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September 2012

Environmental Technology Verification Report

Pall Corporation
Xact 625 Particulate Metals Monitor

Prepared by

Battelle
The Business of Innovation

Under a cooperative agreement with

EPA **U.S. Environmental Protection Agency**

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Columbus, Ohio 43201

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This report was prepared by Battelle to summarize testing supported by EPA's Region 5 and Office of Air Quality Planning and Standards (OAQPS), and conducted in collaboration with the Ohio EPA (OEPA). Neither Battelle, EPA, OEPA nor any person acting on behalf of those organizations

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Foreword

The 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 to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to 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 to 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 (QA) 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.

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List of Abbreviations

AMS	Advanced Monitoring Systems
As	arsenic
Ba	barium
°C	degrees Centigrade
Ca	calcium
Cd	cadmium
CES	Cooper Environmental Services LLC
CI	confidence interval
Co	cobalt
Cr	chromium
Cu	copper
DC	data completeness
EDXRF	energy-dispersive X-ray fluorescence
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
Fe	iron
HF	hydrofluoric acid
Hg	mercury
ICP/MS	inductively coupled plasma mass spectrometry
K	potassium
L/min	liter per minute
mm Hg	millimeter of mercury
m^3/hr	cubic meter per hour
MDL	method detection limit
µg/L	microgram per liter
µm	micrometer
Mn	manganese
Mo	molybdenum
ng/m^3	nanograms per cubic meter
Ni	nickel
NIST	National Institute of Science and Technology
OAQPS	Office of Air Quality Planning and Standards
OEPA	Ohio Environmental Protection Agency
OVESC	Ohio Valley Educational Service Center
Pb	lead
Pd	palladium
PE	performance evaluation
PM	particulate matter
PM_{10}	particulate matter of aerodynamic diameter ≤ 10 micrometers
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QL	quantitation limit

List of Abbreviations

AMS	Advanced Monitoring Systems
As	arsenic
Ba	barium
°C	degrees Centigrade
Ca	calcium
Cd	cadmium
CES	Cooper Environmental Services LLC
CI	confidence interval
Co	cobalt
Cr	chromium
Cu	copper
DC	data completeness
EDXRF	energy-dispersive X-ray fluorescence
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
Fe	iron
HF	hydrofluoric acid
Hg	mercury
ICP/MS	inductively coupled plasma mass spectrometry
K	potassium
L/min	liter per minute
mm Hg	millimeter of mercury
m^3/hr	cubic meter per hour
MDL	method detection limit
µg/L	microgram per liter
µm	micrometer
Mn	manganese
Mo	molybdenum
ng/m^3	nanograms per cubic meter
Ni	nickel
NIST	National Institute of Science and Technology
OAQPS	Office of Air Quality Planning and Standards
OEPA	Ohio Environmental Protection Agency
OVESC	Ohio Valley Educational Service Center
Pb	lead
Pd	palladium
PE	performance evaluation
PM	particulate matter
PM_{10}	particulate matter of aerodynamic diameter ≤ 10 micrometers
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QL	quantitation limit

QMP	quality management plan
r^2	coefficient of determination
Rb	rubidium
RSD	relative standard deviation
SAT	School Air Toxics
Sb	antimony
SD	standard deviation
Se	selenium
SEDO	Southeast District Office
Sr	strontium
Th	thorium
Tl	thallium
TSA	technical systems audit
XRF	X-ray fluorescence
Zn	zinc

QMP	quality management plan
r^2	coefficient of determination
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SEDO	Southeast District Office
Sr	strontium
Th	thorium
Tl	thallium
TSA	technical systems audit
XRF	X-ray fluorescence
Zn	zinc

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (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 tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance and quality control (QA/QC) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The 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 Xact 625 Particulate Metals Monitor produced by Pall Corporation at an ambient air quality monitoring site in Marietta, Ohio. Systems for monitoring of metals in atmospheric particulate matter (PM) were identified as a priority technology category for verification through the AMS Center stakeholder process.

Chapter 1
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Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This report provides results from verification testing of the Xact 625 Particulate Metals Monitor, which was developed and previously manufactured by Cooper Environmental Services LLC (CES) (Portland, OR). Commercial rights to the Xact 625 technology are now owned by Pall Corporation (Port Washington, NY). The following is a description of the Xact 625, based on information provided by the vendor. The information provided below was not verified in this test.

The Xact 625, shown in Figure 2-1, determines metals in airborne PM less than 10 micrometers (μm) in aerodynamic diameter (PM_{10}). Metals determination by the Xact 625 is based on the principle of X-ray fluorescence (XRF), in which X-rays from a source cause removal of an electron from an inner electronic shell of a metal atom in a sample. The vacancy in the inner shell is then filled by an electron from an outer shell, with resulting emission of an X-ray with a wavelength longer than that of the original excitation and characteristic of the metal in question. The Xact 625 uses energy-dispersive XRF (EDXRF), in which the detector and electronics resolve emitted X-rays based on their energy. The EDXRF approach allows use of a relatively simple optical path and a relatively low power X-ray source, and thus reduces the instrument cost. The EDXRF approach also provides acquisition of the entire X-ray spectrum very rapidly, so that many elements in the periodic table can be detected within a few seconds.

To monitor metals in atmospheric PM, the Xact 625 uses an automated moveable filter tape system, in which sample air is drawn through a small spot on the tape, collecting and concentrating PM_{10} onto that spot. The tape then advances, placing the collected sample spot in the X-ray excitation and analysis section of the instrument and initiating sampling onto a previously unexposed spot on the tape. The sequence of sampling and analysis can continue automatically, limited only by the supply of filter tape. The duration of sample collection at each spot can be set at a constant interval, or varied to maintain detection performance in the face of varying atmospheric PM_{10} levels. The Xact 625 samples ambient air at a constant flow rate of 16.7 liters per minute (L/min), i.e., 1 cubic meter per hour (m^3/hr). The Xact 625's sample inlet is designed to provide uniform sample deposition, and the instrument analyzes approximately 90% of the sample spot area to minimize effects of sample inhomogeneity. The Xact 625 incorporates sensors for temperature and atmospheric pressure, and uses those data to maintain a constant volumetric sample flow and

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consequently an accurate PM_{10} inlet size cut. In addition for this verification the vendor of the Xact 625 programmed the monitor to perform the following automatic internal QC checks on a daily basis to assure data quality:

- Internal energy alignment check, performed by XRF analysis of a copper (Cu) rod, conducted over a 15-minute period starting at midnight each day,
- Upscale rod check, performed by XRF analysis of a metal rod containing chromium (Cr), lead (Pb), and cadmium (Cd), conducted once per day over a 15-minute period,
- Flow check, conducted at the same time as the upscale rod check, to determine the Xact 625 sample air flow by insertion of a second mass flow meter into the flow path,
- Palladium (Pd) rod stability check, conducted by XRF analysis of a Pd rod in every ambient sample analysis.

Figure 2-1. Xact 625 installed in field trailer for testing; top to bottom are the control panel/X-ray source, computer, XRF analysis module with sampling tape drive, modem, and datalogger.

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Chapter 3
Test Design and Procedures

3.1 Introduction

Industrial communities are often impacted by emissions of toxic metals such as Pb, manganese (Mn), and Cd. For example, EPA's School Air Toxics (SAT) Monitoring Initiative[1] has reported that Mn, a neurotoxic metal, is one of the pollutants of greatest potential risk near schools in industrialized locations. Standard monitoring methods for metals in airborne PM have significant limitations, in that samples are collected on filters over a 24-hour time period and must be submitted for laboratory analysis, from which results may not be available for several weeks. In contrast, commercially-developed metals monitors can potentially determine 10 or more toxic metals simultaneously in ambient PM_{10} with time resolution of 1 hour or less. The relatively fast response afforded by such monitors can provide advantages such as:

- Improved ability to associate variations in metals concentrations with time of day or meteorological conditions, and thus to attribute metals risk to a particular source
- Ability to compile datasets large enough to conduct source/receptor modeling, and
- Cost reduction and time savings due to the generation of metals data onsite without waiting for laboratory analysis.

Thus, continuous metals monitoring may lead to better characterization of environmental metals exposures and more effective source identification, allowing decision-makers to quickly target industries for enforcement action or voluntary emissions reduction.

This verification test was conducted according to a peer-reviewed quality assurance project plan (QAPP),[2] and conformed to the quality system defined in the ETV[3] and AMS Center[4] Quality Management Plans (QMPs). As indicated in the QAPP[2] the testing satisfied EPA QA Category III requirements. The QAPP and this verification report were reviewed by:

- Rudy Eden, South Coast Air Quality Management District
- Dennis Mikel, U.S. EPA Office of Air Quality Planning and Standards (OAQPS).

The purpose of this verification test was to generate performance data on metals monitoring technologies to inform users about the potential benefits of such technologies. The verification results reported here are from testing that involved the continuous operation of a Xact 625 monitor at an ambient air monitoring site in Marietta, Ohio, operated by the Southeast District Office (SEDO) of the Ohio Environmental Protection Agency (OEPA). The PM_{10} metals data produced hourly by the Xact 625 were averaged and compared to metals data from reference method samples collected daily and analyzed in the laboratory.

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The Xact 625 was verified by evaluating the following performance parameters.

- Comparability
- Correlation
- Bias
- Data completeness
- Operational factors

Comparability, correlation, and bias were assessed by comparison of Xact 625 results to those from inductively coupled plasma/mass spectrometry (ICP/MS) analysis of samples collected by a reference sampling method. Data completeness was determined from the number of hourly periods the metals monitor provided readings of PM_{10} metals concentrations. Data completeness was determined both relative to the entire field test period and relative to each 24-hour reference sampling period. Each of these performance factors was evaluated separately for those target metals detected by both the Xact 625 and the reference sampling/ICP-MS approach. Operational performance factors such as maintenance requirements, ease of use, and effectiveness of data acquisition were determined from observations by the field testing staff. This test was not intended to simulate long-term performance of the metals monitor at a monitoring site, but rather to assess the feasibility of its use for ambient metals monitoring in near-source locations. In long-term use, metals monitoring procedures might be tailored to address the specific conditions, metals concentrations, and sources for a given site.

3.2 Test Procedures

3.2.1 Field Installation

The Xact 625 used in this testing was purchased in 2011 by EPA's OAQPS as a stand-alone monitoring system, designed and built by CES per EPA specifications. The Xact 625 monitor was installed in an environmentally controlled trailer specially designed for field deployment of the monitor. Figure 3-1 shows an external view of the trailer at the Marietta test site with the Xact PM_{10} inlet, reference sampler (see Section 3.2.2) and meteorological sensors located atop the trailer. A view of the Xact 625 installed in the trailer is shown above in Figure 2-1.

The PM_{10} inlet of the Xact 625 extended through the roof of the trailer and was positioned approximately 1.5 m (5 ft) from the inlet of the PM_{10} reference sampler, as shown in Figure 3-1. A contractor employed by EPA/OAQPS transported and installed the Xact 625 trailer in the field, and performed startup checks on the Xact 625 monitor. The vendor of the Xact 625 (Pall Corporation) trained OEPA staff in operation of the monitor, and those OEPA staff oversaw operation of the monitor during the field testing. The automated internal QC checks of the Xact 625 were programmed to take place between midnight and 12:30 am each day. As a result, on each test day, the Xact 625 reported 23 one-hour averages and one half-hour average measurement of metals in ambient PM_{10}. All Xact 625 measurement data and QC results were recorded by the monitor's datalogger, downloaded by EPA/OAQPS, and transferred to Battelle for use in data comparisons.

The Xact 625 was verified by evaluating the following performance parameters.

- Comparability
- Correlation
- Bias
- Data completeness
- Operational factors

Comparability, correlation, and bias were assessed by comparison of Xact 625 results to those from inductively coupled plasma/mass spectrometry (ICP/MS) analysis of samples collected by a reference sampling method. Data completeness was determined from the number of hourly periods the metals monitor provided readings of PM_{10} metals concentrations. Data completeness was determined both relative to the entire field test period and relative to each 24-hour reference sampling period. Each of these performance factors was evaluated separately for those target metals detected by both the Xact 625 and the reference sampling/ICP-MS approach. Operational performance factors such as maintenance requirements, ease of use, and effectiveness of data acquisition were determined from observations by the field testing staff. This test was not intended to simulate long-term performance of the metals monitor at a monitoring site, but rather to assess the feasibility of its use for ambient metals monitoring in near-source locations. In long-term use, metals monitoring procedures might be tailored to address the specific conditions, metals concentrations, and sources for a given site.

