW-25	Bottled Water	20	18	0.58	0.03
MWWE#1-25	Wastewater 1	19	20	1.00	0.05
MWWE#2-25	Wastewater 2	20	26	2.52	0.10
MFWWE-25	Metal Finishing	24	22	1.00	0.05

Shaded values indicate CV ≥0.10

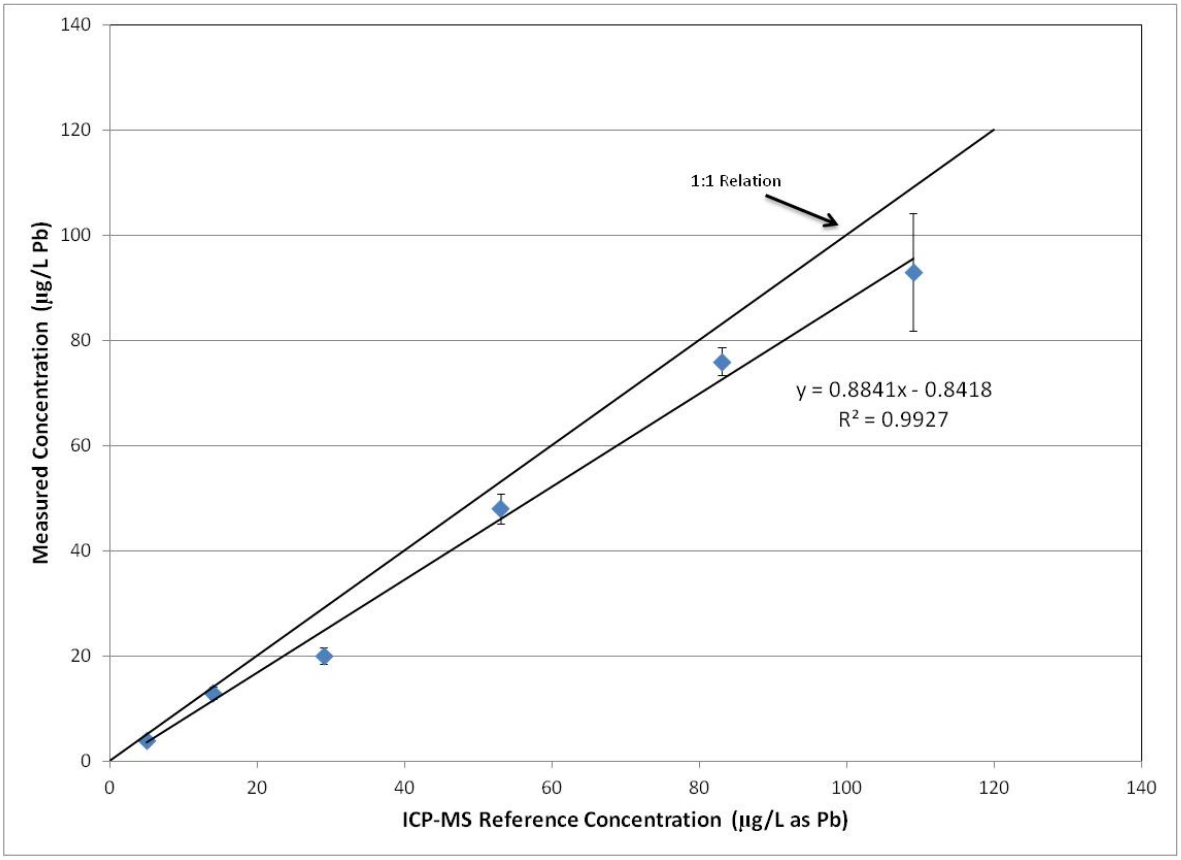


Figure 5. Observations from DLR Sample Testing versus Reference Concentrations

6.4 Limit of Detection

Table 12 presents the results of DLOD testing in addition to some statistical analyses. The Student's t-test value for α of 0.01 and 6 degrees of freedom is 3.143. The LOD of the Lead100/AND1000 was determined by Equation 7 to be 1.534 µg/L Pb, which is below the vendor's estimated detection limit.

Table 13. Results of DLOD Testing

Sample Name	Sample Type	ICP-MS Concentration (µg/L Pb)	Observation (µg/L Pb)	Mean Observation	Standard Deviation
DLOD-10-1	DLOD	9	8	8.3	0.488
DLOD-10-2	DLOD		8		
DLOD-10-3	DLOD		9		
DLOD-10-4	DLOD		8		
DLOD-10-5	DLOD		8		
DLOD-10-6	DLOD		8		
DLOD-10-7	DLOD		9		

6.5 Qualitative Results

Table 13 presents precision results for Seawater samples. The coefficients of variation for Seawater observations were significantly higher than those associated with any other test. This was expected due to the high salinity of the samples as communicated by the vendor prior to testing. However, observations aligned with reference concentrations (i.e., no observations for samples prepared with 20 µg/L Pb were greater than any observations for samples prepared with 40 µg/L Pb). This demonstrates that the Lead100/AND1000 is capable of indicating whether seawater has a high or low concentration of Pb, despite its low precision when analyzing seawater samples.

Table 14. Precision of Seawater Testing

Sample Name	Sample Type	ICP-MS Concentration (µg/L Pb)	Mean Observation (µg/L Pb)	Standard Deviation	CV
SW-25	Seawater	20	24	9.84	0.42
SW-50	Seawater	40	60	18.93	0.32

6.6 Operational Factors

In general, the ease of use of the Lead100/AND1000 was high. In several cases, the rechargeable battery provided with the AND1000 lost power after less than 8 hours. In addition, in one instance, the instrument displayed a screen that was foreign to the user making the instrument unusable. Simply turning the instrument off and rebooting retuned the AND1000 to normal working order. The Lead100 test kits generate a significant amount of solid waste if many tests are performed; this could make field measurements under some conditions difficult, although this claim is specific to field testing conditions and not an issue when testing under laboratory conditions.

Chapter 7
Performance Summary for the Lead100/AND1000

7.1 Performance Summary for the Lead100/AND1000

The performance of the Lead100/AND1000 was evaluated for its accuracy, precision, linearity of response, LOD, and other operational factors. Prevailing water quality characteristics dictated by environmental conditions (e.g., pH, major anions, major cations) and water quality characteristics artificially imparted on synthetic environmental or laboratory samples, including synthetic matrices and Pb spikes, were varied to challenge the Pb detection technology under a variety of conditions.

The accuracy of the Lead100/AND1000 was evaluated by comparing percent recovery to reference observations for samples with a variety of prevailing water quality characteristics and characteristics artificially imparted on the laboratory samples. Average percent recoveries for IDC and ICC testing were determined to be 74% and 100%, respectively. Average percent recoveries for DLOD and DLR testing were determined to be 92% and 86%, respectively. Average percent recovery for DEI testing was determined to be 96%. Average percent recoveries for River Water, Reservoir Water, and Raw Well Water were determined to be 113%, 105%, and 168%, respectively. Average percent recoveries for Finished Well Water, WF, and Bottled Water were determined to be 88%, 108%, and 88%, respectively. Average percent recoveries for Wastewater Effluent and Metal Finishing Wastewater Effluent were determined to be 117% and 92%, respectively.

The precision of the Lead100/AND1000 was evaluated by statistical analysis of triplicate observations, summarized by the mean value, SD, and CV presented in Table 12. Average CV across all triplicate samples was determined to be 0.09. Moreover, the greatest CV determined for triplicate observations was 0.19 (for pretreated Raw Well Water), indicating that SD of less than 20% of the mean value should be expected during proper operation of the Lead100/AND1000 within its reported operating range by a trained individual.

The linearity of response of the Lead100/AND1000 was evaluated by statistical analysis of DLR testing observations, summarized by the linear regression equation. Linearity was calculated in terms of slope, intercept, and the square of the correlation coefficient (r^2) as 0.8841, -0.8418, and 0.9927, respectively. This is indicative of a nearly linear response across the reported operating range of the Lead100/AND1000 for synthetic samples prepared with reagent grade water.

The LOD of the Lead100/AND1000 was evaluated by statistical analysis of DLOD testing observations. The LOD of the Lead100/AND1000 was determined to be 1.534 µg/L Pb, which is below the vendor's estimated detection limit of 2 µg/L.

Observations of Seawater testing were evaluated qualitatively rather than quantitatively. Average percent recovery for Seawater was determined to be 131% and CV was reported as high as 0.42 for Seawater samples. However, high Pb observations in Seawater samples coincided directly with high Pb reference concentrations. This verifies that the Lead100/AND1000 is capable of indicating high or low Pb concentrations in seawater, albeit with less precision and accuracy than in other matrices.

Operational factors were also evaluated for the Lead100/AND1000. Observations of short battery life (i.e., power loss after less than 8 hours of operation) were recorded, as well as observations of unexplained errors necessitating device restart. However, these observations were infrequent. In addition, if it were necessary to conduct many tests over a short period of time, a significant amount of waste would be generated. Recalibration was necessary for 5 LFM and LFMD samples and retesting was required for 17 LFM and LFMD samples during Round 2 testing due to QC inconsistencies. However, in some instances, QC inconsistencies were misidentified during testing due to actual spike concentrations being outside of acceptable ranges. Total training time for the VTC included three days of vendor training between Rounds 1 and 2 and one week of vendor observation during Round 2 testing to ensure proper sample preparation and preservation due to Round 1 retesting.

Other general limitations were identified during the performance evaluation. The Lead100/AND1000 detects only lead in the dissolved phase. Water treatment systems are required to monitor for total (particulate and dissolved) lead under the Lead and Copper Rule and research indicates that a significant proportion of lead in drinking water systems at the customer tap may be particulate lead. Secondly pH is an important parameter to measure when using the technology because samples must be in a limited pH range to ensure accurate results, according to vendor specifications..

Chapter 8
References

1. *Quality Assurance Project Plan for Verification of ANDalyze Lead100 Test Kit and AND1000 Fluorimeter*. U.S. Environmental Technology Verification Program, Battelle, 2012.
2. *Quality Management Plan for the ETV Advanced Monitoring Systems Center, Version 8.* U.S. EPA Environmental Technology Verification Program, Battelle, April 2011.
3. *Quality Assurance Project Plan Deviation Report: "Verification of ANDalyze Lead100 Test Kit and AND1000 Fluorimeter" (July 3, 2012).* U.S. Environmental Technology Verification Program, Battelle, 2012.
4. Touring Ohio Magazine. 2012. Scioto River. Available at: http://www.touring-ohio.com/central/columbus/scioto-river.html.
5. *Standard Methods for the Examination of Water and Wastewater, 22nd Edition,* American Public Heath Association/American Water Works Association, Rice, E.W., Baird, R.B., Eaton, A.D. and Clesceri, L.S. (ed.).

Appendix A
Summary of Deviations from the QAPP

Deviation (Date)	**Description**	**Cause**	**ETV Report Location**	**Original QAPP Location**
No. 1 (11/13/12)	In order to ensure that lead-spiked samples used for ANDalyze tests and ICP-MS were identical in treatment, lead spikes were made after specific sample matrices have been filtered to remove suspended material (the putative sequestration phase).	ANDalyze analysis is designed to detect only dissolved lead for this verification. During the previous testing Battelle and ANDalyze discovered that matrix composition (especially environmental waters) can have a significant effect on lead partitioning between bioavailable and sequestered phases, which can lead to low recoveries compared to expected values. This deviation was to clarify experimental procedures which were believed to lead to low recovery of Pb using both ICP-MS and Lead100/AND1000 during testing conducted according to procedures described in the original QAPP	Section 3.3	Section B 1.1
No. 2 (11/13/12)	ANDalyze document AND-Sol-Env-02-2012 ("Environmental Water Testing: Surface Water, Groundwater, Hard Water, Wastewater, & Seawater") was revised to clarify the specific protocol for on-site calibration of environmental samples (to be included as a replacement to Appendix C of the QAPP; see below). Specifically, this document was revised to include filtration and incubation requirements for environmental samples.	ANDalyze analysis is designed to detect only dissolved lead for this verification. During the previous testing Battelle and ANDalyze discovered that matrix composition (especially environmental waters) can have a significant effect on lead partitioning between bioavailable and sequestered phases, which can lead to low recoveries compared to expected values. This deviation was to clarify experimental procedures which were believed to lead to low recovery of Pb using both ICP-MS and Lead100/AND1000 during testing conducted according to procedures described in the original QAPP.	Section 3.3	Section B1.1 and Appendix C
No. 3 (11/13/12)	Utilizing the requirements for QA/QC samples detailed in Standard Methods for the Examination of Water and Wastewater, 22nd Edition 1020 B and 40 CFR part 136.7, QA/QC requirements have been added to standard QA/QC requirements of EPA Method 200.8. These requirements are discussed in detail in Section 4.3 of this document.	It was believed that the root cause of low recoveries determined by ICP-MS lied in the QA/QC procedures employed by the commercial laboratory.	Section 4.3	Section B5.2 and Appendix J
No. 4 (11/13/12)	Procedures for preparation of the HFe sample were clarified. As stated in ANDalyze document AND-Sol-Lead-05-2012 ("Iron Interference with Lead100 Sensor"), pH must be adjusted carefully to 6.5-8.0 using a pH meter before lead is spiked. It is important to carefully adjust pH with constant stirring and to wait two minutes and re-test the pH to ensure no drift has occurred.	In prior sample testing the Battelle-prepared HFe sample had a starting pH ~ 3 due to the acidic iron solution that was used in their preparation. This is not typical for natural ground water samples that have high iron content.	Section 3.3	Section B1.1 and Appendix D

Deviation (Date)	**Description**	**Cause**	**ETV Report Location**	**Original QAPP Location**
No. 5 (11/13/12)	Battelle and ANDalyze agreed that the tests would be conducted in three phases. The test results, which include ANDalyze sensor test results, root cause analyses (if applicable), and the ICP-MS results were reviewed by ANDalyze and discussed with Battelle at the end of each phase or during each phase before commencement of the next phase. The three phases are described as: • Phase 1: Performance testing • Phase 2: Finished drinking water testing and environmental water testing • Phase 3: Wastewater testing	Testing was not able to be completed in the timeframe allotted by the QAPP when root cause analyses were required. Communication between phases of testing reduces the risk of repeating large portions of testing due to unforeseen QA/QC issues.	Section 3.1	Section B1.1

Appendix B

QAPP Document Replacement Appendices (C and D) and Additional Appendices (I and J)

Environmental Water Testing: Surface Water, Groundwater, Hard Water, Wastewater, & Seawater

Matrix-specific sample preparation and testing methods for environmental waters

Problem Statement

1. ANDalyze metal test kits are designed for use out of the box with drinking water; however they can be used for environmental water analysis with some minor protocol modifications.
2. Below are instructions for testing samples obtained from sources such as:
   - Surface Water (rivers, lakes, ponds)
   - Ground Water (wells, aquifers)
   - Hard or Very Hard Water (multiple sources)
   - Treated Wastewater – Finished or treated and diluted tenfold
   - Seawater (from the surface, not the sediment/water column interface)

Materials

Each matrix type may require one or more of the following pre-treatment kits. Read guidelines for each matrix. Kits may be purchased from ANDalyze wherever indicated or individual components for pre-treatment may be purchased through a scientific supply company.

ANDalyze Dilution Kit
- 50 mL Self-standing sample tube
- 5 mL Fixed Volume Pipette
- Reagent grade water

ANDalyze pH Adjustment Kit
- Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide in a dropper bottle
- Nitric Acid Neutralization Solution, 1.5% (v/v) nitric acid in a dropper bottle
- pH paper

ANDalyze Iron Interference Kit
- Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide in a dropper bottle
- Hydrogen Peroxide Solution, 30% (w/w) hydrogen peroxide in a dropper bottle

ANDalyze Filtration Kit **(Available now from ANDalyze)**
- 0.2 µm Nylon filter, 25 mm diameter (Nalgene)
- 20 mL Syringe
- 50 mL Self-standing sample tube

Solution Statement

ANDalyze kits may be used to test many different environmental waters. Each matrix may require different pretreatment steps. Please see the general protocols below for: (1) Dilution, (2) pH Adjustment, (3) Filtration, and (4) Environmental Water On-site Calibration. Matrix-specific instructions, including necessary protocols, are presented following the protocols.

Note: Our tests have shown that the percent recovery for lead in environmental samples is ~60 % for less than 25 ppb lead and 75-125 % for 25-100 ppb lead. The percent recovery for uranium in environmental samples is > 60% for less than 30 ppb uranium and 75 – 125 % for 30 – 60 ppb uranium. Copper is less well characterized in environmental matrices, though the copper sensor is tolerant of high salt conditions.

General Protocols

---

(1) General Protocol - Dilution

Dilution is needed for accurate readings if the target metal ion is present at a concentration higher than the linear detection range stated in the *Testing and Calibration* manual. Linear detection ranges are noted below:

Lead100 sensor – 2-100 ppb Lead
Uranium100 sensor – 2-60 ppb Uranium
Copper High Range – 0.6-3 ppm Copper
Copper Low Range – 40-200 ppb Copper
Mercury100 Range – 2-50 ppb Mercury

The ANDalyze Copper sensor is available in two ranges and therefore dilution is usually not required.

1. **Dilution is best performed using standard laboratory glassware** and reagent grade water – one volume sample to nine volumes reagent grade water.
2. **Dilution may also be performed in the field**, with a decrease in accuracy, by withdrawing 5 mL sample with a 5 mL fixed volume pipette, adding the aliquot to a 50 mL self-standing tube, and filling to the 50 mL mark with reagent grade water. Shake well.
3. **If the sample is diluted**, on-site calibration must be performed with the diluted sample.

(2) General Protocol - pH Adjustment

ANDalyze Lead, Mercury and Copper sensors perform best when the sample pH is between 5 and 8 (pH 4-7 for Uranium). Samples with a pH greater than 8 or below 5 will not test reliably for Lead, Mercury, or Copper (greater than 7 or below 4 for Uranium). It is required to adjust the pH into this range before sample preparation steps and testing can continue. Samples above pH 10 should not be tested even with pH adjustment.

1. **Check the sample pH** using pH paper.
2. **Prepare the following solutions** if pH adjustment is required
    1. Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide
    2. Nitric Acid Neutralization Solution, 1.5% (v/v) nitric acid
3. **Adjust the sample pH**
    1. **If the sample is below pH 5** (or pH 4 for U) addition of a dilute sodium hydroxide solution is necessary. To a 50 mL volume of sample add the Sodium Hydroxide Neutralization Solution dropwise with stirring or with shaking between addition of each drop. Do not titrate beyond pH 5 for Lead, Mercury, and Copper and pH 4 for Uranium.

        Note: pH change from 4-5 is rapid, requiring a half drop or less. **Check the pH multiple times during titration.** The number of drops required depends heavily on matrix constituents. As few as four drops may be sufficient to increase pH from 3 to 4, or many more may be required.

    2. **If the sample is above pH 8** for Lead, Mercury, and Copper (above pH 7 for Uranium) addition of a dilute nitric acid (1.5 %) solution is necessary. Samples above pH may be unsuitable for testing even with pH adjustment as metal ion may have already precipitated out.

        Note: pH change from 9-8 is rapid, requiring a half drop or less depending on matrix. **Check the pH multiple times during titration.** The number of drops required depends heavily on matrix constituents. As few as four drops may be sufficient to decrease pH from 10 to 7, or many more may be required.

Note: For highly basic water samples, acidification may be insufficient to solubilize precipitated metals.

(3) – General Protocol - Filtration

1. **Obtain an ANDalyze Filtration Kit.** Before testing or spiking any environmental water sample, it must be filtered to remove suspended solids.

2. **Filter the water sample.** Draw ~20 mL water sample into a 20 mL syringe, securely attach the filter, and dispense into the self-standing vial.

   Note: If the sample is collected off-site and transported to a laboratory for testing, ensure that the sample is stirred (*e.g.*, stir-bar in the bottom of a 1 L HDPE Nalgene bottle filled with sample on a stir plate) while filling the syringe to ensure homogeneity.

3. The sample should be clear and the filter may no longer be white.

   Note: If a sample contains a great deal of suspended solids the syringe filter may clog after elution of 10-20 mL sample. In this case, discard the clogged filter and use a fresh filter to continue filtering the sample.

(4) General Protocol - Environmental Water On-site Calibration

On-site calibration is performed for all new samples and any time a matrix may have changed, *e.g*. new sampling day, change in matrix composition, new sensor batch, temperature change, etc. If in doubt, perform On-site Calibration.

Important: For environmental samples, filtration (with 0.2 µm Nylon filter) is required before the 100 µL standard metal solution spike. After filtration and spiking, it is required to incubate the calibration spike with the sample for at least 5 minutes as the spiked metal takes some time to reach equilibrium between dissolved and bound states. Failure to allow spike incubation in the sample will lead to lower recovery.

1. **Perform on-site calibration as described in the Product Manual.** After adding the 100 µL standard metal solution spike as per the instructions in the product manual, shake, and **let it sit for ~ 5 minutes** before the analysis is performed.

2. **Use all spiked solutions** within 15 minutes.

Note: The ANDalyze test kit is designed to test for bioavailable metals and not total metals without acid digestion, which is beyond the scope of this procedure.

Matrix-Specific Protocols

Surface Water Testing Protocol

ANDalyze has performed extensive testing of our kits in surface waters such as rivers, lakes, and streams. Some surface waters, such as runoff from industrial sites, heavily contaminated bodies of water, mine runoff, or areas affected by acid rain may exceed interference levels and the acceptable pH range. Special care may be needed in handling as well as testing these samples. Please contact ANDalyze with any questions.

Important: Testing of surface waters from rivers, lakes, and streams usually does not require dilution, pH adjustment, or iron interference removal. If required, perform those steps as stated in the protocols. Filtration, however, is always required.

Follow this order of steps:

1. **Check the pH using pH paper** and adjust if required.
2. **Filtration** is required as per the Filtration Protocol.
3. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of calibration spike) and instructions in the *Testing and On-site Calibration* manual.

Groundwater Testing Protocol

Important: Testing of raw or treated groundwater usually does not require dilution or pH adjustment. If required, perform those steps as stated in the protocols. Iron interference may be an issue and the solution color should be noted – yellow/orange color may be indicative of iron. Filtration is always required.

Follow this order of steps:

1. **Check the pH using pH paper** and adjust if required.
2. **Verify that iron interference is not an issue.** If interference is suspected, follow the Iron Interference Solution Note.
3. **Filtration** is required as per the Filtration Protocol.
4. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of calibration spike) and instructions in the *Testing and On-site Calibration* manual.

Note: ANDalyze has performed extensive testing of our kits in ground waters from across the U.S.A as well as in artificial matrices based on those in Standard Methods for the Examination of Water & Wastewater, Centennial Edition. As a general rule, performance in soft waters exceeds that of very hard waters, which are much more likely to exceed the interference level or pH range.

Hard Water Testing Protocol

ANDalyze, Inc. has performed extensive testing of our kits in simulated hard waters, including hard and moderately hard waters according to Standard Methods for the Examination of Water & Wastewater, Centennial Edition.

Important: Testing of hard waters usually does not require dilution, pH adjustment, or iron interference removal. If required, perform those steps as stated in the protocols. Filtration, however, may be required.

Follow this order of steps:

1. **Check the pH using pH paper** and adjust if required.
2. **Filtration** is required as per the Filtration Protocol **IF** the water is cloudy.
3. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of metal spike) and instructions in the *Testing and On-site Calibration* manual.

Wastewater Testing Protocol

Important: ANDalyze has tested multiple **finished or treated** wastewater matrices and analysis can be challenging depending on matrix constituents. **Raw wastewater** is **NOT** suitable for testing. Dilution of the sample (1:10) is absolutely required, which increases the **effective detection range tenfold**, *e.g.* the detection range for Lead after dilution is 20-1000 ppb. Analyte concentrations measured at the low end of the sensor ranges are **qualitative** rather than quantitative and the relative standard deviation of results is larger than experienced in drinking water.

Follow this order of steps:

1. **Precautions!** Wastewaters are complicated matrices and may contain interferences beyond other metal ions.
    - **Chelators** such as EDTA will cause false negatives. Chelators are present in many cleaning products and industrial processes, so check wastewater components carefully.
    - **Fluorescent compounds** will give a high background signal and results may be unreliable
    - **Very high concentration of other metal ions** – Example: Known metals from a metal finisher plant
    - **Wear personal protective equipment**. Wastewaters may have extreme pH values and contain hazardous components. Wear appropriate laboratory attire and use a fume hood as appropriate.

2. **Follow the Dilution Protocol to dilute the sample tenfold.** Remember that your effective detection range has increased tenfold.
3. **Check the pH using pH paper** and adjust if required.
4. **Verify that iron interference is not an issue.** If interference is suspected, follow the Iron Interference Solution Note.
5. **Filtration** is required as per the Filtration Protocol. If filters clog rapidly then pre-filtration through Whatman 3MM paper or acid digestion may be necessary.
6. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol and instructions in the *Testing and On-site Calibration* manual.
    1. **If on-site calibration fails, repeat.**
    2. **If on-site calibration fails again**, further dilution may be necessary. Dilute the sample another tenfold (total 100-fold dilution). Be aware that the analyte concentration may be out of the linear detection range upon 100-fold (total) dilution.

Note: Some waste water matrices have many interferences and cannot be effectively analyzed without acid digestion or other treatment procedures, which are beyond the scope of this solution note.

Seawater Testing Protocol

Important: Sample preparation steps for seawater are normally not necessary beyond filtration unless the sample is taken from a polluted area. This protocol is intended for analysis of seawater from the surface or water column with minimal sediment. Analyte concentrations measured are **qualitative/ semi quantitative** rather than quantitative and the relative standard deviations of results are larger than experienced in drinking water.

Follow this order of steps:

1. **Follow the Dilution protocol to dilute the sample tenfold**. Remember that your effective detection range has increased
2. **Filtration** is required as per the Filtration Protocol.
3. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol and instructions in the *Testing and On-site Calibration* manual.

Note: Bittern Water is a concentrated solution left over after crystallization of NaCl from seawater. It contains very high concentrations of interfering ions, notably magnesium. ANDalyze test kits may work in bittern water upon dilution of the sample by at least ten-fold if not 100-fold. Contact ANDalyze for further details.

Iron Interference with the Lead100 Sensor

Minimization of interference from soluble iron in environmental water

Problem Statement

The presence of soluble iron has a negative effect on sensor performance. The interference level for the ANDalyze Lead sensor is defined as the level of an ion at which the signal of a 30 ppb Pb^{2+} solution is changed by ±10%. The interference level for soluble Fe(III) is 40 ppb. Insoluble iron in the form of precipitates may be removed, at least in part, through natural settling or filtration. Steps to minimize interference are provided below.

Materials

ANDalyze pH Adjustment Kit

- Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide in a dropper bottle
- Nitric Acid Neutralization Solution, 1.5% (v/v) nitric acid in a dropper bottle
- pH paper

ANDalyze Iron Interference Kit

- Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide in a dropper bottle
- Sodium Hydroxide Neutralization Solution, 0.1% (w/w) sodium hydroxide in a dropper bottle
- Hydrogen Peroxide Solution, 30% (w/w) hydrogen peroxide in a dropper bottle

ANDalyze Filtration Kit **(Available now from ANDalyze)**

- 0.2 µm Nylon filter, 25 mm diameter (Nalgene)
- 20 mL Syringe
- 50 mL Self-standing sample tube

Solution Statement

Important: Ground water samples visibly orange in color are likely to contain high levels of iron (low ppm), though lower levels may not be easily detected with the naked eye. If it is suspected that the water sample to be tested contains interfering levels of iron, it may be prudent to test the iron concentration using a commercial iron test kit.

Important Safety Note: Refer to the product manual for general guidelines on safety, proper use, and general sample testing procedures before using the testing protocol listed in this solution note. Be very careful when handling the sodium hydroxide solution and the hydrogen peroxide solution. Wear gloves and eye protection. Exposure to concentrated hydrogen peroxide will result in burns. See the manufacturer Material Safety Data Sheet for further information.

Note: Although no individual ion may exceed the interference levels, a combination of many interfering ions close to the maximum levels may have an effect meeting or exceeding that of a single ion at the interference level.

pH Adjustment Protocol for Iron Interference

ANDalyze Lead sensors perform best when the sample pH is between 5 and 8. Samples with a pH greater than 8 or below 5 will not test reliably for Lead. Iron interference removal requires a narrower pH range of pH 6.5 to pH 8. It is **required** to adjust the pH into this range before sample preparation steps and testing can continue. **Samp~~les abov~~e pH 10 should not be tested for Lead**, even with pH adjustment.

