



South Coast Air Quality Management District

21865 Copley Drive, Diamond Bar, CA 91765-4182
(909) 396-2000 • www.aqmd.gov

EMAILED and MAILED: February 16, 2017

February 16, 2017

Mr. Scott Bevans
Quemetco Inc
720 S. 7th Ave
City of Industry, CA 91745-3124

Subject: Rejection of Rule 1402 Risk Reduction Plan for
Quemetco Inc, City of Industry (SCAQMD No. 8547)

Dear Mr. Bevans:

The South Coast Air Quality Management District (SCAQMD) staff received the proposed Risk Reduction Plan (RRP) for Quemetco Inc. located at 720 S. 7th Ave, City of Industry (Facility ID# 8547) submitted on November 16, 2016. The SCAQMD staff appreciates that Quemetco is proposing to set a new, enforceable lower arsenic emission limit and use an in-stack multi-metals Continuous Emissions Monitoring System (CEMS) to monitor these emissions. The SCAQMD staff supports Quemetco's request for a lower arsenic limit. However, the in-stack multi-metals CEMS as proposed in the RRP lacks sufficient measures to ensure the reliable operation and enforcement of this system. Any new monitoring system must meet standard practices required of other compliance monitoring instruments. As a result, the SCAQMD staff is rejecting the draft RRP and has provided a list of measures that Quemetco can include in a revised RRP that will ensure the reliable operation of the in-stack multi-metals CEMS. Details regarding the arsenic emission limit, measures to ensure the appropriate protocols are used for reliable operation of the in-stack multi-metals CEMS, and supplemental information to enhance the RRP that is needed prior to approval of a revised RRP are discussed below.

Arsenic Emission Limit

The submitted RRP proposes an arsenic emission limit of 6.50 pounds per year from the Wet Electro-Static Precipitator (WESP) stack as continuously measured by an XACT 640 multiple metals CEMS, or an equivalent device. Both the new arsenic emission limit and the CEMS requirement would need to be included in Quemetco's SCAQMD permit if the RRP is approved. The approved HRA found that arsenic makes up 80% of the cancer risk at the maximum receptor and that the WESP is the source of 88% of arsenic emissions from the facility. By maintaining an emission rate lower than 6.50 pounds per year of arsenic from the WESP, the modeling contained within the RRP demonstrates that the cancer burden will stay at least 10% below the SCAQMD Rule 1402 threshold. SCAQMD staff has reviewed this dispersion modeling analysis and concurs with the results.

The proposed XACT 640 CEMS would take hourly measurements, and evaluate compliance with the RRP's emission limit based on a rolling 30-day average. A 30-day rolling average would be used instead of a shorter average because the health risk endpoint of concern from arsenic is lifetime cancer risk, and not short-term impacts. Preliminary CEMS data submitted by Quemetco on January 29, 2017 shows that WESP arsenic emissions throughout calendar year 2016 were below the RRP's proposed limit. This data submittal did not contain any of the QA/QC information described below and SCAQMD staff cannot verify the validity of these results without this information.

In-Stack Multi-Metal CEMS and QA/QC

The SCAQMD staff conducted a pilot study of this instrument at Quemetco in 2015 and verified that the levels detected are within acceptable limits compared to more traditional stack testing techniques when it was operated under specific conditions (Attachment 1). In order to ensure that this relatively new technology continues to report reliable results, the RRP must include enforceable measures demonstrating its proper operation, including provisions for maintenance and QA/QC, recordkeeping, reporting, and contingency plans in case of failure of the XACT 640 CEMS. The key parameters to include are described below, and a recommended detailed approach is included in Attachment 2.

- Recordkeeping
The revised RRP must provide timelines for recordkeeping of all data collected by the CEMS, as well as data generated by maintenance and QA/QC activities specified above. These records must be made available to SCAQMD upon request.
- Reporting
For SCAQMD oversight and QA/QC purposes, Quemetco must provide SCAQMD direct, realtime access to the metal CEMS data as specified in Attachment 2. In order to facilitate public access of this data, Quemetco should also establish and maintain a website with SCAQMD input that provides the real-time rolling 30-day averages from both the WESP and the onsite fenceline monitoring stations.
- Contingency Plan
In the revised RRP Quemetco must demonstrate how it will operate the CEMS in an uninterrupted manner. The revised RRP should also specify the maximum amount of time that the facility can operate while the CEMS is not operating (e.g., 95% CEMS uptime with downtime allowed only for periodic instrument maintenance). The revised RRP should also specify what the facility will do if the instrument cannot operate within this limit.

For equipment maintenance purposes, Quemetco must present an operation and maintenance program for the XACT 640 CEMS, especially where it differs from manufacturer's specification. For quality assurance / quality control (QA/QC), Quemetco must prepare and submit plans for upscale, zero, and flow calibration drift checks; for an initial and regular follow-up x-ray

fluorescence (XRF) audit; for an initial and regular follow-up relative accuracy test audit (RATA) using CARB Method 436 and a quantitative aerosol generator (QAG); and for acceptable meter accuracy and raw data completeness.

Supplements to the RRP

There are two additional components that should be included in the revised RRP, as described below.

- Description of Arsenic Reductions
The revised RRP should contain a description of the steps Quemetco has taken to reduce its arsenic emissions since 2013. This information should be substantiated where possible.
- Full Metals Reporting from the CEMS
Although arsenic is the primary driver of cancer risk, other pollutants like lead also contribute to this risk. The proposed CEMS is capable of evaluating emissions of multiple metals simultaneously, without additional cost. As part of the recordkeeping and reporting requirements outlined above, SCAQMD staff requests that the RRP commit to providing the full suite of metals data made available from this instrument.

In conclusion, by including the provisions outlined above and in the attachments to the satisfaction of SCAQMD staff, the proposed RRP should meet the requirements of Rule 1402. However, without sufficient maintenance, recordkeeping, reporting, and contingency measures for the multi-metals in-stack CEMS, the RRP does not demonstrate how the proposed approach will sufficiently maintain facility health risks below SCAQMD thresholds. Pursuant to Rule 1402(f)(3)(B) and Rule 216, you have 30 days to either submit a revised RRP in response to this rejection, or appeal this matter to the SCAQMD Hearing Board. Should you have any questions, don't hesitate to contact me at (909) 396-3244.

Sincerely,



Ian MacMillan
Planning and Rules Manager

Cc: Phil Fine, SCAQMD
Susan Nakamura, SCAQMD
Laki Tisopulos, SCAQMD
Kurt Wiese, SCAQMD
Mike Buckantz, Quemetco

Attachment 1: *Summary of Installation and Evaluation of the XACT 640 under South Coast Air Quality Management District Contract #C14337*, March 30, 2016 prepared by Cooper Environmental

Attachment 2: *Potential Quemetco XACT 640 Multi-Metals CEMS Requirements for Risk Reduction Plan*

**Summary of Installation and Evaluation of the Xact 640 under South Coast Air Quality
Management District Contract #C14337**

Krag Petterson and Chris Koch

March 30, 2016

1. Project Introduction

On March 7, 2014, the Board of the South Coast Air Quality Management District (SCAQMD) adopted a provision in Rule 1420.1 for operators of large lead-acid battery recycling facilities to implement and fund a multi-metals continuous emissions monitoring system (CEMS) demonstration program. The goal of the demonstration project was to gather emissions data to determine if the Xact 640 multi-metals CEMS is a feasible and effective means of continuously monitoring lead, arsenic and other toxic metals. The demonstration project originally was to consist of deploying a Xact 640 rented from Cooper Environmental Services, LLC (CES) at two battery recycling facilities (Quemetco, Inc. and Exide Technologies) in the greater Los Angeles area with approximately five months at each site. In the time since this project was approved by SCAQMD, one of the facilities (Exide Technologies) has shut down and the Xact was deployed at Quemetco for the entire 10 month duration of the project.

2. Xact Instrument Background

The Xact 640 is a multi-metal CEMS based on X-ray fluorescence (XRF) and reactive filter tape technology. The Xact operates by withdrawing a large sample of stack gas (approximately 250 lpm) through a relatively large diameter (approximately 1 inch) probe and transporting that sample through large diameter heated lines. A small subsample (approximately 1.5 lpm) is extracted through a chemically reactive filter tape where both particulate and vapor phase metals are captured. (In some cases, dilution air is added to the subsample of stack gas to lower the sample dew point, however, the stack conditions at Quemetco did not warrant this). The sample flow passing through the tape is dried and the total dry sample flow is measured. After sampling for a period of time (60 minutes was used throughout the duration of the study period) the aerosol deposited on the filter tape is advanced into the analysis area where the sample is analyzed by XRF for metals content. The resulting XRF determined mass (μg) is divided by the totalized flow (dscm) to give an aerosol concentration in $\mu\text{g}/\text{dscm}$.

The Xact has been evaluated for accuracy and precision using EPA Method 301 which is the method by which the US EPA evaluates new stack sampling methods^{1,2}. In addition, the Xact was accepted by EPA as a compliance metals monitor as part of an Alternative Monitoring Petition (AMP) at Eli Lilly's Tippecanoe Laboratories³. It operated at the facility from 2005 to 2011. As part of Eli Lilly's Alternative Monitoring Petition the Xact had to meet certain initial and on-going quality assurance criteria. These criteria and procedures are currently recognized by the US EPA as Other Test Methods (OTM) 16 (initial performance criteria) and 20 (on-going

quality assurance criteria).^{4,5} The required quality assurance tests from these documents are described below and formed the basis for much of the evaluation of the Xact's ongoing performance during this project.

1. Daily Upscale Calibration Drift Check

This check evaluates the precision of the Xact XRF system's response to a standard once per day. During this check, a rod containing metals is injected into the analysis area and the stability of the analyzer response is evaluated. The CEMS must report a concentration that is within 15% of known value of the upscale standard each day.

2. Daily Zero Calibration Drift Check

This check evaluates the Xact XRF system's response to a zero concentration produced by analyzing an un-sampled section of filter tape. The instrument passes the test if the result of the zero drift check for each monitored metal is less than 20% of the applicable emission limit. The emission limits for arsenic (As) and lead (Pb) at Quemetco's facility are in lbs/hr (0.01 lbs/hr for Pb and 0.00114 lbs/hr for As). Based on average stack flow rates (82,000 dscfm) the following approximate limits in micrograms per dry standard cubic meter ($\mu\text{g}/\text{dscm}$) were calculated:

Pb – 32.5 $\mu\text{g}/\text{dscm}$

As – 3.7 $\mu\text{g}/\text{dscm}$

3. Daily Flow Calibration Drift Check

The Xact utilizes a quality assurance flow sensor to check the flow reading from the sample flow sensor once per day. The difference in flow between the quality assurance flow sensor and the sample flow sensor must be less than 20% of the full scale value of the flow measurement (5 slpm) device to pass the test.

4. Initial and Quarterly XRF Audit

During installation, and at least once per quarter the XRF analysis portion of the Xact is challenged using a traceable-to-NIST thin film standard. These standards are produced by depositing metal vapor on a filter substrate and the mass of the metal deposit is determined gravimetrically. These standards are recommended by the US EPA⁶ for the calibration of XRF equipment used to analyze ambient air filters.

5. Initial and Annual RATA

During installation and at least once per year, the Xact is challenged with a reference aerosol containing a known concentration of the metals of interest at three different concentration levels. Although OTM16 describes several different approaches to this test, the one that was used at Eli Lilly was a dynamic spiking approach in which the reference aerosol is introduced

into a sample of stack gas. The same dynamic spiking procedure was performed at Quemetco along with several other spiking procedures (described in Section 7) as part of South Coast Air Quality Management District's evaluation of the Xact 640.