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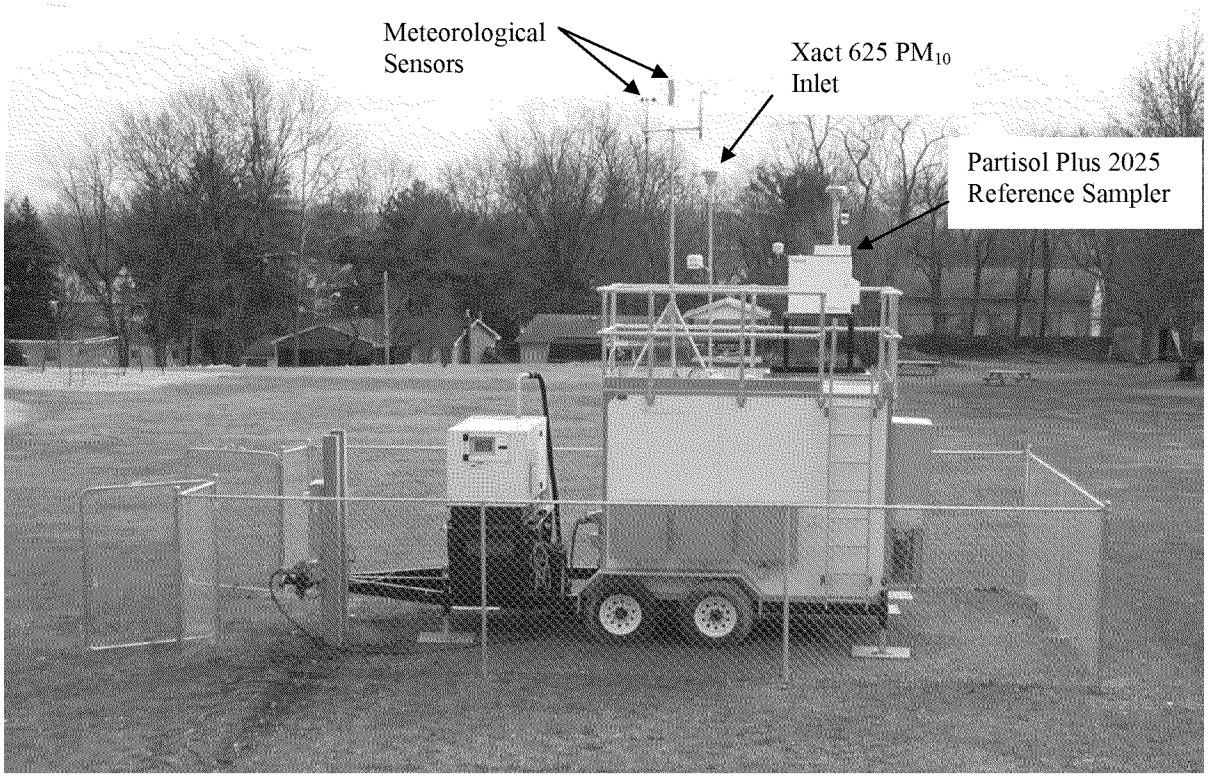
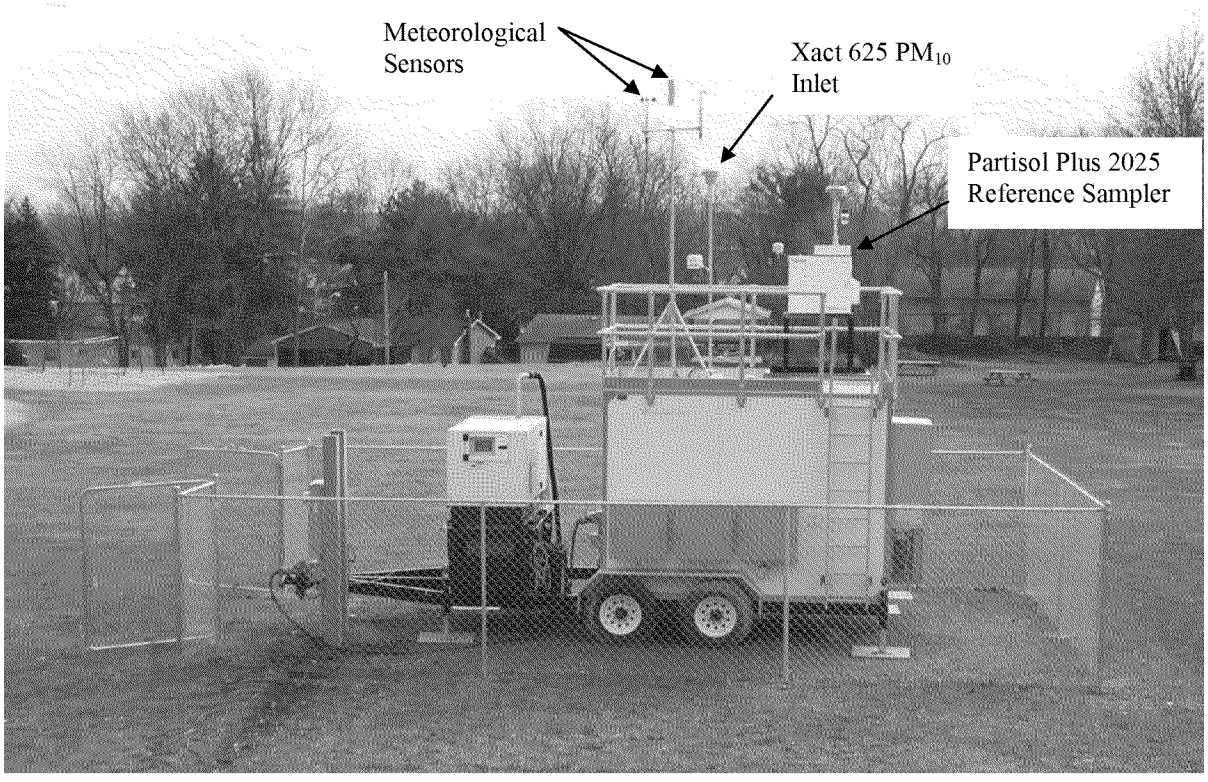


Figure 3-1. Field trailer used in verification test, showing Xact 625 PM_{10} inlet, reference PM_{10} automated sampler, and meteorological sensors on the roof.

3.2.2 Reference Sampling and Analysis

Ambient PM_{10} samples for reference metals analysis were collected according to EPA Method IO-3.1[5] using a Partisol Plus 2025 Sequential Ambient Particulate Sampler (Thermo Scientific, Hopkinton, MA) equipped with a PM_{10} size-selective inlet. This sampler is designated by EPA as Reference Method RFPS-1298-127 for sampling of ambient PM_{10}. The Partisol Plus 2025 uses 47 mm diameter Teflon® sample filters which are exchanged automatically after a pre-set sampling interval. The Partisol Plus 2025 can hold up to 16 filter cassettes, sufficient for more than two weeks of unattended daily sampling. Sample air is pulled by an internal pump through the filter currently being sampled, with the sample air flow regulated by a mass flow controller. Ambient temperature and pressure readings are used along with mass flow control to maintain a constant volumetric sampling rate of 16.7 L/min. Previously sampled and yet-to-be-sampled filters are sealed off within the Partisol Plus 2025 to prevent contamination. The sampler stores sampling and meteorological data in internal memory, including the average ambient temperature, ambient pressure, and average ambient relative humidity for each filter sample.

The Partisol Plus 2025 sampler was installed on the roof of the field trailer as shown in Figure 3-1 and was operated by OEPA personnel. Samples were collected every day



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The Partisol Plus 2025 sampler was installed on the roof of the field trailer as shown in Figure 3-1 and was operated by OEPA personnel. Samples were collected every day

throughout the field period with a 23.5 hour sampling duration, chosen so that reference sampling did not take place during the 0.5 hours per day when the Xact 625 performed its internal QC checks. Thus, the reference and Xact 625 sampling intervals were identical throughout the test period.

The ICP/MS laboratory contracted by EPA/OAQPS delivered blank 47 mm Teflon® filters to the field site in individual pre-labeled containers accompanied by chain of custody forms. Collected filter samples were removed from the Partisol Plus 2025 sampler approximately once per week without interruption of sampling. Collected samples were then shipped to the ICP/MS laboratory for extraction and analysis approximately every 2 weeks.

The reference PM_{10} filter samples were extracted and analyzed by the ICP/MS laboratory for metals content according to the procedures of EPA Method IO-3.5,[6] but using a modified acid digestion that included hydrofluoric acid (HF) to improve digestion for some elements. The extraction and analysis were performed according to Standard Operating Procedures that are incorporated into the laboratory's QAPP for sampling and analysis in EPA's national monitoring programs.[7] The QC requirements of Method IO-3.5[6] were followed, including the use of blanks, QC samples, laboratory fortified blanks, internal standards, and tuning solutions. An instrument performance demonstration program included duplicate samples, standards, blanks, interference check standards, continuing calibration blanks and verification standards, and laboratory control and matrix spikes.[7] The ICP/MS laboratory's stated detection limits for the PM_{10} metals are summarized in Table 5-1 in Section 5.1.

3.2.3 Verification Sites and Schedule

The Xact 625 operated from August 19 to November 3, 2011 at an OEPA field site in East Liverpool, Ohio. Battelle conducted a technical systems audit (TSA) of the field procedures and a performance evaluation (PE) audit of the Partisol Plus 2025 reference sampler at the East Liverpool site that confirmed both adherence to the field procedures and valid reference sampler operation. However, during operation at the East Liverpool site, clearly erroneous ambient temperature and pressure readings were reported by the Xact 625 sensors. Because of those readings it was determined that the reliability of the monitor's sample flow (and consequently its PM_{10} particle size cut) was questionable. The temperature and pressure sensors in the Xact 625 were not repaired until the end of the sampling period in East Liverpool, and therefore it was concluded that none of the Xact 625 data from the East Liverpool site were of sufficient quality to be used for performance verification. It should be noted that the failure of those sensors was not caused by a fault in the Xact 625 itself, but by the exposed location of the wiring connections for those sensors on the roof of the field trailer in which the Xact 625 was installed. The design of those connections was subsequently corrected by installation of more durable and weather resistant connections.

Following repair of the ambient temperature and pressure sensors in the Xact 625, the field trailer and Partisol Plus 2025 reference sampler were installed at an OEPA site at the Ohio Valley Educational Service Center (OVESC) in Marietta, Ohio. The Xact 625 operated continuously at the Marietta site from December 10, 2011 to February 27, 2012, and with minor interruptions daily reference samples were collected with the Partisol Plus 2025 sampler from December 23, 2011 through February 25, 2012. Thus, data for comparison of

throughout the field period with a 23.5 hour sampling duration, chosen so that reference sampling did not take place during the 0.5 hours per day when the Xact 625 performed its internal QC checks. Thus, the reference and Xact 625 sampling intervals were identical throughout the test period.

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Xact 625 and reference results were obtained over a 65-day period, within an approximately 80-day period of continuous operation of the Xact 625. The daily reference method samples were collected over 23.5-hour sampling intervals, i.e., from 12:30 am to midnight each day. This sampling schedule synchronized the reference and Xact 625 sampling periods and avoided reference sampling during the half hour each day when the Xact 625 performed its internal QC checks. Throughout the period in which the Xact 625 was operating at the Marietta site, the monitor's automated QC check results were reviewed frequently and confirmed proper operation of the instrument.

Both the East Liverpool and Marietta air quality monitoring sites were located in industrialized areas near the Ohio River characterized by restricted air flow due to local terrain. Both sites were chosen in part based on elevated levels of Mn and other metals found in ambient total suspended particulate in EPA's SAT Monitoring Initiative. Figure 3-2 shows a map view of the Marietta area, indicating the location of the OVESC sampling site and of an industrial facility thought to be a key source of metals emissions in the area.

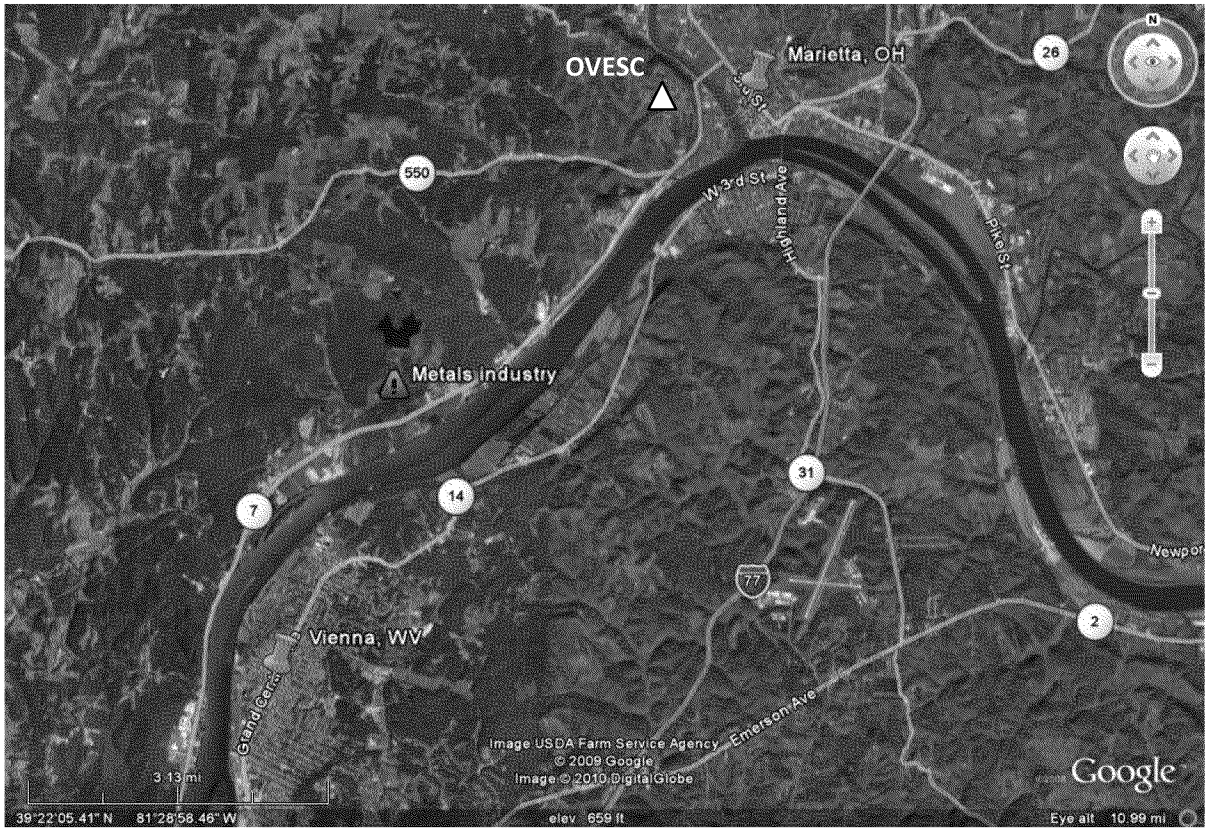

Figure 3-2. Map view of Marietta, Ohio area showing location of OVESC sampling site (white triangle near top of figure) and of suspected metals emission source (red triangle at left center of figure).