1. **Check the sample pH** using pH paper.
    1. **Prepare or purchase from ANDalyze the following solutions** if pH adjustment is required
    2. Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide
    3. Sodium Hydroxide Neutralization Solution, 0.1% (w/w) sodium hydroxide
    4. Nitric Acid Neutralization Solution, 1.5% (v/v) nitric acid
2. **Adjust the sample pH**
    1. **If the sample is below pH 6.5** addition of a dilute sodium hydroxide solution is necessary. This is a strict limit and use of a pH meter instead of pH paper will ensure that the sample is at ~~leas~~t ~~pH 6.5. To a 50 mL volume of sample add the Sodium Hydroxide Neutralization Solution dropwi~~se with stirring or with shaking between addition of each drop. Do not titrate beyond pH 8 for Lead as it will precipitate out of solution. Once the correct pH has been achieved, wait 2 minutes and re-check to ensure that pH has stabilized

        Note: The number of drops required depends heavily on matrix constituents. As few as four drops of 1% (w/w) sodium hydroxide solution may be sufficient to increase pH from 3 to 4, or many more may be required. pH change from 4-6.5 is rapid; add 0.1% (w/w) sodium hydroxide solution to avoid over titration. **Check the pH multiple times during titration.**

    2. **If the sample is above pH 8** for Lead, addition of a dilute nitric acid (1.5 %) solution is necessary. Samples above pH 10 should not be tested even with pH adjustment.

        Note: pH change from 9-8 is rapid, requiring a half drop or less depending on matrix. **Check the pH multiple times during titration.** The number of drops required depends heavily on matrix constituents.

        Note: For highly basic water samples, acidification may be insufficient to solubilize precipitated metals.

Peroxide Treatment Protocol

The addition of hydrogen peroxide converts soluble iron to insoluble iron which can then be removed by filtration.

1. **Hydrogen peroxide addition.** Add 4 drops of the hydrogen peroxide solution to each ~50 mL water sample using a dropper, replace cap on the sample tube, mix well by inversion, then let sit on the bench for 20 min.

2. **After the 20 min incubation** continue with the Filtration Protocol described below.

Filtration Protocol

1. **Obtain an ANDalyze Filtration Kit.** Before testing or spiking any environmental water sample, it must be filtered to remove suspended solids.

2. **Filter the water sample.** Draw ~20 mL water sample into a 20 mL syringe, securely attach the filter, and dispense into the self-standing vial.

   Note: If the sample is collected off-site and transported to a laboratory for testing, ensure that the sample is stirred (e.g., stir bar in the bottom of a 1 L HDPE Nalgene bottle filled with sample on a stir plate) while filling the syringe to ensure homogeneity.

3. The sample should be clear and the filter may no longer be white.

   Note: If a sample contains a great deal of suspended solids the syringe filter may clog after elution of 10-20 mL sample. In this case, discard the clogged filter and use a fresh filter to continue filtering the sample.

After completion of the Filtration Protocol continue with On-site Calibration as described in the *Testing and On-site Calibration* manual.

Summary/Notes/References

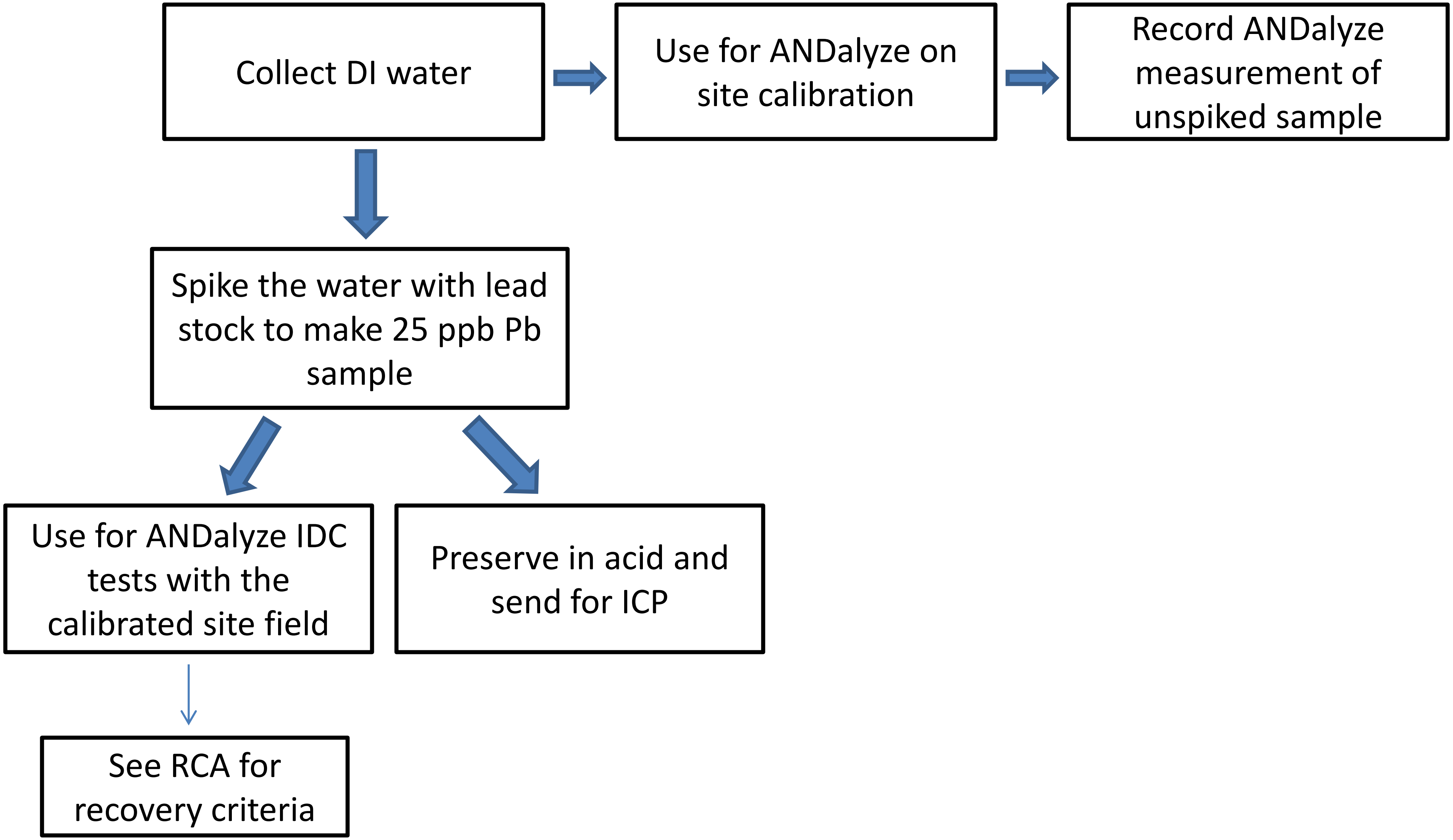
It is expected that, upon completion of this procedure, the interference from Iron will be greatly reduced and that a more accurate reading of Lead concentration will be obtained. It should be noted that some co-precipitation of Iron and Lead may be possible.

Appendix 1
QAPP Deviation -1

Flowchart for sample preparation, ANDalyze analysis, ICP analysis

Prepared by: Dr. Priya Mazumdar
(ANDalyze)

IDC Testing (page 47, section B1.1.8.1)



Collect DI water

Use for ANDalyze on site calibration

Record ANDalyze measurement of unspiked sample

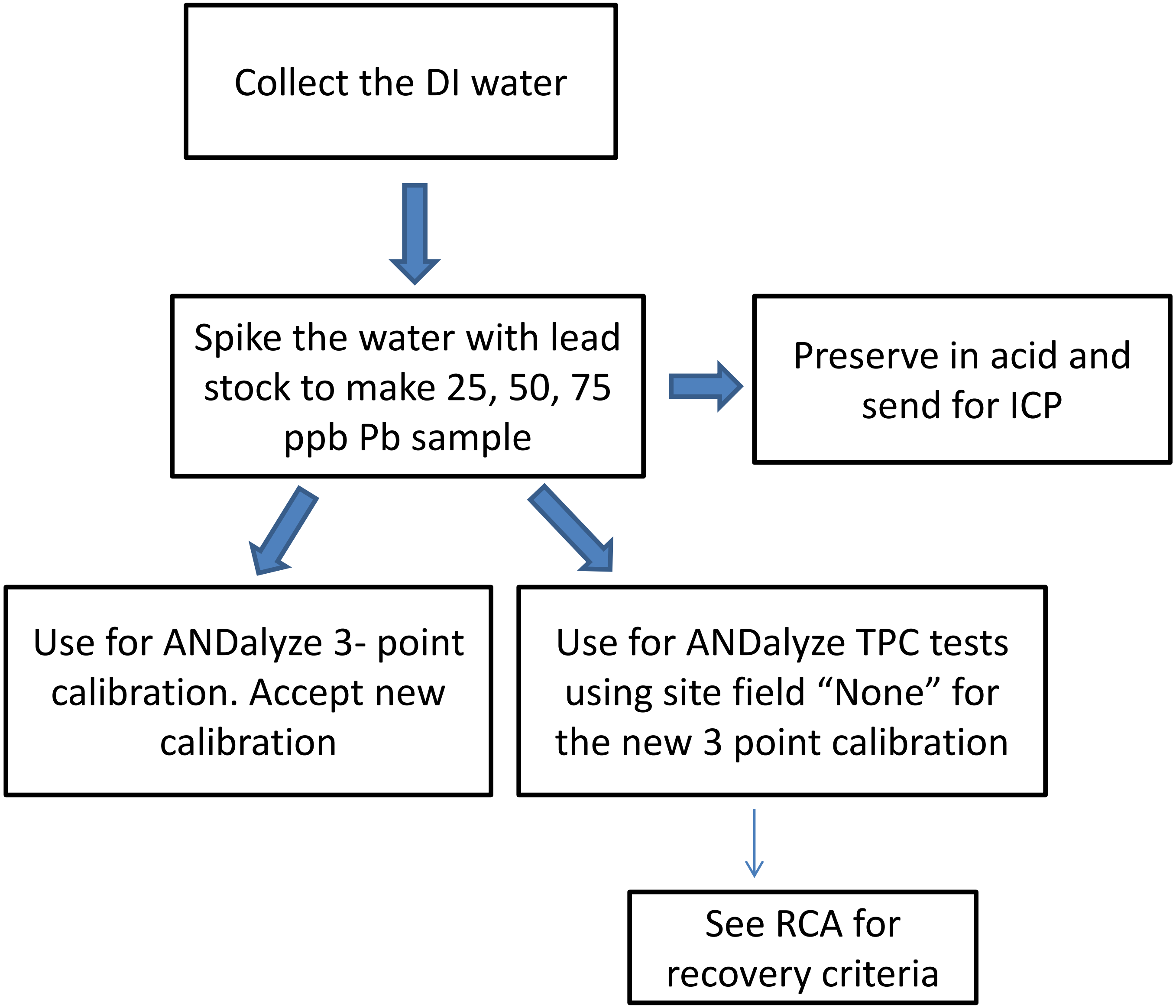
Spike the water with lead stock to make 25 ppb Pb sample

Use for ANDalyze IDC tests with the calibrated site field

Preserve in acid and send for ICP

See RCA for recovery criteria

TPC (page 47, section B1.1.8.2)



Collect the DI water

Spike the water with lead stock to make 25, 50, 75 ppb Pb sample

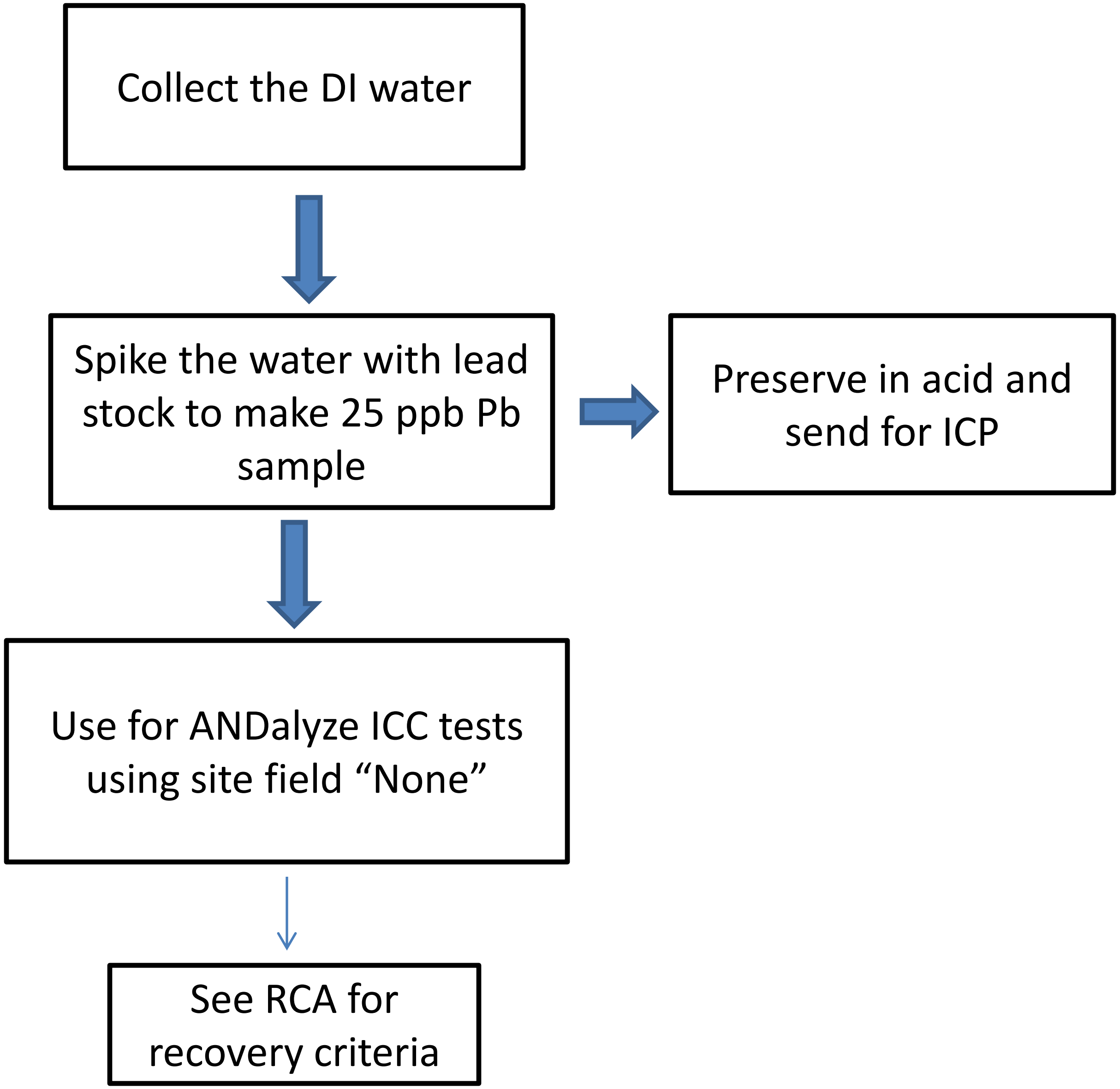
Preserve in acid and send for ICP

Use for ANDalyze 3- point calibration. Accept new calibration

Use for ANDalyze TPC tests using site field “None” for the new 3 point calibration

See RCA for recovery criteria

ICC (page 49, section B1.1.8.3)



Collect the DI water

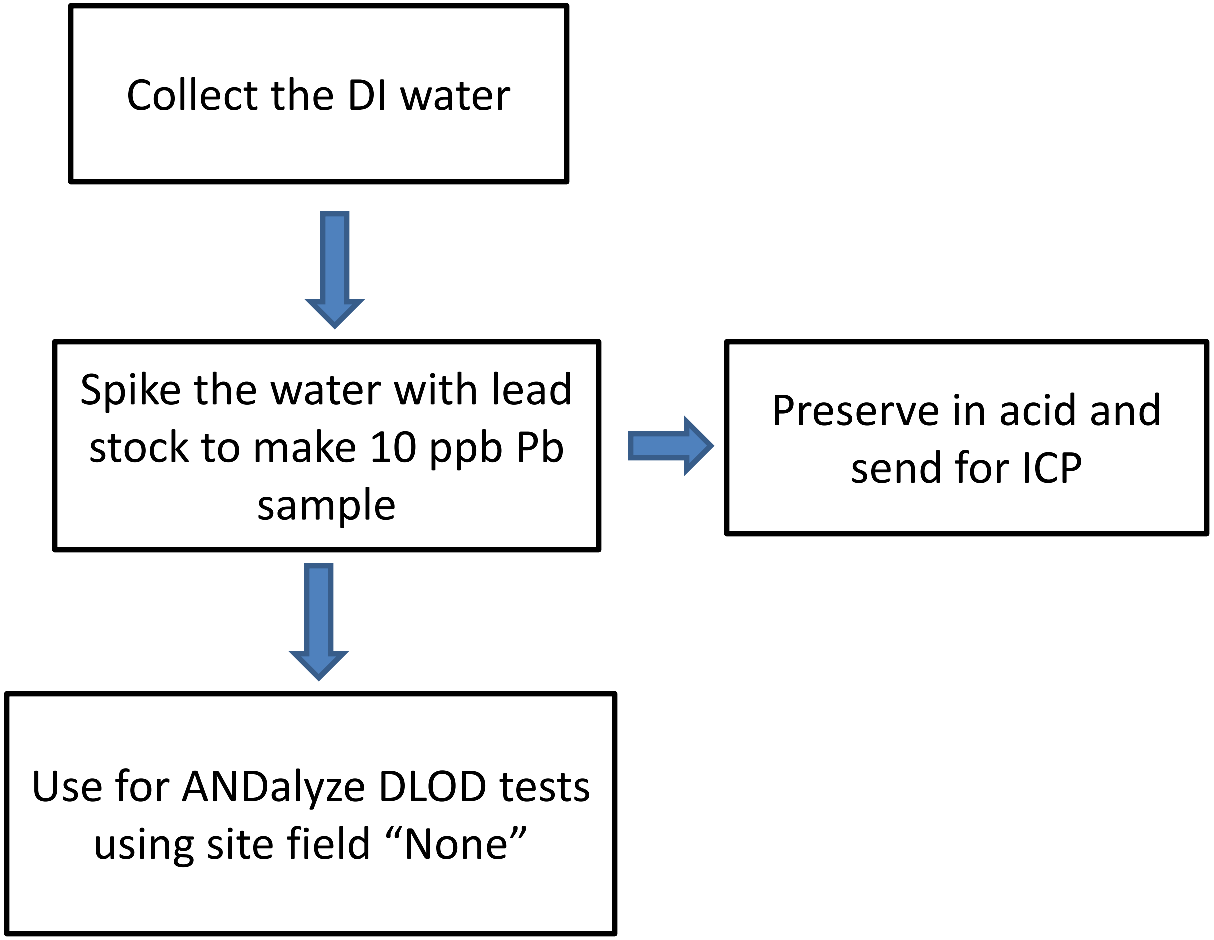
Spike the water with lead stock to make 25 ppb Pb sample

Preserve in acid and send for ICP

Use for ANDalyze ICC tests using site field “None”

See RCA for recovery criteria

DLOD (page 49, section B1.1.8.4)



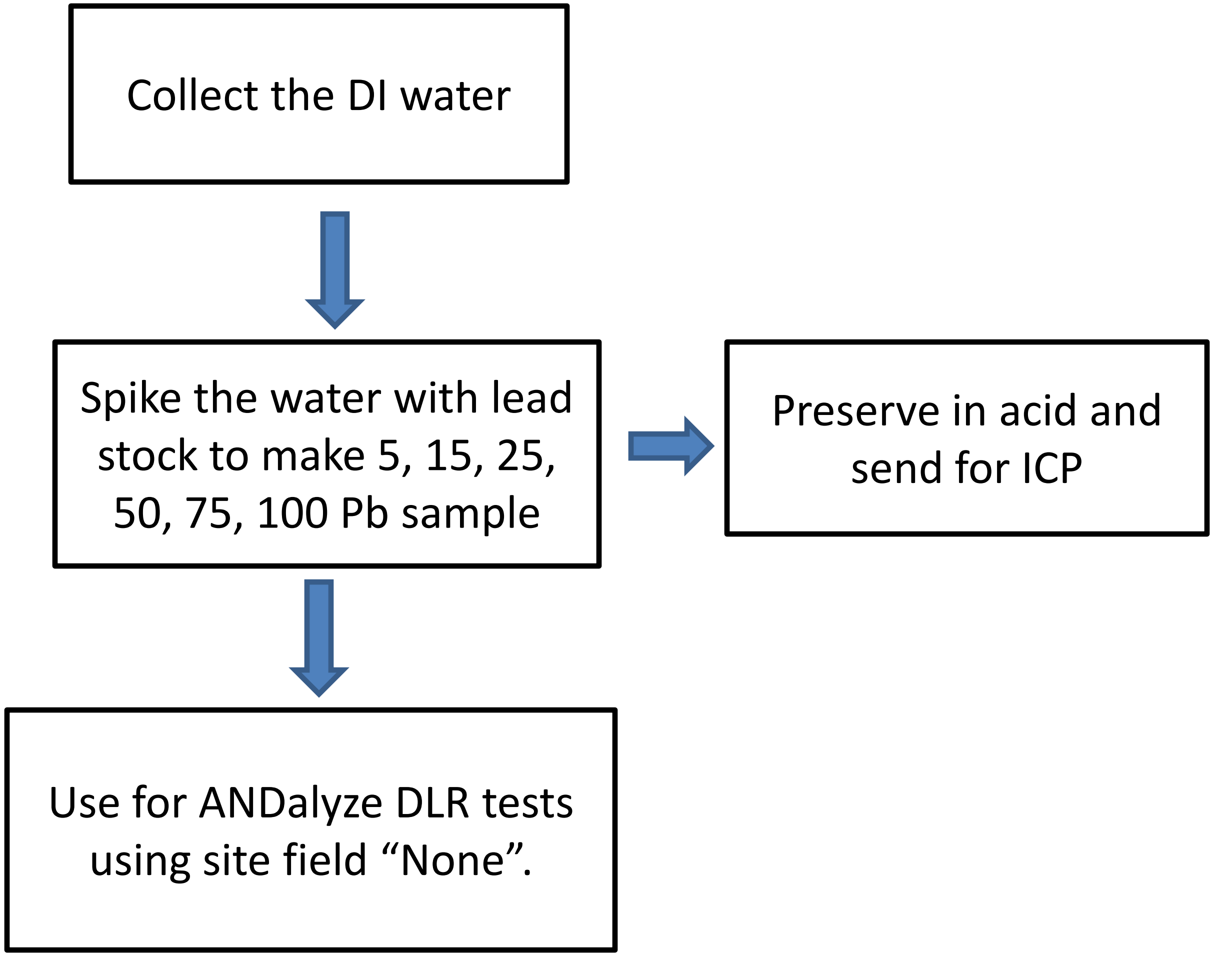
Collect the DI water

Spike the water with lead stock to make 10 ppb Pb sample

Preserve in acid and send for ICP

Use for ANDalyze DLOD tests using site field “None”

DLR (page 50, section B1.1.8.5)



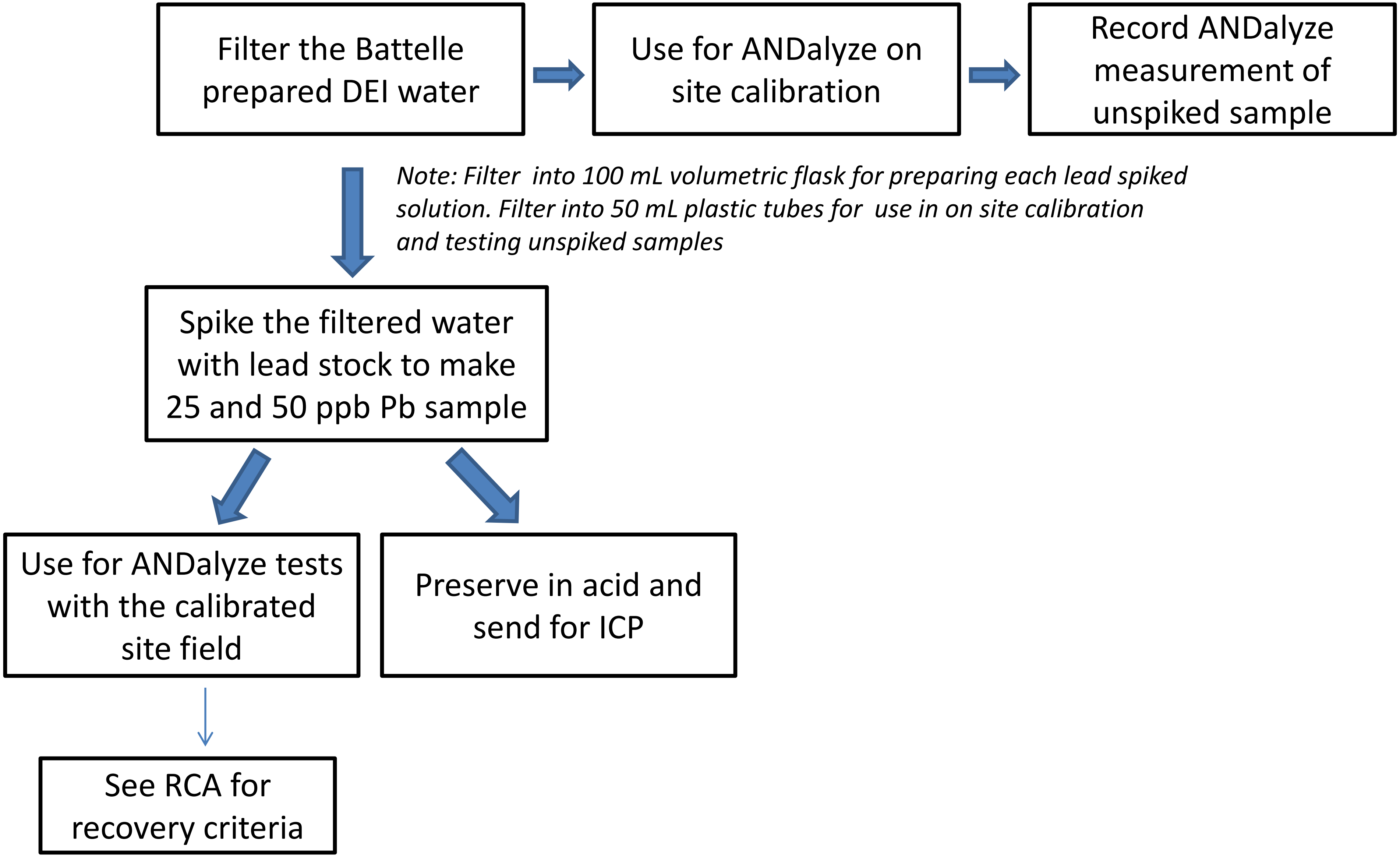
Collect the DI water

Spike the water with lead stock to make 5, 15, 25, 50, 75, 100 Pb sample

Preserve in acid and send for ICP

Use for ANDalyze DLR tests using site field “None”.