The dynamic spiking procedures include challenging the Xact at three separate spiked concentration levels with a reference aerosol produced using CES' Quantitative Aerosol Generator (QAG). The Xact reported concentration is plotted against the QAG spiked concentration and a linear least squares regression analysis is performed. The Xact is evaluated on the basis of slope, intercept and correlation coefficient. The instrument passes the relative accuracy test assessment if the slope of the best fit line is between 0.85 and 1.15, if the correlation coefficient is 0.9 or greater and if the intercept is less than 20% of the applicable emission limit.

3. Calculations

The equations used to calculate the metrics associated with each of the tests are given in Sections 3.1 to 3.4.

3.1. Daily Upscale and Blank Calibration Drift Check

$$CD = \frac{|R - A|}{L} \times 100 \quad \text{Equation 1}$$

Where:

- CD = Either the upscale or zero calibration drift check.
- R = Either the upscale or zero standard reference value
- A = Either the Xact CEMS response to the upscale or zero standard
- L = The emission limit expressed in the $\mu\text{g}/\text{m}^3$ or the known concentration of the upscale standard

3.2. Flow Drift Check

$$FD = \frac{|F_p - F_{QA}|}{FS} \times 100 \quad \text{Equation 2}$$

Where:

- FD = The flow drift
- F_p = The flow as measured by the primary flow measurement device in the Xact.
- F_{QA} = The flow as measured by the CEMS's secondary quality assurance flow meter.

FS = The full scale value of the flow sensor

3.3. XRF Audit

$$AE = \frac{|C_s - C_c|}{C_s} \times 100 \quad \text{Equation 3}$$

Where:

AE = XRF Analyzer Error

C_s = Concentration (or mass) of the metal analyte on the traceable to NIST standard

C_c = Concentration (or mass) of the metal analyte as reported by the Xact

3.4. Flow Audit

$$FE = \frac{|F_s - F_c|}{F_s} \times 100 \quad \text{Equation 4}$$

Where

FE = The flow error

F_s = The flow as measured by the reference flow sensor

F_c = The flow as measured by the Xact flow sensor

4. Physical Installation

A Xact 640 was installed on the sampling platform of the Wet Electrostatic Precipitator (WESP) exhaust stack at Quemetco's City of Industry facility. The instrument was placed approximately 10 feet from its sampling port. A one inch diameter sampling probe was placed into the stack with the tip located between the second and third traverse points as defined by US EPA Method 1.⁷ The port is located at least 8 diameters downstream of any flow disturbance and at least 2 diameters upstream of the stack exit. The probe was connected to the instrument using approximately one inch diameter heat traced Teflon line. The flow rate through the tubing was set to approximately 250 lpm which corresponds to a nominally isokinetic flow rate through the probe (based on Quemetco's average stack flow). From this flow, approximately 1.5 slpm is drawn through the filter tape. The remaining flow was originally returned back to the same port from which the sample was drawn however, this flow disturbed the plant's volumetric flow

sensor so the return flow was vented to atmosphere. Physical installation of the Xact 640 was completed on March 6th, 2015.

5. Initial Test Procedures and Results

5.1. XRF Audit

Immediately following the physical installation of the Xact an XRF audit was performed. During the XRF audit the Xact was challenged with several thin film standards with known concentrations of metals. The Xact reported concentration was compared with the certified concentration of the standard. Data from the initial XRF audit can be found in Table 1.

Table 1. Initial XRF Audit Results

Atomic number	Element	Micromatter Standard Composition	Standard ID	Mass (ng)	Reported Mass (ng)	% Error
25	Mn	Mn	37705	35.43	37.72	6.47%
34	Se	Se	37714	38.33	39.01	1.77%
82	Pb	Pb	37727	41.11	42.02	2.21%
48	Cd	CdSe	37718	22.29	20.74	-6.94%

5.2. Seven-Day Calibration Drift Check

Once per day from April 10th to April 16th the instrument performed an automatic flow, upscale and zero drift check. The zero drift check occurred at 12:30 AM each day while the upscale and flow drift occurred at 12:45 AM. Table 2 shows the results from each of the seven days for the upscale and flow drift check results. The instrument passed both the upscale and flow drift check on each of the seven days. The zero drift results showed no detectable arsenic or lead during the test.

Table 2. Seven Day Calibration Drift Check Results

Time	XRF Upscale Percent Difference			Flow Percent Difference
	Cr	Cd	Pb	
4/10/2015 0:45	-5.74%	-1.96%	-4.06%	0.20%
4/11/2015 0:45	-5.98%	-1.98%	-3.99%	0.40%
4/12/2015 0:45	-6.10%	-4.14%	-4.78%	0.40%
4/13/2015 0:45	-7.66%	-5.03%	-6.30%	0.20%
4/14/2015 0:45	-5.98%	-3.83%	-4.71%	0.20%
4/15/2015 0:45	-5.86%	-2.00%	-3.56%	0.00%
4/16/2015 0:45	-7.54%	-3.05%	-5.51%	0.20%

5.3. QAG RATA Testing

As part of the performance specifications and on-going quality assurance requirements for compliance measurements on Eli Lilly's hazardous waste incinerator, periodic relative accuracy

test audits (RATA) were performed on the Xact. The RATA procedures involved dynamically spiking sampled stack gas with an aerosol of a known concentration. These reference aerosols were generated using CES' Quantitative Aerosol Generator (QAG). The guidelines for these procedures have been recognized by EPA in Other Test Methods 16 and 20.^{4,5}

There are several benefits to dynamic spiking. One benefit is the ability to test the instrument's response over a wide range of concentration levels rather than just relying on the native stack gas concentrations. In addition, dynamic spiking, as opposed to spiking with a clean dry air, challenges the instrument and tests for any potential effects of the stack matrix.

There are some differences between the hazardous waste incinerator and a secondary lead recycler in the source operation that provide additional challenges to dynamic spiking. Lilly's hazardous waste incinerator was able to burn waste during the RATA procedure that did not contain significant metal concentrations. This means that there was no need to correct for background concentrations of the spiked metals. The secondary lead smelting facility included in this study was not able to provide a metals free background when under normal operation. To resolve this issue CES alternated between background (non-spiked) and spiked concentrations during its dynamic spiking procedures. The background concentration for spiked metal is determined by calculating the average concentration from the background samples taken immediately before and immediately after each spiked concentration. This procedure is similar to approach that EPA has taken to dynamic spiking procedures on HCl CEMS (PS-18).⁸

Prior to performing the dynamic spiking procedures CES also demonstrated the measurement accuracy of the instrument itself independently of these relatively new procedures by challenging it with a QAG generated reference aerosol spiked into sampled ambient air. These procedures are described in more detail in Sections 5.5 to 5.11.

5.4. QAG Summary

The Quantitative Aerosol Generator (QAG) provides a traceable-to-NIST metal and particulate matter (PM) aerosol concentrations. The QAG nebulizes a solution containing a traceable to NIST concentration of metals at a measured rate (using liquid flow sensors or by measuring mass loss on a balance) into a measured flow. The concentration of the aerosol is obtained by dividing the product of the solution concentration ($\mu\text{g/g}$) and the mass loss rate (g/min) by the flow rate (m^3/min). Each of the key measurements is traceable to NIST standards making the resulting concentration traceable to NIST standards.

$$C_i^{QAG} = \frac{C_i^{sln} \times R}{F_T}$$

Equation 5

Where:

C_i^{QAG} = The QAG aerosol concentration of the i^{th} metal

C_i^{sln} = The concentration of the i^{th} metal in the nebulized solution

R = The solution mass loss rate

F_T = The total flow

5.5. Spiking Arrangement

Figure 1 shows the spiking arrangement used during the testing. Ambient air is drawn into the spike mixing chamber through carbon trap which acts as a particulate filter as well as preventing any metals from escaping into the ambient air should the system backflow for any reason. The spiked aerosol is introduced to the approximately 250 lpm ambient air flow and then air is allowed to mix and be transported to the heated flexible sample line. The spike mixing chamber is approximately three inches in diameter while the heated flexible line is approximately one inch in diameter. After traveling through the heated sample line the aerosol is transported to the Xact stilling chamber where approximately 1.5 lpm of aerosol is drawn through the reactive filter tape. The flow then passes through the stilling chamber and into a tee where the aerosol can be sampled using a CARB Method 436 sampling train. The probe for CARB Method 436 train was inserted into a 1.5 inch sanitary tee and positioned so that it is 3 inches upstream from the start of the tee (2 diameters) and at least 12 inches (8 diameters) downstream from the bend in the stilling chamber. The CARB Method 436 sample probe was modified so that it is straight (rather than having a button hook configuration) and had tapered sampling tip. The majority of the aerosol passed through the tee and into a carbon trap which removes any of the spiked metals as well as the acid gases generated when nebulizing the solutions of dissolved metals in dilute nitric acid. Finally the flow is measured using a calibrated Rosemount differential pressure flow sensor that is capable of measuring the flow in standard liters per minute.

During spiking procedures that involve CARB Method 436 sampling the total flow used to calculate QAG aerosol concentration in Equation 4 is the sum of the flow measured using the Rosemount flow sensor and the flow measured with CARB Method 436. During spiking procedures not using CARB Method 436 the probe was removed and replaced with a sanitary cap. The total flow in those situations was the flow as measured with the Rosemount flow sensor. Finally during dynamic spiking procedures the carbon trap at the inlet of the system was removed and the Xact probe was inserted in the stack.

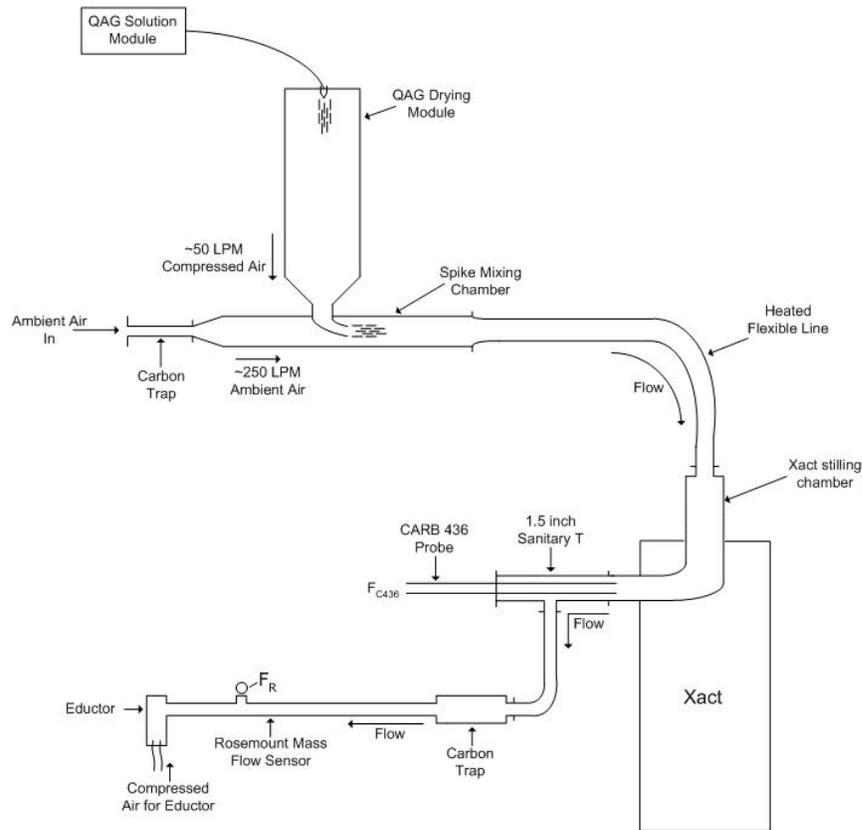


Figure 1. QAG Spiking Arrangement

5.6. Spiked Concentration Levels

The Rule 1420.1 emission limits for Quemetco after January 15, 2015 are 0.01 lb/hr for single point source and 0.00114 lb/hr for facility for lead (Pb) and arsenic (As), respectively. At average stack flow rates (82000 dscfm) this converts to concentration limits of 32.5 and 3.7 $\mu\text{g}/\text{m}^3$ respectively. The spiked concentration levels were based in part on these emission limits. Three concentration levels for lead and arsenic were spiked. The target concentration for the low spiking level was at 0.2 $\mu\text{g}/\text{dscm}$ for lead and arsenic. The target mid-level concentrations were 2.25 and 16.25 $\mu\text{g}/\text{dscm}$ for arsenic and lead respectively while the high concentrations were 4.5 and 32.5 $\mu\text{g}/\text{dscm}$. Table 3 summarizes the concentrations used at each level as well as the solution concentration and mass loss rate required to achieve each concentration level. The total flow for all concentrations is approximately 300 lpm.