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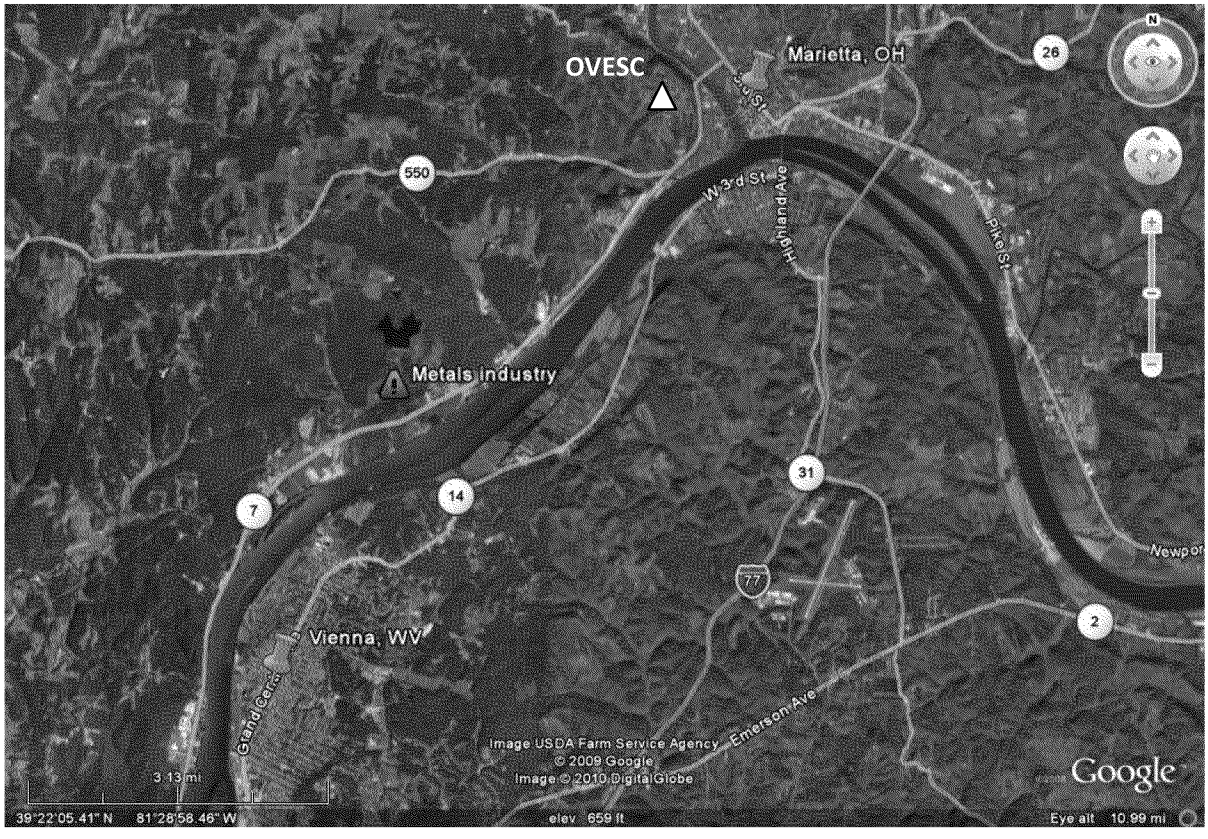

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Chapter 4
Quality Assurance/Quality Control

QA/QC procedures and all verification testing were performed in accordance with the QAPP for this verification test and the QMP for the AMS Center except where noted below. QA/QC procedures and results are described below.

4.1 Amendments/Deviations

Three deviations to the test/QA plan were prepared, approved, and retained in the test documentation. Those deviations collectively established the following modifications and corrections to the test/QA plan and the test procedures:

- The period of testing at the East Liverpool site was shortened due to startup difficulties with the Partisol Plus 2025 sampler.
- At the request of the analytical laboratory, reference filter samples were shipped from the field site to the analytical laboratory every 2 weeks, rather than every week as stated in the QAPP, to provide more efficient handling and analysis of each batch of samples.
- Testing was conducted at one site (Marietta) rather than two sites as originally planned, due to the failure of the Xact 625's ambient temperature and pressure sensors at the East Liverpool site, as noted in Section 3.2.3.
- The filters used in the Partisol Plus 2025 sampler were not weighed before shipment to the field because determination of PM_{10} mass concentration was not needed.
- The analytical laboratory returned ICP/MS analysis results within 7 days of the end of the week in which samples were received, rather than within 7 days of sample receipt.
- The sample extraction procedure used by the analytical laboratory was modified slightly from the procedure in Method IO-3.5, by the inclusion of HF in the digestion reagent. This fact was specified in the laboratory's standard operating procedure but was not stated in the QAPP.

These deviations are not considered to have had any significant effects on the verification data obtained at the Marietta site.

4.2 Reference Methods

The QA/QC procedures for the reference metals sampling and ICP/MS analysis adhered to the requirements of the methods used.[5-7] The QC results were reported to EPA/OAQPS by the analytical laboratory as part of the analytical data package for the reference samples.

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4.3 Review of Xact 625 QC Data

The results of the automated daily internal QC checks performed by the Xact 625 were reviewed approximately weekly, each time data were downloaded from the instrument. Those results showed stability in Xact 625 operations throughout the entire period of operation at both the East Liverpool and Marietta sites. Over that entire period the relative standard deviation (RSD) of the Pd internal standard readings determined in every Xact 625 XRF analysis was 2.04%. The instrument's average flow error was -0.69% (± 0.004%), where the value in parentheses is the standard deviation (SD) of the daily flow check results. The average accuracy relative to upscale rod check standards analyzed daily was 100.21% (±0.004%) for Cr, 100.55% (±0.013%) for Cd, and 99.79% (±0.007%) for Pb, where accuracy of 100% represents perfect agreement with the upscale rod check standard.

4.4 Audits

Three types of audits were performed during the verification test: a TSA of the verification test performance, a PE audit of the reference method sampling and analysis, and a data quality audit. Audit procedures are described further below.

4.4.1 Technical Systems Audit

The Battelle QA Officer performed two TSAs as part of this verification test. The field TSA was performed at the East Liverpool test site on October 6, 2011, and focused on observation of the sampling material handling, Xact 625 oversight, reference method sampling, and field data recording procedures. The first two deviations listed in Section 4.1 were noted in that TSA. The second Battelle TSA consisted of a visit on February 23, 2012 to the analytical laboratory contracted by EPA/OAQPS to conduct the ICP/MS analyses. That TSA focused on laboratory QA/QC, chain of custody, and analytical procedures. No significant findings resulted from the laboratory TSA.

An EPA QA representative also conducted a field TSA at the East Liverpool site on October 13, 2011. Two findings from that audit addressed communication among the several organizations involved in the test, and the failures of the temperature and pressure sensors in the Xact 625 that are described in Section 3.2.3. Those sensor failures were the cause of the third deviation listed in Section 4.1. Both of these findings were addressed prior to the start of testing at the Marietta site, the former by instituting regular conference calls among all parties, and the latter by replacement of the temperature and pressure sensor and confirmation of their correct operation.

4.4.2 Performance Evaluation Audit

A PE audit of the Partisol Plus 2025 reference method sampler was performed at the East Liverpool site on December 2, 2011, prior to moving the field test to the Marietta site. The PE flow audit was conducted by measuring the sample air flow rate through the sampler by means of a National Institute of Science and Technology (NIST)-traceable flow transfer standard (BIOS DryCal, Serial No. 103777). The results of that PE audit showed that the Partisol 2025 sample flow rate was within 1.9% of the target rate of 16.7 L/min, well within

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the target ±5% tolerance of the flow rate. The PE audit of the ambient temperature and pressure sensors of the Partisol Plus 2025 sampler was conducted using a Kestrel® Model 4500 Pocket Weather Tracker (Nielsen-Kellerman, Boothwyn, PA) obtained from Battelle's Instrumentation Services Laboratory (No. LN-269475). The PE audit showed that the Partisol Plus 2025 temperature and pressure sensors agreed with the PE audit device within 0.3 degrees Centigrade (°C) and 1 millimeter of mercury (mm Hg) pressure, respectively. These PE audit results were well within the target tolerances of ± 2 °C and ± 4 mm Hg (i.e., ± 5.3 millibars), respectively.

Battelle also conducted a PE audit of the reference metals analysis by submitting sample solutions of eight target metals to the reference laboratory for analysis. Those PE audit samples were prepared by Battelle by dilution of individual aqueous metals standards traceable to NIST. The metals concentrations in the PE audit samples were unknown to the reference laboratory. Two PE audit samples containing different levels of the eight metals were submitted for analysis, and the reference laboratory analyzed each sample both with and without dilution. The results from those two analyses agreed closely for each target metal in each of the two PE audit samples, so the average of the undiluted and diluted sample results was used for comparison to the spike value for each metal. The acceptance criterion for the PE audit was that the concentrations reported by the laboratory should be within ±10% of the prepared concentrations. The results of the laboratory PE audit are summarized in Table 4-1, and show that the reference analyses met that acceptance criterion for all metals in both PE audit samples.

Table 4-1. Summary of PE Audits of Reference Analytical Method

Sample	Metal	Standard Concentration (µg/L)[a]	Measured Concentration (µg/L)	Percent Difference
# 1	As	8.0	8.27	3.4
	Cd	2.0	2.06	2.8
	Cr	8.0	8.34	4.2
	Mn	2.0	1.97	-1.3
	Ni	2.0	2.14	6.9
	Pb	2.0	2.06	3.0
	Sb	2.0	1.86	-7.0
	Se	8.0	8.77	9.6
# 2	As	30	30.3	1.1
	Cd	7.0	7.36	5.1
	Cr	30	30.4	1.3
	Mn	7.0	7.12	1.7
	Ni	7.0	7.37	5.3
	Pb	7.0	7.21	3.0
	Sb	7.0	6.73	-3.9
	Se	30	32.9	9.7

a: µg/L = microgram per liter

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	Sb	2.0	1.86	-7.0
	Se	8.0	8.77	9.6
# 2	As	30	30.3	1.1
	Cd	7.0	7.36	5.1
	Cr	30	30.4	1.3
	Mn	7.0	7.12	1.7
	Ni	7.0	7.37	5.3
	Pb	7.0	7.21	3.0
	Sb	7.0	6.73	-3.9
	Se	30	32.9	9.7

a: µg/L = microgram per liter

4.4.3 Data Quality Audit

At least 10% of the data acquired during the verification test were audited. Battelle's QA Officer traced the data from the acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked. Only minor and readily correctable data issues were noted in the data quality audit, with no effect on the overall quality of the verification results.

4.5 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center. The Battelle Verification Test Coordinator prepared formal responses to all audit findings and observations, including any corrective actions taken. The results of the audits and Battelle's corrective actions were reviewed, approved, and submitted to EPA.

4.6 Data Review

All data received from EPA for the Xact 625 and the reference method underwent 100% review and validation by Battelle technical staff before being used for any statistical calculations. Records generated in the verification test received a one-over-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test.

4.4.3 Data Quality Audit

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Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.1 are described in this chapter. All results from the Xact 625 monitor and from the reference sampling and ICP/MS analysis were reported as ambient metals concentrations in nanograms per cubic meter (ng/m^3) of air at ambient (i.e., not standard) conditions. Non-detect results from the reference method for any metal were flagged as such, and excluded from any data comparisons.

5.1 Averaging of Xact 625 Hourly Data

The Xact 625 readings on each test day consisted of one half-hour measurement and 23 one-hour measurements, with all sampling done at the same flow rate (i.e., 16.7 L/min). Consequently, integration of the Xact 625 results over a daily 23.5-hour time period required simple arithmetic averaging of the 24 total concentration results, but with the 0.5-hour result given half the weight of the 23 1-hour results, i.e.:

$$23.5 \text{ Hour Average} = (0.5c_1 + c_2 + \ldots c_{24})/23.5 \qquad (1)$$

where c_1, c_2, $\ldots c_{24}$ are the metals concentrations reported each hour by the Xact 625.

Before the resulting daily average results from the Xact 625 monitor were compared to the corresponding daily integrated sample results from the reference method, they were compared to a daily quantitation limit (QL) of the Xact 625 for each target metal. The QL is a defined value for each target metal and roughly corresponds to 10% uncertainty in an interference-free situation.[8] Three distinct hourly QL values were applicable to the Xact 625 data for each metal, and were used to determine the daily QL value for each metal. Those three hourly QL values were:

- The normal hourly QL value for a Xact 625 sample collected over 1 hour and analyzed by XRF over the following hour. This QL value applies to 22 of the 24 hourly readings reported each day by the Xact 625.
- The QL value for an Xact 625 sample collected between 11:00 pm and midnight, which was collected over 1 hour but only analyzed by XRF for 0.5 hour (due to the internal QC checks performed by the Xact 625 between midnight and 12:30 am). This QL value equals the normal hourly QL value times $\sqrt{2}$ (i.e., times 1.414).

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- The QL value for a Xact 625 sample collected between 12:30 am and 1:00 am, which was collected for 0.5 hour (due to the internal QC checks performed by the Xact 625 between midnight and 12:30 am) but analyzed by XRF for 1 hour. This QL value equals the normal hourly QL value times 2.

Daily QL values for each metal reported by the Xact 625 were determined as the appropriately weighted average of the three different hourly QL values. Table 5-1 lists the three hourly QL values for each of the 23 metals reported by the Xact 625, along with the resulting daily QL value. A footnote to the table illustrates the calculation procedure used. Daily average Xact 625 results for any metal that were less than the Xact 625 daily QL for that metal were excluded from the statistical calculations summarized below. For comparison, the detection limits reported by the ICP/MS analysis laboratory for each metal are also shown in the last column of Table 5-1.

Table 5-1. Calculation of the Xact 625 Daily QL for Elements Reported in Ambient Air at the Marietta Site and Comparison to ICP/MS Detection Limits

Element	Xact 625 Quantitation Limits				Laboratory ICP/MS Detection Limit (ng/m^3)
	Normal 1-hour QL (ng/m^3)[a]	11:00 pm to Midnight QL (ng/m^3)[b]	12:30 to 1:00 am QL (ng/m^3)[c]	Calculated Daily QL (ng/m^3)[d]	
As	0.81	1.14	1.62	0.84	0.17
Ba	6.68	9.45	13.4	6.95	0.66
Br	1.31	1.85	2.61	1.35	[e]
Ca	6.38	9.02	12.8	6.62	113
Cd	40.6	57.5	81.3	42.2	0.01
Co	2.24	3.17	4.48	2.32	0.03
Cr	2.04	2.88	4.08	2.12	24.2
Cu	1.89	2.67	3.78	1.96	2.51
Fe	5.37	7.59	10.7	5.57	[e]
Hg	1.33	1.89	2.67	1.38	0.05
K	16.7	23.7	33.5	17.4	[e]
Mn	2.00	2.83	4.00	2.08	0.32
Mo	6.94	9.81	13.9	7.21	0.19
Ni	1.60	2.26	3.19	1.66	0.40
Pb	1.54	2.18	3.09	1.60	0.07
Rb	2.43	3.44	4.86	2.52	0.02
Sb	4.69	6.63	9.38	4.88	0.28
Se	0.99	1.41	1.99	1.03	0.35
Sr	3.16	4.47	6.33	3.29	0.09
Th	11.3	16.0	22.6	11.7	0.01
Ti	2.69	3.80	5.37	2.80	[e]
Tl	1.30	1.84	2.60	1.35	0.003
Zn	1.64	2.31	3.27	1.70	5.93

a: Sample collected over 1 hour and analyzed by XRF over 1 hour; b: Sample collected over 1 hour and analyzed by XRF over 0.5 hour; c: Sample collected over 0.5 hour and analyzed by XRF over 1 hour.
d: Calculated as (22 × Normal QL + (11 pm to midnight QL) + 0.5 × (12:30 to 1:00 am QL))/23.5; e.g., for As daily QL = (22 × 0.81 + 1.14 + 0.5 × 1.62)/23.5 = 0.84 ng/m^3.
e: Element not reported from ICP/MS analysis.