DEI Testing – for high TDS, low TDS, High Fe Water (page 50, section B1.1.8.1)



Filter the Battelle prepared DEI water

Use for ANDalyze on site calibration

Record ANDalyze measurement of unspiked sample

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

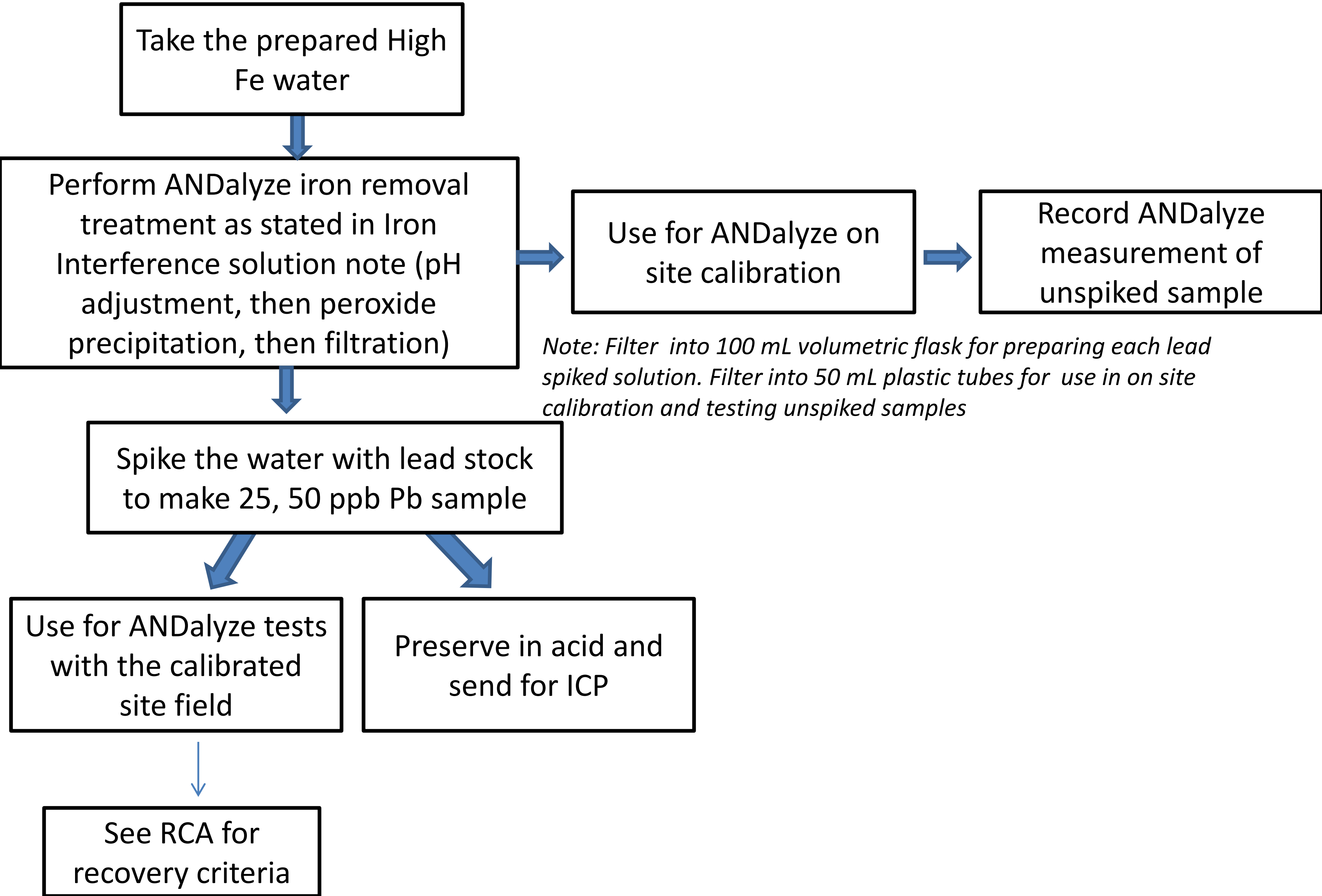
Spike the filtered water with lead stock to make 25 and 50 ppb Pb sample

Use for ANDalyze tests with the calibrated site field

Preserve in acid and send for ICP

See RCA for recovery criteria

DEI Testing – High Fe Water (page 50, section B1.1.8.1) with ANDalyze iron interference treatment



Take the prepared High Fe water

Perform ANDalyze iron removal treatment as stated in Iron Interference solution note (pH adjustment, then peroxide precipitation, then filtration)

Use for ANDalyze on site calibration

Record ANDalyze measurement of unspiked sample

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

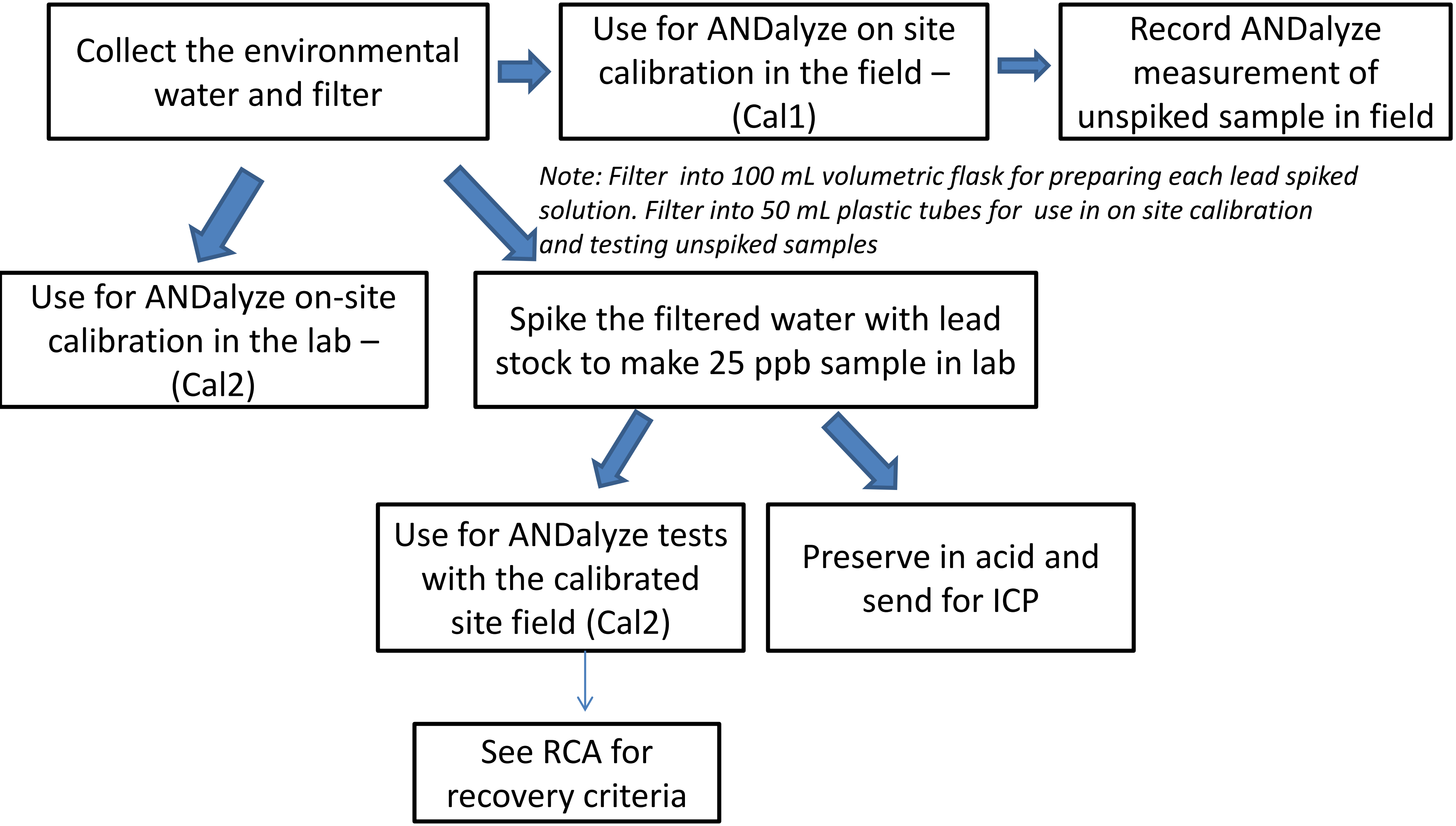
Spike the water with lead stock to make 25, 50 ppb Pb sample

Use for ANDalyze tests with the calibrated site field

Preserve in acid and send for ICP

See RCA for recovery criteria

Finished drinking Water (page 51, section B1.1.8.7) – Field test + Lab test



Collect the environmental water and filter

Use for ANDalyze on site calibration in the field – (Cal1)

Record ANDalyze measurement of unspiked sample in field

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

Use for ANDalyze on-site calibration in the lab – (Cal2)

Spike the filtered water with lead stock to make 25 ppb sample in lab

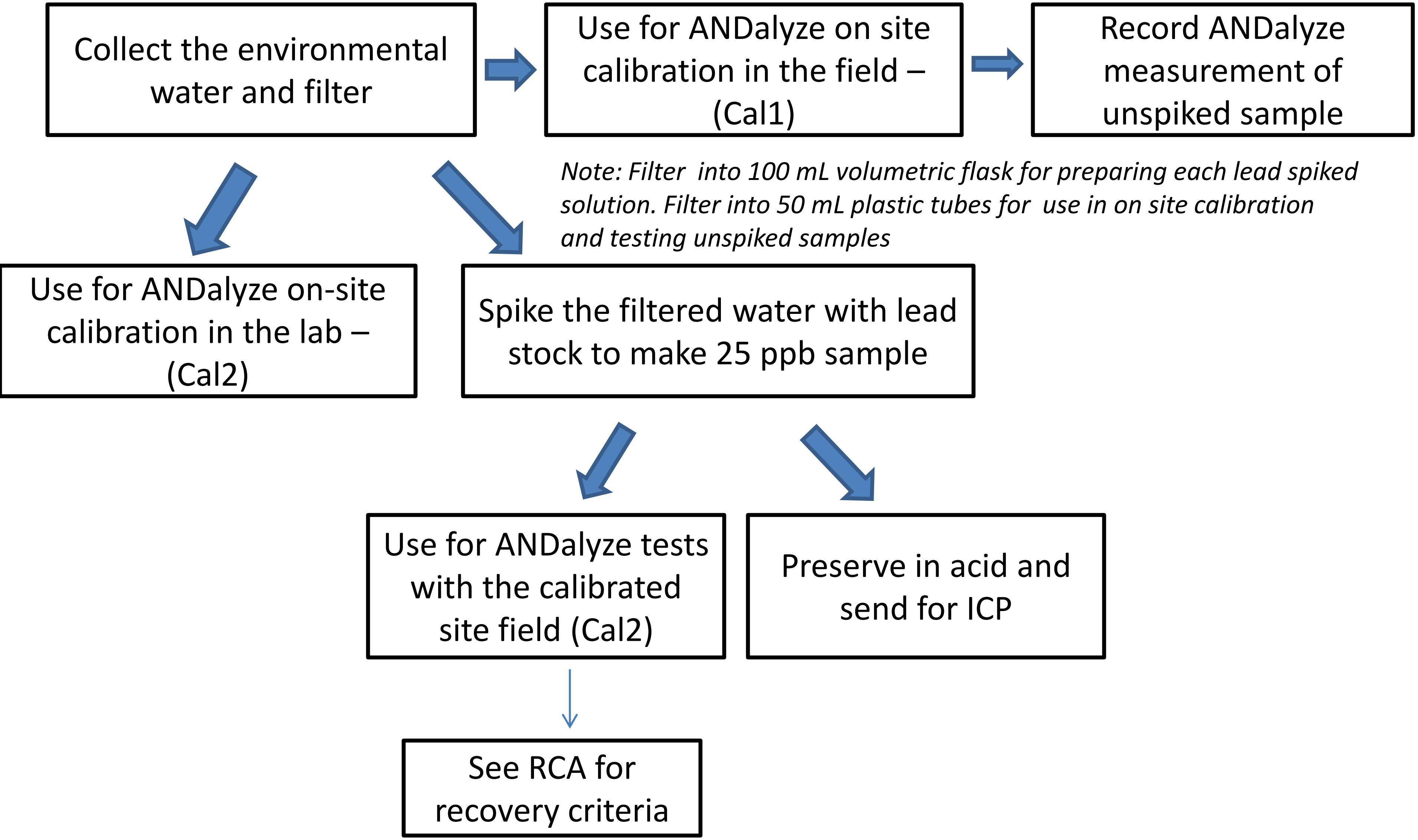
Use for ANDalyze tests with the calibrated site field (Cal2)

Preserve in acid and send for ICP

See RCA for recovery criteria

Note: For bottled water, fountain water: data will be collected in lab only. No field tests
For *each* sample that is to be tested both in the field and in the lab, two on-site calibrations will be performed – one in the field (cal1) and one in the lab (cal2).

Environmental Water (page 53, section B1.1.8.8), except sea water – Field test + Lab test



Collect the environmental water and filter

Use for ANDalyze on site calibration in the field – (Cal1)

Record ANDalyze measurement of unspiked sample

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

Use for ANDalyze on-site calibration in the lab – (Cal2)

Spike the filtered water with lead stock to make 25 ppb sample

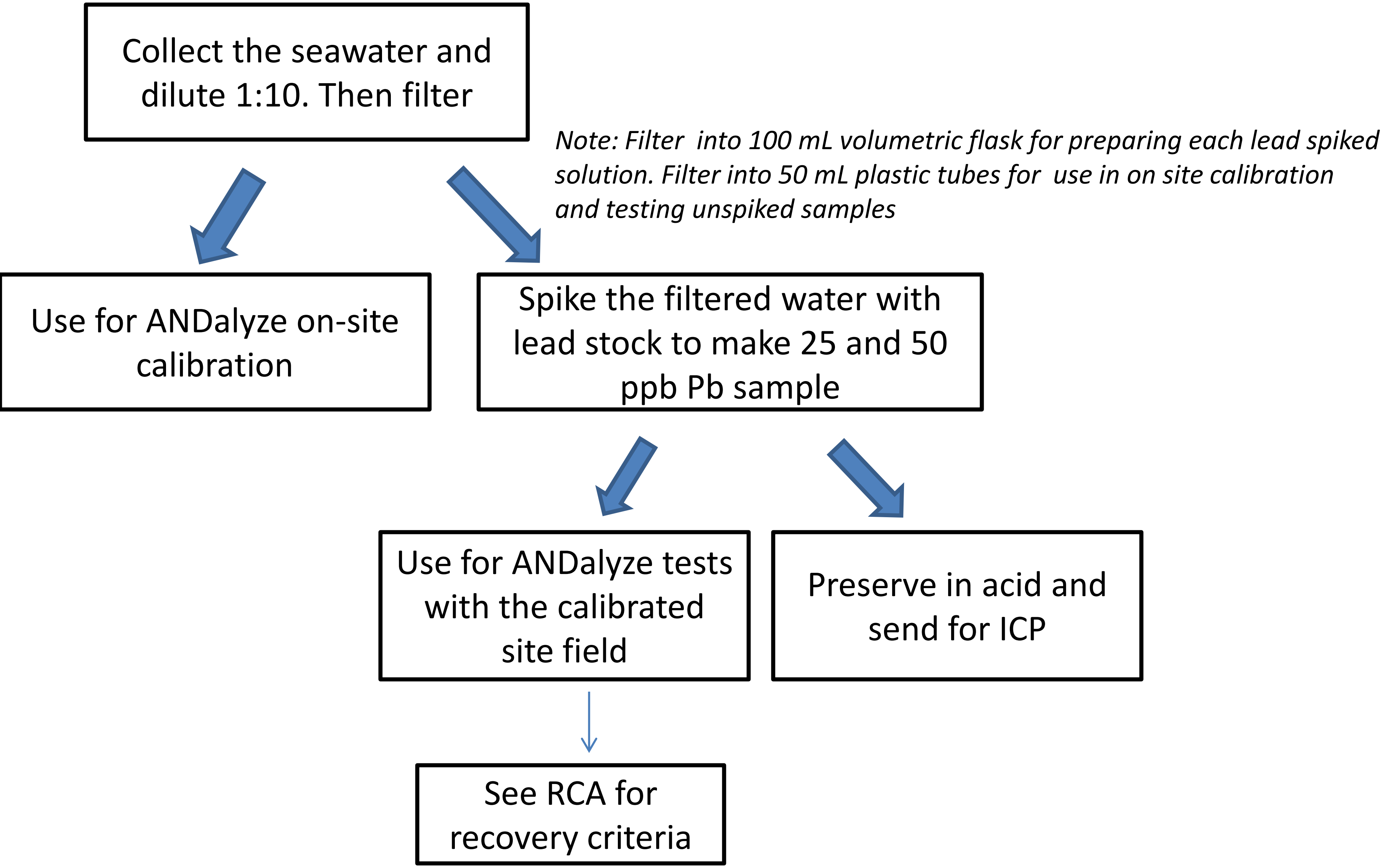
Use for ANDalyze tests with the calibrated site field (Cal2)

Preserve in acid and send for ICP

See RCA for recovery criteria

Note: For *each* sample that is to be tested both in the field and in the lab, two on-site calibrations will be performed – one in the field (cal1) and one in the lab (cal2).

Seawater (page 55, section B1.1.8.8)



Collect the seawater and dilute 1:10. Then filter

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

Use for ANDalyze on-site calibration

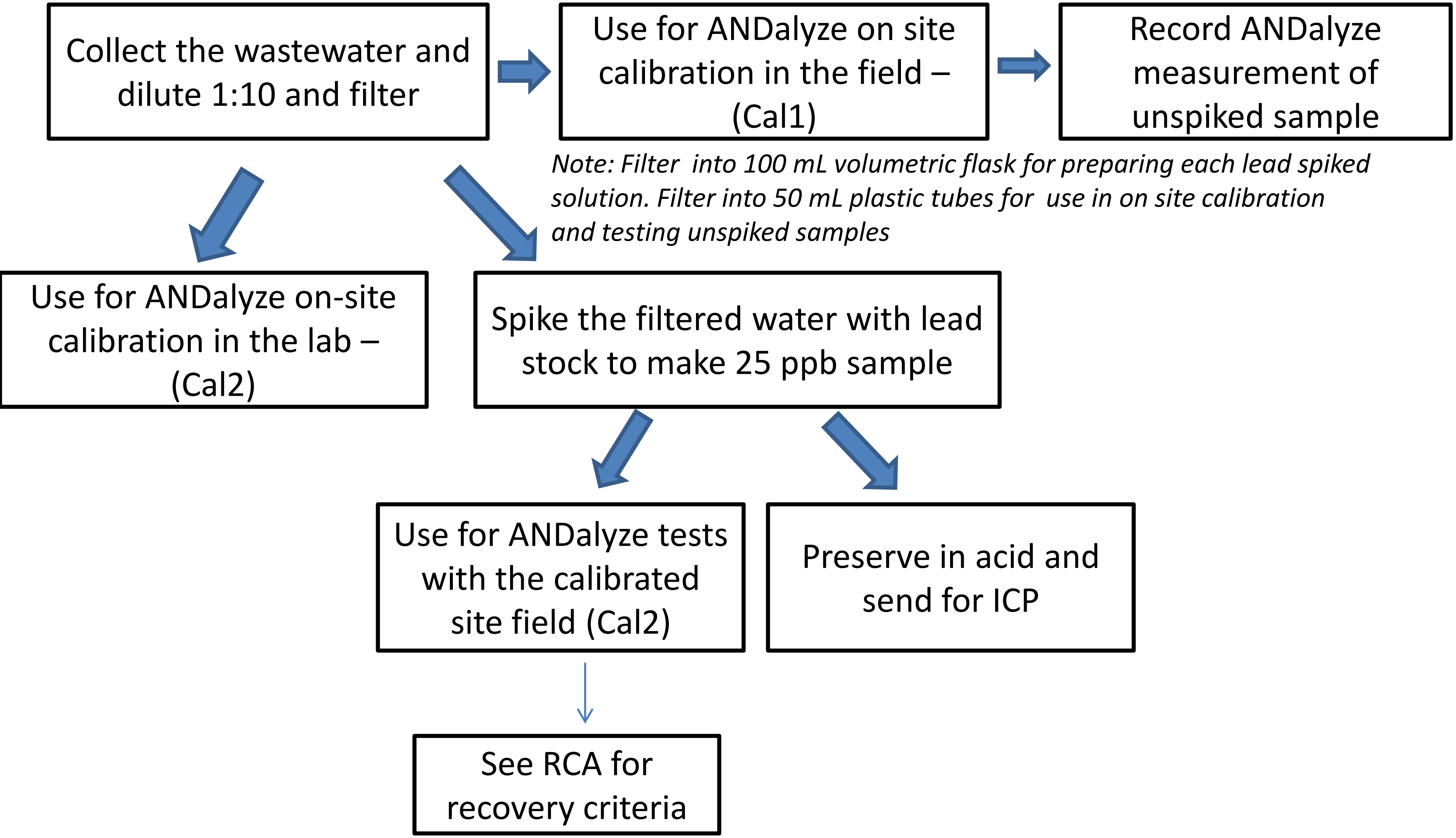
Spike the filtered water with lead stock to make 25 and 50 ppb Pb sample

Use for ANDalyze tests with the calibrated site field

Preserve in acid and send for ICP

See RCA for recovery criteria

Wastewater (page 56, section B1.1.8.9) – Field test + Lab test



Collect the wastewater and dilute 1:10 and filter

Use for ANDalyze on site calibration in the field – (Cal1)

Record ANDalyze measurement of unspiked sample

Note: Filter into 100 mL volumetric flask for preparing each lead spiked solution. Filter into 50 mL plastic tubes for use in on site calibration and testing unspiked samples

Use for ANDalyze on-site calibration in the lab – (Cal2)

Spike the filtered water with lead stock to make 25 ppb sample

Use for ANDalyze tests with the calibrated site field (Cal2)

Preserve in acid and send for ICP

See RCA for recovery criteria

Note: For *each* sample that is to be tested both in the field and in the lab, two on-site calibrations will be performed – one in the field (cal1) and one in the lab (cal2).

Appendix 2

ICP-MS Quality Control Requirements for ANDalyze Instrument ETV Study

Edward F. Askew

Askew Scientific Consulting

Updated November 8, 2012

Table of Contents

Table of Figures

Introduction

ANDalyze has contracted with Battelle Laboratories through the EPA Environmental Technology Verification Program to evaluate the ANDalyze instrument for the determination of lead in aqueous matrixes. A Quality Assurance Project plan (QAPP) was developed by Battelle to perform the ETV project.

The initial ICP-MS data received from the 3rd party contract laboratory, DHL Analytical, for QC samples and aqueous matrix samples prepared by Battelle did not show acceptable agreement between the expected value and the experimental value.

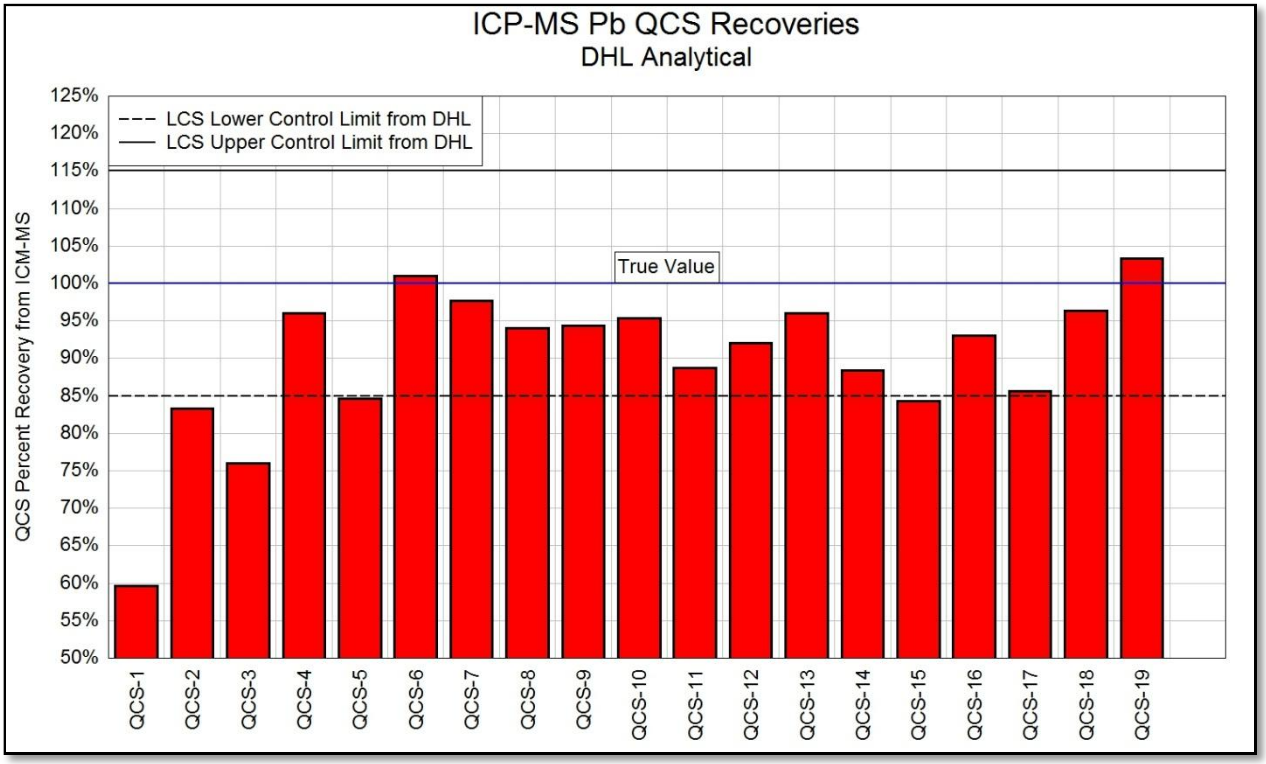


Figure A: DHL QCS Percent recoveries

Figure A summarizes the quality control samples (QCS) prepared by Battelle consisting of 25 PPB lead. These samples should be accurate and are the analog of the LCS (laboratory control sample) prepared by DHL. In DHLs report, they have set the recovery limits for their LCS to 85% and 115%. These control limits were used to evaluate the QCS recoveries. As can be seen in the Figure A, there are disturbing trends on DHL's QCS recoveries by ICP-MS. Their recoveries are very low to start with and only twice did they exceed 100%.

As per Standard Methods for the Examination of Water and Wastewater 19th Edition, 1020 B(7) these QCS recoveries must vary above or below the true value when plotted. Ideally, the variation of the analytical results must occur such that over a 5 sample sequential sequence the observed (determined) value must vary on either side of the 100% true value indicates that the bias is random and not due to a correctable analyst or instrument error. This has not happened with the DHL reported values and indicates a correctable bias is present.

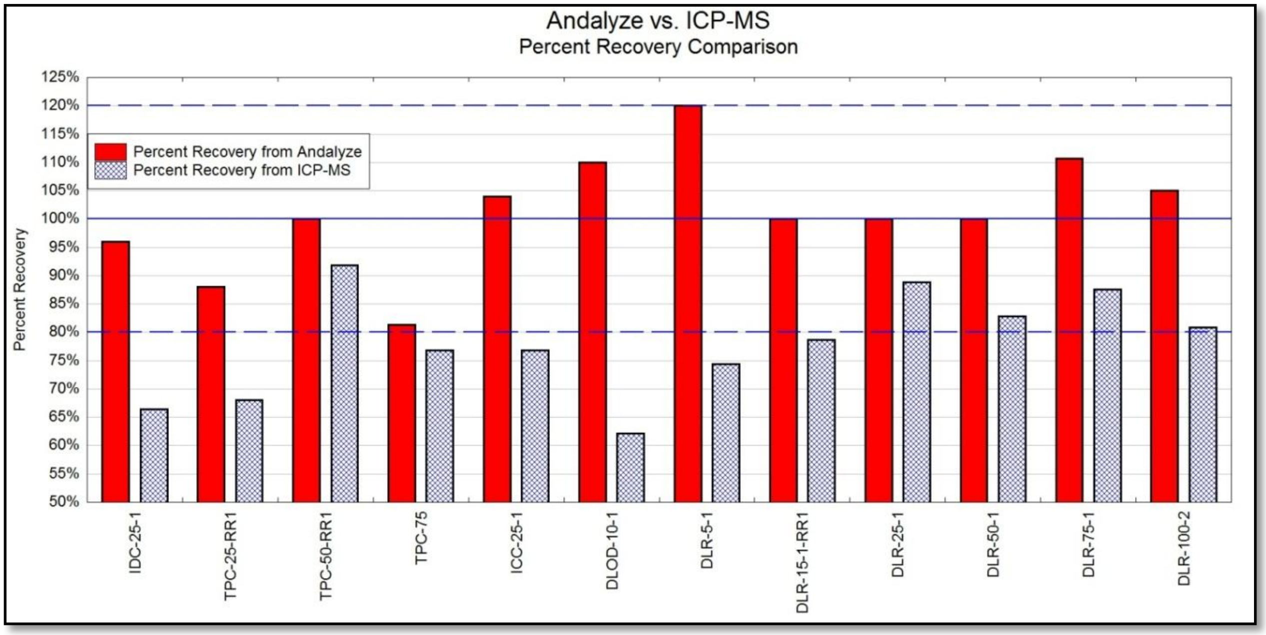


Figure B: DHL vs. ANDalyze Different Aqueous Sample Matrix Recoveries

Figure B summarizes the ANDalyze vs. ICP-MS recoveries for samples prepared in DI water. The control range limits of 80% and 120% emphasizes the difference between the Andalyze instrument recoveries and supposedly the more accurate ICP-MS. It is evident the DHL samples did not have acceptable recoveries when compared to the ANDalyze instrument or to the maximum recoveries acceptable for an ICP-MS instrument. This points to the samples analyses bias.

The final area of concern is the DHL concentrations used for lead in the following QC samples. They are:

ICV	100 PPB
CCV	200 PPB
LCS	200 PPB
MS and MSD	200 PPB
PDS	200 PPB

The Andalyze samples had spike concentrations for the majority of the samples in the range of 25-30 PPB lead. The DHL concentrations of the MS, MSD, and PDS were 6-8 times higher than the actual sample concentration. Referring to the current EPA method 200.8, the MS/MSD only has to be at the concentration of the LFB (LCS). But, if this concentration is too high, it fails to show the effect of the matrix on the sample analyse.

Standard Methods for the Examination of Water and Wastewater, 22nd Edition 1020 B (7) provides more guidance in this area: *"**<u>Add a concentration that is at least 10 times the MRL,</u>***

less than or equal to the midpoint of the calibration curve, or method-specified level to the selected sample(s). ***Preferably use the same concentration as for the LFB to allow analysts to separate the matrix's effect from laboratory performance.*** *Prepare the LFM from the same reference source used for the LFB/LCS. Make the addition such that sample background levels do not adversely affect recovery (preferably adjust LFM concentrations if the known sample is more than five times the background level).* ***For example, if the sample contains the analyte of interest, then add approximately as much analyte to the LFM sample as the concentration found in the known sample.****"*

So, the MRL reported by DHL is 1 PPB for lead. Utilizing Standard Methods, the LCS, MS, MSD, and PDS should have been between 10 PPB lead and no higher than the 25-30 PPB QCS spike.