Table 3. QAG Aerosol Concentration Levels and Settings

Concentration Level		Low Conc	Mid Conc	High Conc
Solution Mass Loss Rate (g/min)		0.125	0.125	0.25
As	Target Aerosol Conc (µg/dscm)	0.2	2.25	4.5
	Required Solution Conc (µg/g)	0.48	5.4	5.4
Pb	Target Aerosol Conc (µg/dscm)	0.2	16.25	32.5
	Required Solution Conc (µg/g)	0.48	39	39

5.7. Xact Sampling Times During Spiking Procedures

The detection limit of the Xact is a function of the sampling time – the longer the sampling time (and the subsequent analysis time) the better the detection limits. Currently, the Xact 640 can sample in 15, 30, 60, and 120 minute intervals. For the purpose of the spiking tests the Xact time interval was selected so that the spiked concentration level is at least 10 times the detection limit – this will assure at least 10% analytical uncertainty in the Xact’s reported results. The detection limits (1 sigma, interference free) are given for arsenic and lead in Table 4.

Table 4. Xact 640 Minimum Detection Limits in µg/dscm

Element	Sampling Time (min)			
	15	30	60	120
As	0.06	0.02	0.007	0.003
Pb	0.11	0.04	0.014	0.005

Given the Xact’s minimum detection limits, the sampling time for the low concentration level should be set to 60 minutes. Sampling times for the mid and the high concentration levels were set at 15 minutes to save testing time.

5.8. Test 1 – Spiking Ambient Air

5.8.1. Purpose and Description

The purpose of this test was to evaluate the measurement accuracy of the Xact in the absence of any complicating factors provided by the dynamic spiking procedures. During this procedure the Xact was disconnected from the stack and sampled filtered ambient air which was then spiked with QAG aerosol. After passing through the Xact's stilling chamber the spiked flow passed through a carbon filter to remove any metal and acid gas species. After the carbon filter the total flow was measured using a Rosemount differential pressure (DP) flow sensor equipped with a temperature and pressure sensor to correct the flow to standard conditions. The motive force for flow was provided by the eductor used during normal sampling. The concentration levels used were those described in Section 5.6 with five or six data points gathered at each level.

5.8.2. Ambient Air Spiking Test Results

Table's 5 and 6 show the results from the ambient air QAG spiking for arsenic (As) and lead (Pb) respectively. For each sample the concentration reported by the Xact is compared to the concentration of the QAG generated aerosol and a percent difference is calculated. Over all three concentration levels the average percent difference was -2.8% for arsenic and -2.5% for lead.

Table 5. Ambient Air Spiking Results for Arsenic (As)

Concentration Level	Time	QAG Conc (µg/dscm)	Xact Conc (µg/dscm)	% Difference
Low Conc. Level (0.2 µg/dscm)	3/19/2015 19:00	0.22	0.22	2.00%
	3/19/2015 20:00	0.21	0.23	7.03%
	3/19/2015 21:00	0.21	0.22	3.23%
	3/19/2015 22:00	0.22	0.23	6.15%
	3/19/2015 23:00	0.22	0.23	6.32%
Mid Conc. Level (2.25 µg/dscm)	3/19/2015 11:45	2.23	2.14	-4.19%
	3/19/2015 12:00	2.23	2.21	-0.98%
	3/19/2015 12:15	2.20	2.02	-8.24%
	3/19/2015 12:30	2.21	2.11	-4.66%
	3/19/2015 12:45	2.23	2.11	-5.32%
	3/19/2015 13:00	2.23	2.12	-5.12%
High Conc Level (4.5 µg/dscm)	3/19/2015 13:45	4.35	3.97	-8.66%
	3/19/2015 14:00	4.35	3.86	-11.33%
	3/19/2015 14:15	4.35	3.99	-8.27%
	3/19/2015 15:30	4.34	3.96	-8.67%
	3/19/2015 15:45	4.33	4.17	-3.77%

Table 6. Ambient Air Spiking Results for Lead (Pb)

Concentration Level	Time	QAG Conc (µg/dscm)	Xact Conc (µg/dscm)	% Difference
Low Conc. Level (0.2 µg/dscm)	3/19/2015 19:00	0.22	0.21	-3.23%
	3/19/2015 20:00	0.22	0.19	-12.13%
	3/19/2015 21:00	0.21	0.21	-2.07%
	3/19/2015 22:00	0.22	0.19	-12.85%
	3/19/2015 23:00	0.22	0.19	-12.71%
Mid Conc. Level (16.25 µg/dscm)	3/19/2015 11:45	16.85	16.59	-1.52%
	3/19/2015 12:00	16.83	16.62	-1.27%
	3/19/2015 12:15	16.60	16.61	0.04%
	3/19/2015 12:30	16.68	16.95	1.60%
	3/19/2015 12:45	16.81	16.63	-1.06%
	3/19/2015 13:00	16.85	17.03	1.07%
High Conc Level (32.5 µg/dscm)	3/19/2015 13:45	32.77	33.06	0.87%
	3/19/2015 14:00	32.82	33.62	2.43%
	3/19/2015 14:15	32.80	33.51	2.17%
	3/19/2015 15:30	32.70	32.56	-0.43%
	3/19/2015 15:45	32.68	32.26	-1.27%

In addition, the Xact reported concentrations for each metal were plotted against the QAG reference aerosol concentrations and a linear least squares fit for each plot was performed. Figures 2 and 3 show these plots and regression fits for arsenic and lead respectively. In general a slope of unity indicates perfect agreement between the QAG and the Xact while a high coefficient of determination indicates good precision of the data.

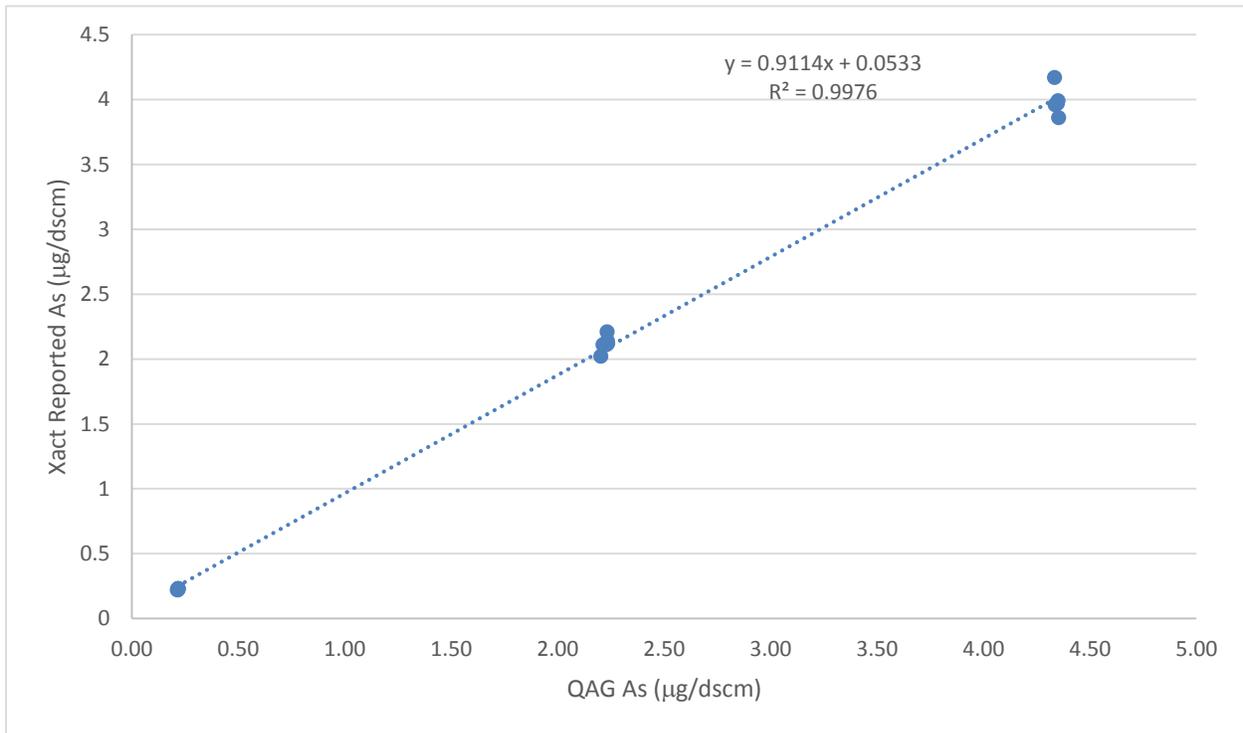


Figure 2. Ambient Air Spiking Regression Fit for Arsenic

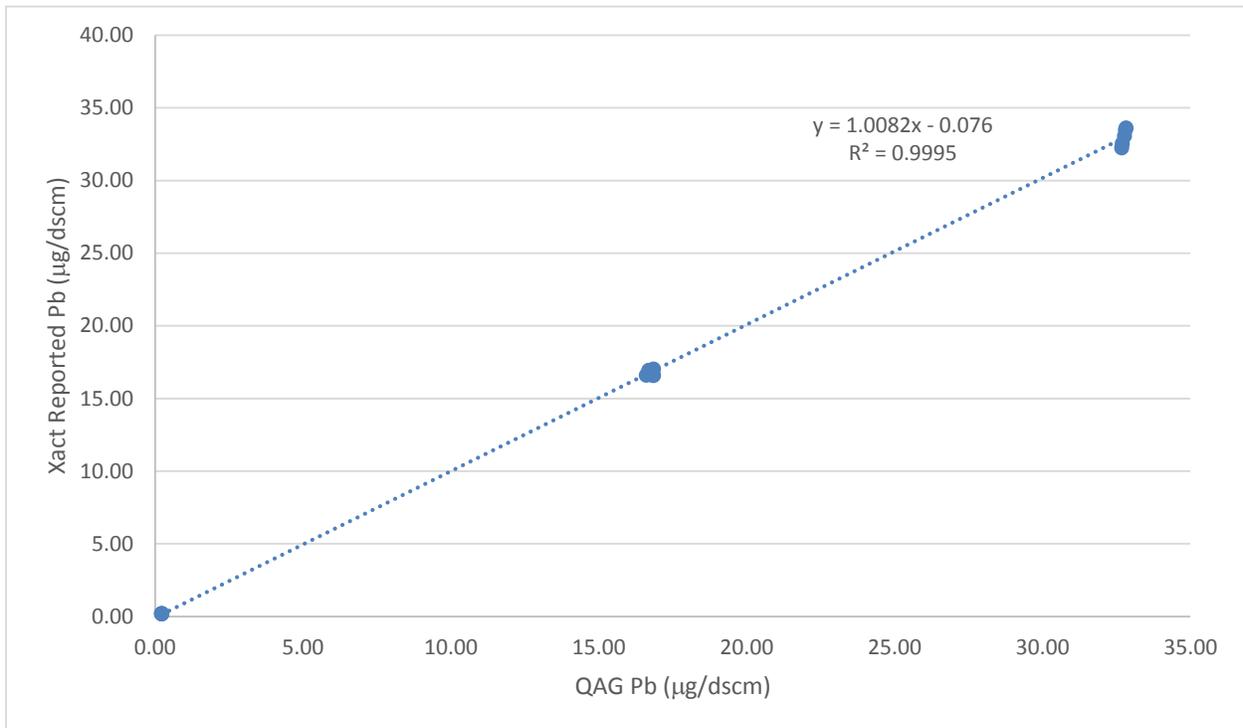


Figure 3. Ambient Air Regression Fit for Lead (Pb)

The slopes for arsenic and lead are 0.91 and 1.01 respectively – indicating excellent agreement between the Xact and the QAG over the entire concentration range. Both fits also showed excellent coefficients of determination ($r^2 < 0.99$) indicating excellent precision. Finally, the intercepts for both are very low (0.05 and 0.08 respectively) indicating very little blank bias.