- The QL value for a Xact 625 sample collected between 12:30 am and 1:00 am, which was collected for 0.5 hour (due to the internal QC checks performed by the Xact 625 between midnight and 12:30 am) but analyzed by XRF for 1 hour. This QL value equals the normal hourly QL value times 2.

Daily QL values for each metal reported by the Xact 625 were determined as the appropriately weighted average of the three different hourly QL values. Table 5-1 lists the three hourly QL values for each of the 23 metals reported by the Xact 625, along with the resulting daily QL value. A footnote to the table illustrates the calculation procedure used. Daily average Xact 625 results for any metal that were less than the Xact 625 daily QL for that metal were excluded from the statistical calculations summarized below. For comparison, the detection limits reported by the ICP/MS analysis laboratory for each metal are also shown in the last column of Table 5-1.

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Ba	6.68	9.45	13.4	6.95	0.66
Br	1.31	1.85	2.61	1.35	[e]
Ca	6.38	9.02	12.8	6.62	113
Cd	40.6	57.5	81.3	42.2	0.01
Co	2.24	3.17	4.48	2.32	0.03
Cr	2.04	2.88	4.08	2.12	24.2
Cu	1.89	2.67	3.78	1.96	2.51
Fe	5.37	7.59	10.7	5.57	[e]
Hg	1.33	1.89	2.67	1.38	0.05
K	16.7	23.7	33.5	17.4	[e]
Mn	2.00	2.83	4.00	2.08	0.32
Mo	6.94	9.81	13.9	7.21	0.19
Ni	1.60	2.26	3.19	1.66	0.40
Pb	1.54	2.18	3.09	1.60	0.07
Rb	2.43	3.44	4.86	2.52	0.02
Sb	4.69	6.63	9.38	4.88	0.28
Se	0.99	1.41	1.99	1.03	0.35
Sr	3.16	4.47	6.33	3.29	0.09
Th	11.3	16.0	22.6	11.7	0.01
Ti	2.69	3.80	5.37	2.80	[e]
Tl	1.30	1.84	2.60	1.35	0.003
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a: Sample collected over 1 hour and analyzed by XRF over 1 hour; b: Sample collected over 1 hour and analyzed by XRF over 0.5 hour; c: Sample collected over 0.5 hour and analyzed by XRF over 1 hour.
d: Calculated as (22 × Normal QL + (11 pm to midnight QL) + 0.5 × (12:30 to 1:00 am QL))/23.5; e.g., for As daily QL = (22 × 0.81 + 1.14 + 0.5 × 1.62)/23.5 = 0.84 ng/m^3.
e: Element not reported from ICP/MS analysis.

5.2 Comparability

For each target metal, comparability was determined by a linear regression of the data using the reference method results as the independent variable and the Xact 625 results as the dependent variable, as follows.

$$C_i = (m \cdot R_i) + b \qquad (2)$$

where R_i is the ith daily reference measurement, C_i is the average of the Xact 625 measurements over the same 23.5-hour time period, and *m* and *b* are the slope and intercept of the linear regression, respectively. Comparability is reported in terms of the *m* and *b* values obtained from the linear regression for each metal determined by the Xact 625 and the reference method. Comparability results also indicate whether each reported slope or intercept value is significantly different from 1.0 or from zero, respectively (i.e., whether the 95% confidence interval [CI] excludes a slope of 1.0 or an intercept of zero, respectively).

5.3 Correlation

The degree of correlation between the Xact 625 results and the reference method results was determined by the coefficient of determination (r^2) of the linear regression between the daily reference method results and the corresponding daily averages of the Xact 625 measurements over the same time periods. The r^2 value was determined separately for each metal measured.

5.4 Bias

The bias of the Xact 625 readings was evaluated in terms of the percent difference of the daily average Xact 625 readings relative to the corresponding daily average reference method results. That is, for each target metal (i) in each 23.5-hour reference method period (j), bias for that metal in that period ($B_{i,j}$) was calculated as:

$$B_{i,j} = \frac{(\text{Average Monitor Reading - Reference Reading}) \times 100}{\text{Reference Reading}} \qquad (3)$$

The bias results are reported in terms of the mean, median, range, and SD of the individual $B_{i,j}$ results for each metal. Also, the individual $B_{i,j}$ results for each metal were compared to the ambient metal concentrations to determine whether bias is a function of the ambient concentration of the metal.

5.5 Data Completeness

Data completeness (DC) was determined in two ways. The first was as the percentage of all hours in the field period in which the metals monitor reported ambient metals data, relative to the total number of hours in the field period:

$$DC1 = (\text{\# Hours data return/Total hours in period}) \times 100 \qquad (4)$$

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where R_i is the ith daily reference measurement, C_i is the average of the Xact 625 measurements over the same 23.5-hour time period, and *m* and *b* are the slope and intercept of the linear regression, respectively. Comparability is reported in terms of the *m* and *b* values obtained from the linear regression for each metal determined by the Xact 625 and the reference method. Comparability results also indicate whether each reported slope or intercept value is significantly different from 1.0 or from zero, respectively (i.e., whether the 95% confidence interval [CI] excludes a slope of 1.0 or an intercept of zero, respectively).

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DC was also calculated as the percentage of all 23.5-hour reference measurement periods during which the monitor reported at least 12 hours of monitoring data (i.e., produced data for at least half of the reference monitoring period):

$$DC2 = (\text{\# Periods with} \geq 12 \text{ hours monitor data/\# Reference periods}) \times 100 \qquad (5)$$

Both forms of DC were calculated for each target metal.

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Chapter 6
Test Results

This chapter summarizes the metals monitoring results from the Xact 625 at the Marietta site, and the comparisons of those results to the corresponding results of the reference sampling and ICP/MS analysis. Section 6.1 shows illustrative results from the Xact 625 and the reference method, and Sections 6.2 through 6.4 show results for the quantitative performance parameters identified in Section 3.1. Section 6.5 summarizes observations on operational factors of the Xact 625.

6.1 Xact 625 Ambient Metals Results

Mn was the predominant toxic metal determined in ambient air during the field period in Marietta, OH. To illustrate the ambient levels observed, Figure 6-1 shows the hourly Xact 625 readings of Mn, potassium (K), iron (Fe), and zinc (Zn) from December 10, 2011 to February 27, 2012. Although most hourly Mn concentrations were below 10 ng/m^3, Figure 6-1 shows approximately 20 hourly Mn concentrations exceeding 1 µg/m^3, with a maximum hourly reading of 5.9 µg/m^3 on February 7. K, Fe, and Zn are shown in Figure 6-1 because analysis of the Xact 625 data showed those metals to have the highest degree of correlation with the Mn data. Figure 6-1 shows that K and Fe concentrations were similar, and that peak concentrations of these metals often, but not always, coincided with peak concentrations of Mn. The peak concentrations of Mn usually exceeded the simultaneous concentrations of Fe and K. The median hourly Zn concentration was 12 ng/m^3, but the maximum Zn concentration was 965 ng/m^3, and occurred on February 7, coincident with the maximum hourly Mn concentration. The concentrations of other metals in Marietta were much lower in this time period. For example, Pb exhibited mean and median concentrations of 5.2 and 3.9 ng/m^3, respectively, with a maximum hourly reading of 98 ng/m^3.

The episodes of elevated Xact 625 metals readings in Marietta did not typically consist of single hourly spikes, but rather were periods of elevated concentrations lasting from a few hours to several hours. As an example, Figure 6-2 shows the period from February 5 to 7, 2012, in which the highest Mn levels were observed. Figure 6-2 shows that those levels occurred as two separate peaks in an episode that lasted approximately 12 hours.

Table 6-1 summarizes the 1,829 hourly readings of the 23 metals reported by the Xact 625 in continuous operation at the Marietta site. That table shows the mean, median, maximum, and minimum hourly reading of each metal, and for comparison the Xact 625's hourly method detection limit (MDL) and hourly QL for each metal, in ng/m^3.

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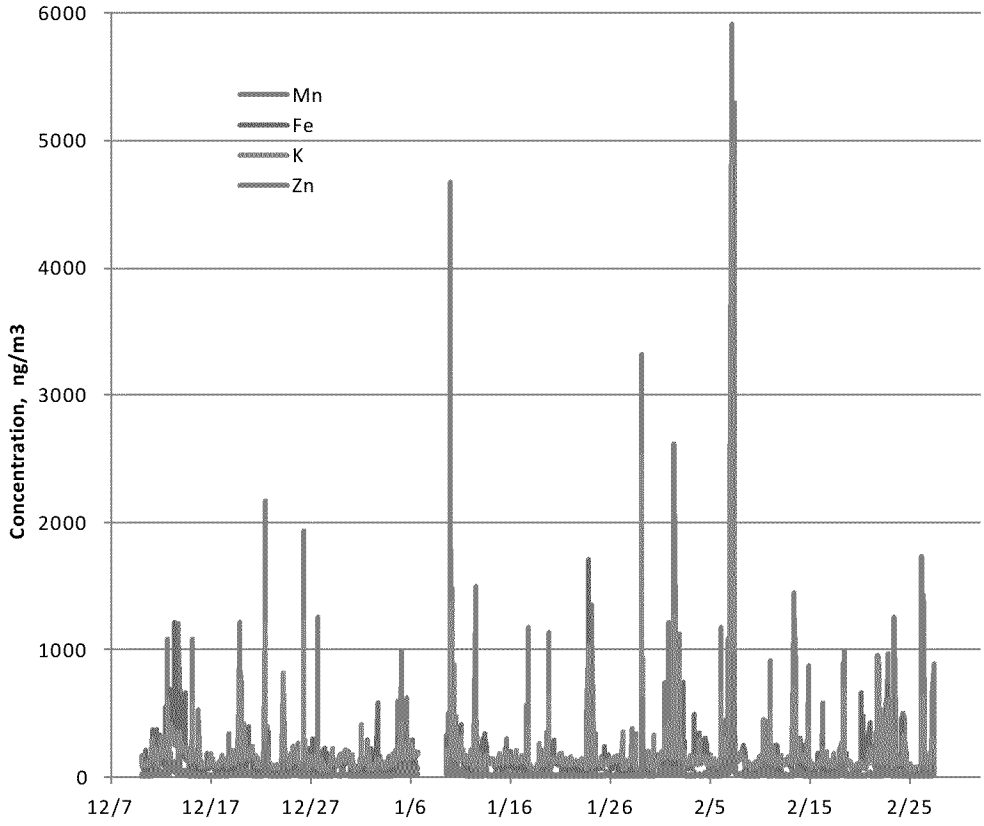

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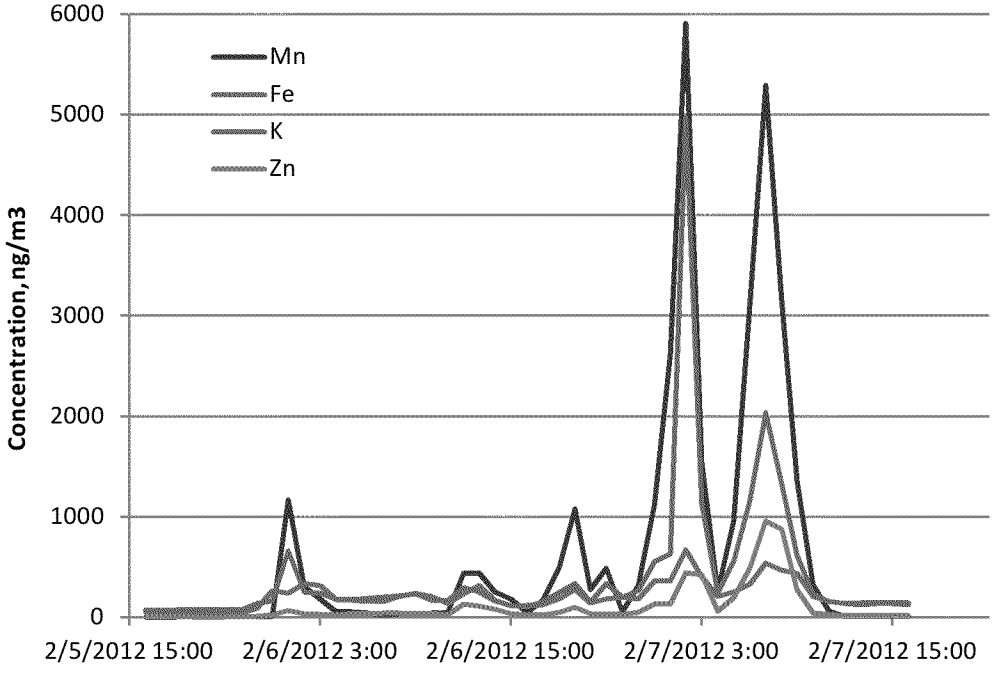
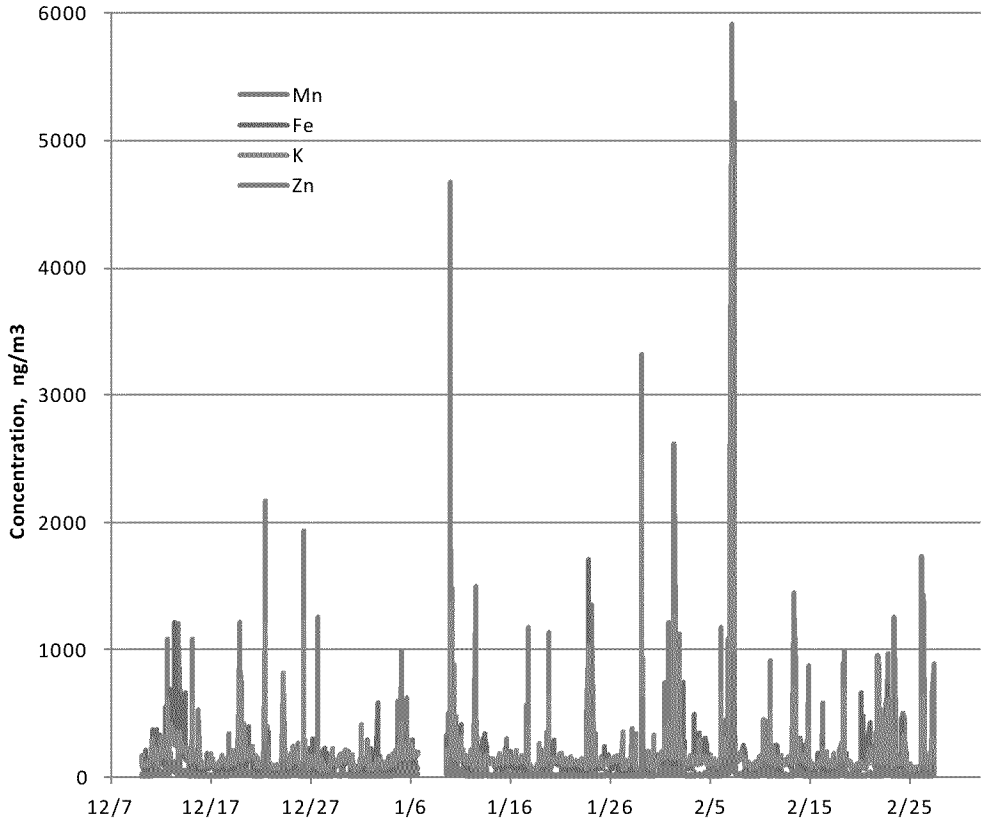