Definitions

Calibration Blank: A volume of reagent water with the same sample preparation matrix as in the calibration standards.

Calibration Standard: A solution prepared from the dilution of stock standard solutions. These solutions are used to calibrate the instrument response with respect to analyte concentration

Continuing Calibration Standard Check: Analyte standard that has a concentration between the lower calibration standard and upper calibration standard. A continuing calibration standard check will be run at least once per batch.

Control Charts: Graphical charts that contain the expected value (the central line) and the acceptable range of occurrence. The acceptable range is determined from the control limits and warning limits. Refer to Part 1000 of Standard Methods for the Examination of Water and Wastewater for further explanation and guidance.

Laboratory Fortified Blank (LFB): An aliquot of analyte free reagent water to which known quantities of analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

Laboratory Fortified Sample Matrix/Duplicate (LFM/LFMD) also called a Matrix Spike/Duplicate (MS/MSD): An aliquot of an environmental sample to which known quantities of analyte is added in the laboratory. The LFM/LFMD are analyzed exactly like a sample, and there purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM/LFMD corrected for background concentrations.

Laboratory Reagent Blank (LRB): An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

Ongoing Demonstration of Capability (ODC) also called Ongoing Precision and Recovery (OPR): ODC/OPR is performed at least once per sample batch to demonstrate proficiency with the method. Reagent water is spiked with known quantities of analyte. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Sample Batch: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch. A batch cannot span between laboratory work days (24 hrs). New batches must be started each laboratory work day.

Quality Control Requirements for the ICP-MS

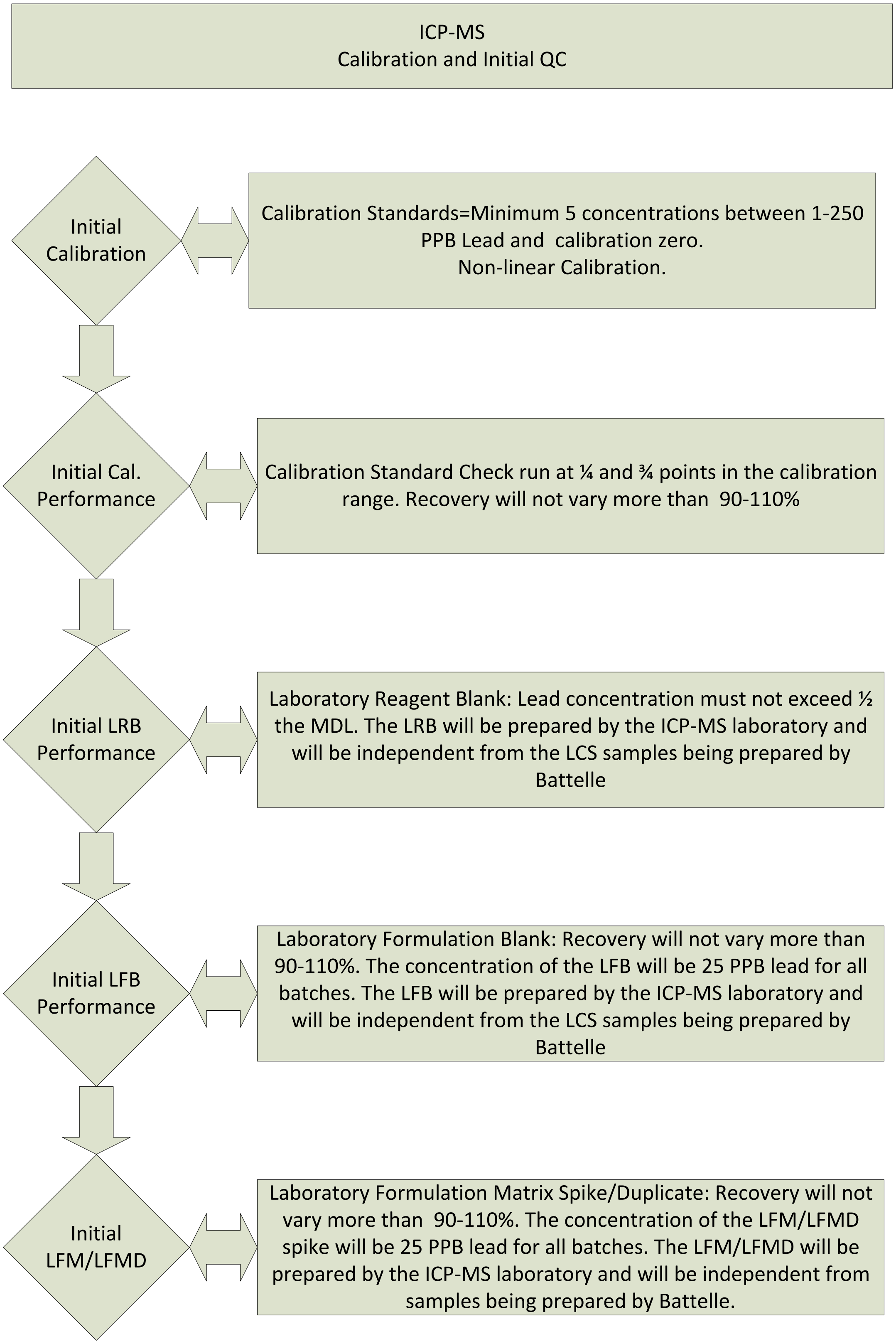
Utilizing the requirements for QC samples detailed in Standard Methods for the Examination of Water and Wastewater, 22nd Edition 1020 B and 40 CFR part 136.7, the following QC analysis per batch will be performed for the ICP-MS analysis of the ANDalyze samples;

Analytical Batch

1. Initial Calibration and QC. (Figure C)
    a. Meet the QC requirements Figures E-H
2. 10 unique ANDalyze analytical samples.
3. Ongoing Calibration and QC.(Figure D)
    a. Meet the QC requirements Figures E-H
4. 10 unique ANDalyze analytical samples.
5. Continue sequence of 10 samples until end of batch with Ongoing QC .(Figure D) until end of sample batch.

QC Failure Requirements:

If by following the flow charts in Figures E-H, the analyst reaches the point where a Root Cause Analyses, RCA, must be performed, contact Battelle. All RCA results must be recorded and submitted for approval by Battelle prior to restarting the ICP-MS analyses.



Calibration Standards=Minimum 5 concentrations between 1-250 PPB Lead and calibration zero.
Non-linear Calibration.

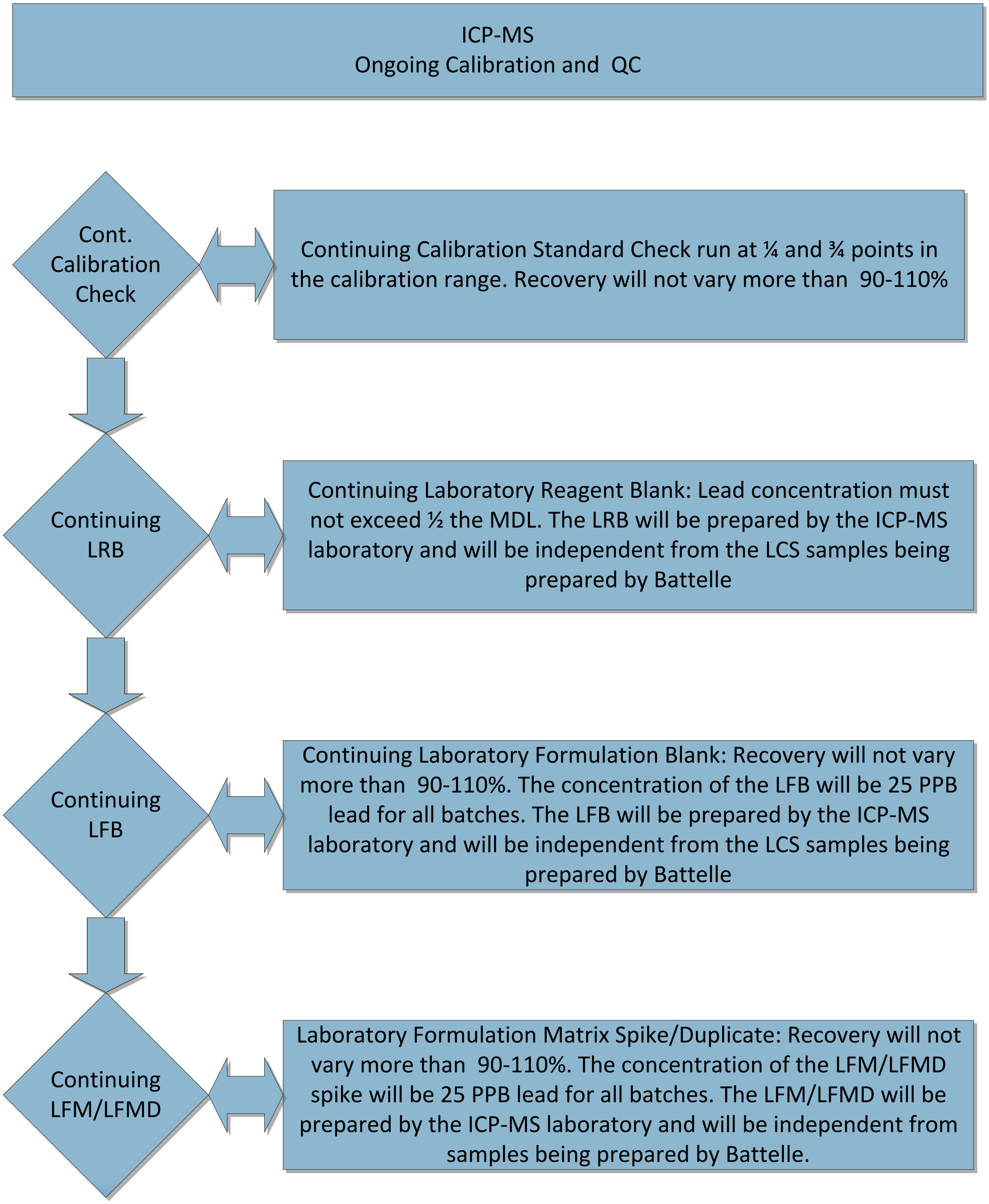
Calibration Standard Check run at ¼ and ¾ points in the calibration range. Recovery will not vary more than 90-110%

Laboratory Reagent Blank: Lead concentration must not exceed ½ the MDL. The LRB will be prepared by the ICP-MS laboratory and will be independent from the LCS samples being prepared by Battelle

Laboratory Formulation Blank: Recovery will not vary more than 90-110%. The concentration of the LFB will be 25 PPB lead for all batches. The LFB will be prepared by the ICP-MS laboratory and will be independent from the LCS samples being prepared by Battelle

Laboratory Formulation Matrix Spike/Duplicate: Recovery will not vary more than 90-110%. The concentration of the LFM/LFMD spike will be 25 PPB lead for all batches. The LFM/LFMD will be prepared by the ICP-MS laboratory and will be independent from samples being prepared by Battelle.

Figure C: Initial ICP-MS Calibration and QC



Continuing Calibration Standard Check run at ¼ and ¾ points in the calibration range. Recovery will not vary more than 90-110%

Continuing Laboratory Reagent Blank: Lead concentration must not exceed ½ the MDL. The LRB will be prepared by the ICP-MS laboratory and will be independent from the LCS samples being prepared by Battelle

Continuing Laboratory Formulation Blank: Recovery will not vary more than 90-110%. The concentration of the LFB will be 25 PPB lead for all batches. The LFB will be prepared by the ICP-MS laboratory and will be independent from the LCS samples being prepared by Battelle

Laboratory Formulation Matrix Spike/Duplicate: Recovery will not vary more than 90-110%. The concentration of the LFM/LFMD spike will be 25 PPB lead for all batches. The LFM/LFMD will be prepared by the ICP-MS laboratory and will be independent from samples being prepared by Battelle.

Figure D; ICP-MS ongoing Calibration and QC

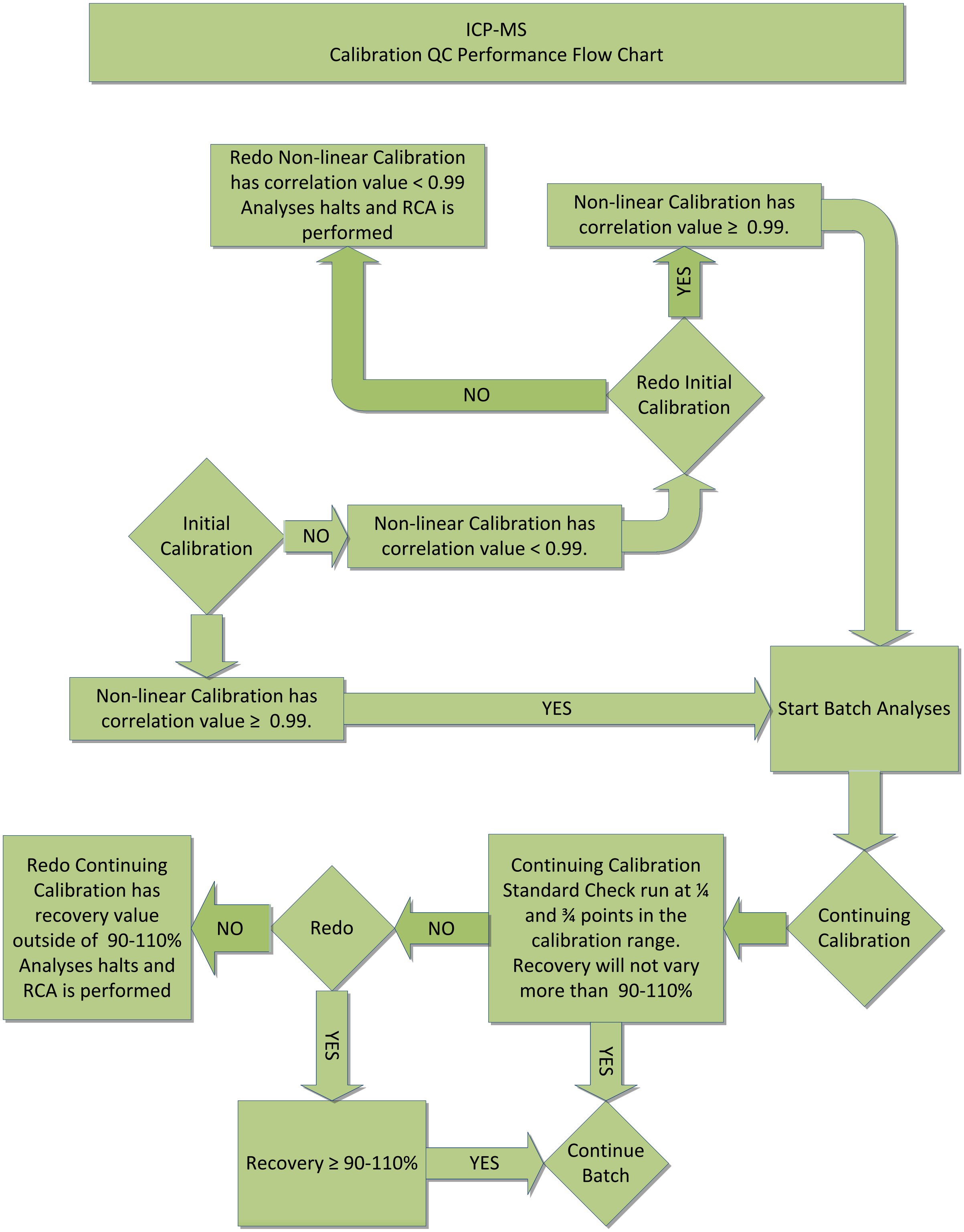


Figure E: Calibration Performance Flow Chart

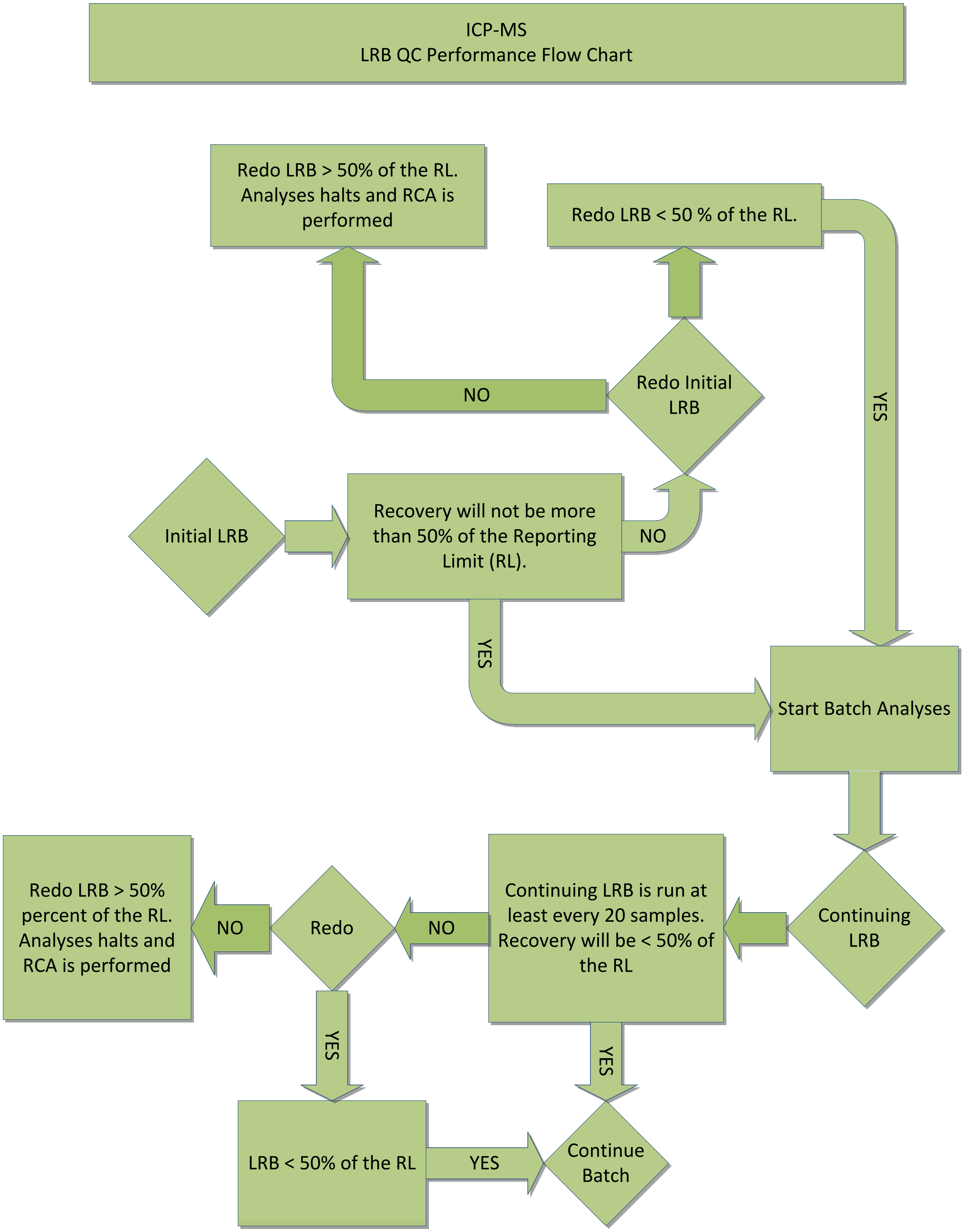


Figure F: Laboratory reagent Blank (LRB) QC Flowchart

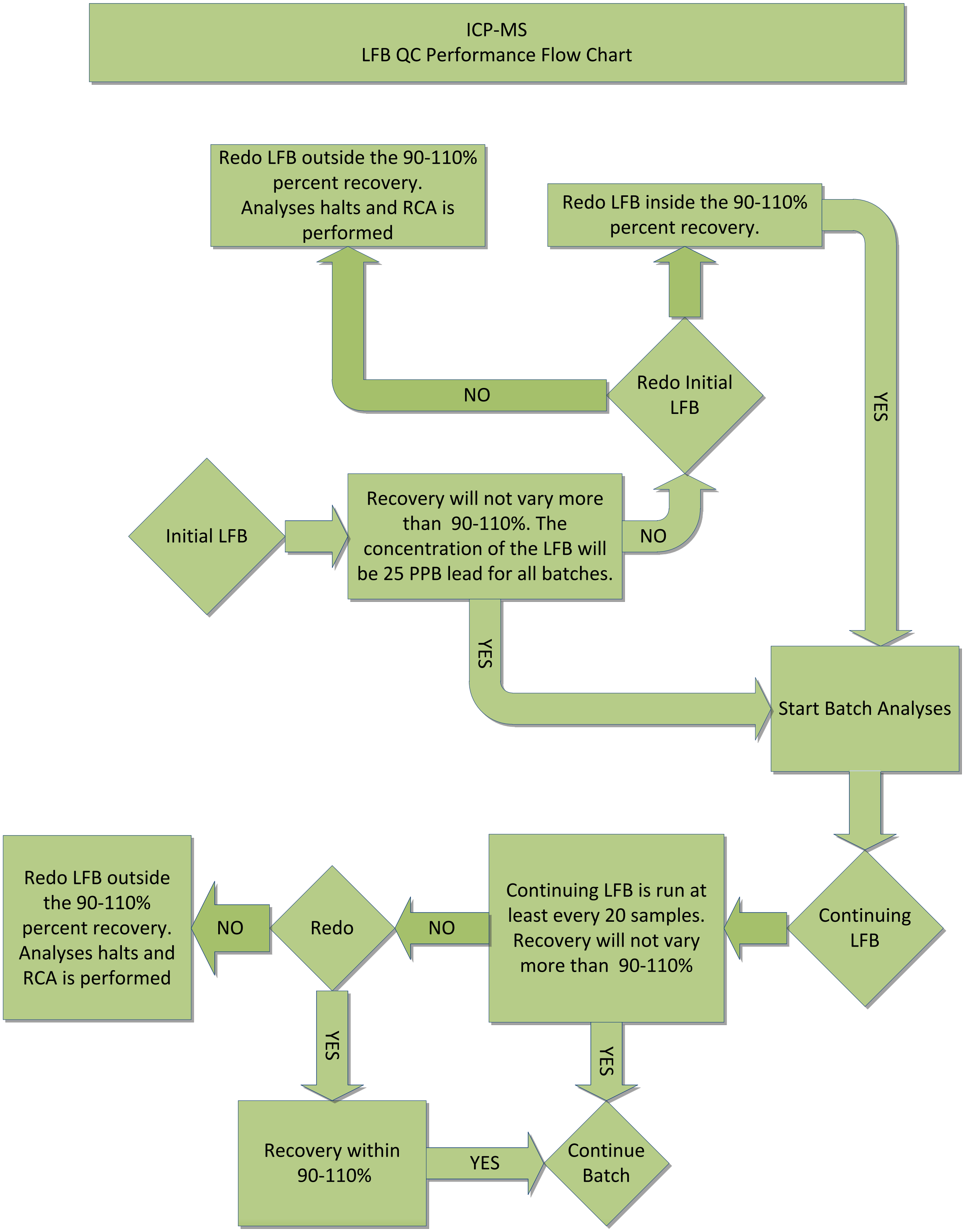


Figure G: Laboratory Formulation Blank (LFB) QC Flowchart

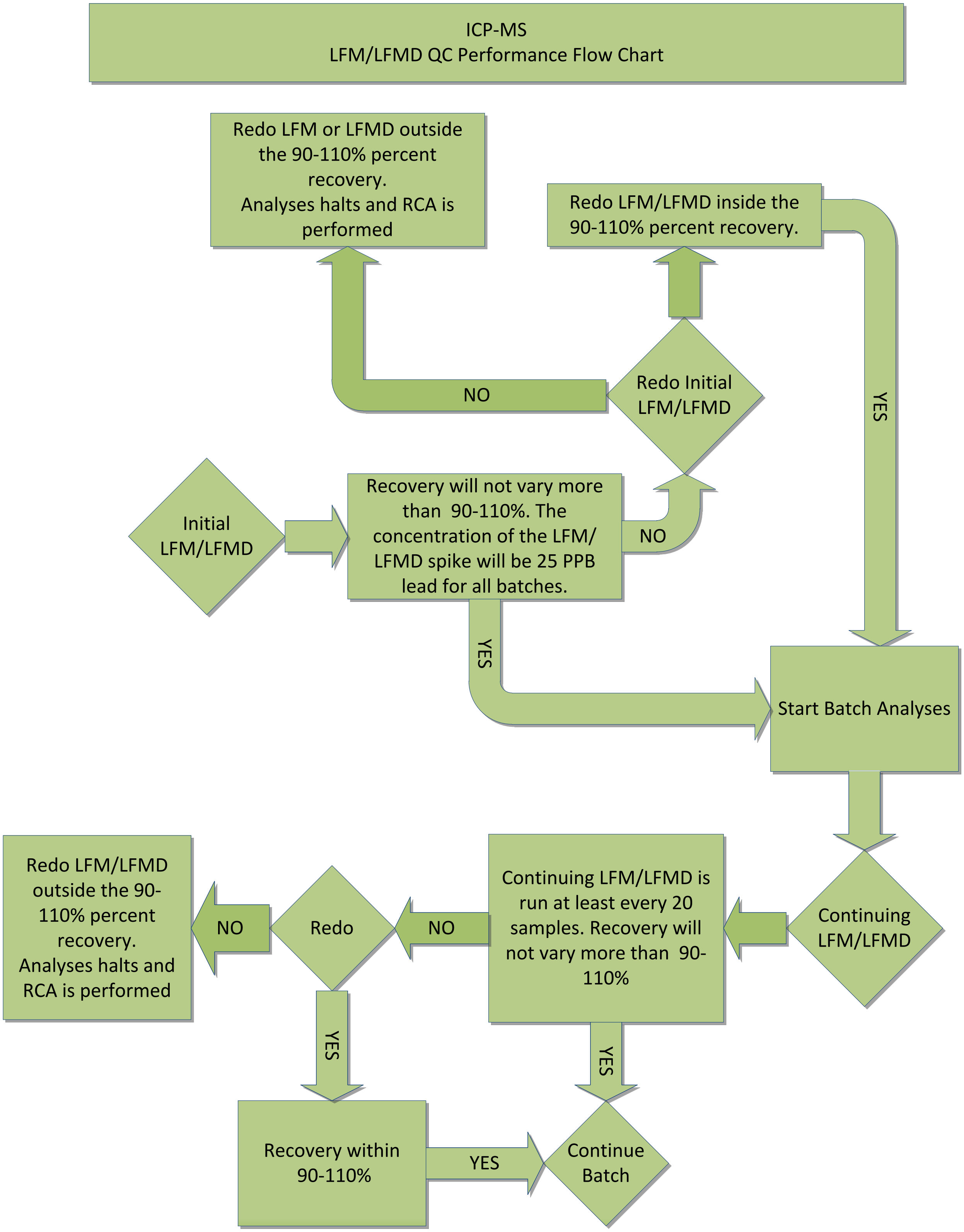


Figure H: Laboratory Formulation Matrix Spike 7 Duplicate (LFM/LFMD) QC Flowchart

Appendix C
Round 1 Testing Results

Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
7/10/2012	1	QCS-1	30	27	Not Analyzed	None		
	2	IDC-25-1	25	18	Not Analyzed	Percent recovery < 75%	Perform on-site calibration and rerun sample	
	3	IDC-25-1-RR1	25	16	Not Analyzed	Percent recovery < 75%	Root cause analysis. Reprepare IDC-25 sample and repeat onsite calibration	Reanalysis of IDC-25-1
	4	IDC-25-1-RR2	25	22	Not Analyzed	None		Assume sample preparation error for IDC-25
	5	IDC-25-2	25	16	Not Analyzed	Percent recovery < 75%	Repeat on-site calibration and rerun sample	
	6	IDC-25-2-RR2	25	18	Not Analyzed	Percent recovery < 75%	pH and temperature of each sample measured (6.92-6.94)	Contacted ANDalyze and agreed that ANDalyze will be present to *observe only* a repeat of the performance testing on 7/13/12
7/13/2012	7	QCS-1	30	22	18	Percent recovery < 75%	Repeat on-site calibration and rerun sample	Failed first on-site calibration
	8	QCS-1-RR1	30	27	18	None		Reanalysis of QCS-1
	9	IDC-25-1	25	24	17	None		
	10	IDC-25-2	25	31	17	Sample above UCL		Sample should have been reanalyzed
	11	IDC-25-3	25	24	17	None		
	12	TPC-25	25	36	17	Percent recovery > 125%	Three point calibration (25, 50 and 75 ppb) completed and saved to AND1000	
	13	TPC-25-RR1	25	22	17	None		Reanalysis of TPC-25
	14	TPC-50	50	65	46	Percent recovery > 125%	Repeat on-site calibration and rerun sample	
	15	TPC-50-RR1	50	50	46	None		Reanalysis of TPC-50
	16	TPC-75	75	61	58	None		

Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
	17	ICC-25-1	25	26	19	None		
	18	ICC-25-2	25	23	19	None		
	19	ICC-25-3	25	22	19	None		RB-1 analyzed (below limit reported)
	20	QCS-2	30	27	25	None		
	21	DLOD-10-1	10	11	6	None		DLOD has no explicit QC requirement for percent recovery. These samples must conform to the control chart
	22	DLOD-10-2	10	12	6	None		
	23	DLOD-10-3	10	11	6	None		
	24	DLOD-10-4	10	8	6	None		
	25	DLOD-10-5	10	11	6	None		
	26	DLOD-10-6	10	7	6	None		
	27	DLOD-10-7	10	8	6	None		
	28	DLR-5-1	5	6	4	None		DLR has no explicit QC requirement for percent recovery. These samples must conform to the control chart
	29	DLR-5-2	5	6	4	None		
	30	DLR-5-3	5	7	4	None		This sample was mistakenly observed above the UCL and reanalyzed. Reanalysis unnecessary and results of reanalysis results not reported RB-2 analyzed: first reading 3 ppb. RB-2 reanalyzed: second reading below limit
	31	QCS-3	30	35	23	Four out of five samples are outside one standard deviation of the mean percent recovery	QCS-3 reanalyzed	
	32	QCS-3-RR1	30	22	23	Percent recovery < 75%. Four out of five samples are outside one standard deviation of the mean percent recovery	QCS-3 reanalyzed	Reanalysis of QCS-3

Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
	33	QCS-3-RR2	30	29	23	None		Reanalysis of QCS-3
	34	DLR-15-1	15	18	12	Four out of five samples are outside one standard deviation of the mean percent recovery	DLR-15-2 reanalyzed	
	35	DLR-15-1-RR1	15	15	12	None		Reanalysis of DLR-15-3
	36	DLR-15-2	15	14	12	None		
	37	DLR-15-3	15	14	12	None		
	38	DLR-25-1	25	25	22	None		
	39	DLR-25-2	25	21	22	None		
	40	DLR-25-3	25	23	22	None		
	41	DLR-50-1	50	50	41	None		
	42	DLR-50-2	50	51	41	None		
	43	DLR-50-3	50	45	41	None		
	44	DLR-75-1	75	83	66	None		
	45	DLR-75-2	75	60	66	None		
	46	DLR-75-3	75	63	66	None		
7/18/2012	47	QCS-4	30	35	29	None		RB-2 analyzed (below limit reported)
	48	DLR-100-1	100	141	81	None		This sample was mistakenly observed above the UCL and reanalyzed. Reanalysis unnecessary and results of reanalysis results not reported
	49	DLR-100-2	100	105	81	None		
	50	DLR-100-3	100	95	81	None		
	51	HTDS-25-1	25	19	21	Four out of five measurements in decreasing order	Reanalyze HTDS-25-1	
	52	HTDS-25-1-RR1	25	14	21	Percent recovery < 75%	Repeat on-site calibration and reanalyze HTDS-25-1	Reanalysis of HTDS-25-1
	53	HTDS-25-1-RR2	25	27	21	None		Reanalysis of HTDS-25-1
	54	HTDS-25-2	25	25	21	None		
	55	HTDS-25-3	25	33	21	Percent recovery > 125%	Repeat on-site	

Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
							calibration and reanalyze HTDS-25-3	
	56	HTDS-25-3-RR1	25	19	21	None		Reanalysis of HTDS-25-3
	57	HTDS-50-1	50	52	43	None		
	58	HTDS-50-2	50	45	43	None		
	59	HTDS-50-3	50	40	43	None		
	60	QCS-5	30	29	25	None		RB-4 analyzed (2 ppb reported). RB-4 reanalyzed (below limit reported)
	61	LTDS-25-1	25	20	19	None		
	62	LTDS-25-2	25	21	19	None		
	63	LTDS-25-3	25	19	19	None		
	64	LTDS-50-1	50	53	39	None		
	65	LTDS-50-2	50	41	39	None		
	66	LTDS-50-3	50	33	39	Percent recovery < 75%	Repeat on-site calibration and reanalyze LTDS-50-3	
	67	LTDS-50-3-RR1	50	50	39	None		Reanalysis of LTDS-50-3
	68	QCS-6	30	35	30	None		HFe water analyzed with and without pretreatment. Samples without pretreatment do not have explicit percent recovery QC criteria nor are they reported in the control chart. RB-5 analyzed (below limit reported)
	69	HFe-25-PT-1	25	2	27	Percent recovery < 75%. Sample is below LCL	Repeat on-site calibration and reanalyze HFe-25-PT-1	
	70	HFe-25-PT-1-RR1	25	2	27	Percent recovery < 75%. Sample is below LCL	HFe-25 analysis terminated	Reanalysis of HFe-25-1
	71	HFe-50-PT-1	50	3	51	Percent recovery < 75%. Sample is below LCL.	Repeat on-site calibration and	

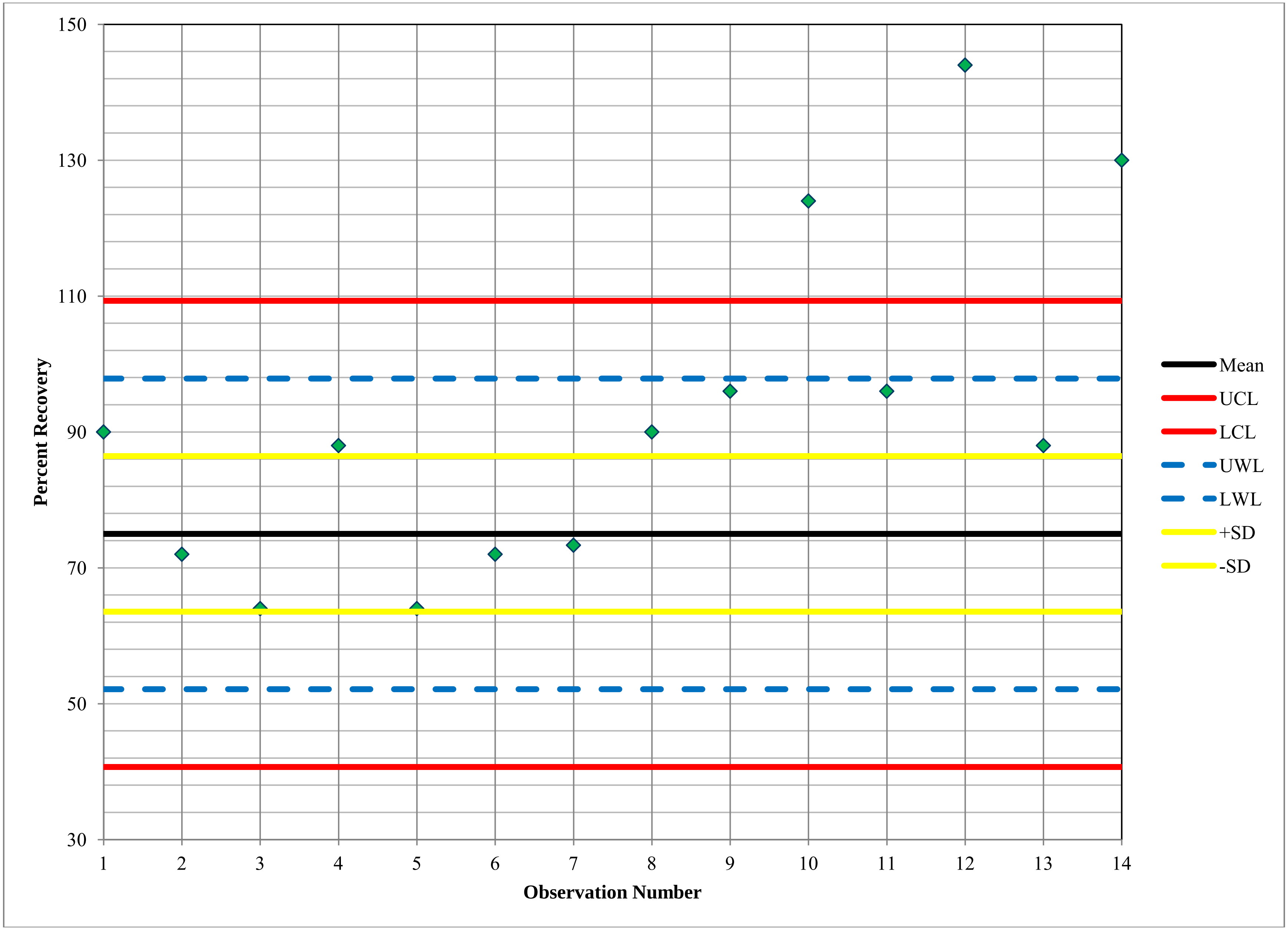
Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
						Fourth out of five samples outside of one standard deviation from mean percent recovery	reanalyze HFe-50-PT-1	
	72	HFe-50-PT-1-RR1	50	4	51	Percent recovery < 75%. Sample is below LCL	HFe-50 analysis terminated.	Reanalysis of HFe-50-1. RB-6 analyzed (below limit reported)
	73	QCS-7	30	38	29	Percent recovery > 125%	Reanalyze QCS-7	
	74	QCS-7-RR1	30	36	29	None		Reanalysis of QCS-7
7/19/2012	75	QCS-8	30	23	28	None		This sample was mistakenly observed as the fourth out of five samples outside of one standard deviation from mean percent recovery. Reanalysis unnecessary and results of reanalysis results not reported
	76	WF-25-1	25	21	15	None		
	77	WF-25-2	25	16	15	Percent recovery < 75%	Repeat on-site calibration and reanalyze WF-25-2	Repeated on-site calibration 3 times as the readings did not seem correct (12 ppb and 29 ppb) for WF water
	78	WF-25-2-RR1	25	14	15	Percent recovery < 75%. LFM/LFMD RPD > 30 %	Repeat on-site calibration and reanalyze WF-25-2	Reanalysis of WF-25-2. Testing should have been abandoned at this point
	79	WF-25-2-RR2	25	12	15	Percent recovery < 75%. LFM/LFMD RPD > 30 %	Repeat on-site calibration and reanalyze WF-25-2	Reanalysis of WF-25-2.
	80	WF-25-2-RR3	25	19	15	None		Reanalysis of WF-25-2.
	81	WF-25-3	25	19	15	None		
	82	BW-25-1	25	20	16	None		
	83	BW-25-2	25	21	16	None		
	84	BW-25-3	25	18	16	Percent recovery < 75%	Repeat on-site calibration and reanalyze BW-25-3	
	85	BW-25-3-RR1	25	25	16	None		Reanalysis of BW-25-3. RB-7 analyzed (below limit reported)
	86	QCS-9	30	32	28	None		This sample was mistakenly

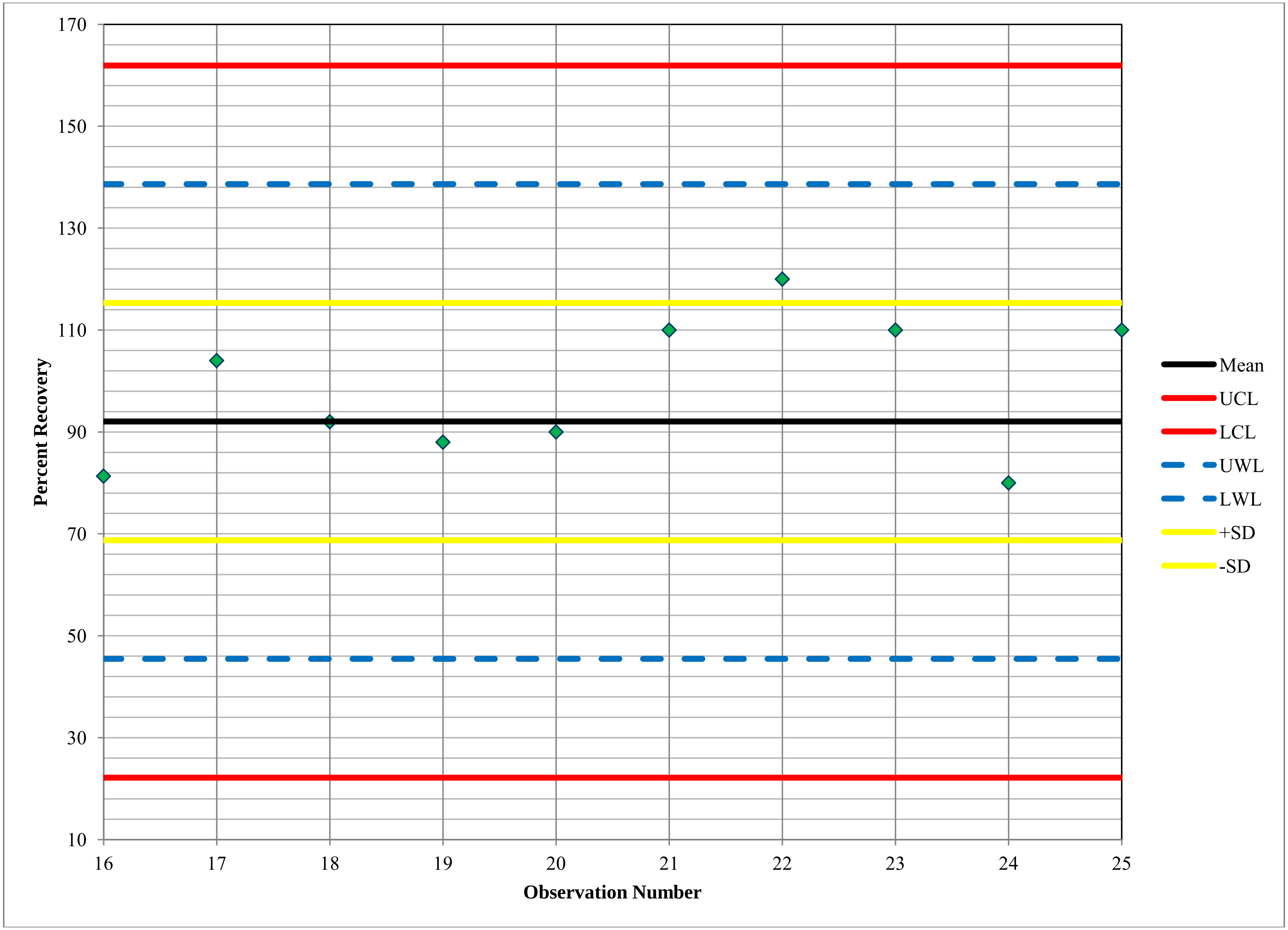
Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
								observed as the fourth out of five samples in increasing order. Reanalysis unnecessary and results of reanalysis results not reported
	87	FWW-25-1	25	15	23	Percent recovery < 75%	Repeat on-site calibration and reanalyze FWW-25-1	Attempted recalibration, however, AND1000 reported that the test water was not suitable for accurate analysis and to contact the vendor. As a result, FWW analysis was terminated
	88	RWW-25-1	25	23	7	None		
	89	RWW-25-2	25	21	7	None		
	90	RWW-25-3	25	19	7	None		
	91	QCS-10	30	32	29	None		
7/24/2012	92	QCS-11	30	25	27	None		RB-8 analyzed (below limit reported)
	93	QCS-12	30	35	28	None		
	94	ReW-25-1	25	3	8	Percent recovery < 75%	Repeat on-site calibration and reanalyze ReW-25-1	
	95	ReW-25-1-RR1	25	9	8	Percent recovery < 75%. LFM/LFMD RPD > 30 %	Repeat on-site calibration and reanalyze ReW-25-1	Reanalysis of ReW-25-1.
	96	ReW-25-1-RR2	25	0	8	Percent recovery < 75%. LFM/LFMD RPD > 30 %	Reservoir water analysis terminated	Reanalysis of ReW-25-1.
	97	RiW-25-1	25	9	4	Percent recovery < 75%. LFM/LFMD RPD > 30 %	Repeat on-site calibration and reanalyze RiW-25-1	
	98	RiW-25-1-RR1	25	22	4	None		Reanalysis of RiW-25-1
	99	RiW-25-2	25	19	4	None		
	100	RiW-25-3	25	13	4	Percent recovery < 75%	Repeat on-site calibration and reanalyze RiW-25-3	
	101	RiW-25-3-RR1	25	13	4	Percent recovery < 75%	River water analysis terminated	Reanalysis of RiW-25-3

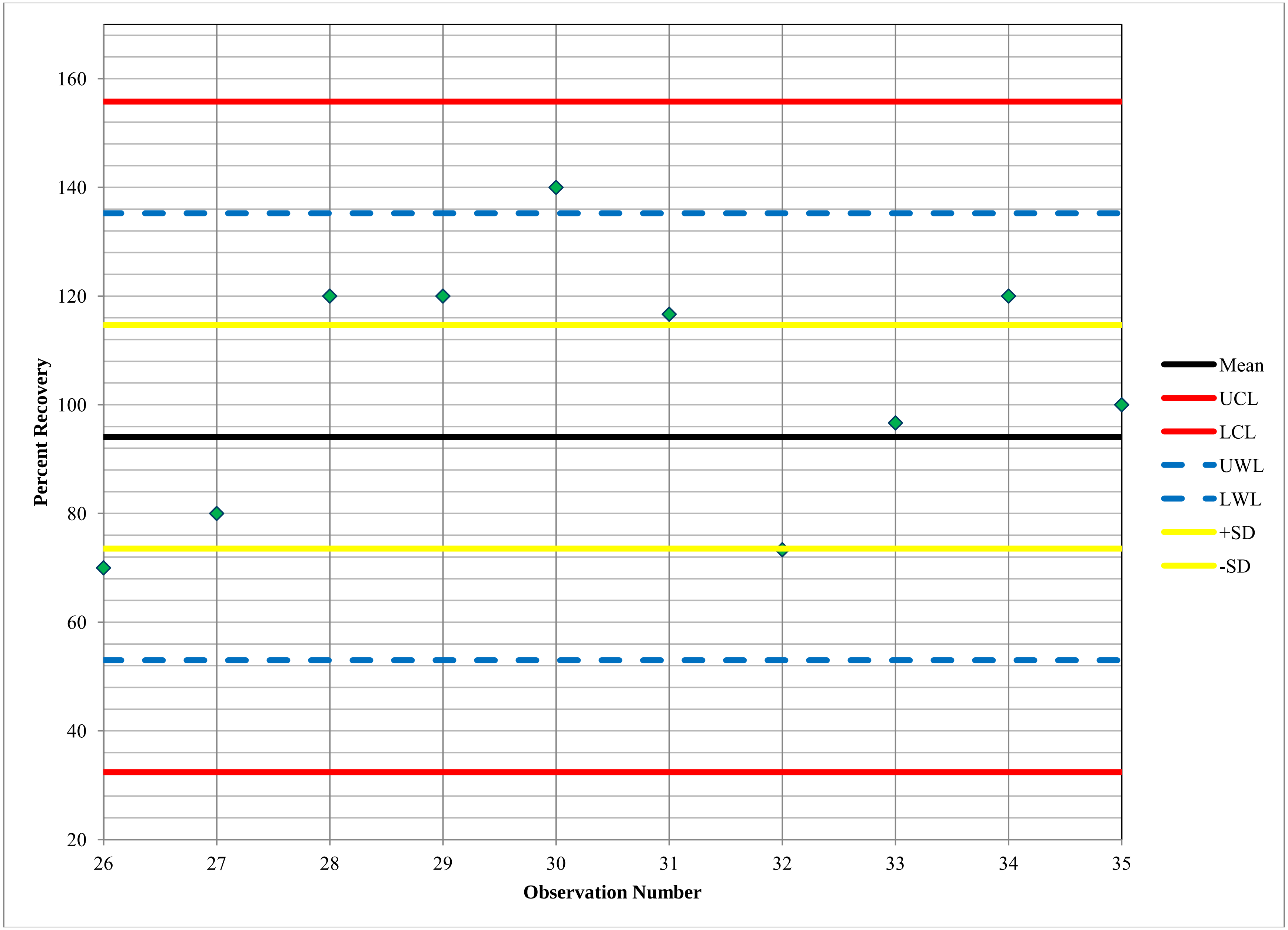
Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
	102	SW-25-1	25	23	20	None		Seawater samples were diluted 10:1 and filtered through 0.20 µm Nylon filter before any further analysis or manipulation. Seawater samples required pH adjustment. Seawater samples have no explicit QC requirement for percent recovery. These samples must conform to the control chart.
	103	SW-25-2	25	30	20	None		
	104	SW-25-3	25	18	20	None		
	105	SW-50-1	50	48	46	None		
	106	SW-50-2	50	42	46	None		
	107	SW-50-3	50	51	46	None		
	108	QCS-13	30	32	29	None		RB-9 analyzed (below limit reported)
7/25/2012	109	QCS-14	30	29	27	None		
	110	QCS-15	30	25	25	None		RB-10 analyzed (below limit reported)
	111	MWWE#1-25-1	25	22	19	None		All wastewater samples were diluted 10:1 and filtered through 0.20 µm Nylon filter before any further analysis or manipulation
	112	MWWE#1-25-2	25	20	19	None		
	113	MWWE#1-25-3	25	17	19	Percent recovery < 75%	Repeat on-site calibration and reanalyze MWWE#1-25-3	
	114	MWWE#1-25-3-RR1	25	22	19	None		Reanalysis of MWWE#1-25-3
	115	QCS-16	30	30	28	None		RB-11 analyzed (below limit reported)
	116	MWWE#2-	25	21	17	None		All wastewater samples were

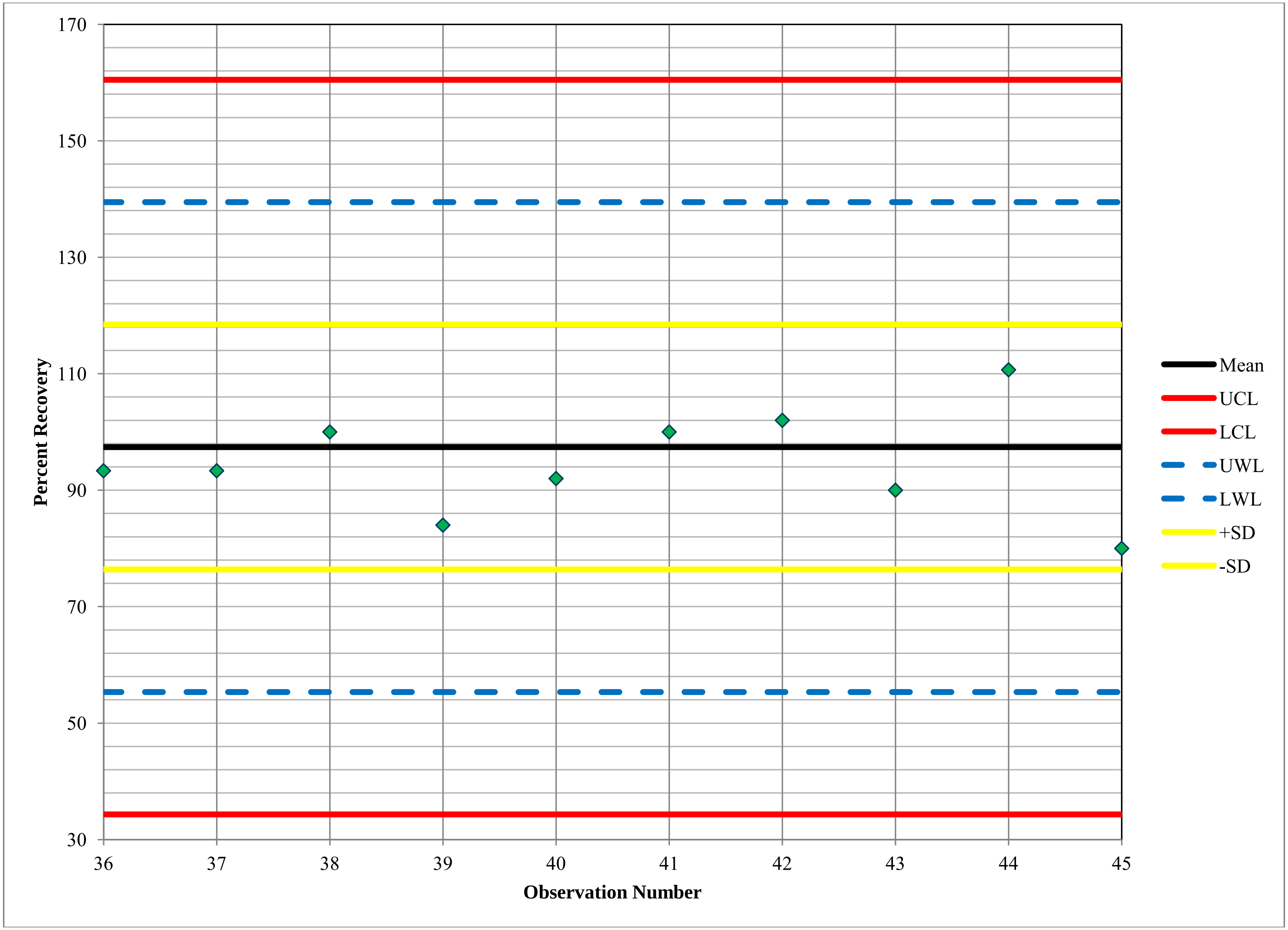
Date	Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Abnormal Anticipated Percent Recovery/Control Chart Result (vs. Expected Results)	Resolution	Comments
		25-1						diluted 10:1 and filtered through 0.20 µm Nylon filter before any further analysis or manipulation
	117	MWWE#2-25-2	25	20	17	None		
	118	MWWE#2-25-3	25	15	17	Percent recovery < 75%	Repeat on-site calibration and reanalyze MWWE#2-25-3	
	119	MWWE#2-25-3-RR1	25	12	17	Percent recovery < 75%	MWWE#2 analysis terminated	Reanalysis of MWWE#2-25-3
7/27/2012	120	QCS-18	30	22	29	Percent recovery < 75%	Reanalyze QCS-18	MFWWE analysis attempted on 7/26/12 however, operator failure to follow QAPP resulted in reanalysis on 7/27/12
	121	QCS-18-RR1	30	29	29	None		Reanalysis of QCS-18
	122	QCS-19	30	26	31	None		Attempted recalibration, however, AND1000 reported that the test water was not suitable for accurate analysis and to contact the vendor. As a result, MFWWE analysis was terminated. RB-12 analyzed (below limit reported)