5.8.3. Unknown Solution Concentration Test

During the ambient air spiking testing South Coast Air Quality Management District provided CES with a solution containing arsenic and lead at concentrations unknown to CES. This solution was then spiked using the QAG and the resulting aerosol was sampled and measured using the Xact. The Xact reported aerosol concentrations and the operating parameters from the QAG (solution mass loss rate and total air flow) were used to calculate the concentration of the unknown solution. The CES reported concentration was provided to SCAQMD and compared against the concentrations reported by SCAQMD’s laboratory as well as those reported by an independent third party laboratory. The results from this test are provided in Table 7.

Table 7. Solution Concentration Determination Results

Element	Xact 640 Result (µg/g)	SCAQMD Lab Analysis (µg/g)	Independent Lab Result (µg/g)	Xact with SCAQMD (% Diff)	Xact with Ind. Lab (% Diff)
As	6.95	7.3	7.5	-4.8%	-7.3%
Pb	6.82	6.7	7.4	1.8%	-7.8%

As can be seen the concentration reported by the Xact agrees very well with the concentrations determined by SCAQMD and with the independent lab.

5.8.4. Spiking Ambient Air and Sampling with CARB 436

The purpose of this test was to identify any potential bias between the Xact and CARB Method 436 when both measurement methods are presented with an identical aerosol. During this test the Xact and a CARB Method 436 sampling system were challenged with each of the three QAG generated concentration levels described in Section 5.6. For the test the CARB sampling train start and end times corresponded with the start and end times of a Xact sampling period. For the low concentration level (0.2 µg/dscm) the Xact sampled for two 1 hour periods while the CARB Method 436 acquired a single 2 hour sample. For the mid-level concentration the Xact acquired four 15 minute samples to the CARB Method 436’s single 1 hour sample. Finally, for the high sample the Xact acquired six 15 minute samples and CARB Method 436 acquired a single 90 minute sample.

Tables 8 and 9 below show the results of the comparison between the Xact and the QAG and CARB Method 436 for arsenic and lead respectively. In general, the Xact agrees well with both the QAG and CARB Method 436. The percent difference between the Xact 640 and either the QAG reference aerosol or the CARB Method 436 is less than 20%. The CARB Method 436 results also seem to agree well with the QAG reference aerosol. The only exception to this is for

the low level arsenic concentration where the CARB Method 436 reported result is 40% higher than the QAG generated aerosol, however, it is worth pointing out, that at these low concentrations the absolute error is relatively low (0.08 µg/dscm) even if the relative difference (40%) seems high.

Table 8. QAG, CARB 436 and Xact Comparison for Arsenic

Testing Mode	CARB 436 Concentration (µg/dscm)	QAG Concentration (µg/dscm)	Xact 640 Concentration (µg/dscm)	Xact 640 Percent Difference with CARB 436	Xact 640 Percent Difference with the QAG	CARB 436 and QAG Percent Difference
Ambient Air Low Concentration	0.28	0.20	0.24	-16.07%	17.50%	40.00%
Ambient Air Mid Concentration	1.87	2.03	1.75	-6.42%	-13.79%	-7.88%
Ambient Air High Concentration	4.33	4.43	4.23	-2.31%	-4.51%	-2.26%

Table 9. QAG, CARB 436 and Xact Comparison for Lead

Testing Mode	CARB 436 Concentration (µg/dscm)	QAG Concentration (µg/dscm)	Xact 640 Concentration (µg/dscm)	Xact 640 Percent Difference with CARB 436	Xact 640 Percent Difference with the QAG	CARB 436 and QAG Percent Difference
Ambient Air Low Concentration	0.22	0.20	0.22	-2.27%	7.50%	10.00%
Ambient Air Mid Concentration	13.56	15.32	15.03	10.84%	-1.89%	-11.49%
Ambient Air High Concentration	30.52	32.81	34.12	11.80%	3.99%	-6.98%

5.9. Test 3 Dynamic Spiking

The purpose of this test was to evaluate the accuracy of the Xact in the presence of stack gas constituents. For this test the Xact probe was inserted into the stack so that the instrument was sampling stack effluent. This sampled gas was spiked with the same three concentration levels defined in Section 5.6.

One key difference between dynamic spiking and the spiking of ambient air is that it is likely that both lead and arsenic will be present at appreciable concentration levels. To evaluate these background concentration levels the Xact alternated between sampling unspiked aerosol and spiked aerosol concentrations. The average concentration of lead and arsenic for the two unspiked time periods before and after each spiked concentration was calculated and this average concentration was subtracted from the Xact reported aerosol concentration. The resulting Xact reported background subtracted aerosol concentration was compared with the expected QAG aerosol concentration.

At the low concentration level the Xact operated in sixty minute sampling mode. Spiking and background testing periods were alternated every hour. At the high and the mid concentrations the Xact operated in thirty minute sampling and analysis mode. Spiking and background testing periods were alternated 30 minutes. Table 10 shows the percent difference between the background corrected Xact data and QAG reference concentration.

Table 10. Dynamic Spiking Results

Concentration Level	Arsenic			Lead		
	QAG Conc As ($\mu\text{g/dscm}$)	Xact-Bknd ($\mu\text{g/dscm}$)	% Difference	QAG Conc As ($\mu\text{g/dscm}$)	Xact-Bknd ($\mu\text{g/dscm}$)	% Difference
Low	0.197	0.09	-54%	0.194	0.155	-20%
	0.196	0.33	69%	0.193	0.15	-22%
	0.199	0.445	124%	0.196	0.21	7%
	0.199	0.135	-32%	0.196	0.155	-21%
	0.201	-0.01	-105%	0.199	0.14	-30%
Mid	2.48	2.34	-5.6%	18.35	15.37	-16.2%
	2.49	2.71	8.9%	18.42	18.3	-0.7%
	2.48	2.51	1.1%	18.38	18.2	-1.0%
	2.49	2.855	14.6%	18.44	18.575	0.7%
	2.49	2.68	7.8%	18.40	18.635	1.3%
High	4.37	4.565	4.4%	32.37	33.01	2.0%
	4.42	4.33	-2.0%	32.70	33.48	2.4%
	4.51	4.28	-5.1%	33.37	34.34	2.9%
	4.48	4.955	10.5%	33.18	33.69	1.5%
Mid and High Average			3.8%			-0.8%

At the mid and high concentration levels the Xact reported concentration agrees very well with the QAG aerosol concentration. The average percent difference between the Xact and the QAG is 3.8% and -0.8% for arsenic and lead respectively. The relative differences between the Xact and the QAG at the low concentrations are quite large, however, even if the relative difference is large the absolute differences are still quite low (less than 0.3 $\mu\text{g/dscm}$). At the low concentration level differences are typically greater than 20% and in some case substantially greater than that. For arsenic the reason for the large differences between the Xact and QAG seem clear fairly clear. The stack background concentrations for arsenic during the low concentration testing were high relative to the spiking level and variable (0.36, 0.28, 0.34, 0.35, 0.18 and 0.60 $\mu\text{g/dscm}$). This meant that the background corrections were larger than the spiking levels themselves. For lead the background concentration levels were generally lower than spiking level and somewhat more stable (0.13, 0.04, 0.04, 0.04, 0.01 and 0.13 $\mu\text{g/dscm}$) however, these levels may still be high enough and variable enough to cause problems during the QAG spike.

In addition to calculating the percent difference at each data point the Xact 640 blank corrected concentrations were plotted against the QAG reference aerosol concentrations and a linear least squares regression was performed on the data. Figures 4 and 5 show these plots along with the linear least squares fit for arsenic and lead respectively.