Figure 6-2. Example of elevated metals concentrations over a period of several hours.



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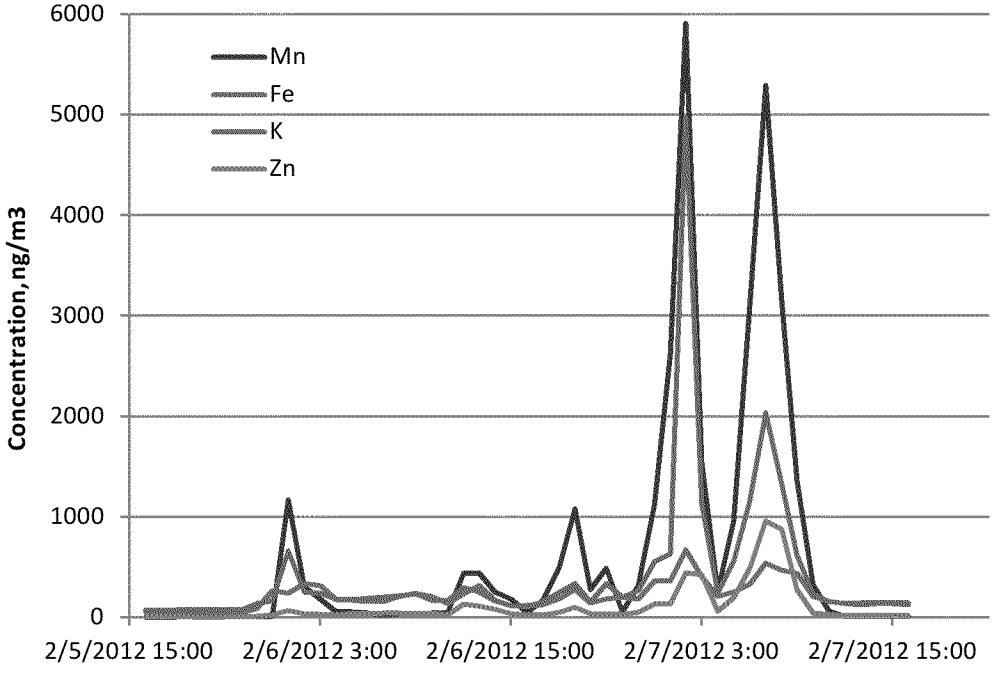

Figure 6-2. Example of elevated metals concentrations over a period of several hours.

Table 6-1. Summary of Hourly Values of All Metals Reported by the Xact 625 in Marietta, Ohio from December 10, 2011 to February 27, 2012

Metal	Ambient Concentration[a] (ng/m^3)				MDL[b] (ng/m^3)	QL[b] (ng/m^3)
	Mean	Median	Maximum	Minimum		
As	0.15	< MDL	31.5	< MDL	0.11	0.81
Ba	1.82	< MDL	148	< MDL	0.95	6.68
Br	4.09	3.22	126	< MDL	0.18	1.31
Ca	212	142	1,830	< MDL	0.90	6.38
Cd	< MDL	< MDL	21.1	< MDL	5.75	40.64
Co	< MDL	< MDL	0.43	< MDL	0.32	2.24
Cr	0.73	< MDL	106	< MDL	0.29	2.04
Cu	3.11	2.37	450	0.77	0.27	1.89
Fe	126	95.1	1,711	7.91	0.76	5.37
Hg	< MDL	< MDL	0.62	< MDL	0.19	1.33
K	158	122	4,970	49.8	2.37	16.7
Mn	95.5	6.45	5,910	< MDL	0.28	2.00
Mo[c]	11.8	11.3	37.3	9.02	0.98	6.94
Ni	0.48	0.30	31.2	< MDL	0.23	1.60
Pb	5.21	3.92	97.7	0.79	0.22	1.54
Rb	0.36	< MDL	26.9	< MDL	0.34	2.43
Sb	< MDL	< MDL	3.65	< MDL	0.66	4.69
Se	1.28	0.95	11.6	< MDL	0.14	0.99
Sr	1.33	1.07	37.7	< MDL	0.45	3.16
Th	< MDL	< MDL	4.68	< MDL	1.60	11.3
Ti	9.64	5.93	491	< MDL	0.38	2.69
Tl	< MDL	< MDL	2.78	< MDL	0.18	1.30
Zn	19.2	12.0	965	1.25	0.23	1.64

a: Based on 1,829 hourly readings.
b: MDL = method detection limit, QL = quantitation limit, for normal hourly data. QL corresponds to 10% uncertainty in an interference-free situation.[8] MDL corresponds to ±1 SD interference free, consistent with EPA Method IO 3.3.[8,9]
c: See text.

Of the 23 metals reported by the Xact 625, 19 were also determined by the ICP/MS analysis of reference samples. For those 19 metals, the daily 23.5-hour averages of the Xact 625 data were calculated as described in Section 5.1 and compared to the respective daily QL values listed in Table 5-1. For 12 of those 19 metals (arsenic [As], barium [Ba], Cd, cobalt [Co], Cr, mercury [Hg], nickel [Ni], rubidium [Rb], antimony [Sb], strontium [Sr], thorium [Th], and thallium [Tl]), the resulting daily averages of the Xact 625 hourly data were almost always below the respective daily QL values of the Xact 625, and consequently no statistical comparison could be made to the reference metals data.

Also, the Xact 625 reported ambient molybdenum (Mo) concentrations that were almost always approximately 12 ng/m^3 throughout the entire field period. This observation is illustrated in Table 6-1, in that the minimum hourly Mo value was over 9 ng/m^3, and the mean and median were 11.8 and 11.3 ng/m^3, respectively. Those Xact 625 Mo results were identified as a detection artifact by the vendor through inspection of Xact 625 spectral data. Although the Mo data from the field test were affected by this artifact and cannot be used for

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	Mean	Median	Maximum	Minimum		
As	0.15	< MDL	31.5	< MDL	0.11	0.81
Ba	1.82	< MDL	148	< MDL	0.95	6.68
Br	4.09	3.22	126	< MDL	0.18	1.31
Ca	212	142	1,830	< MDL	0.90	6.38
Cd	< MDL	< MDL	21.1	< MDL	5.75	40.64
Co	< MDL	< MDL	0.43	< MDL	0.32	2.24
Cr	0.73	< MDL	106	< MDL	0.29	2.04
Cu	3.11	2.37	450	0.77	0.27	1.89
Fe	126	95.1	1,711	7.91	0.76	5.37
Hg	< MDL	< MDL	0.62	< MDL	0.19	1.33
K	158	122	4,970	49.8	2.37	16.7
Mn	95.5	6.45	5,910	< MDL	0.28	2.00
Mo[c]	11.8	11.3	37.3	9.02	0.98	6.94
Ni	0.48	0.30	31.2	< MDL	0.23	1.60
Pb	5.21	3.92	97.7	0.79	0.22	1.54
Rb	0.36	< MDL	26.9	< MDL	0.34	2.43
Sb	< MDL	< MDL	3.65	< MDL	0.66	4.69
Se	1.28	0.95	11.6	< MDL	0.14	0.99
Sr	1.33	1.07	37.7	< MDL	0.45	3.16
Th	< MDL	< MDL	4.68	< MDL	1.60	11.3
Ti	9.64	5.93	491	< MDL	0.38	2.69
Tl	< MDL	< MDL	2.78	< MDL	0.18	1.30
Zn	19.2	12.0	965	1.25	0.23	1.64

a: Based on 1,829 hourly readings.
b: MDL = method detection limit, QL = quantitation limit, for normal hourly data. QL corresponds to 10% uncertainty in an interference-free situation.[8] MDL corresponds to ±1 SD interference free, consistent with EPA Method IO 3.3.[8,9]
c: See text.

Of the 23 metals reported by the Xact 625, 19 were also determined by the ICP/MS analysis of reference samples. For those 19 metals, the daily 23.5-hour averages of the Xact 625 data were calculated as described in Section 5.1 and compared to the respective daily QL values listed in Table 5-1. For 12 of those 19 metals (arsenic [As], barium [Ba], Cd, cobalt [Co], Cr, mercury [Hg], nickel [Ni], rubidium [Rb], antimony [Sb], strontium [Sr], thorium [Th], and thallium [Tl]), the resulting daily averages of the Xact 625 hourly data were almost always below the respective daily QL values of the Xact 625, and consequently no statistical comparison could be made to the reference metals data.

Also, the Xact 625 reported ambient molybdenum (Mo) concentrations that were almost always approximately 12 ng/m^3 throughout the entire field period. This observation is illustrated in Table 6-1, in that the minimum hourly Mo value was over 9 ng/m^3, and the mean and median were 11.8 and 11.3 ng/m^3, respectively. Those Xact 625 Mo results were identified as a detection artifact by the vendor through inspection of Xact 625 spectral data. Although the Mo data from the field test were affected by this artifact and cannot be used for

comparison to reference data, the vendor indicates that in the future this artifact can be prevented by narrowing the X-ray energy window used for determination of Mo.

For the remaining six metals determined by the Xact 625 (calcium [Ca], Cu, Mn, Pb, selenium [Se], and Zn) quantitative comparisons could be made between the daily average Xact 625 results and the daily ICP/MS results. Figures 6-3 through 6-8 show the linear regression of Xact 625 daily average results against the ICP/MS method results for Ca, Cu, Mn, Pb, Se, and Zn, respectively. Each of these figures also shows the linear regression equation and r^2 value.

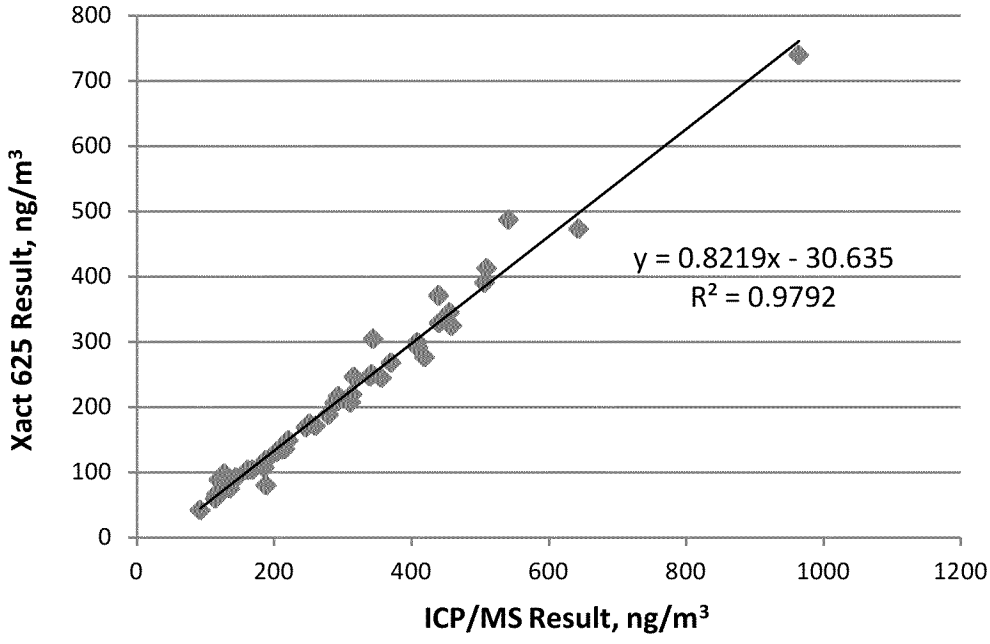

Figure 6-3. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Ca.