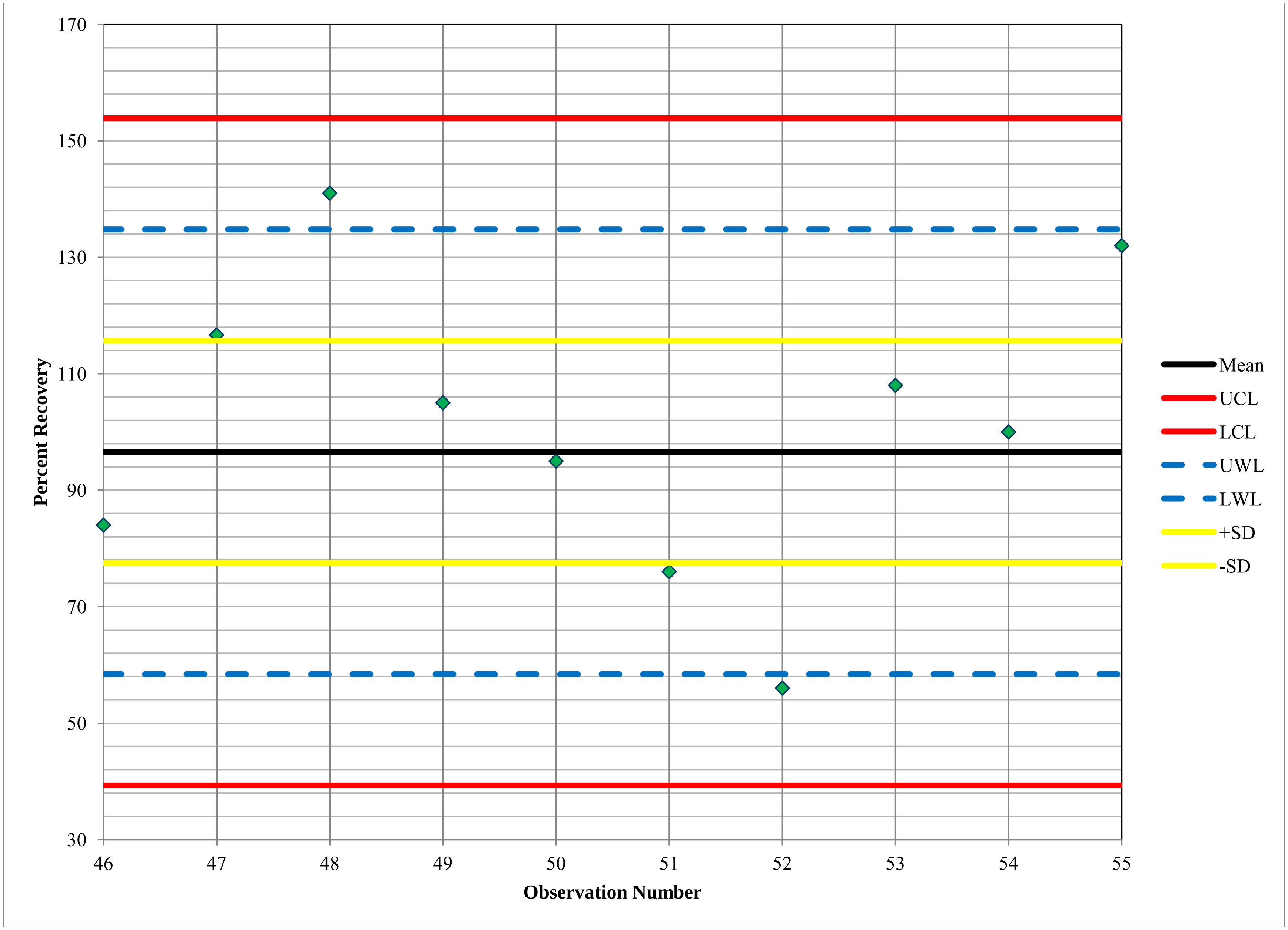
Appendix D
Round 1 Control Charts

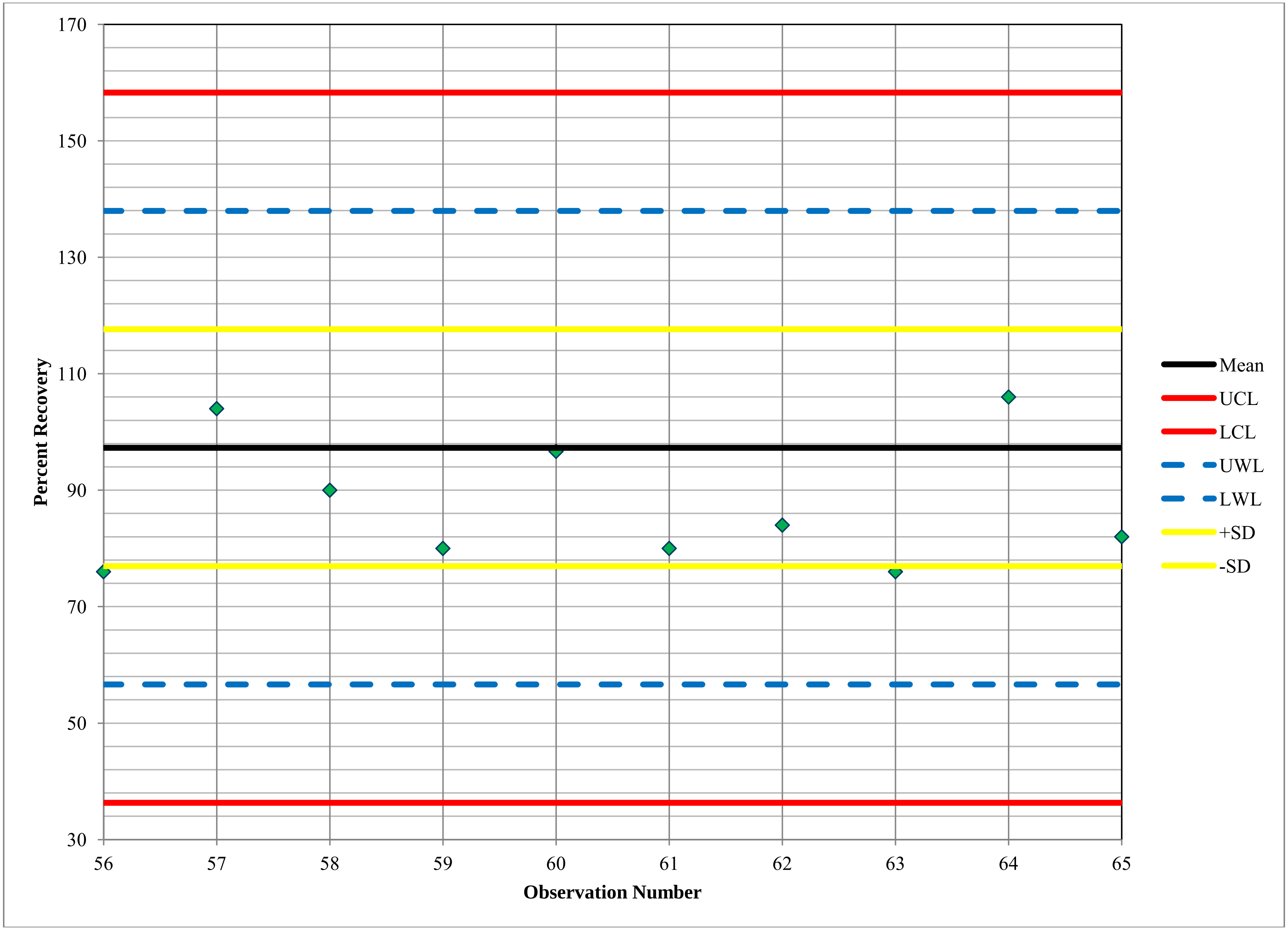

150
130
110
90
70
50
30
Percent Recovery
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

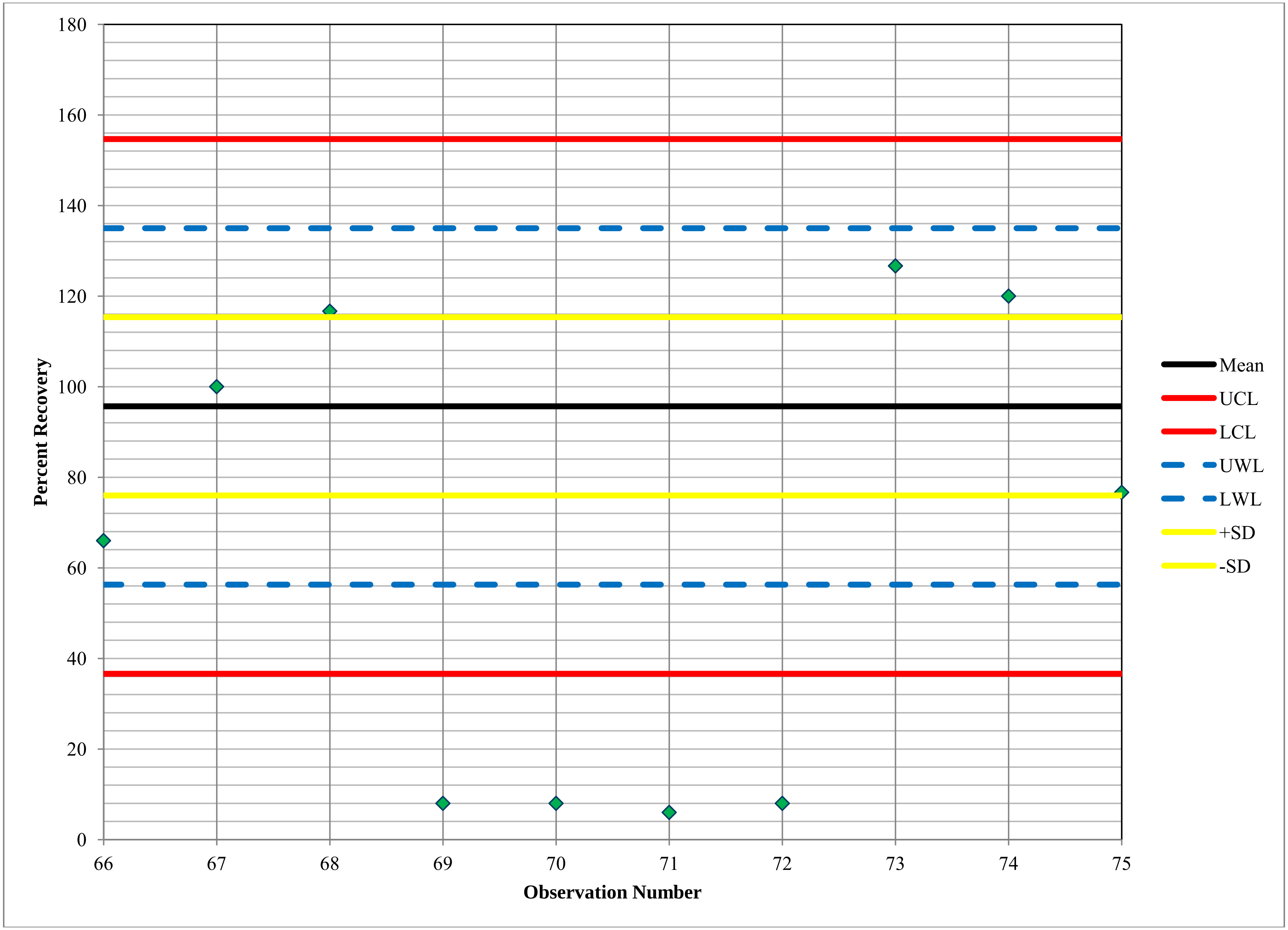

Percent Recovery
170
150
130
110
90
70
50
30
10
16
17
18
19
20
21
22
23
24
25
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

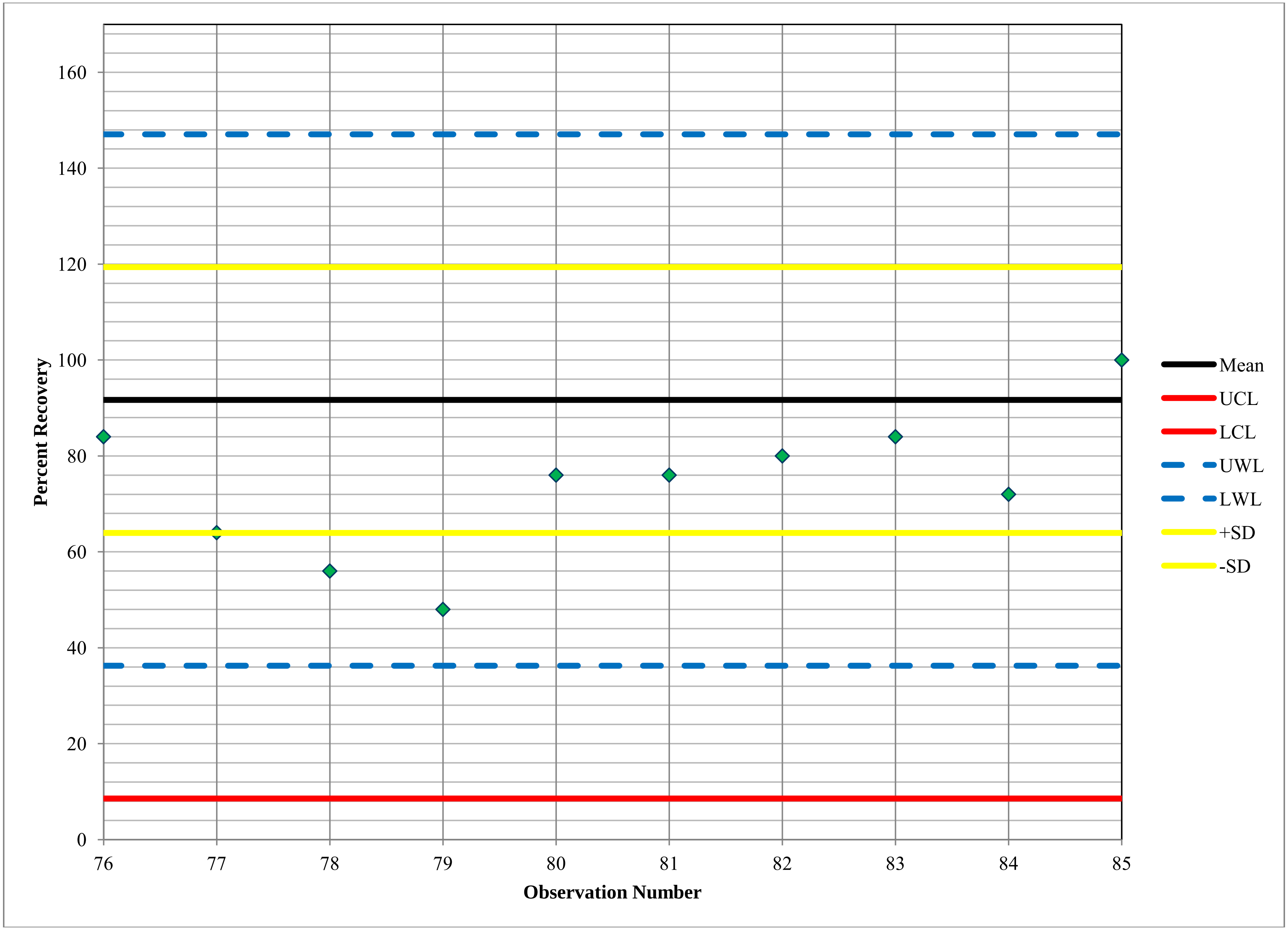

Percent Recovery
160
140
120
100
80
60
40
20
26
27
28
29
30
31
32
33
34
35
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

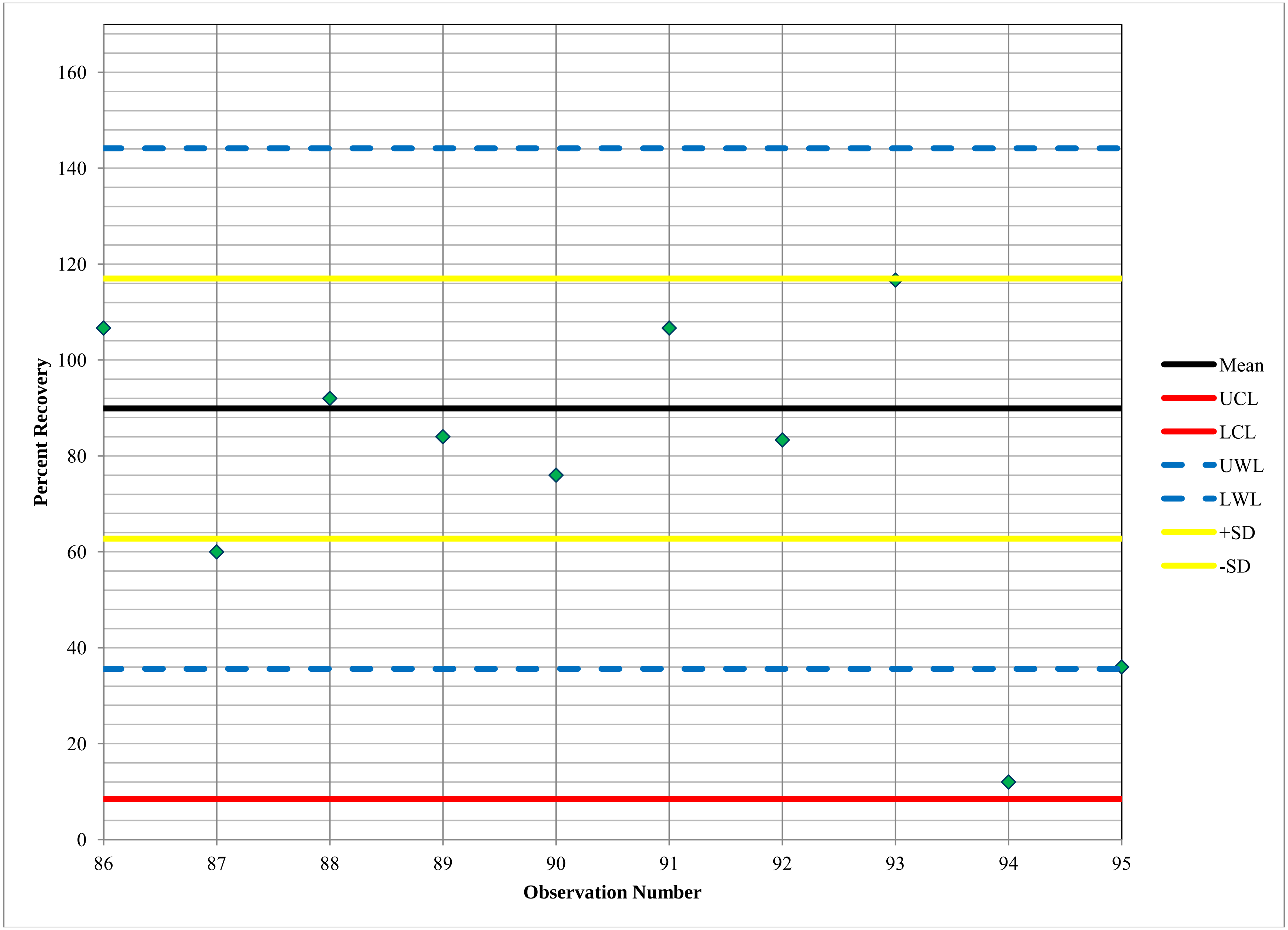

Percent Recovery
170
150
130
110
90
70
50
30
36
37
38
39
40
41
42
43
44
45
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD


170
150
130
110
90
70
50
30
Percent Recovery
46
47
48
49
50
51
52
53
54
55
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

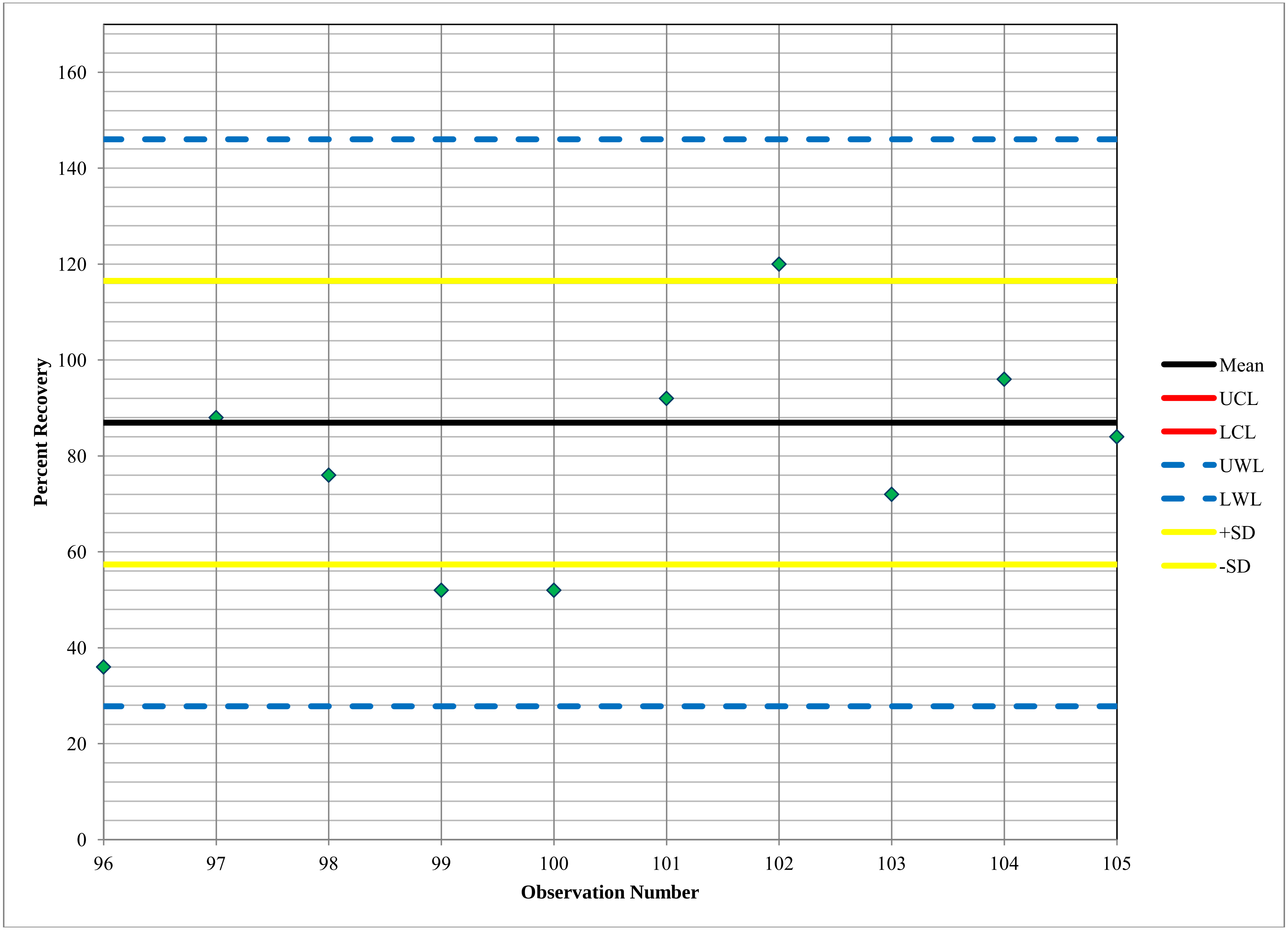

170
150
130
110
90
70
50
30
Percent Recovery
56
57
58
59
60
61
62
63
64
65
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

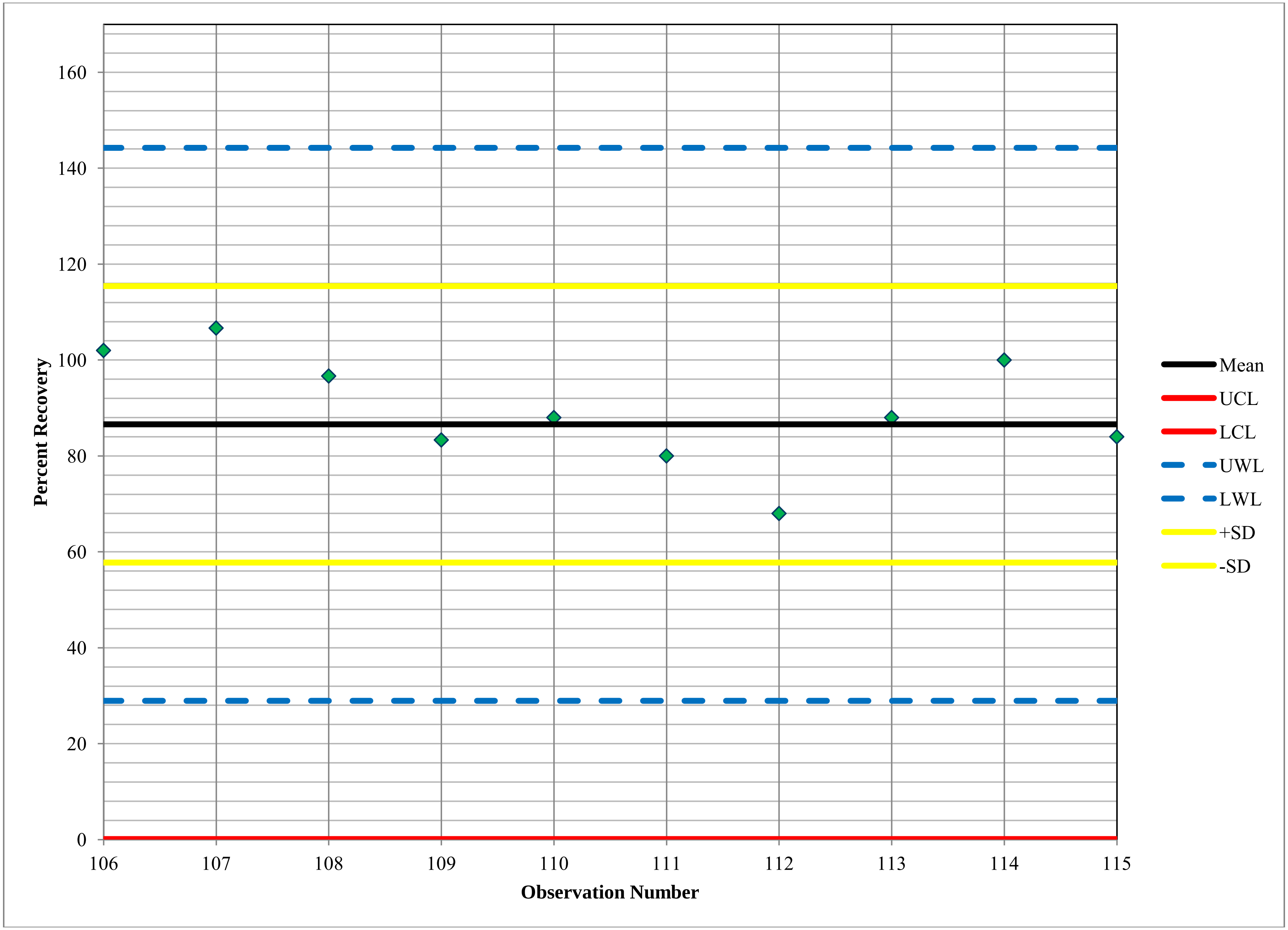

180
160
140
120
100
80
60
40
20
0
Percent Recovery
66
67
68
69
70
71
72
73
74
75
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

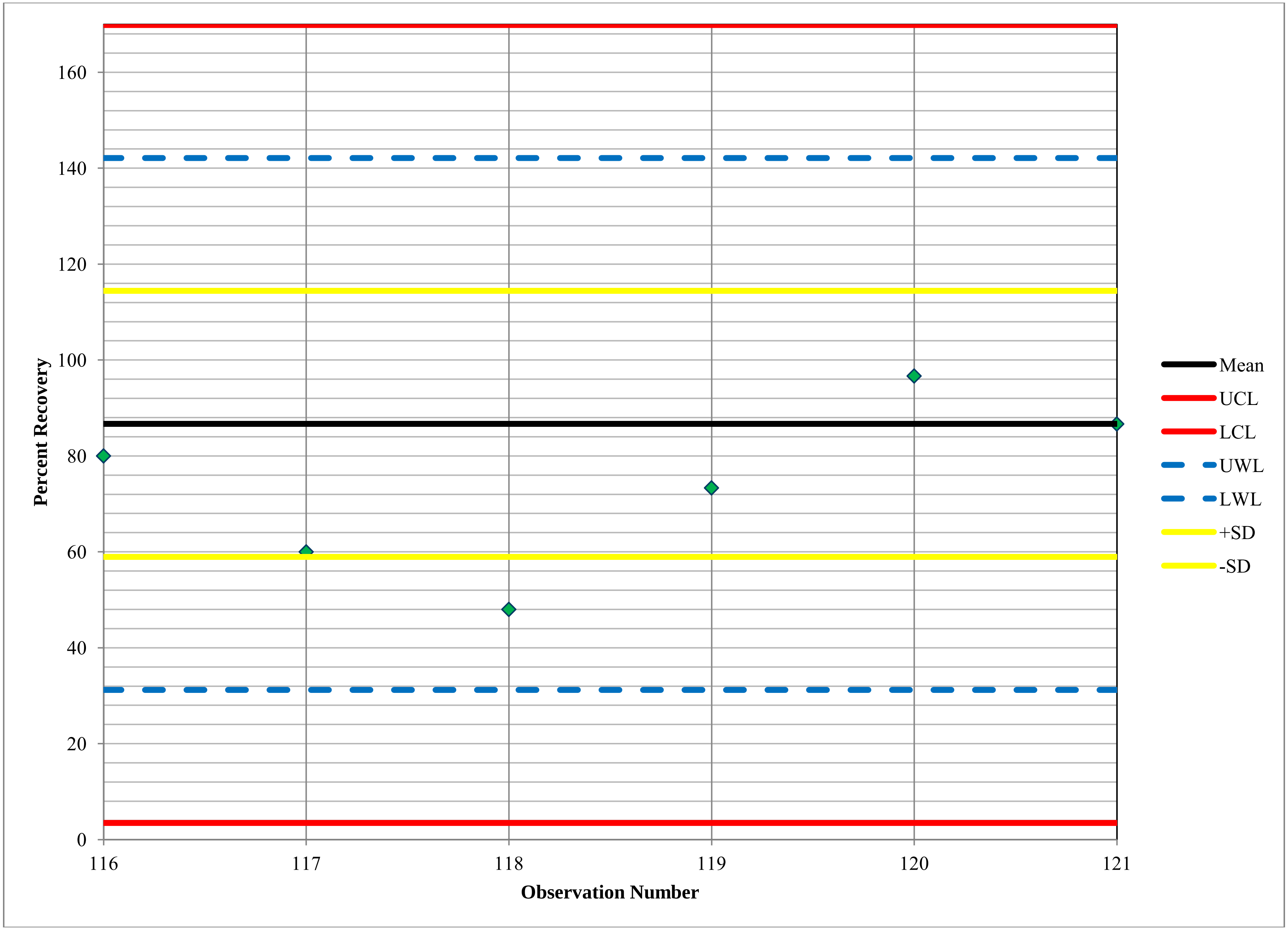

Percent Recovery
160
140
120
100
80
60
40
20
0
76
77
78
79
80
81
82
83
84
85
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD



Percent Recovery
0
20
40
60
80
100
120
140
160
Observation Number
86
87
88
89
90
91
92
93
94
95
Mean
UCL
LCL
UWL
LWL
+SD
-SD


Percent Recovery
0
20
40
60
80
100
120
140
160
96
97
98
99
100
101
102
103
104
105
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD


Percent Recovery
160
140
120
100
80
60
40
20
0
106
107
108
109
110
111
112
113
114
115
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD



Percent Recovery
0
20
40
60
80
100
120
140
160
116
117
118
119
120
121
Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