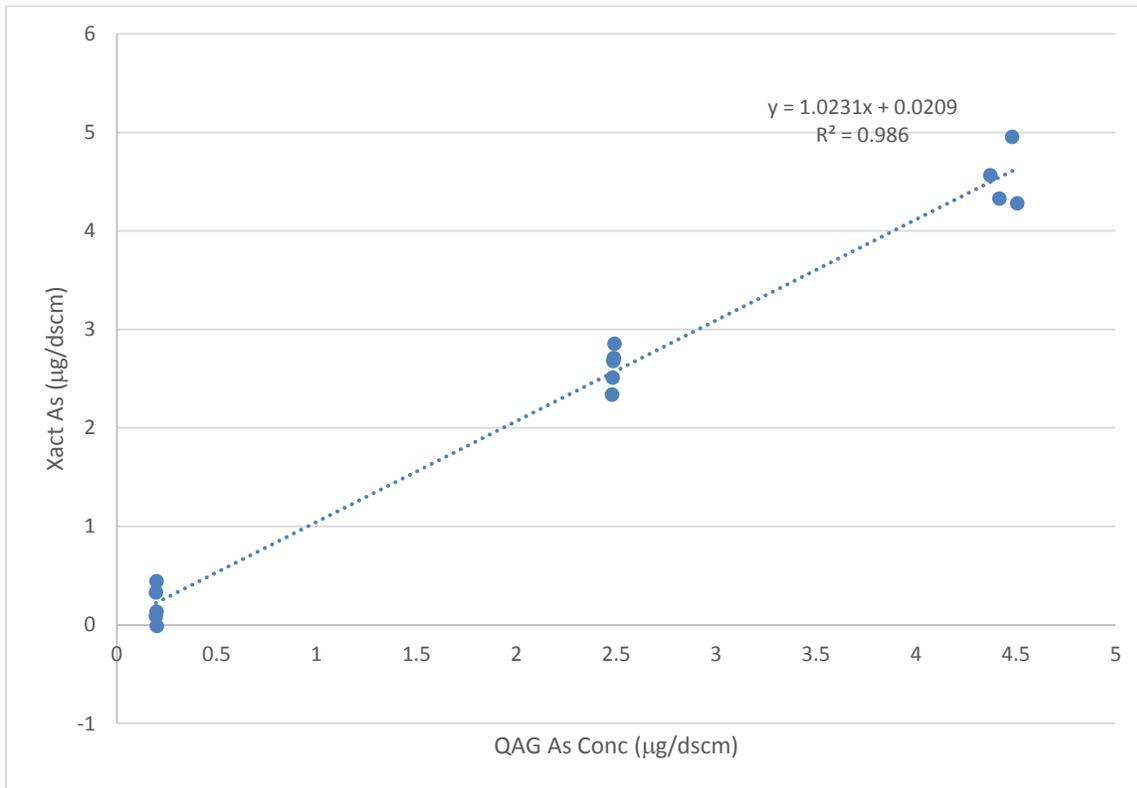


Figure 4. Dynamic Spiking Linearity for Arsenic

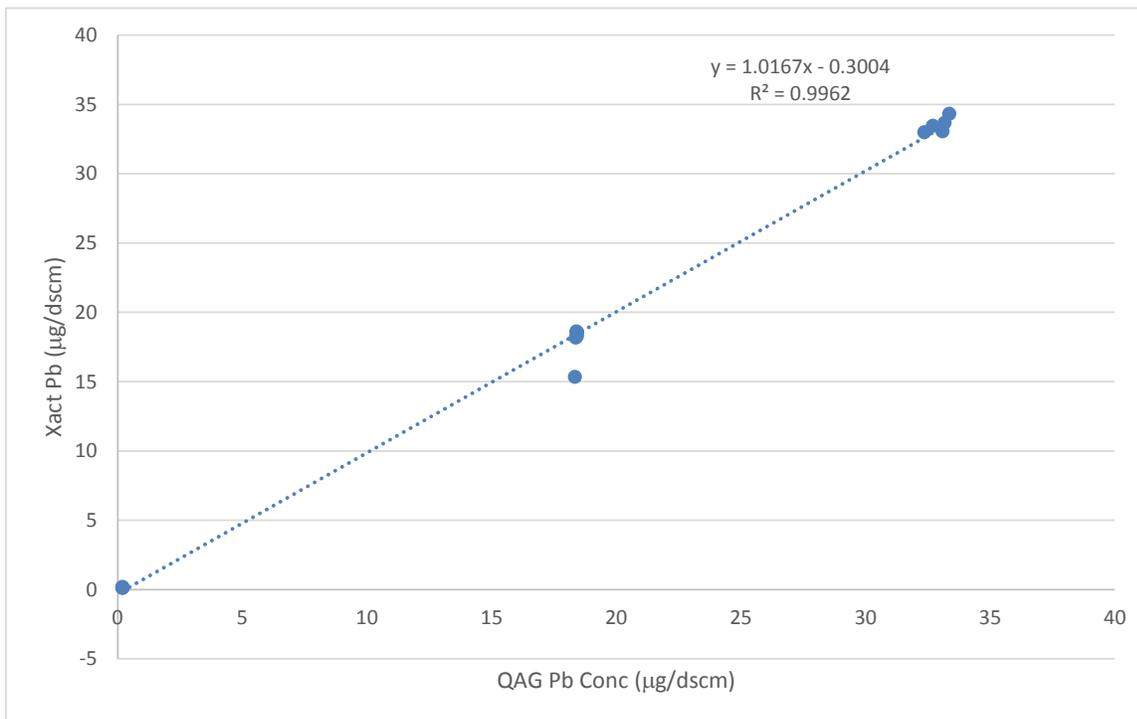


Figure 5. Dynamic Spiking Results for Pb

Again the regression fits for both arsenic and lead indicate excellent agreement between the Xact and the QAG. The slope of both fits is approximately 1.02 with both coefficients of determination being greater than 0.98.

5.9.1. Test 4. Dynamic Spiking with CARB Method 436

The purpose of this test was to identify if there is any bias between the Xact and CARB Method 436 in presence of stack gas. For this test the Xact reported concentrations for lead and arsenic were compared to the CARB Method 436 results at the high QAG concentration level. The test was performed in a similar manner to the CARB testing done when spiking ambient air except that stack effluent was sampled. The CARB probe was inserted into the same two inch port described in section 5 and the start and stop times for the CARB Method 436 sample train were timed to correspond with start and stop times on the Xact. For this test the CARB Method 436 was run for 90 minutes corresponding to three 30 minute Xact sampling periods. Table 11 below shows the results for this test.

Table 11. Comparison Xact, CARB 436 and QAG during Dynamic Spiking

Element	CARB 436 Concentration (µg/dscm)	QAG Concentration (µg/dscm)	Xact 640 Concentration (µg/dscm)	Xact 640 Percent Difference with CARB 436	Xact 640 Percent Difference with the QAG	CARB 436 and QAG Percent Difference
Arsenic	5.48	5.36	4.66	-14.96%	-13.06%	2.24%
Lead	32.27	33.39	33.70	4.43%	0.93%	-3.35%

As with the ambient air spiking – there is good general agreement between the CARB Method 436 and the Xact and they both compare well with the QAG.

6. CARB Method 436 Testing Results

On May 6th, 7th, and 12th, 2015 South Coast Air Quality Management District performed three separate CARB Method 436 tests at Quemetco’s City of Industry facility. During this testing SCAQMD used the CARB Method 436 sampling method to measure WESP stack emissions (not QAG produced aerosols). The CARB Method 436 reported emission rates (lb/hr) were compared to the Xact 640 reported emission rates during these time periods. The percent difference between the Xact 640 reported emission and the CARB Method 436 emission rate was calculated using equation 6. In addition, the relative accuracy for each set of three measurements was calculated using equation 7. The relative accuracy calculation used is identical to those outlined in Performance Specification 2 – Specifications and Test Procedures for SO₂ and NO_x Continuous Emission Monitoring Systems in Stationary Sources.⁹ It should be pointed out, however, that a typical CEMS relative accuracy test assessment requires at least nine test runs and in this case only three runs were performed. Tables 12 and 13 show the results for both arsenic and lead.

$$PD = \frac{C_{Xact} - C_{RM}}{C_{RM}} \quad \text{Equation 6}$$

Where:

PD = Percent difference

C_{Xact} = The emission rate reported by the Xact

C_{RM} = Emission rate by the reference method

$$RA = \left[\frac{|\bar{d}| + |CC|}{\overline{RM}} \right] \quad \text{Equation 7}$$

Where:

RA = Relative accuracy of the data set

$|\bar{d}|$ = The arithmetic mean of the differences

CC = Confidence coefficient (See Equation 8)

\overline{RM} = Average reference method value or in cases where the average emissions for the test are less than 50 percent of the applicable standard, substitute the applicable standard, which in this case are the Rule 1420.1 emissions limits for As and Pb.

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \quad \text{Equation 8}$$

Where:

CC = Confidence Coefficient

$t_{0.975}$ = T-value for 97.5% confidence (for n=3 this is 4.303)

n = Number of samples

S_d = Standard deviation of the samples

Table 12. Comparison of the Xact 640 and CARB 436 Measurements of WESP Stack Arsenic Emissions

Test Date	CARB 436 Emissions (lb/hr)	Xact 640 Emissions (lb/hr)	% Difference	Relative Accuracy	R1420.1 Limit (lb/hr)
May 6, 2015 13:00 –17:00	9.38×10^{-5}	8.63×10^{-5}	-8.0%	7.2%	1.14×10^{-3}
May 7, 2015 13:00 –17:00	2.63×10^{-4}	2.82×10^{-4}	+7.2%		1.14×10^{-3}
May 12, 2015 13:00 – 17:00	1.80×10^{-4}	2.24×10^{-4}	+24.4%		1.14×10^{-3}
Average			+8		

Table 13. Comparison of the Xact 640 and CARB 436 Measurements of WESP Stack Lead Emissions

Test Date	CARB M436 Emissions (lb/hr)	Xact 640 Emissions (lb/hr)	% Difference	Relative Accuracy	R1420.1 Limit (lb/hr)
May 6, 2015 13:00 –17:00	6.29×10^{-5}	4.15×10^{-5}	-34.0%	1.5%	1.00×10^{-2}
May 7, 2015 13:00 –17:00	6.59×10^{-5}	5.50×10^{-5}	-16.5%		1.00×10^{-2}
May 12, 2015 13:00 –17:00	1.18×10^{-4}	2.85×10^{-5}	-75.8%		1.00×10^{-2}
Average			-42.1%		

The average percent difference for arsenic is 7.9% while the relative accuracy is 7.2% indicating very good agreement between the Xact and CARB Method 436 for arsenic. For lead the average percent difference is -42.1% which would appear to indicate less than ideal agreement between the two methods. However, these reported emission levels are very low relative to the rule limit of 1.00×10^{-2} lb/hr for lead. In this case and also in the case for arsenic, relative accuracy is calculated using the rule limit as the denominator - resulting in a relative accuracy of 1.5%. This means the average difference between the Xact reported concentration and CARB Method 436 is small relative to the emission limit. In the case of the lead results, the CARB Method 436 results are all biased high in comparison to the Xact measurements, and it is possible that there was lead contamination from the glassware used in the CARB Method 436 sampling apparatus.

7. Line Rinse Testing

At the request of the host site, the Xact's probe and transport line were rinsed on four different occasions throughout the study period starting in July of 2015. The probe and line were rinsed with 5% nitric acid and the rinsate was captured in a pre-weighed polyethylene bottle. The bottle and the rinsate were weighed to determine the total mass of the rinsate and two aliquots of this rinsate were extracted and submitted to separate laboratories (WECK labs and SCAQMD) for lead and arsenic analysis. The total mass of lead and arsenic in the solution was determined using the mass data and the concentrations reported by each laboratory. This mass was divided by the total flow through the transport line between rinsate tests to get an average aerosol concentration lost during the test period in $\mu\text{g}/\text{dscm}$. This concentration was divided by the average Xact measured concentration over the same time period to calculate a percent loss for each element. The average percent loss in the probe and transport line for each of the four measurements can be found in Table 14.

Table 14. Percent Loss of Arsenic and Lead in the Xact 640 Probe and Transport Line

Date	Arsenic						Lead					
	Weck Labs			SCAQMD			Weck Labs			SCAQMD		
	% Loss			% Loss			% Loss			% Loss		
	Line	Probe	Total	Line	Probe	Total	Line	Probe	Total	Line	Probe	Total
Jul-15	3.41%	0.81%	4.17%	3.54%	0.76%	4.25%	10.27%	5.41%	14.66%	10.46%	5.40%	14.81%
Sep-15	10.35%	0.36%	10.64%	10.01%	0.32%	10.28%	9.73%	12.02%	19.64%	9.43%	11.05%	18.59%
Oct-15	2.79%	0.15%	2.93%	-	-	-	2.79%	2.29%	4.96%	-	-	-
Dec-15	3.00%	0.44%	3.42%	3.11%	0.44%	3.55%	2.15%	2.78%	4.81%	2.18%	2.33%	4.51%
Average	4.89%	0.44%	5.29%	5.56%	0.51%	6.03%	6.24%	5.62%	11.02%	7.35%	6.26%	12.63%

In general the results indicate relatively little loss of material in the sampling system. The average percent loss for arsenic is around 6% and about 12% for lead. Interestingly, for lead, the percent loss for the last two samples was much smaller than for the first two.

8. Operation

8.1. General Time Line

The Xact was installed on the sampling platform on the WESP stack from March 1st to March 4th, 2015. The instrument started sampling stack gas on March 4th. From March 16th to April 8th the Xact underwent extensive testing with the QAG. From April 8th through the remainder of the test which was completed on January 6th, 2016 the unit sampled WESP stack emissions. A detailed time line can be found in Appendix A.

8.2. On-going Quality Assurance Data

8.2.1. Upscale Check Data

Once per day for the duration of the testing period, the XRF portion of the Xact 640 was checked by injecting a rod containing chromium (Cr), cadmium (Cd) and lead (Pb) into the analysis area. The percent difference between the calibrated and reported concentrations for each element was determined each day. Figure 6 shows the percent difference between calibrated and reported

value for each of the standards for all 279 data points. In general, the vast majority of data was within the 15% criteria. Those points that fell outside of this range resulted from a faulty detector which was replaced.