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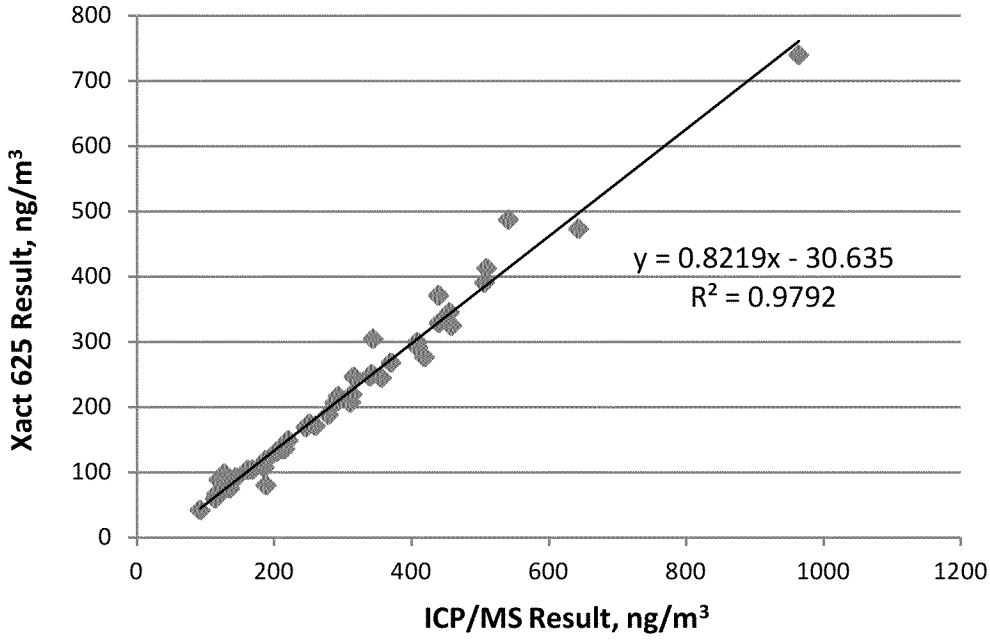


Figure 6-3. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Ca.

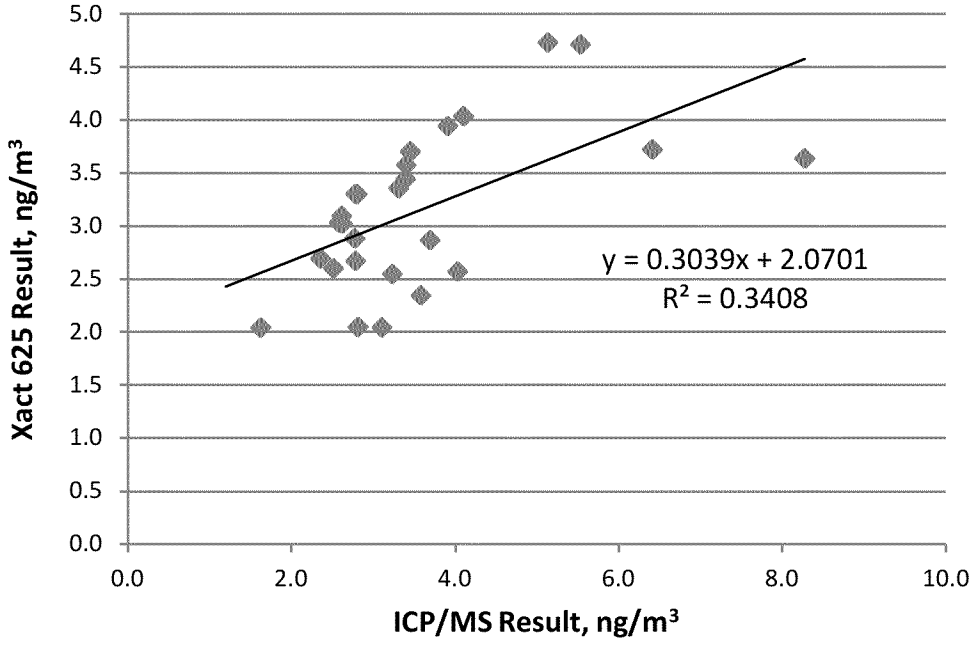


Figure 6-4. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Cu.

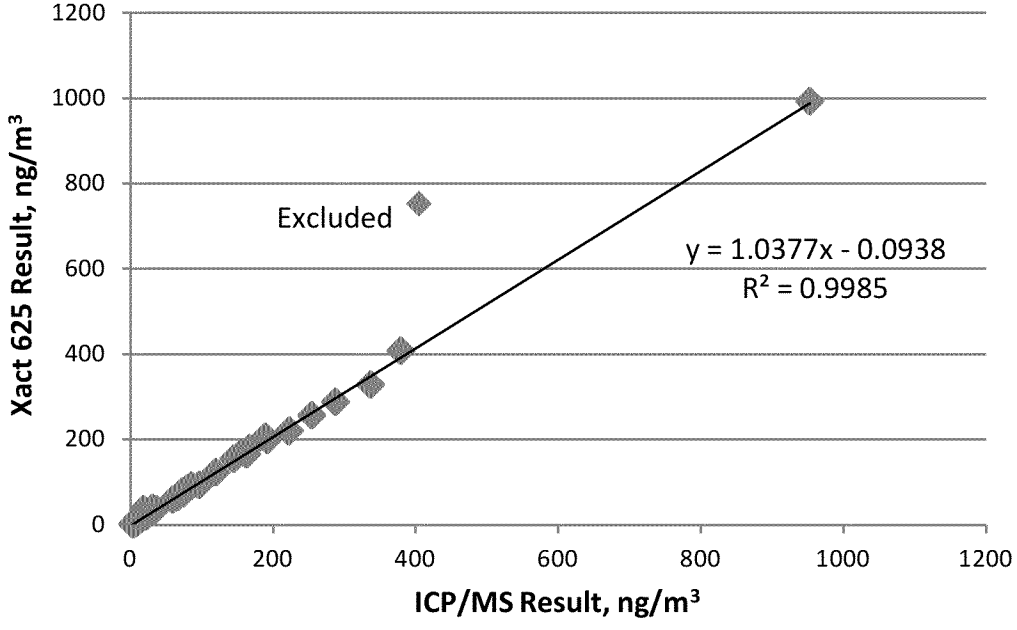
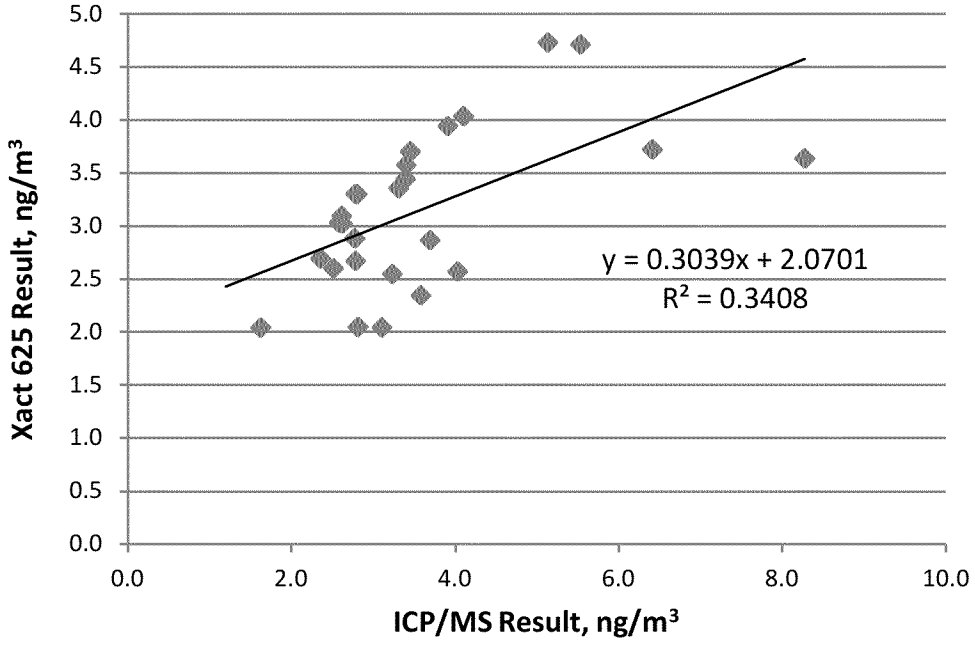


Figure 6-5. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Mn.



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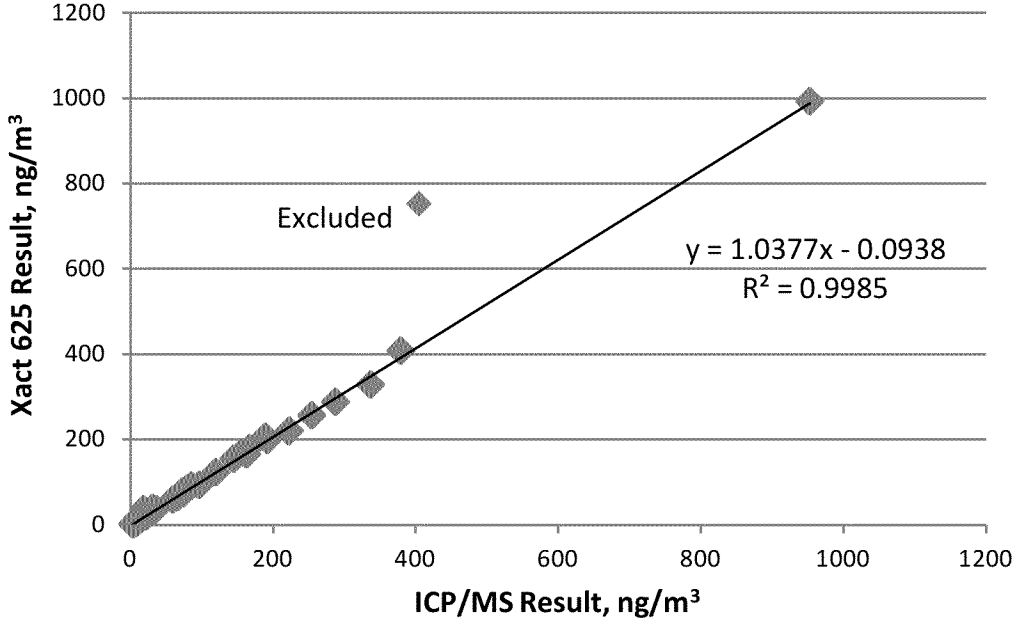

Figure 6-5. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Mn.

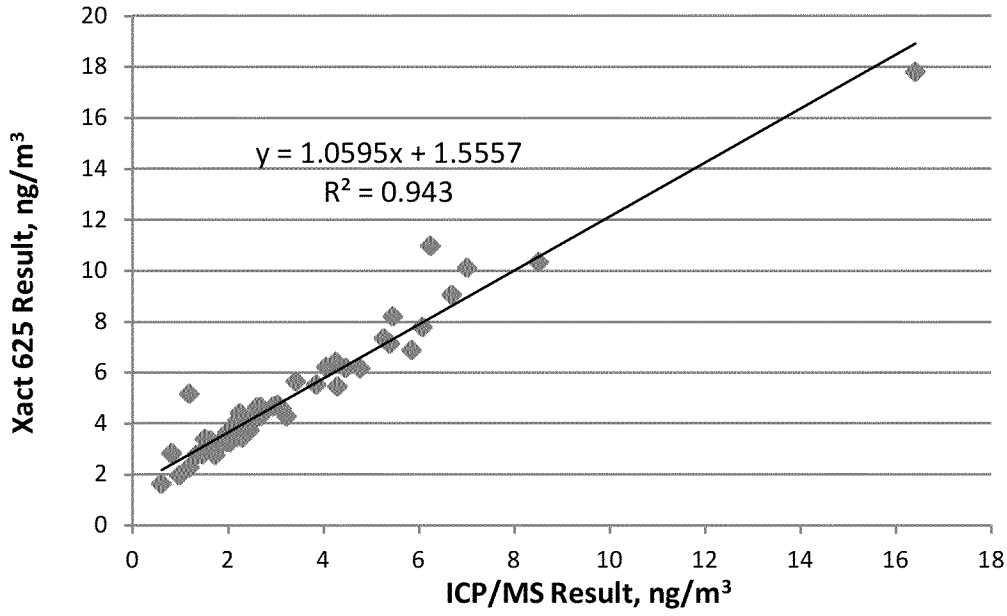

Figure 6-6. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Pb.

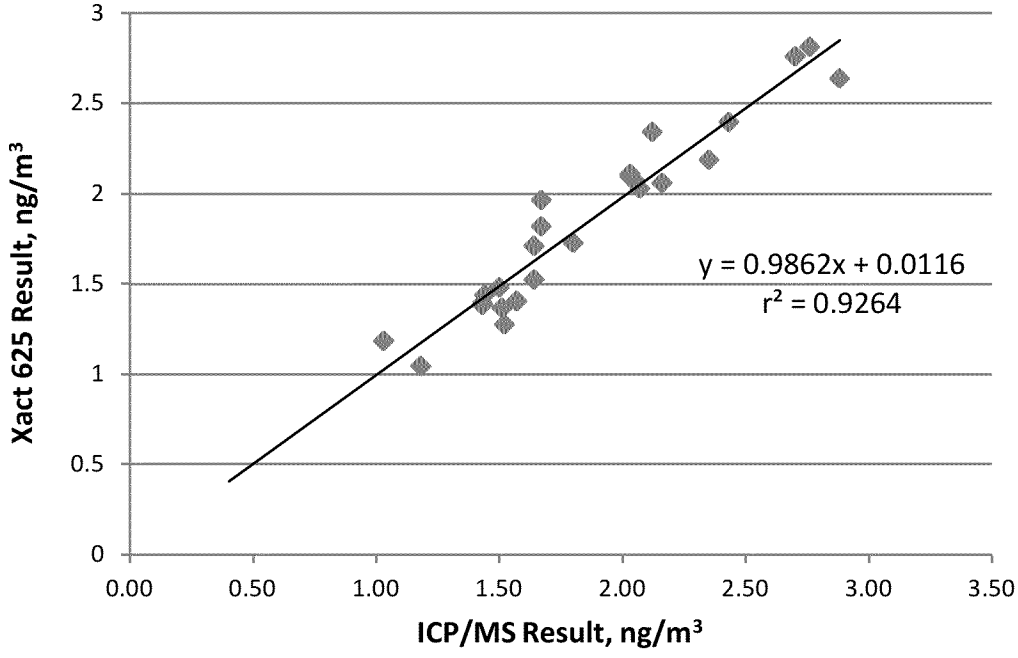

Figure 6-7. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Se.