Appendix E
Round 2 Testing Results

Date	Phase 1 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
2/12/2013	1	QCS-1	30	31	30	103	103			
	2	IDC-25-1	25	20	27	80	74			
	3	IDC-25-2	25	18		72	67	Percent recovery < 75%	Rerun IDC-2	
	4	IDC-25-2-RR1	25	16		64	59	Percent recovery < 75%	Repeat on-site calibration	
	5	IDC-25-2-RR2	25	19		76	70			
	6	IDC-25-3	25	18		72	67	Percent recovery < 75%		
	7	IDC-25-3-RR1	25	21		84	78		Continue to TPC	TPC completed and applied. Site "None" used for all remaining DI water samples
	8	ICC-25-1	25	20	22	80	91			
	9	ICC-25-2	25	25		100	114			
	10	ICC-25-3	25	21		84	95			
	11	QCS-2	30	20	31	67	65	Percent recovery < 75%	Rerun QCS-2	
	12	QCS-2-RR1	30	25		83	81			
	13	DLOD-10-1	10	8	9	80	89	No Percent recovery criterion		
	14	DLOD-10-2	10	8		80	89	No Percent recovery criterion		
	15	DLOD-10-3	10	9		90	100	No Percent recovery criterion		
	16	DLOD-10-4	10	8		80	89	No Percent recovery criterion		
	17	DLOD-10-5	10	8		80	89	No Percent recovery criterion		
	18	DLOD-10-6	10	8		80	89	No Percent recovery criterion		
	19	DLOD-10-7	10	9		90	100	No Percent recovery criterion		

Date	Phase 1 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
	20	DLR-5-1	5	4	5	80	80	No Percent recovery criterion		
	21	DLR-5-2	5	4		80	80	No Percent recovery criterion		
	22	DLR-5-3	5	5		100	100	No Percent recovery criterion		
	23	QCS-3	30	24	32	80	75			
	24	DLR-15-1	15	12	14	80	86	No Percent recovery criterion		
	25	DLR-15-2	15	14		93	100	No Percent recovery criterion		
	26	DLR-15-3	15	12		80	86	No Percent recovery criterion		
	27	DLR-25-1	25	20	29	80	69	No Percent recovery criterion		
	28	DLR-25-2	25	19		76	66	No Percent recovery criterion		
	29	DLR-25-3	25	22		88	76	No Percent recovery criterion		
	30	DLR-50-1	50	51	53	102	96	No Percent recovery criterion		
	31	DLR-50-2	50	46		92	87	No Percent recovery criterion		
	32	DLR-50-3	50	46		92	87	No Percent recovery criterion		
	33	QCS-4	30	28	29	93	97			
	34	DLR-75-1	75	77	83	103	93	No Percent recovery criterion		
	35	DLR-75-2	75	78		104	94	No Percent recovery criterion		
	36	DLR-75-3	75	73		97	88	No Percent recovery criterion		
	37	DLR-100-1	100	105	109	105	96	No Percent recovery criterion		
	38	DLR-100-2	100	91		91	83	No Percent recovery criterion		
	39	DLR-100-3-RR1	100	83		83	76	First reading was 157 ppb and above the UCL	DLR-100-3 will be rerun	

Date	Phase 1 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
	40	QCS-5	30	34	34	113	100			
2/13/13/	41	QCS-6	30	20	27	67	74	Percent recovery < 75%	rerun QCS-6	
	42	QCS-6-RR1	30	27		90	100			
	43	LTDS-25-1	25	19	25	76	76			All LTDS samples prefiltered
	44	LTDS-25-2	25	17		68	68	Percent recovery < 75%	Rerun LTDS-25-2	
	45	LTDS-25-2-RR1	25	23		92	92			
	46	LTDS-25-3	25	25		100	100			
	47	LTDS-50-1	50	46	47	92	98			
	48	LTDS-50-2	50	38		76	81			
	49	LTDS-50-3	50	41		82	87			
	50	HTDS-25-1	25	18	21	72	86	Percent recovery < 75%	Rerun HTDS-25-1	All HTDS samples prefiltered
	51	HTDS-25-1-RR1	25	26		104	124			
	52	HTDS-25-2	25	22		88	105			
	53	HTDS-25-3	25	24		96	114			
	54	QCS-7	30	26	31	87	84			
	55	HTDS-50-1	50	46	49	92	94			
	56	HTDS-50-2	50	41		82	84			
	57	HTDS-50-3	50	47		94	96			
	58	HFe-25-1	25	24	22	96	109			After filtration, pH adjustment and

Date	Phase 1 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
										pretreatment
	59	HFe-25-2	25	18		72	82			
	60	HFe-25-2-RR1	25	19		76	86			
	61	HFe-25-3	25	20		80	91			
	62	HFe-50-1	50	42	45	84	93			
	63	HFe-50-2	50	44		88	98			
	64	HFe-50-3	50	45		90	100			
	65	QCS-8	30	33	31	110	106			

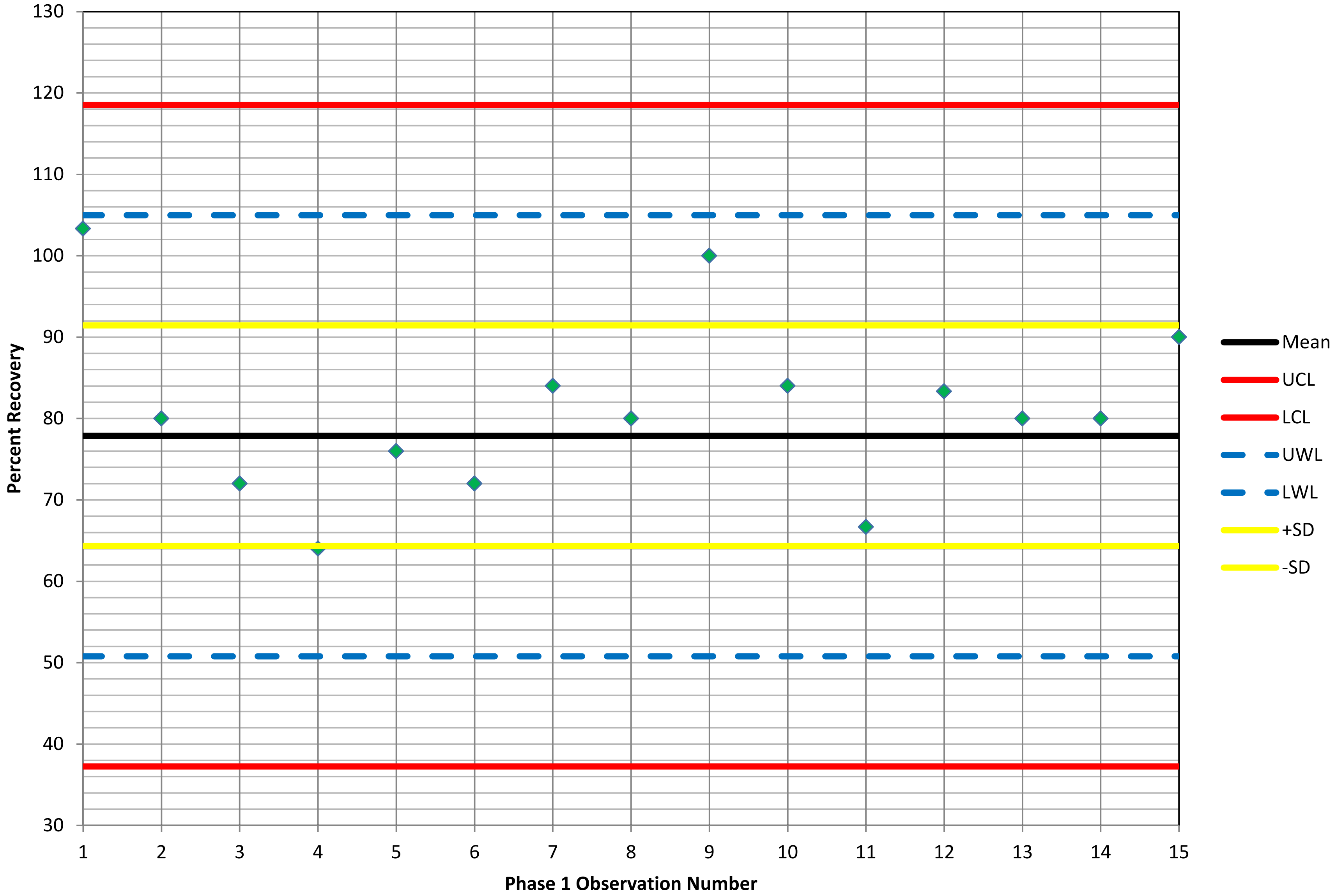
Date	Phase 2 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
3/12/2013	1	QCS-9	30	24	29	80	83			
	2	RiW-25-1	25	21	20	84	105			
	3	RiW-25-2	25	24		96	120			
	4	RiW-25-3	25	16		64	80	Percent recovery < 75%	Rerun RiW-25-3	
	5	RiW-25-3-RR1	25	23		92	115			
	6	ReW-25-1	25	23	21	92	110			
	7	ReW-25-2	25	20		80	95			
	8	ReW-25-3	25	23		92	110			
	9	RWW-25-1	25	13	18	52	72	Percent recovery < 75%	Rerun RWW-25-1	
	10	RWW-25-1-RR1	25	12		48	67	Percent recovery < 75%	Repeat on-site calibration and rerun RWW-25-1	
	11	QCS-10	30	24	26	80	92			
	12	RWW-25-1-RR2	25	16	18	64	89	Percent recovery < 75%	Rerun RWW-25-1-RR2	

Date	Phase 2 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
	13	RWW-25-1-RR3	25	21		84	117			
	14	RWW-25-2	25	18		72	100	Percent recovery < 75%	Rerun RWW-25-2	
	15	RWW-25-2-RR1	25	14		56	78	Percent recovery < 75%	Proceed with iron interference procedure	Assume that residual iron in the sample is causing the low readings
	16	RWWPT-25-1	35	43	21	123	205			
	17	RWWPT-25-2	35	32		91	152			
	18	RWWPT-25-3	35	26		74	124	Percent recovery < 75%	Rerun RWWPT-25-3	
	19	RWWPT-25-3-RR1	35	31		89	148			
	20	FWW-25-1	25	23	24	92	96			
	21	FWW-25-2	25	21		84	88			
	22	QCS-11	30	43	28	143	154	Percent Recovery > 125%	Rerun QCS-11	
	23	QCS-11-RR1	30	37		123	132			
	24	FWW-25-3	25	19	24	76	79			
	25	QCS-12	30	40	28	133	143	Percent Recovery > 125%	Rerun QCS-12	
	26	QCS-12-RR1	30	46		153	164	Percent Recovery > 125%	Repeat on-site calibration and rerun QCS-12-RR1	
	27	QCS-12-RR2	30	33		110	118			
3/13/2013	28	QCS-13	30	27	29	90	93			
	29	WF-25-1	25	19	21	76	90			
	30	WF-25-2	25	24		96	114			

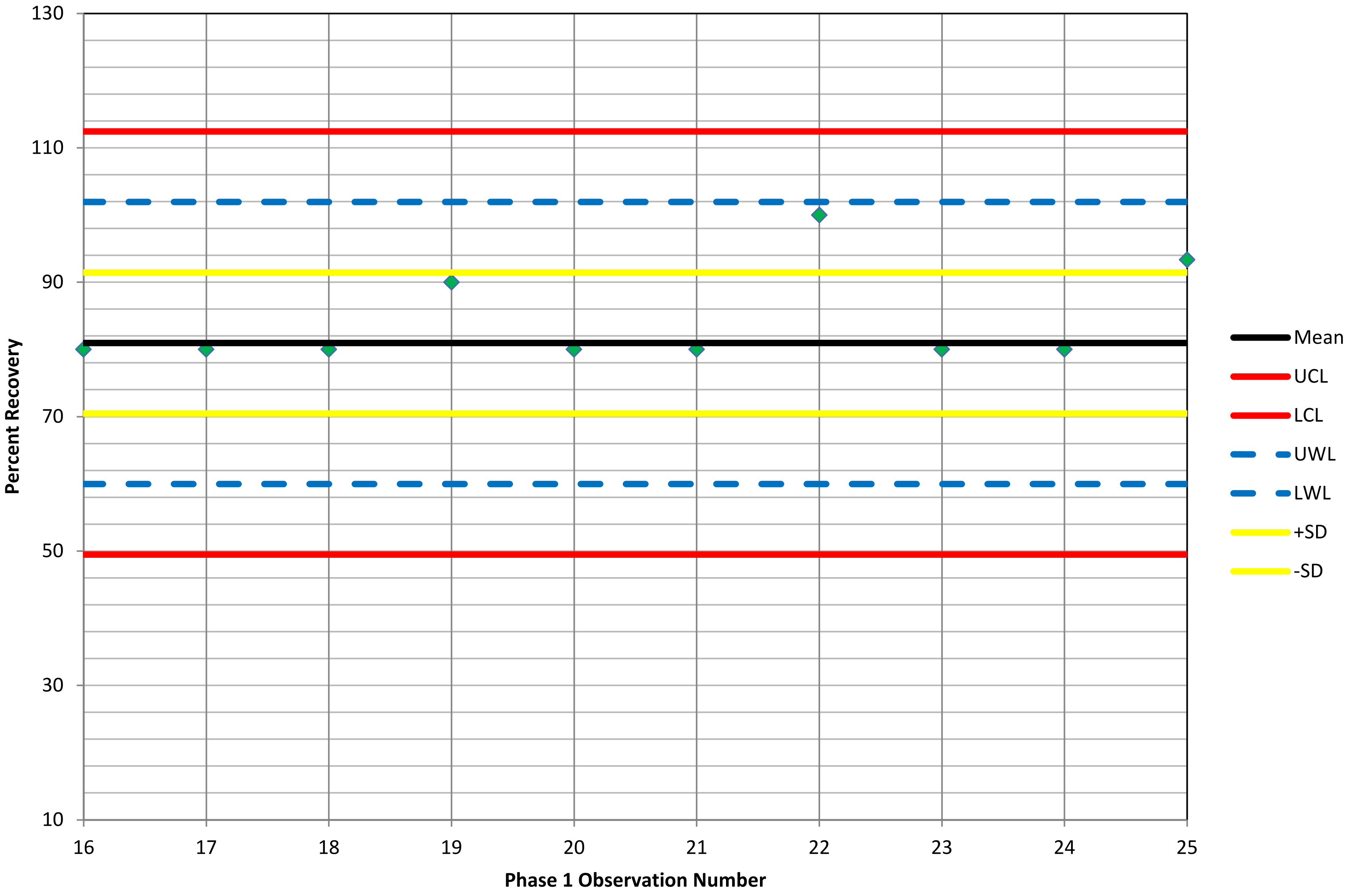
Date	Phase 2 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
	31	WF-25-3	25	25		100	119			
	32	BW-25-1	25	18	20	72	90	Percent Recovery < 75%	Rerun BW-25-1	
	33	BW-25-1-RR1	25	17		68	85	Percent Recovery < 75%	Repeat on-site calibration	
	34	BW-25-1-RR2	25	16		64	80	Percent Recovery < 75%	Rerun BW-25-1-RR2	
	35	BW-25-1-RR3	25	17		68	85	Percent Recovery < 75%	Rerun BW-25-1-RR3 as a final BW sample	
	36	BW-25-1-RR4	25	18		72	90	Percent Recovery < 75%		
	37	MWWE#1-25-1	25	20	19	80	105			
	38	MWWE#1-25-2	25	19		76	100			
	39	MWWE#1-25-3	25	17		68	89	Percent Recovery < 75%	Rerun MWWE#1-25-3	
	40	MWWE#1-25-3-RR1	25	21		84	111			
	41	QCS-14	30	23	30	77	77			
	42	MWWE#2-25-1	25	28	20	112	140			
	43	MWWE#2-25-2	25	34		136	170	Percent Recovery > 125%	Rerun MWWE#2-25-2	
	44	MWWE#2-25-2-RR1	25	33		132	165	Percent Recovery > 125%	Repeat onsite calibration	
	45	MWWE#2-25-2-RR2	25	26		104	130			
	46	MWWE#2-25-3	25	23		92	115			

Date	Phase 2 Sample Number	Sample Name	Expected Concentration (µg/L Pb)	Measured Concentration (µg/L Pb)	ICP-MS Concentration (µg/L Pb)	Percent Recovery to Target (%)	Percent Recovery to ICP-MS (%)	Abnormal Anticipated Percent Recovery/Control Chart Result	Resolution	Comments
	47	MWWE#2-25-4	25	26		104	130			This sample run because of LFM/LFMD requirement after new on-site calibration
	48	MFWWE-25-1	25	22	24	88	92			
	49	MFWWE-25-2	25	21		84	88			
	50	MFWWE-25-3	25	23		92	96			
	51	QCS-15	30	31	30	103	103			

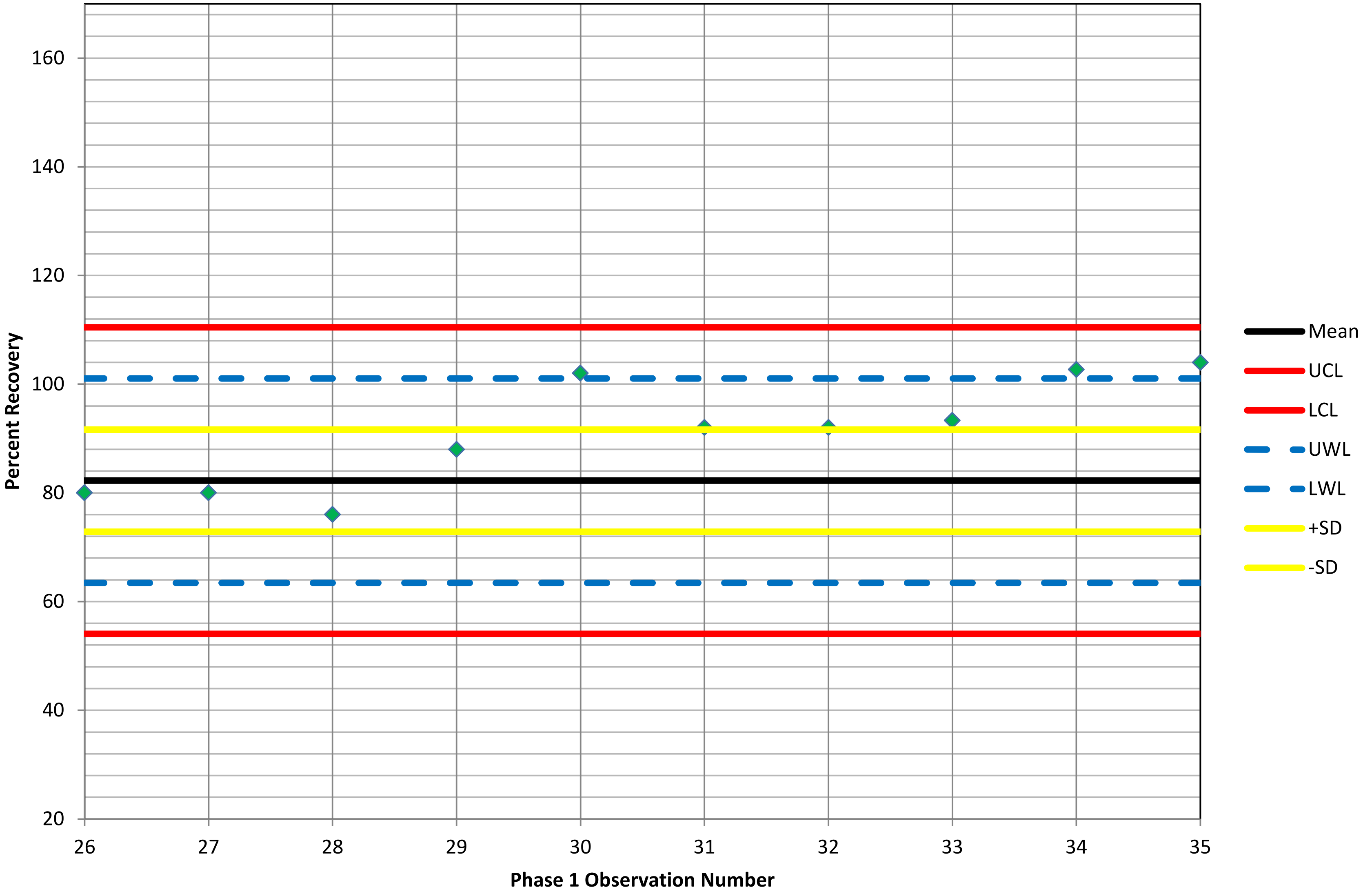
Appendix F
Round 2 Control Charts

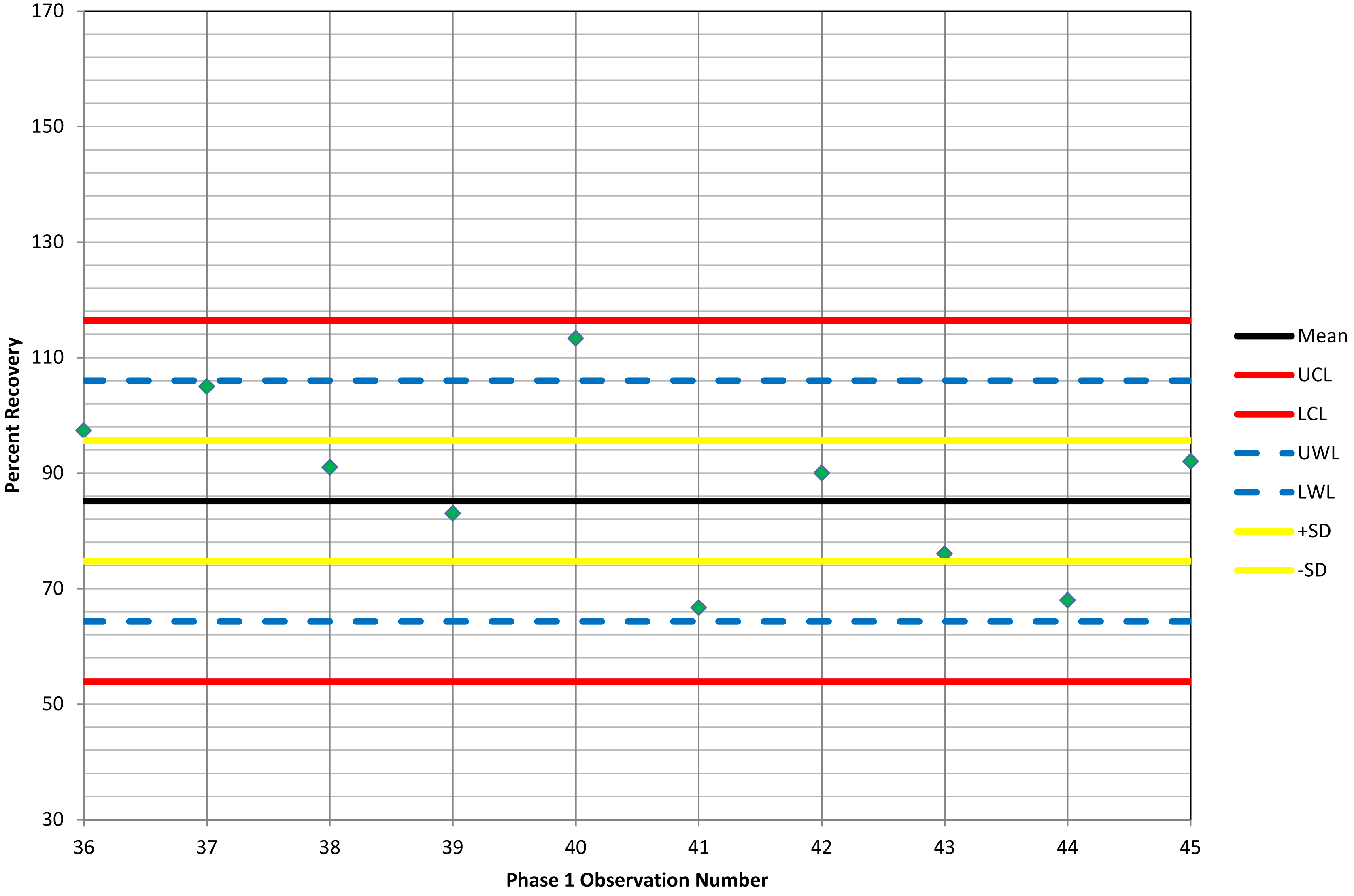


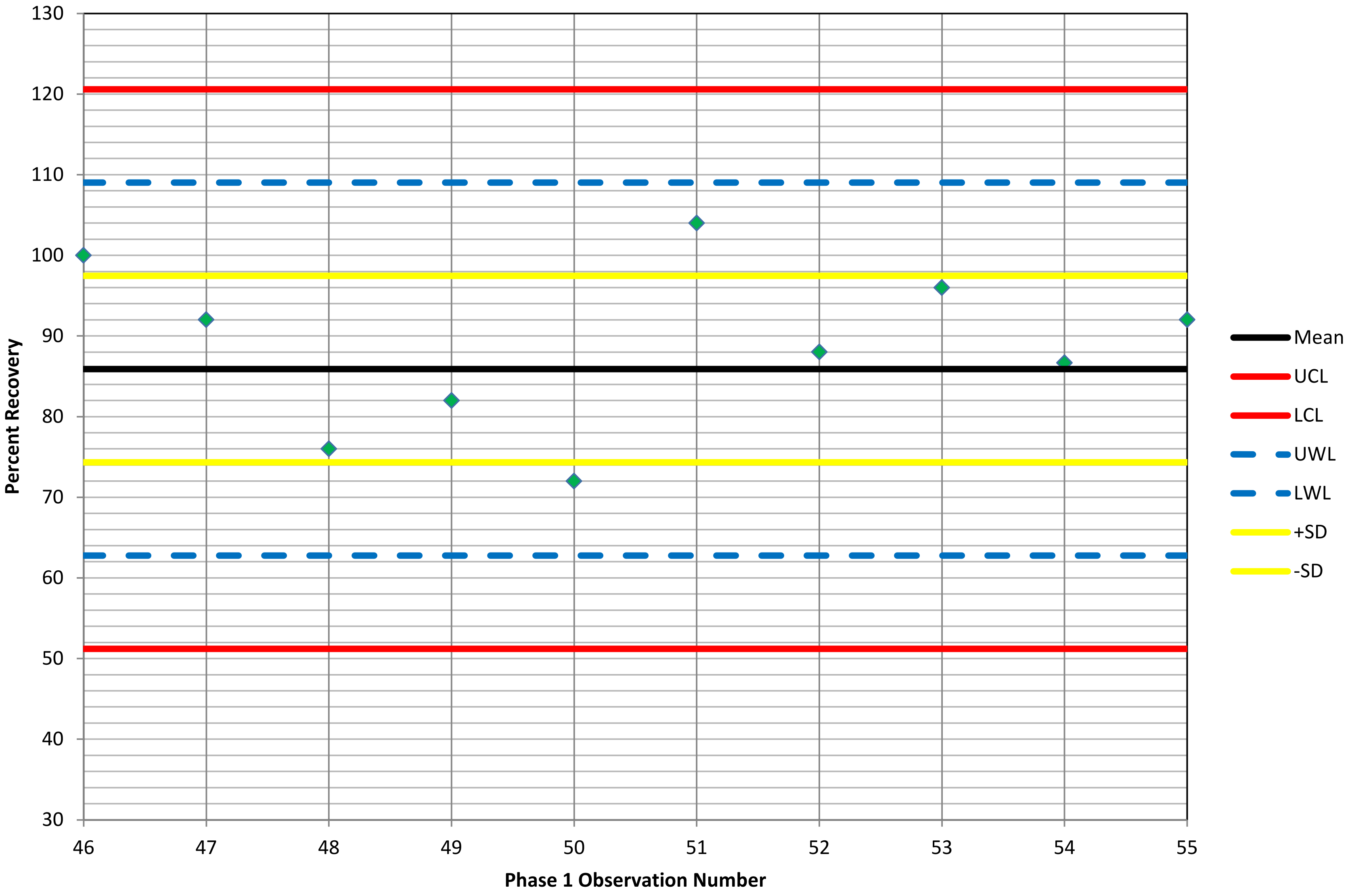
130
120
110
100
90
80
70
60
50
40
30
Percent Recovery
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