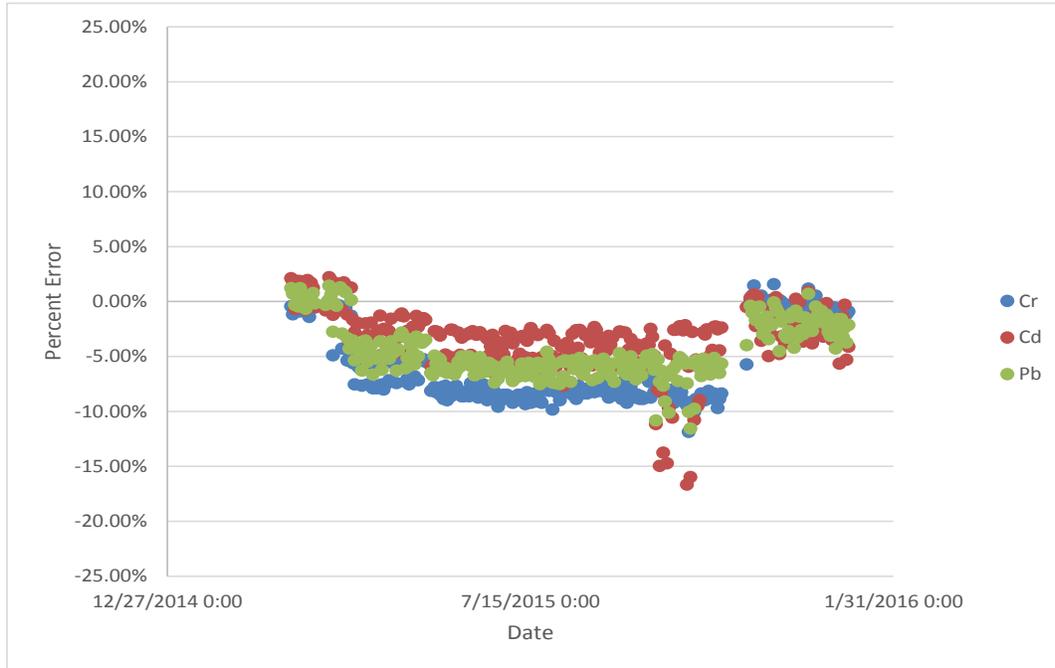


Figure 6. Upscale Rod Percent Difference

8.2.2. Zero Drift Check

Once per day the Xact 640 also analyzed a blank (unsampled) section of filter tape for a 15 minute period. The reported concentrations for each element were divided by the emission limit (converted to $\mu\text{g}/\text{dscm}$) to determine the percent zero drift. For most all of the data points the instrument zero drift was 0% - well within the 20% zero drift criteria.

8.2.3. Per Sample XRF Stability Check Data (Palladium Rod Check)

The stability of the XRF system in the Xact 640 is evaluated with each and every sample using a fixed rod of palladium that is installed beneath the tape. The concentration for this palladium rod is determined at the time of calibration and then the Xact's reported concentration for palladium is recorded with each and every sample. The difference between the Xact's reported value for palladium and the calibrated value must be less than 15% for the data from that sample to meet quality assurance criteria. Table 15 below shows the results for the palladium rod stability check throughout the test period. The average percent difference was -1.77% over the course of 6546 samples. Nearly 98.5% of the data met the criteria for palladium stability.

Table 15. Palladium Rod Stability Test Data

Average	-1.77%
N	6546
Number over 15%	99
Percent of data meeting QA requirements	98.49%

There were two main reasons for the time periods where the Xact did not meet palladium stability criteria. The first was because of a detector failure that occurred on November 3, 2015. The detector was replaced and the instrument experienced no problems after that. The second major reason was temperature. The instrument was housed inside of a temperature controlled NEMA rated enclosure equipped with an air conditioner. On very hot days (approximately 100°F) the air conditioner was unable to provide sufficient cooling to the instrument. The resulting increase in outside temperature caused the inside of the enclosure to warm up and the gain of the detector to shift. This shift resulted in underreporting of palladium. Figure 7 below shows palladium concentration and enclosure temperature (the temperature inside the cabinet containing the X-ray equipment) over several days in August 2015.

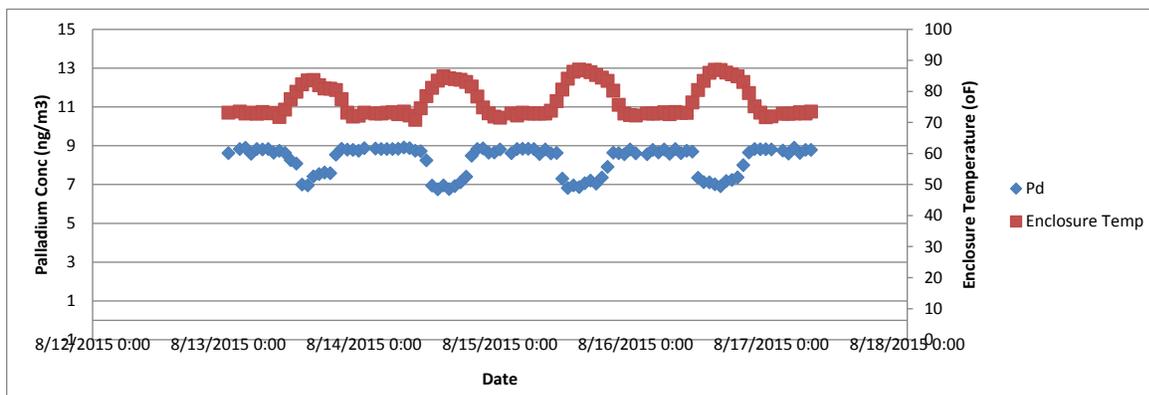


Figure 7. Palladium Concentration and Enclosure Temperature on Several Hot Days

The figure clearly shows a reduction of palladium concentration when the enclosure temperature rises. The problem was reduced in frequency when the thermistor controlling the air conditioner was relocated to more accurately reflect the temperature in the Xact’s XRF cabinet. To completely eliminate this problem, however, the instrument should be shaded from the sun or provided with a larger air conditioner.

8.2.4. Flow Check Data

Once per day the Xact’s sample flow sensor was checked using a secondary QA flow sensor and the difference as a percentage of the full scale of the flow sensor was determined. All of the flow checks met the 20% criteria and in fact, the percent difference was always 1% or less over the course of the entire testing period. Figure 8 shows the percent difference between the sample and quality assurance flow sensor throughout the testing period.

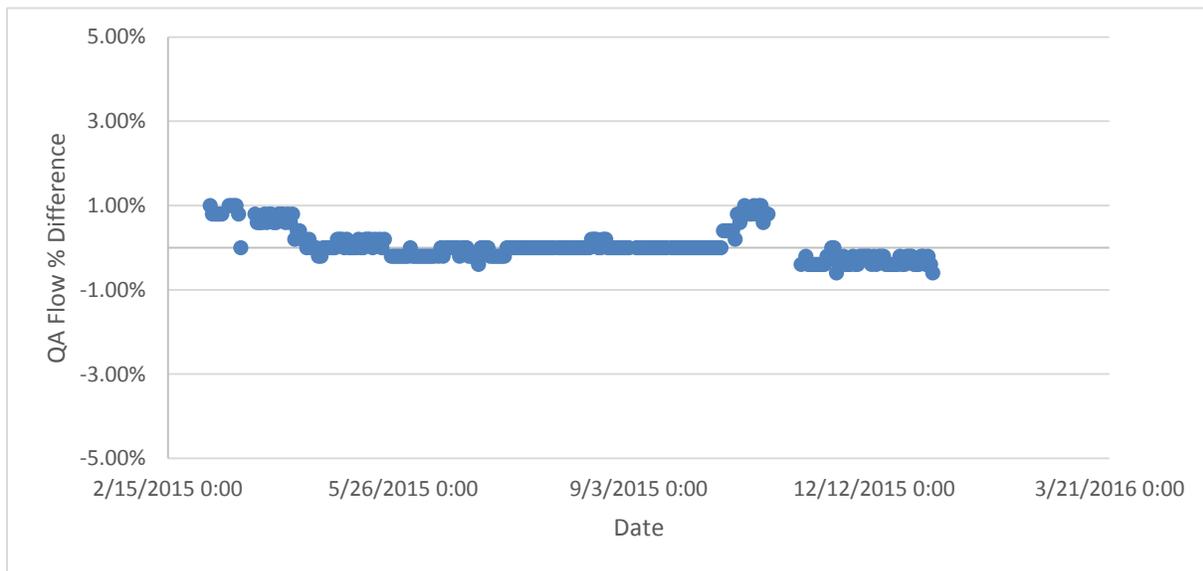


Figure 8. Flow Drift during the Evaluation Period

8.3. Uptime

Percent uptime was calculated for the time period between April 14th 2015 (following all QAG testing and training activities) and January 16th, 2016. Over this time period the percent uptime was approximately 93%.

8.4. Variability in Emissions

During operation the Xact concentration data was converted into emission data in pounds per hour using flow data from the facility's RECLAIM flow monitor. The variability in emissions (lbs/ hr) are shown for both arsenic and lead.

8.4.1. Arsenic

Figures 9 and 10 show the hourly arsenic concentration reported by the instrument and the daily average arsenic concentrations. During the 10-month demonstration project at Quemetco, in some cases the Xact 640 CEMS measured arsenic emissions at the WESP stack that exceeded the Rule 1420.1 facility limit of 0.00114 lb/hr. However, because this is a demonstration project, these measurements were not used for rule based compliance and/or enforcement purposes. The applicable Rule 1420.1 lead emissions limit is 0.01 lb/hr for a single point source.

Figure 9. Hourly Arsenic Emissions Reported Throughout the Test Period

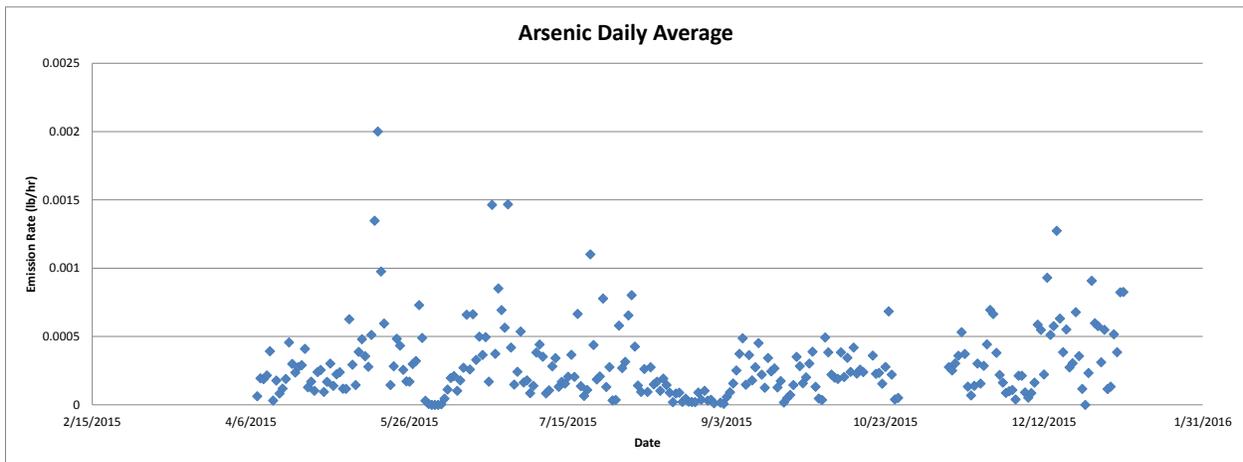
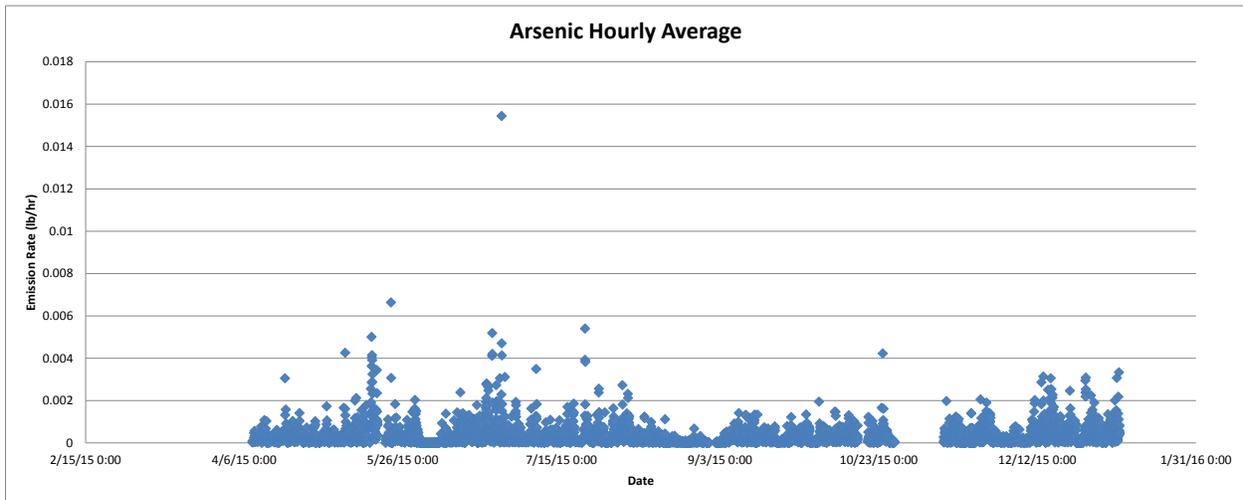


Figure 10. Xact Daily Average Arsenic Emissions

8.4.2. Lead

Figures 11 and 12 show the hourly and the daily average lead concentrations as reported by the Xact throughout the test period.

Figure 11. Xact Reported Hourly Lead Emissions

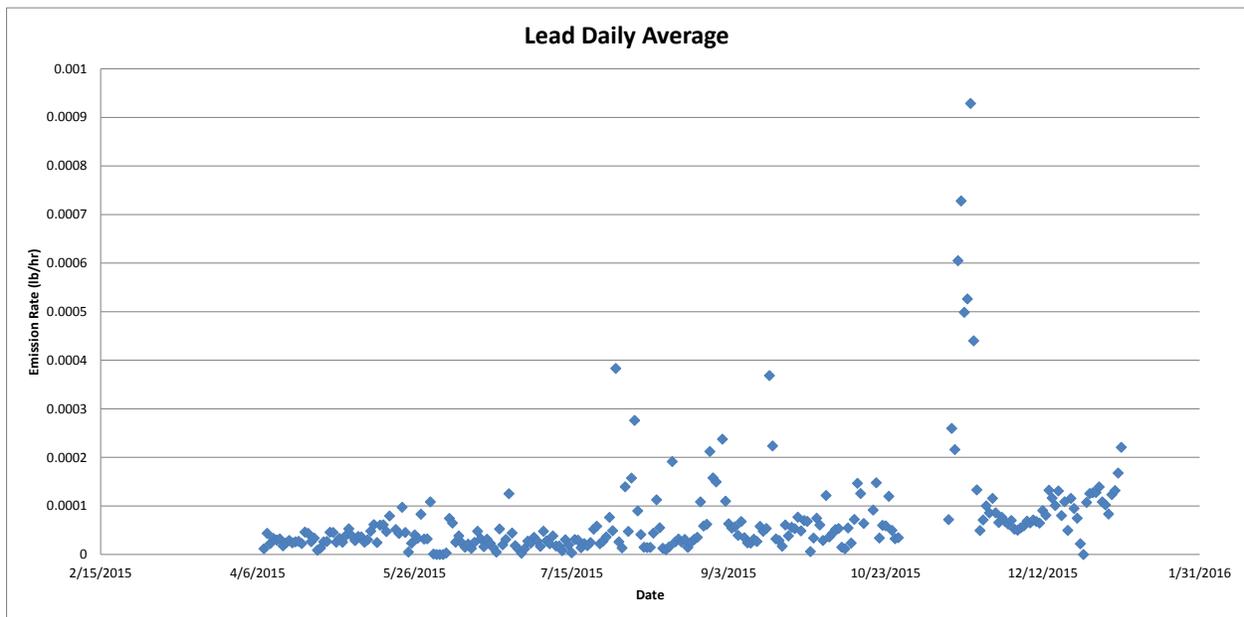
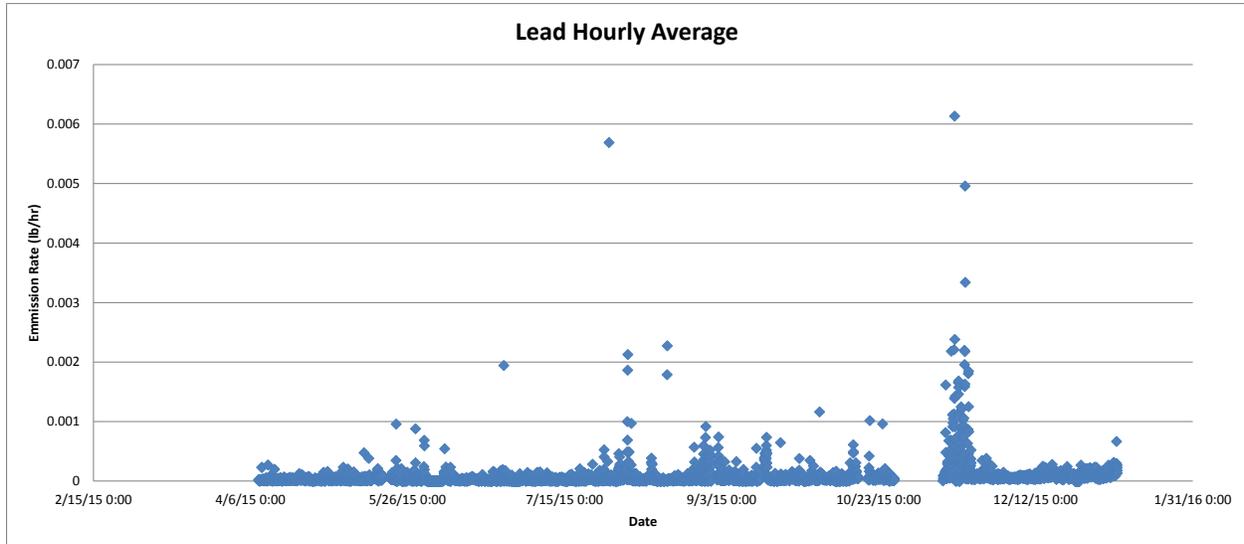


Figure 12. Xact Reported Daily Average Lead Emissions

9. Modem and Remote Data Transmittal

A Sixnet SN series cellular modem was connected to the Xact 640 CEMS's computer so that SCAQMD staff could remotely communicate with the Xact 640 unit installed at Quemetco's WESP stack. By remotely communicating with the Xact 640 from SCAQMD headquarters, staff downloaded real-time emissions data from the CEMS, diagnosed operating and malfunctioning

issues; and remotely controlled the CEMS to change sampling time and other operating parameters. The modem service was provided by AT&T Wireless.

For data encryption and security, a Virtual Private Network (VPN) was configured between the modem and SCAQMD's network. Remote control software was utilized to control the instrument. Cooper Environmental staff was granted this remote access capability to facilitate technical support.

The Xact 640 produces emissions concentration data in terms of $\mu\text{g}/\text{m}^3$. In order to convert concentrations in $\mu\text{g}/\text{m}^3$ to mass emission rates in terms of lb/hr as required by Rule 1420.1, stack gas flowrate data in dry standard cubic feet from the RECLAIM stack flow monitor was used.

For majority of the time, during this 10-month demonstration period, 1-hour sampling time was used. The one hour sampling time reflected a balance between the need for time resolution of the data and good quantitation and precision at low concentration levels.

10. Summary

A Xact 640 was installed and operated over a 10 month period at a secondary lead smelter in the greater Los Angeles area. During this time the Xact was evaluated by challenging it with a reference aerosol (produced using CES Quantitative Aerosol Generator) containing known concentrations of arsenic and lead – the air toxic metals of regulatory interest – at three concentration levels. The Xact reported concentrations were plotted against the QAG reference concentrations and a linear least squares regression fit was performed. The slopes of the best fit lines for arsenic and lead were 1.02 indicating excellent agreement between the Xact reported value and the concentration of the reference aerosol. In addition the Xact was also compared to CARB Method 436 while sampling WESP stack gas concentrations. The relative accuracy between the Xact 640 multi-metals CEMS and CARB Method 436 are 7.2% and 1.5% for arsenic and lead, respectively, which shows a good correlation between the two techniques.

The Xact operated over a period of approximately 8.5 months following the initial testing and training period. During that time the instrument met its on-going quality assurance criteria and achieved an uptime of approximately 93% while reported hourly concentrations for both lead and arsenic as well as several additional metals. Overall this test demonstrated that the Xact can make reliable and accurate measurements at the secondary lead smelter were the test took place.

With the modem installed on the Xact 640 CEMS, SCAQMD and Cooper Environmental staff controlled the CEMS to change sampling time and other operating parameters using office PCs.

After the successful completion of this demonstration project in January 2016, Quemetco acquired the Xact 640 CEMS and it is currently operating at Quemetco's facility in the City of Industry, CA.

In a separate demonstration project, SCAQMD deployed Cooper Environmental's Xact 625 multi-metals ambient monitor at Quemetco, Inc. and Gerdau North America, Rancho Cucamonga, CA, in 2014 and 2015 for a period of approximately six months. The Xact 625 is similar to the Xact 640 and both instruments use X-ray fluorescence technology for multi-metals analysis. The ambient monitor was used to compare Xact 625 multi-metals measurements with Federal Reference Method (FRM) and established method measurements at these two facilities. The Xact multi-metals measurements compare reasonably well with these two techniques.

11. References

1. Cooper Environmental Services, LLC (2006). *Method 301 Evaluation of Three Methods for Multi-Metals Measurement and Validation, Volume 1*. Portland, OR: Submitted to US EPA
 2. Yanca, C. (2006) Validation of Three New Methods for the Determination of Metal Emissions Using a Modified EPA Method 301. *Journal of Air and Waste Management*, 56: 1733-1742.
 3. Eli Lilly and Company. 2005. Alternative Monitoring Petition for the Solid-Liquid Incinerator, Tippecanoe Laboratories: Lafayette, IN.
 4. Other Test Method 16. Specifications for X-ray Fluorescence Based Multi-Metals CEMS at Stationary Sources. <http://www.epa.gov/ttnemc01/prelim/otm16.pdf>. Accessed June 24, 2011.
 5. Other Test Method 20. Quality Assurance Requirements for X-Ray Fluorescence Based Multi-Metals CEMS at Stationary Sources. <http://www.epa.gov/ttnemc01/prelim/otm20.pdf>. Accessed June 24, 2011
 6. EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. June, 1999. Compendium Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy. EPA/625/R-96/010a. U.S. Environmental Protection Agency. 2005. Method 301, Field Validation of Pollution Measurement Methods for Various Media; *Code of Federal Regulations, 40 CFR 56*; U.S. Government Printing Office: Washington, DC.
 7. United States Environmental Protection Agency. Method 1. Sample and Velocity Traverses for Stationary Sources. <https://www3.epa.gov/ttnemc01/promgate/m-01.pdf> accessed February 25, 2016.
 8. United States Environmental Protection Agency (2014). Performance Specification 18 - Specifications and Test Procedures for Gaseous HCl Continuous Emission Monitoring Systems at Stationary Sources. *Code of Federal Regulations, 40 CFR 60*; U.S. Government Printing Office: Washington, DC.
-



9. United States Environmental Protection Agency. Performance Specification 2 – Specifications and Test Procedures for SO₂ and NO_x Continuous Emissions Monitoring Systems in Stationary Sources. *Code of Federal Regulations, 40 CFR 60*; U.S. Government Printing Office: Washington DC.

Appendix A

SCAQMD MMCEMS 10-Month Testing

This document summarizes the events of a 10-month study involving South Coast Air Quality Management District (SCAQMD), Quemetco RSR and Cooper Environmental Services (CES). This study used a MMCEMS provided by CES to primarily measure arsenic (As) and lead (Pb) emissions from a secondary lead smelter operated by Quemetco RSR.

3/1 – 3/4: MMCEMS instrument delivered to Quemetco and installed on stack downstream of WESP.

3/4 14:30 – 3/4 15:30: Instrument was sampling ambient air

3/4 15:45 – 3/16 10:00: Instrument was sampling stack gas

3/13: CES installed program to convert data from $\mu\text{g}/\text{dscm}$ to lbs/hr . Converted data written to data.csv file on MMCEMS computer.

3/16 – 3/19: Ambient air was sampled; QAG setup and preliminary testing performed

3/19 10:00 – 13:30: Ambient air QAG testing Mid-Level [2.25, 17] $\mu\text{g}/\text{dscm}$ [As,Pb]

3/19 13:45 – 16:45: Ambient Air QAG testing High Level [4.5, 33.9] $\mu\text{g}/\text{dscm}$ [As,Pb]

3/19 19:00 – 23:00: Ambient Air QAG testing Low Level [0.2, 0.2] $\mu\text{g}/\text{dscm}$ [As,Pb]

3/25 12:00 – 13:00: Ambient Air QAG testing Low Level with CARB 436 [0.2, 0.2] $\mu\text{g}/\text{dscm}$ [As,Pb]. Suspected improperly mixed solution during testing therefore a 'failed' test.

3/26 8:00 – 11:00: Ambient Air QAG testing Mid Level with CARB 436 [2.03, 15.3] $\mu\text{g}/\text{dscm}$ [As,Pb]

3/26 11:45 – 13:00: Ambient Air QAG testing High Level with CARB 436 [4.5, 33.7] $\mu\text{g}/\text{dscm}$ [As,Pb]. System reset error on Xact at 11:30 led to issues with data accuracy; data during this test is unusable

4/1 11:45 – 14:45: Ambient Air QAG testing High Level with CARB 436 [4.5, 33.7] $\mu\text{g}/\text{dscm}$ [As,Pb]

4/2 9:00 – 11:00: Dynamic Spike (stack gas) QAG testing High level with CARB 436 [4.5, 33.7, 4.5] $\mu\text{g}/\text{dscm}$ [As,Pb,Pt]

4/2 13:00 – 15:00: Ambient Air QAG testing Low Level with CARB 436 [0.2, 0.2] $\mu\text{g}/\text{dscm}$ [As,Pb]

4/4 14:00 – 23:00: Dynamic Spike (stack gas) QAG testing Low Level [0.2, 0.2] $\mu\text{g}/\text{dscm}$ [As, Pb]
Spiked data points at 14:00, 16:00, 18:00, 20:00, 22:00

4/5 12:30 – 17:30: Dynamic Spike (stack gas) QAG testing Mid Level. Spiked data points at 13:00, 14:00, 15:00, 16:00, 17:00. [2.5, 18.6, 2.5] $\mu\text{g}/\text{dscm}$ [As,Pb,Pt]

4/5 18:00 – 23:30: Dynamic Spike (stack gas) QAG testing High Level. Spiked data points at 18:00, 19:00, 20:00, 21:00, 22:00. [4.5, 33.7, 4.5] $\mu\text{g}/\text{dscm}$ [As,Pb,Pt]

4/6 15:00: Dopant removed from the calibration and replaced with Bromine



4/7 12:00 – 23:00: Dynamic Spike (stack gas) QAG testing Low Level [0.2, 0.2] µg/dscm [As, Pb]. Spiked Data points at 14:00, 16:00, 18:00, 20:00, 22:00

4/8 0:00: QAG testing concluded; regular stack sampling begins

5/15: Xport Error, tape ran out

5/20: Xport Error, tape sticking to vane. Thermistor for Air Conditioner moved into Sampling and Analysis module to better regulate temperature inside cabinet which was causing detector to overheat

6/9: Xport Error, tape ran out

6/16: Transport line data logger installed

7/7: Probe Rinse performed to measure As and Pb loss in probe and transport line

7/23: Power failure at Quemetco, instrument shut down for 7 hours

7/30: Xport error, SCAQMD did not ramp down x-rays when changing tape

8/13 13:00 – 18:00: QA Palladium out of bounds due to overheating of detector

8/14 12:00 – 18:00: QA Palladium out of bounds due to overheating of detector

8/15 11:00 – 19:00: QA Palladium out of bounds due to overheating of detector

8/16 11:00 – 19:00: QA Palladium out of bounds due to overheating of detector

8/28 12:00 – 17:00: QA Palladium out of bounds due to overheating of detector

9/1: Xport Error, tape ran out during the weekend

9/2: Probe rinse performed to measure As and Pb loss in probe and transport line

9/8 13:00 – 16:00: QA Palladium out of bounds due to overheating of detector

9/9 11:00 – 17:00: QA Palladium out of bounds due to overheating of detector

9/16: Xport Error, tape stuck to vane due to moisture buildup on tape

9/19 12:00 – 18:00: QA Palladium out of bounds due to overheating of detector

9/20 11:00 – 18:00: QA Palladium out of bounds due to overheating of detector

9/29 13:00 – 16:00: QA Palladium out of bounds due to overheating of detector

10/9 10:00 – 20:00: QA Palladium out of bounds due to overheating of detector

10/10 10:00 – 18:00: QA Palladium out of bounds due to overheating of detector

10/12 10:00 – 19:00: QA Palladium out of bounds due to overheating of detector

9/22 – 10/13: QA Upscale values out of bounds intermittently, cause was unknown at the time

10/28 – 11/3: Xport Error, tape ran out. Probe Rinse performed to measure As and Pb loss in probe and transport line. Quemetco plant shut down for repairs



11/3 - 11/10: Autocurrent error occurred, after extensive troubleshooting problem was identified as a bad detector. Likely the cause of the intermittent QA Upscale values 9/22 - 10/13. Detector replaced and instrument recalibrated

12/11: Probe Rinse performed to measure As and Pb loss in probe and transport line

1/6 23:00: 10-month study comes to an end

**Quemetco Xact 640 Multi-Metals CEMS
Recommended Requirements for Risk Reduction Plan**

1. CEMS Relative Accuracy Test Audit using CARB Method 436

The Xact 640 multi-metals continuous emission monitoring system (CEMS) mass emission rate shall meet a relative accuracy requirement of being less than or equal to 20% of the mean value of the reference CARB Method 436 in units of lb/hr for arsenic. Relative accuracy is calculated by the equations in Section 8 of 40 CFR, Part 60, Appendix B, Performance Specification 2. Nine valid CARB Method 436 tests shall be conducted and compared with corresponding CEMS measurements to obtain the relative accuracy for arsenic. This relative accuracy test audit (RATA) shall be conducted on an annual basis. This procedure is similar to the requirements of RECLAIM, Rules 2011A and 2012A.

2. CEMS Quality Assurance Tests

The required quality assurance tests for the Xact 640 multi-metals CEMS are as follows. These tests are listed in detail along with the calculation procedures in the document “Summary of Installation and Evaluation of the Xact 640 under South Coast Air Quality Management District Contract #C14337, March 30, 2016” which was prepared by Cooper Environmental.

a. Daily Upscale Calibration Drift Check

This check evaluates the precision of the Xact XRF system’s response to a standard once per day. During this check, a rod containing metals is injected into the analysis area and the stability of the analyzer response is evaluated. The CEMS must report a concentration that is within 15% of known value of the upscale standard each day.

b. Daily Zero Calibration Drift Check

This check evaluates the Xact XRF system’s response to a zero concentration produced by analyzing an un-sampled section of filter tape. The instrument passes the test if the result of the zero drift check for each monitored metal is less than 20% of the applicable emission limit. The emission limits for arsenic (As) and lead (Pb) at Quemetco’s facility are in lbs/hr (0.01 lbs/hr for Pb and 0.00114 lbs/hr for As). Based on average stack flow rates (82,000 dscfm) the following approximate limits in micrograms per dry standard cubic meter ($\mu\text{g}/\text{dscm}$) are calculated as:

Pb – 32.5 $\mu\text{g}/\text{dscm}$

As – 3.7 $\mu\text{g}/\text{dscm}$

c. Daily Flow Calibration Drift Check

The Xact utilizes a quality assurance flow sensor to check the flow reading from the sample flow sensor once per day. The difference in flow between the quality assurance flow sensor and the sample flow sensor must be less than 20% of the full scale value of the flow measurement (5 slpm) device to pass the test.

d. Initial and Quarterly XRF Audit

During installation, and at least once per quarter the XRF analysis portion of the Xact is challenged using a traceable-to-NIST thin film standard. These standards are produced by depositing metal vapor on a filter substrate and are available from Cooper Environmental. These standards are recommended by the US EPA for the calibration of XRF equipment used to analyze ambient air filters.

e. Initial and Annual RATA using the QAG

During installation and at least once per year, the Xact shall be challenged with a reference aerosol containing a known concentration of the metals of interest at three different concentration levels. Although EPA OTM16 describes several different approaches to this test, the one to be used is a dynamic spiking approach in which the reference aerosol is introduced into a sample of stack gas. The same dynamic spiking procedure was performed at Quemetco along with several other spiking procedures as part of South Coast Air Quality Management District's evaluation of the Xact 640.

The dynamic spiking procedures include challenging the Xact at three separate spiked concentration levels with a reference aerosol produced using Cooper Environmental's Quantitative Aerosol Generator (QAG). The Xact reported concentration is plotted against the QAG spiked concentration and a linear least squares regression analysis is performed. The Xact is evaluated on the basis of slope, intercept and correlation coefficient. The instrument passes the relative accuracy test assessment if the slope of the best fit line is between 0.85 and 1.15, if the correlation coefficient is 0.9 or greater and if the intercept is less than 20% of the applicable emission limit.

3. Xact 640 Mult-Metals CEMS Remote Modem Access

The Xact 640 CEMS has the provision to install cellular modem for data transmittal. Either SCAQMD or Quemetco shall install a 4G LTE or equivalent modem on the CEMS, and Quemetco shall allow SCAQMD to access the CEMS data remotely via the modem in real-time basis using SCAQMD computers. This type of data monitoring and acquisition was done by SCAQMD during the Xact 640 demonstration project in 2015.