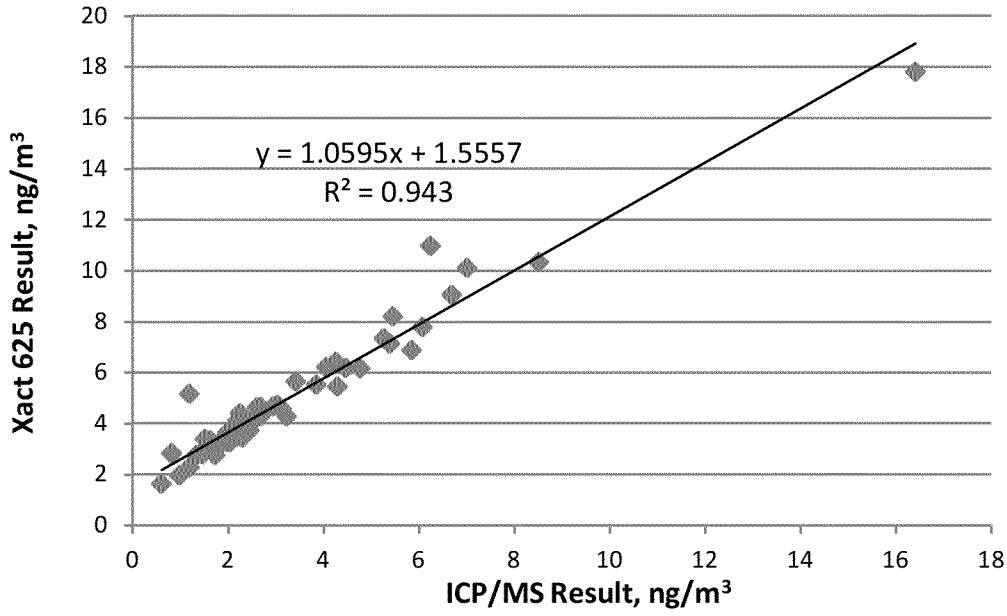

Figure 6-6. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Pb.

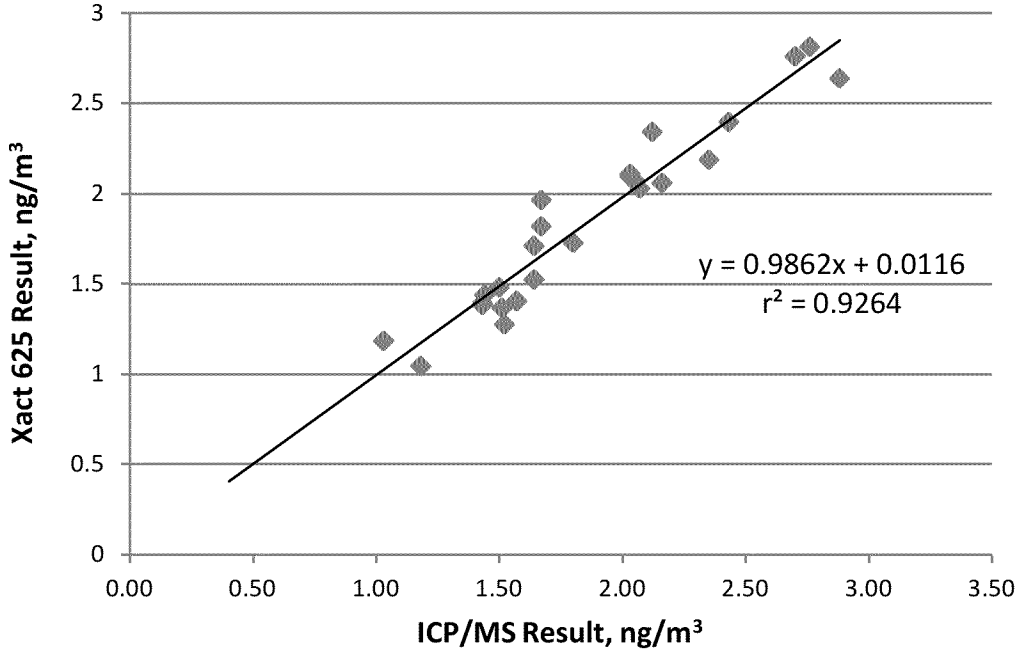

Figure 6-7. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Se.

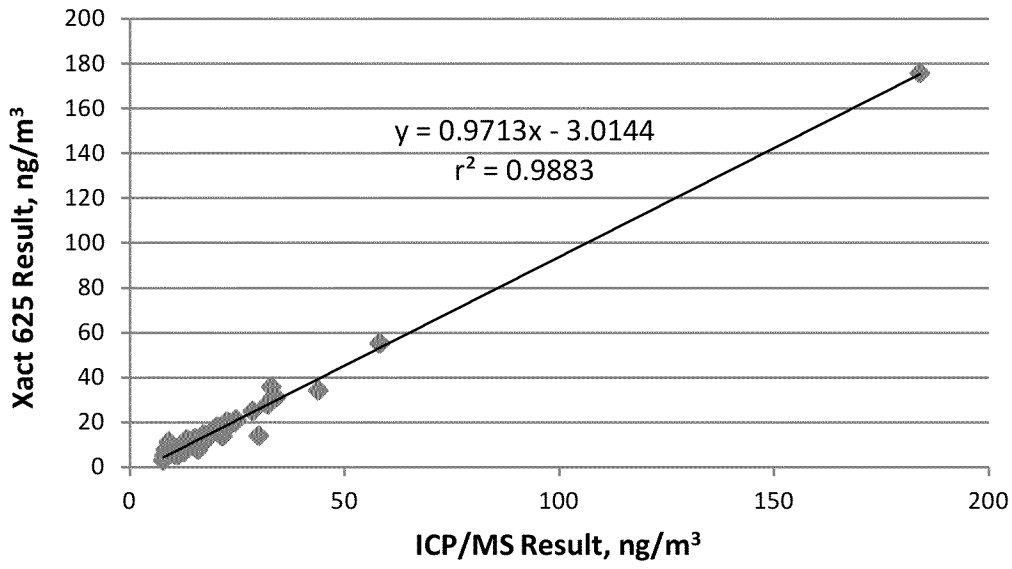

Figure 6-8. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Zn.

It should be noted that one data point for Mn in Figure 6-5 has been excluded from the linear regression calculation shown in that figure. That data point is from January 9, 2012, on which day the Xact 625 reported only 13 hourly readings, for reasons that are described in Section 6.4. This data point is markedly offset from all other Mn results in Figure 6-5, and has a substantial effect if included in the regression. It is likely given the great variability observed in Mn concentrations that the 13 hourly values reported by the Xact 625 on January 9 do not adequately indicate the daily average Mn over that entire day, and as a result agree poorly with the reference sample result. The data for other metals from that same day were also reviewed, and were found not to be outliers and consequently were not excluded from the corresponding regressions. Note that on January 6, 2012 the Xact 625 recorded only 14 hourly readings (see Section 6.4), but no reference sample was collected on that day so there is no impact on the comparison of Xact 625 and reference results.

6.2 Comparability and Correlation

Table 6-2 summarizes the outcome of linear regression of the daily average Xact 625 results against the corresponding reference results for each target metal for which this comparison could be made. For each metal Table 6-2 shows the number of data points in the regression, the slope and intercept of the regression line, and the r^2 value. The slope and intercept results are shown with their associated 95% CI values. Slope results that do not include a value of 1.0 within the 95% CI, and intercept values that do not include a value of 0.0 within the 95% CI, are highlighted by bold font in Table 6-2.

Table 6-2 shows that the regression slopes for Mn, Pb, Se, and Zn are relatively close to 1.0, although a slope of 1.0 falls slightly outside the 95% CI range of the slope for Mn. The slope

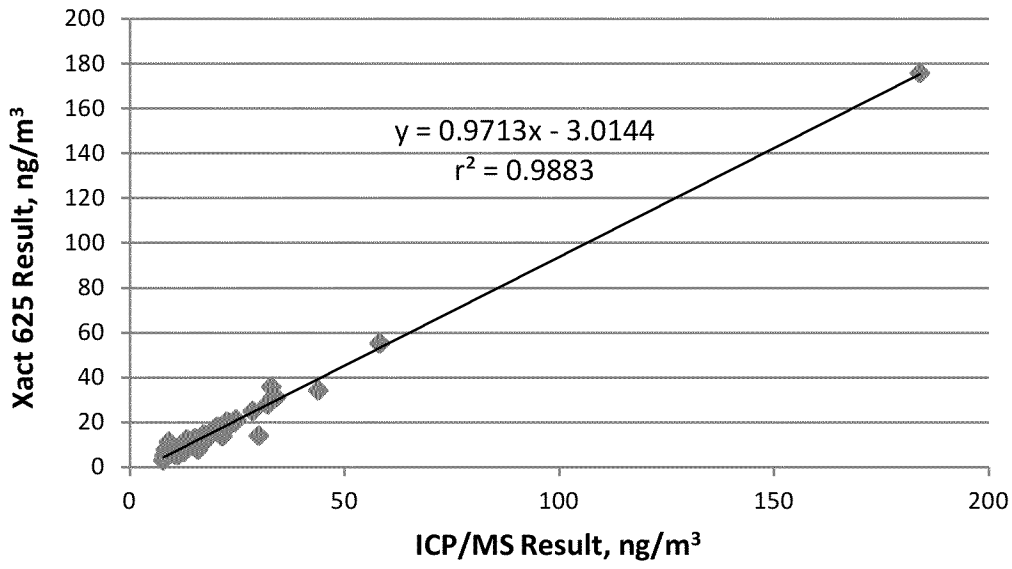

Figure 6-8. Linear regression of Xact 625 daily averages against ICP/MS daily averages for Zn.

It should be noted that one data point for Mn in Figure 6-5 has been excluded from the linear regression calculation shown in that figure. That data point is from January 9, 2012, on which day the Xact 625 reported only 13 hourly readings, for reasons that are described in Section 6.4. This data point is markedly offset from all other Mn results in Figure 6-5, and has a substantial effect if included in the regression. It is likely given the great variability observed in Mn concentrations that the 13 hourly values reported by the Xact 625 on January 9 do not adequately indicate the daily average Mn over that entire day, and as a result agree poorly with the reference sample result. The data for other metals from that same day were also reviewed, and were found not to be outliers and consequently were not excluded from the corresponding regressions. Note that on January 6, 2012 the Xact 625 recorded only 14 hourly readings (see Section 6.4), but no reference sample was collected on that day so there is no impact on the comparison of Xact 625 and reference results.

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Table 6-2. Results of Linear Regression of Xact 625 and Reference Data

Metal	Number of Data Points	Slope[a] (±95% CI)	Intercept[b] (ng/m^3) (±95% CI)	Coefficient of Determination (r^2)
Ca	47	**0.822** (± 0.035)	**-30.6** (± 11.9)	0.979
Cu	26	**0.304** (± 0.169)	**2.07** (± 0.647)	0.341
Mn	48	**1.038** (± 0.012)	-0.094 (± 2.13)	0.999
Pb	52	1.059 (± 0.072)	**1.56** (± 0.301)	0.943
Se	25	0.986 (± 0.114)	0.012 (± 0.219)	0.926
Zn	53	0.971 (± 0.029)	**-3.01** (± 0.977)	0.988

a: Values in bold indicate 95% CI does not include slope of 1.0.
b: Values in bold indicate 95% CI does not include intercept of zero.

for Ca, and especially the slope for Cu, are substantially less than 1.0. Table 6-2 also shows that the regression intercepts for Ca, Cu, Pb, and Zn differ significantly from zero. As shown in Figures 6-3 to 6-8, the concentration ranges of the target metals and the numbers of data points available for regression analysis differ greatly among the six metals. In that regard the strikingly different regression results for Cu and Se are noteworthy, given the similarly low concentration ranges and the relatively small numbers of data points available for these metals (Figures 6-4 and 6-7, respectively). A likely cause of the weak regression for Cu is that the Cu concentrations were near both the detection limit of the ICP/MS analysis and the QL of the Xact 625. In addition, after the field period in Marietta was completed the vendor of the Xact 625 investigated Xact 625 XRF spectra, including a spectrum of a blank section of the Xact 625's filter tape obtained prior to the start of monitoring in Marietta. The vendor indicated a Cu reading on the blank tape equivalent to approximately 6 ng/m^3. A single blank analysis result must be viewed with caution, but this observation suggests that Xact 625 tape background may have contributed to the regression results for Cu, and that analysis of a blank spot on the filter tape should be part of the routine daily QC checks of the Xact 625. Such a blank analysis is generally recommended by the vendor but was not included among the automated QC procedures implemented by the vendor for this verification.

With the exception of Cu Table 6-2 shows strong correlation of the Xact 625 and reference method results, with r^2 values ranging from 0.926 for Se to 0.999 for Mn.

The regression plots for Ca, Mn, Pb, and Zn (Figures 6-3, 6-5, 6-6, and 6-8) each show one data point that is at a much higher concentration than all other data points. To assess whether these single data points unduly influenced the regression results shown for those metals in Table 6-2, the regressions were also calculated without these single data points. The impact of these single points on the respective regression results was found to be minimal. For example, for Ca, Mn, and Zn the regression slope changed by 0.018 or less upon exclusion of the highest data point, r^2 values also changed only slightly, and no changes occurred in the

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significance of the difference of slope values from 1.0 or intercept values from 0.0. A small effect was seen for Pb, for which exclusion of the highest data point increased the regression slope from 1.059 to 1.149 (the latter significantly different from 1.0), decreased the intercept from 1.556 to 1.305 (both significantly different from 0.0), and reduced r^2 from 0.943 to 0.914. Nevertheless, these small differences do not alter the overall picture of the Xact 625's performance relative to the reference method in determining Pb. It was concluded that the single high data points in the regressions for Ca, Mn, Pb, and Zn do not exert undue effect on the regression results for these metals, and these data points were included in the regressions.

6.3 Bias

Table 6-3 summarizes the bias results for the six metals for which Xact 625 results can be compared to the ICP/MS results. The bias values were calculated according to Equation 3 in Section 5.4. Shown in Table 6-3 for each metal are the mean (± SD), median, and range of the individual bias values found by this comparison.

Table 6-3. Bias of Xact 625 Results Relative to Reference Results

Metal	Number of Data Points	Bias (%)		
		Mean (± SD)	Median	Range
Ca	47	-31.3 (± 9.5)	-31.0	-57.0 to -9.8
Cu	26	-5.6 (± 22.1)	1.2	-56.0 to 26.2
Mn	48	1.1 (± 21.8)	-0.6	-33.3 to 103
Pb	52	74.8 (± 54.3)	61.9	8.7 to 339
Se	25	-0.70 (± 8.1)	-1.3	-15.9 to 17.7
Zn	53	-20.5 (± 15.4)	-17.9	-59.3 to 27.6

The percent bias results in Table 6-3 appear to present a different picture than the regression results in Section 6.2, in that (e.g.) a low average bias is indicated for Cu and a relatively large average bias for Pb. The bias results are sensitive to the magnitude of the concentrations being compared, i.e., a small quantitative difference in measurement results can equate to a large percent bias if the reference result is a small concentration. Consequently, a regression equation and r^2 value indicating similarity of results may not correspond to low percent bias values. A good example is Pb, for which the regression line is shown in Figure 6-5. Although the regression slope for Pb is only slightly above 1.0 (i.e., 1.059), the positive intercept of approximately 1.5 ng/m^3 is relatively large compared to the reference Pb concentrations, more than half of which are less than about 3 ng/m^3.

After the field period in Marietta was completed the vendor of the Xact 625 analyzed the XRF spectrum of a blank section of the Xact 625's filter tape obtained prior to the start of monitoring in Marietta, and observed a blank Pb level equivalent to approximately 1 ng/m^3.

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This observation indicates that the Xact 625 filter tape background may have contributed significantly to the positive intercept for Pb, reinforcing the suggestion made in Section 6.2 that analysis of the blank filter tape should be part of the routine daily QC checks of the Xact 625.

In the case of Ca, the combination of a relatively low slope and relatively large negative intercept (Figure 6-3) contribute to the negative bias values shown in Table 6-3. On the other hand, in the case of Cu the relatively random magnitude and direction of the differences between Xact 625 and ICP/MS results shown in Figure 6-3 result in an overall average percent bias close to zero despite a wide range of individual bias values.

The influence of the absolute magnitude of the measured concentrations on the percent bias results is illustrated in Figure 6-9, which plots the individual percent bias values for Pb as a function of the reference method concentrations for that metal. The percent bias values for Pb are all positive, but clearly decline sharply as the reference Pb concentration increases.

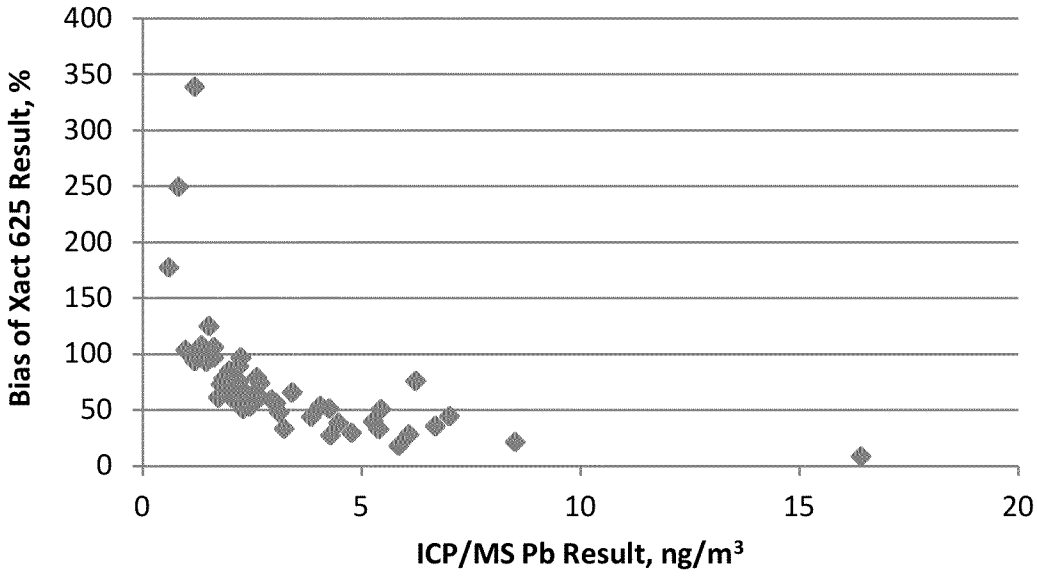

Figure 6-9. Percent bias results for Pb as a function of the reference concentration.

6.4 Data Completeness

The DC for the Xact 625 in operation at the Marietta site was calculated in two ways as described in Section 5.5. DC for each metal was calculated both as the percentage of hourly data collected during the verification testing period, and as the percentage of the 23.5-hour daily averaging periods in which the Xact 625 provided at least 12 readings. Hourly DC was calculated over both the entire period of operation of the Xact 625 in Marietta (December 10, 2011 to February 27, 2012; 1,905 total possible hours) and over the 65-day period during which the reference samples were collected (December 23 to February 25; 1,560 total

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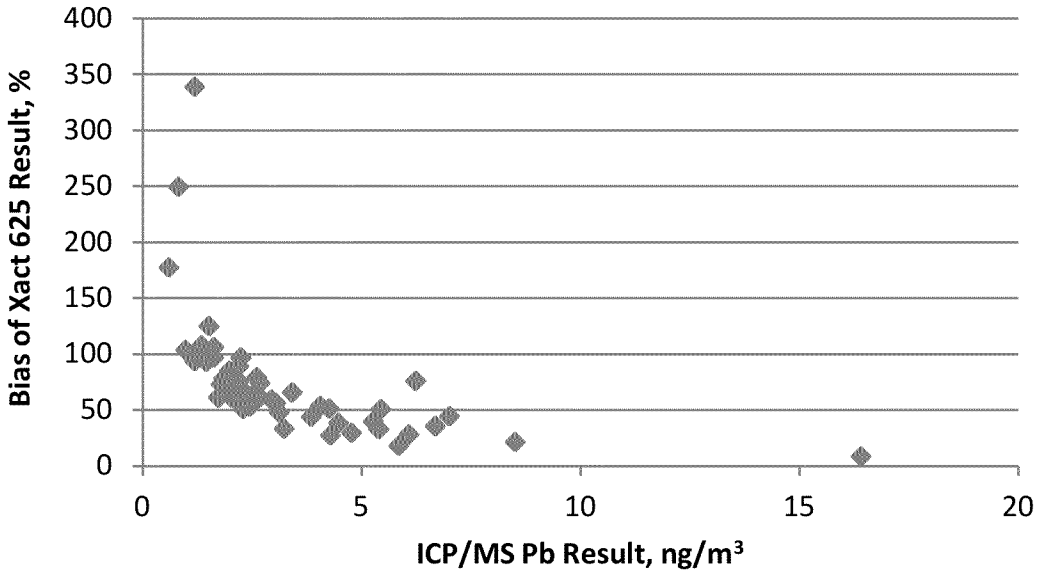

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possible hours). Completeness relative to daily 23.5-hour periods was calculated only for the latter period. Table 6-4 summarizes the DC results.

Table 6-4. Data Completeness for the Xact 625

Measure of Completeness	Time Period	Value (%)
Completeness of Hourly Data	12/10/11 to 2/27/12	96.0
Completeness of Hourly Data	12/23/11 to 2/25/12	95.4
Percentage of Days with ≥12 Hours of Data	12/23/11 to 2/25/12	96.9

Table 6-4 shows that the completeness of the Xact 625's hourly data was greater than 95% over both its entire operational period at the Marietta site and over the 65-day period of reference sampling. By far the largest episode of missing Xact 625 data was from 3:00 pm on Friday, January 6 to 11:00 am on Monday, January 9, 2012. This loss of data resulted when the Xact 625 software opened a second XRF control screen, causing routine sampling to be interrupted. No reason could be found for this event, but because the data loss began on a Friday afternoon, the problem was not discovered and corrected until site operators visited the site on the following Monday. This event caused the Xact 625 to produce only 14 hourly readings on January 6, none on January 7 and 8, and 13 hourly readings on January 9. On all other sampling days between December 23 and February 25, the Xact 625 returned at least 22 hourly readings. Thus, the Xact 625 provided hourly readings for less than 12 hours on only two days out of the 65 days on which reference sampling occurred.

6.5 Operational Factors

The Xact 625 was installed in the field trailer shown in Figure 3-1 prior to its arrival at the field site. Consequently, installation of the Xact 625 was not evaluated in this test. Startup of the Xact 625 was straightforward upon setup of the field trailer at the test site, and the analyzer was ready for routine operation within about one day after electrical power was connected to the trailer. The Xact 625 operated reliably throughout the field test, as indicated by the DC results in Section 6.4, and required minimal operator attention. The filter tape in the analyzer was replaced approximately every 2 weeks, but no other routine maintenance was needed. During the period in which the Xact 625 was installed at the East Liverpool site, the temperature and barometric pressure sensors of the analyzer malfunctioned, invalidating the Xact 625 data from that site. However, that malfunction was caused by the design and installation of connectors for those sensors in an exposed location on the roof of the field trailer, and not by an issue with the Xact 625 itself.

The Xact 625 was programmed to carry out several internal automated QC checks on a daily basis, and did so without interruption during the field period. The results of these QC checks are summarized in Section 4.3, and demonstrated stable performance, minimal flow variation, and close agreement with calibration standards throughout the entire field period at both the East Liverpool and Marietta sampling sites. Analysis of the Xact 625's blank filter

possible hours). Completeness relative to daily 23.5-hour periods was calculated only for the latter period. Table 6-4 summarizes the DC results.

Table 6-4. Data Completeness for the Xact 625

Measure of Completeness	Time Period	Value (%)
Completeness of Hourly Data	12/10/11 to 2/27/12	96.0
Completeness of Hourly Data	12/23/11 to 2/25/12	95.4
Percentage of Days with ≥12 Hours of Data	12/23/11 to 2/25/12	96.9

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tape to determine background metals levels was not part of the monitor's automated daily QC checks. However the results reported above, and investigations conducted by the vendor after the Marietta field period, indicate that inclusion of blank filter analysis in such QC checks may be valuable.

The data files produced by the Xact 625 clearly distinguished the QC analysis periods from the normal hourly ambient sampling periods, and included a variety of analyzer operating data in addition to the measured ambient metals concentrations in ng/m^3. Those operating data included ambient and internal analyzer temperatures, ambient barometric pressure and tape pressure drop, sample flow rates in actual and standard units, sample volumes, and alarm and QC indications. The data files were well organized and allowed quick review to assess Xact 625 operations and QC results, such as those summarized in Section 4.3. Xact 625 data files were reviewed at least weekly by a Pall Corporation representative to assess the analyzer's operating stability, but the data files were clear enough that a similar review could be performed by any user familiar with the file format.

The purchase price of the Xact 625 at the time of preparation of this report was approximately $180,000. This price is subject to change.

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Chapter 7
Performance Summary

Of the 23 ambient PM_{10} metals determined by the Xact 625 in this verification, 19 were also determined by the ICP/MS analysis of reference samples. Of those 19 metals, Xact 625 results for 12 metals were almost always below the respective QLs of the Xact 625, and for one other metal (Mo) the Xact 625 reported a nearly constant and unrealistic ambient concentration due to an incorrect energy window for that metal in the XRF analysis. The vendor of the Xact 625 indicates that this problem can be avoided in the future by narrowing the energy window. Table 7-1 presents a summary of the quantitative performance results of the Xact 625 for the remaining six metals, showing the performance parameters and resulting performance metrics.

Table 7-1. Quantitative Performance Results for the Xact 625

Performance Parameter	Metal	Metric	
Comparability		**Slope**	**Intercept (ng/m^3)**
	Ca	0.822	-30.6
	Cu	0.304	2.07
	Mn	1.038	-0.094
	Pb	1.059	1.56
	Se	0.986	0.012
	Zn	0.971	-3.01
Correlation		**Coefficient of Determination (r^2)**	
	Ca	0.979	
	Cu	0.341	
	Mn	0.999	
	Pb	0.943	
	Se	0.926	
	Zn	0.988	
Bias		**Mean (%)**	**Median (%)**
	Ca	-31.3	-31.0
	Cu	-5.6	1.2
	Mn	1.1	-0.6
	Pb	74.8	61.9
	Se	-0.7	-1.3
	Zn	-20.5	-17.9
Data Completeness		**Hourly Data (%)**	**Daily Averages with ≥ 12 Hours (%)**
	All	95.4 to 96.0	96.9

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Bias		**Mean (%)**	**Median (%)**
	Ca	-31.3	-31.0
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	Mn	1.1	-0.6
	Pb	74.8	61.9
	Se	-0.7	-1.3
	Zn	-20.5	-17.9
Data Completeness		**Hourly Data (%)**	**Daily Averages with ≥ 12 Hours (%)**
	All	95.4 to 96.0	96.9

Table 7-1 indicates that the daily average Xact 625 results were highly correlated and in close quantitative agreement with ICP/MS analysis results for most of the six metals, and that the Xact 625 achieved data completeness of over 95%. The regression results for Cu reflect the fact that Cu concentrations were often near the detection limit of the ICP/MS analysis and the QL of the Xact 625. In addition, investigations conducted after the verification test suggest that the regression results for Cu and the bias results for Pb may have been affected by the levels of these metals in the Xact 625's blank filter tape.

The Xact 625 required minimal operator attention during testing, with routine maintenance consisting of changing the sampling tape approximately every 2 weeks. The monitor conducted several automated internal QC checks on a daily basis, and provided readily understandable data files that distinguished QC from ambient monitoring results and included analyzer flow and internal readings. The RSD of the Pd internal standard readings determined in every Xact 625 XRF analysis was 2.04%. The monitor's average flow error was -0.69% (± 0.004%), where the value in parentheses is the SD of the daily flow check results. The average accuracy relative to upscale rod check standards analyzed daily was 100.21% (±0.004%) for Cr, 100.55% (±0.013%) for Cd, and 99.79% (±0.007%) for Pb, where accuracy of 100% represents perfect agreement with the upscale rod check standard. However, the test results noted above for Cu and Pb strongly indicate that analysis of blank portions of the filter tape should be a component of the Xact 625's automated internal QC checks.

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Chapter 8
References

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