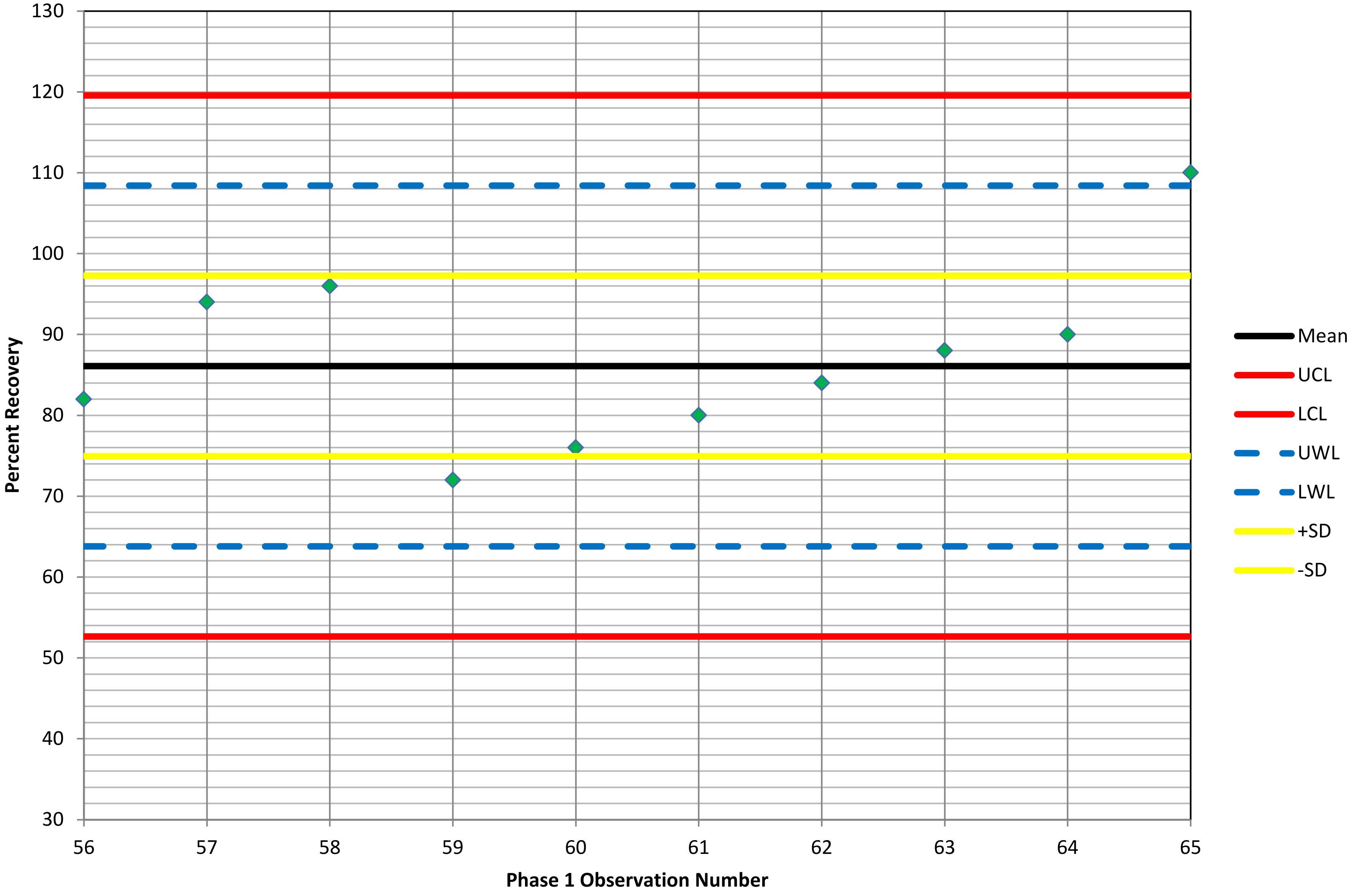


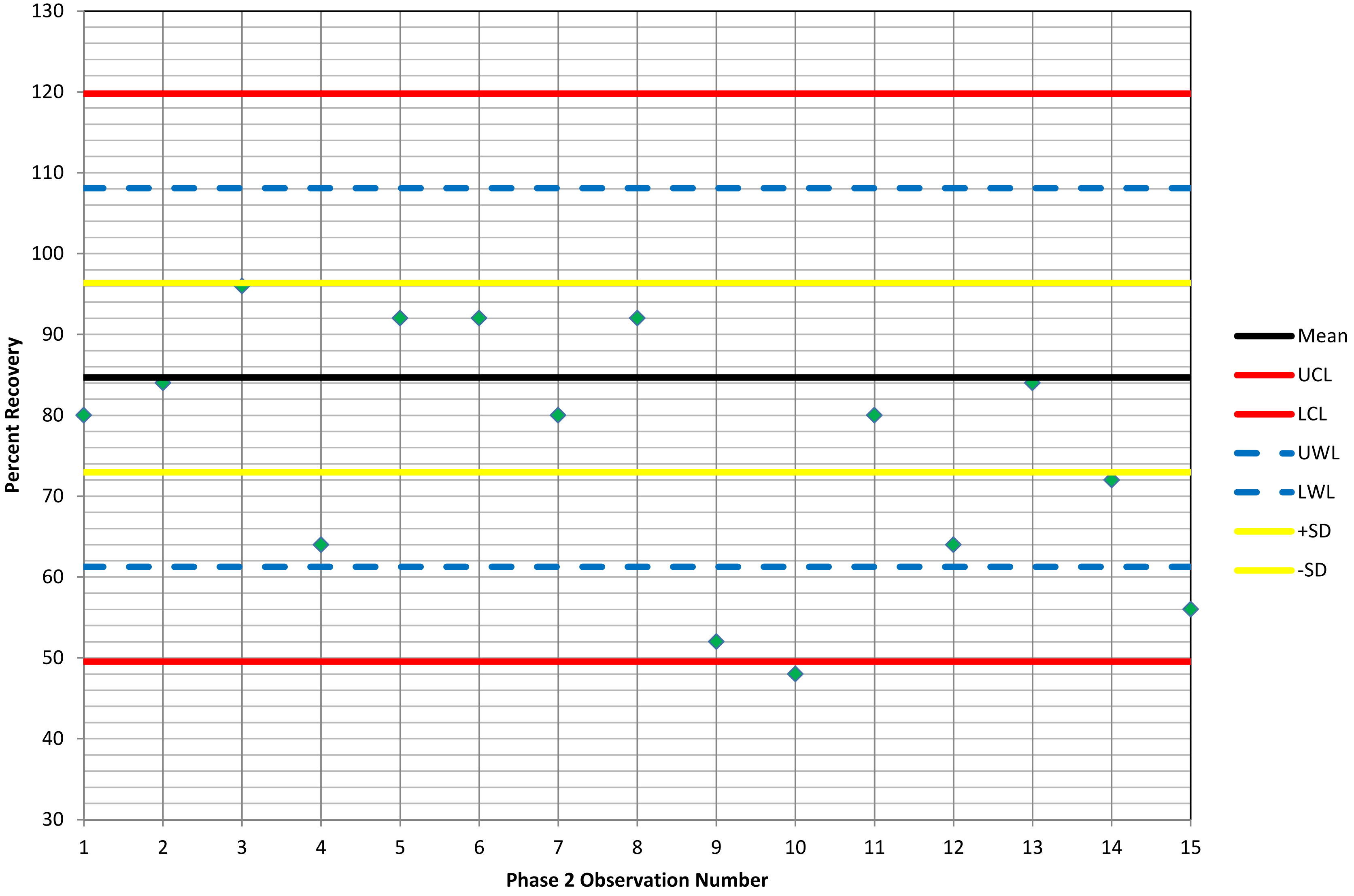
130
110
90
70
50
30
10
Percent Recovery
16
17
18
19
20
21
22
23
24
25
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

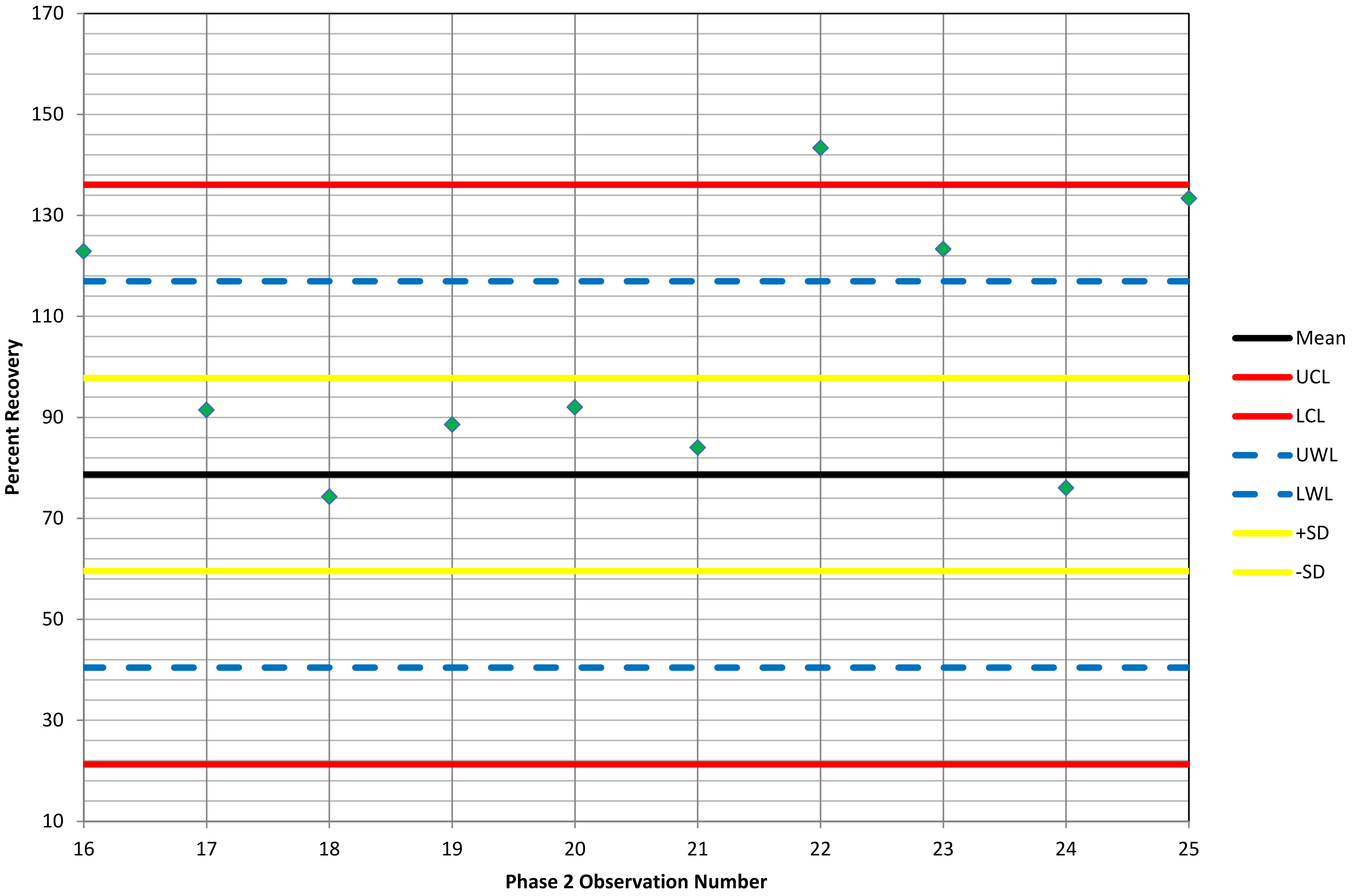

Percent Recovery
160
140
120
100
80
60
40
20
26
27
28
29
30
31
32
33
34
35
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD


170
150
130
110
90
70
50
30
Percent Recovery
36
37
38
39
40
41
42
43
44
45
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

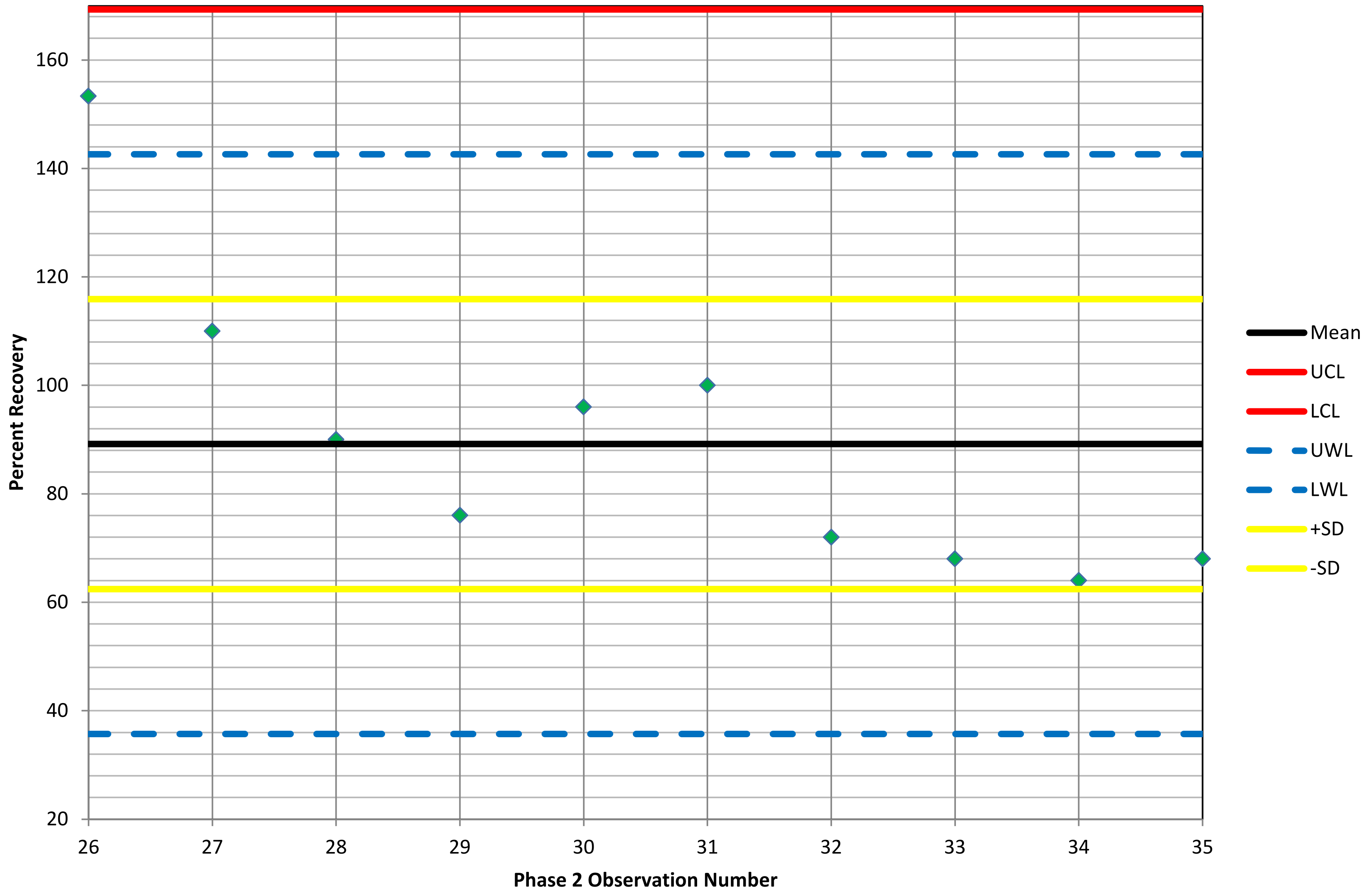

130
120
110
100
90
80
70
60
50
40
30
Percent Recovery
46
47
48
49
50
51
52
53
54
55
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

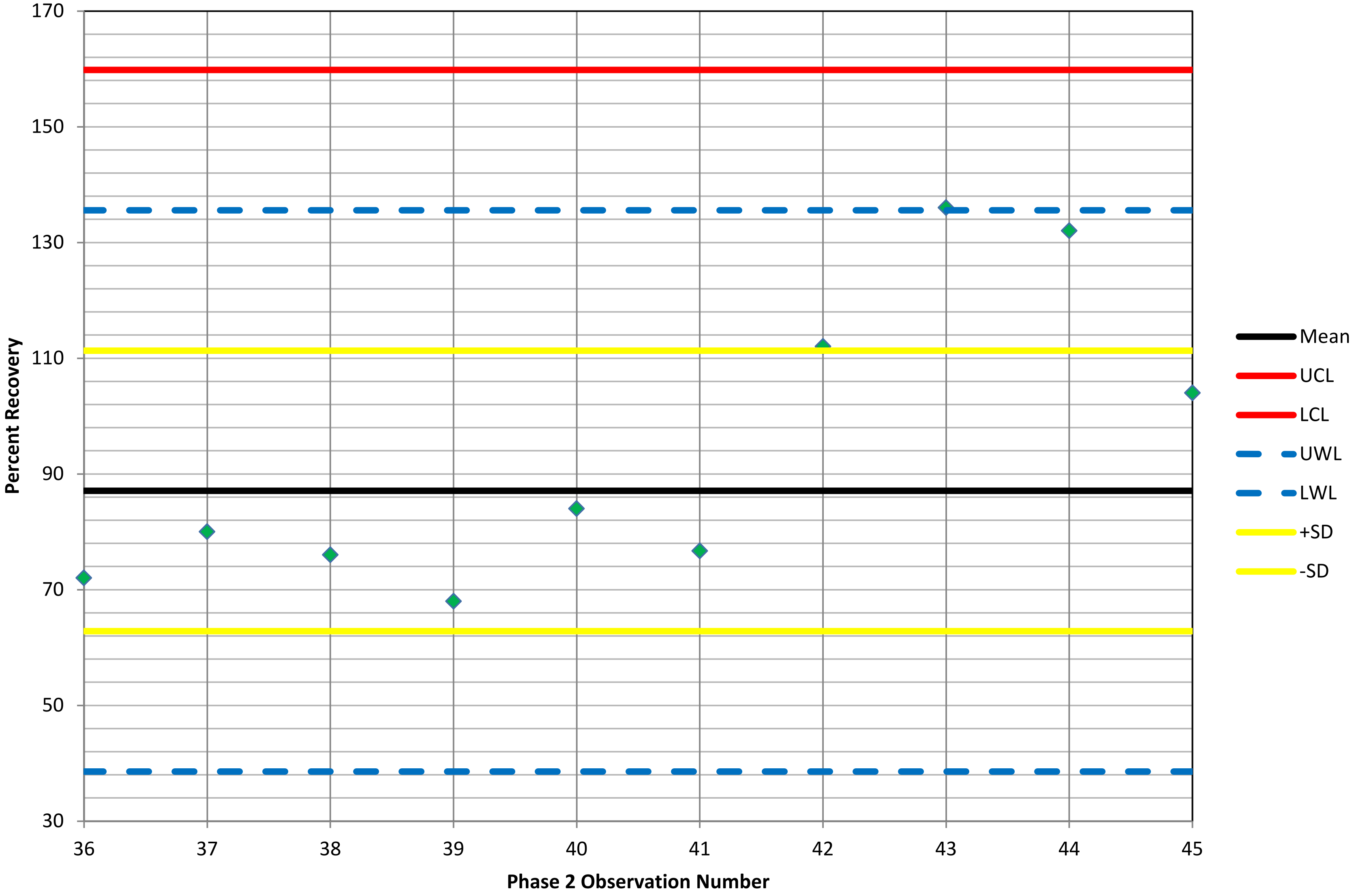

130
120
110
100
90
80
70
60
50
40
30
Percent Recovery
56
57
58
59
60
61
62
63
64
65
Phase 1 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

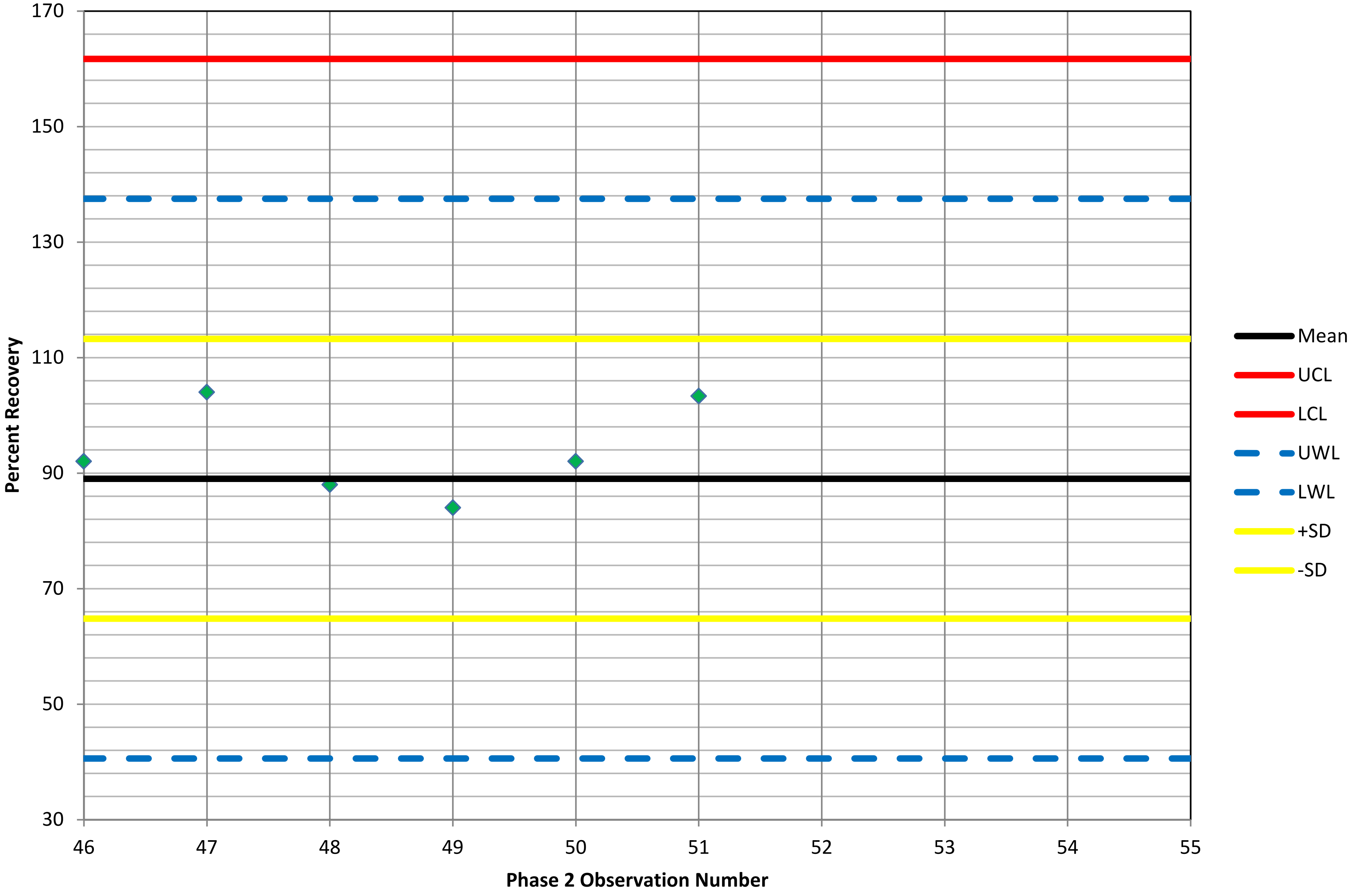

130
120
110
100
90
80
70
60
50
40
30
Percent Recovery
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Phase 2 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD



170
150
130
110
90
70
50
30
10
Percent Recovery
16
17
18
19
20
21
22
23
24
25
Phase 2 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

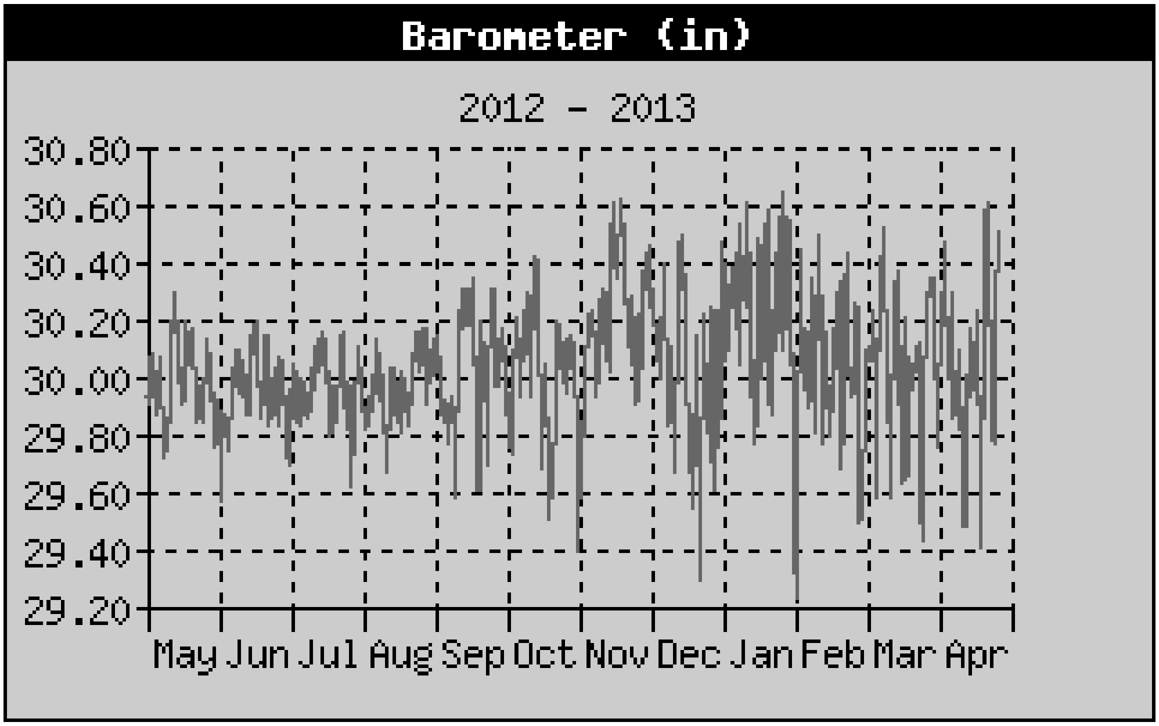

Percent Recovery
160
140
120
100
80
60
40
20
26
27
28
29
30
31
32
33
34
35
Phase 2 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

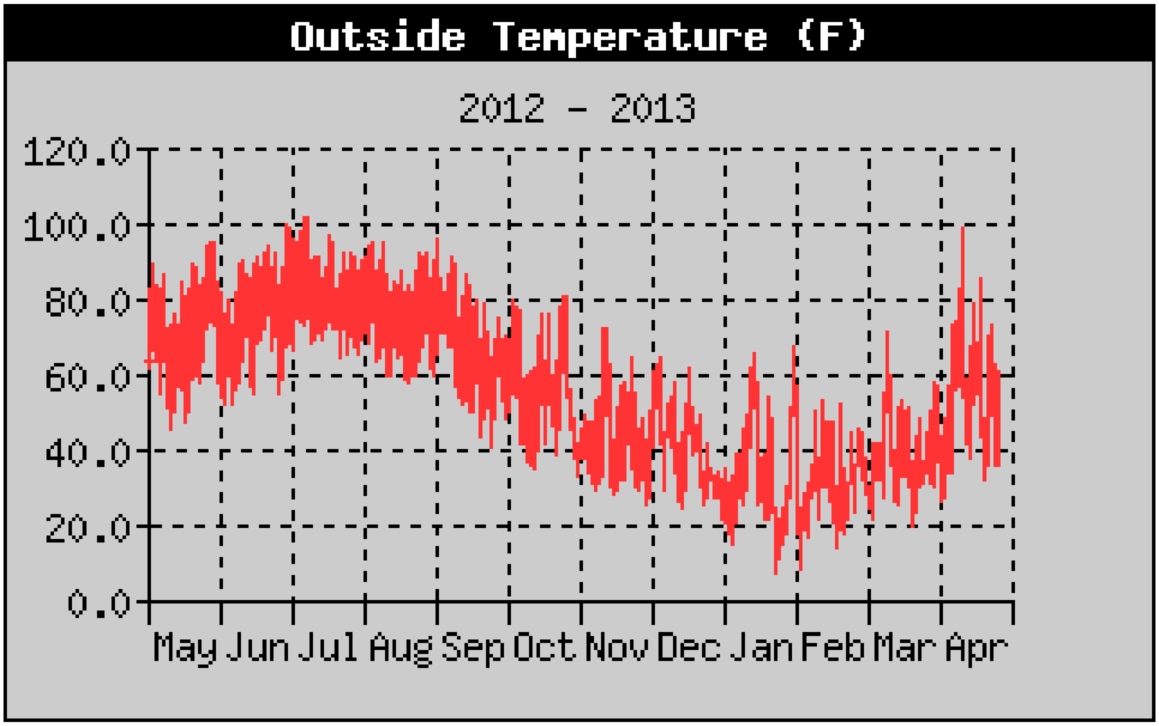

170
150
130
110
90
70
50
30
Percent Recovery
36
37
38
39
40
41
42
43
44
45
Phase 2 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD



170
150
130
110
90
70
50
30
Percent Recovery
46
47
48
49
50
51
52
53
54
55
Phase 2 Observation Number
Mean
UCL
LCL
UWL
LWL
+SD
-SD

Appendix G
Temperature and Barometric Pressure Data


Barometer (in)
2012 - 2013
30.80
30.60
30.40
30.20
30.00
29.80
29.60
29.40
29.20
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr


Outside Temperature (F)
2012 - 2013
120.0
100.0
80.0
60.0
40.0
20.0
0.0
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr