

Field Bias and Precision Demonstration of a Near-Real-Time Multi-Metals Ambient Fence Line Monitor

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Executive Summary

National emissions standards for hazardous air pollutants (HAPs) are required under Section 112 of the Clean Air Act to limit the release of specified HAPs. Permitting, monitoring and enforcement of these emission limits are an integral part of managing air quality to protect human health and the environment. However, this is difficult and highly uncertain in the case of fugitive emissions because of the lack of appropriate monitors. This is of particular concern for fugitive metal emissions because metals represent 8 of 33 pollutants identified by the EPA as posing the greatest potential health threat, and these fugitive emissions may dominate exposure pathways in some airsheds. Fence line monitoring, or monitoring in a neighborhood near the perimeter of a fugitive metals emission source offers the potential to not only greatly increase the accuracy of estimating its local impact, but also has the potential to eliminate the need for costly monitoring of poorly defined emissions from many possible area and fugitive permitted sources. Near-real-time ambient monitoring could also provide hourly or shorter feedback to plant operators to minimize emissions before they become a problem.

Cooper Environmental Services LLC (CES) is currently working on a fence line multi-metals monitoring program sponsored by MACTEC Federal Programs, Inc. and U. S. Environmental Protection Agency (EPA). The objectives of this program are to demonstrate the utility of continuous metals fence line monitors for permitting fugitive metal emissions and compliance demonstration, and develop procedures and protocols for their application. The current phase of this project has focused on demonstrating the field readiness of metals fence line monitors as represented by the CES Xact 620. Evaluation of field readiness was based primarily on performance parameters such as precision, accuracy and detection limits, but also on utility parameters like uptime and stability, reporting times and applicability to fenceline monitoring requirements.

Two Xact 620 continuous fence line metals monitors were deployed to Herculaneum, Missouri along with two PM₁₀ Federal Reference Method samplers. During a month long field test each Xact reported hourly concentrations for 23 different elements including K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Ag, Cd, Sn, Sb, Ba, Hg, Tl, and Pb. The precision of the Xact 620 was determined by comparing the concentrations reported by each Xact. In addition the average daily concentrations reported by the two Xacts were compared with the metals concentrations from filter samples gathered using a federal reference method (FRM) PM₁₀ sampler followed by X-ray fluorescence analysis using USEPA accepted protocol IO 3.3. This field study database was supplemented with similar comparison data collected over the past year with a Xact 620 owned and operated by the State of Missouri (MO), and low and high volume particulate samples collected and analyzed by Washington University. Although there are no defined criteria for the initial certification or acceptance of fence line metals monitors there are a number of other documents that can be used as guides. These guides include EPA Method 301 for evaluating alternative stack monitoring methods and the National Ambient Air Quality Standard (NAAQS) for lead, which establishes

procedures and criteria for alternative analytical methods to obtain Federal Equivalent Method (FEM) status.

Study Results

a. Uptime

Both Xact 620 units reported one hour average concentrations for 23 elements on 27 consecutive days during this study with greater than 99% uptime. The only down time for both instruments was during a five hour period to allow for calibration checks and change of the Xact filter tape.

b. Stability

One Xact 620 used during this study was owned and operated by the Missouri Department of Natural Resources. The X-ray fluorescence (XRF) calibration of that unit was performed in December of 2008 and not changed for this study which occurred nine months later. This unit passed all XRF QA/QC checks and demonstrated less than 5% drift over that time period.

c. Detection Limits

The Xact 620's detection limits were determined both from a calculation based on a single filter blank and statistical analysis of 66 blank samples acquired during normal instrument operation. In general the Xact 620's one hour detection limits were found to be 10 to 20 times better than the detection limits for the standard method of PM metals measurement (24 hour sampling with a FRM sampler followed by laboratory XRF analysis).

d. Precision

The precision of the Xact 620 and FRM sampling followed by XRF analysis were determined using percent difference, EPA Method 301 F-test, lead National Ambient Air Quality Standards (NAAQS), and linear regression as indicators. Using percent difference the Xact 620 was found to be more precise than FRM sampling followed by XRF analysis for 19 out of 21 elements present at concentrations above both method's quantitation limits. When using a Method 301 F-test as an indicator of precision, the Xact 620 was found to be statistically more precise for 17 out of the 21 elements. Precision for lead was determined using the procedures defined by the lead NAAQS. With this method the percent difference for the Xact 620 was found to be 2.6% while for FRM sampling followed by XRF analysis the demonstrated precision was 5.1%. Additionally linear regression analysis was used as an indicator of precision. Figure ES 1 shows a plot of the Missouri Xact lead concentration versus the CES Xact lead

concentration. Both the slope (0.99) and the correlation coefficient (0.99) indicate highly precise measurements on the order of 1% between two collocated Xact 620 instruments.

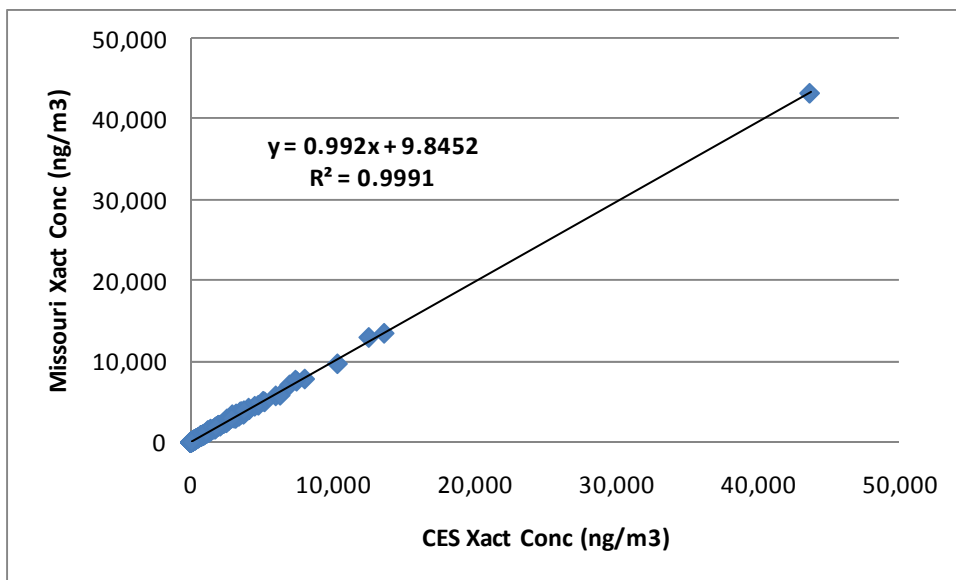


Figure ES 1. Missouri Xact Lead vs CES Xact Lead

e. Accuracy

Linear regression analysis was used to compare the daily average concentrations reported by the Xact 620 with those determined using FRM sampling followed by laboratory XRF analysis. Figure ES 2 shows a plot of the average daily Xact reported concentration versus the average daily lead concentration reported for the FRM sampler. The slope of 1.065 suggests a systematic bias of about 7%. Strong linear relationships were also found for several other elements present at concentrations above quantitation limits for both methods, including calcium (slope = 1.10), titanium (slope = 1.05), iron (slope = 1.19), copper (slope = 1.21) and zinc (slope = 1.06). All of these elements also met the EPA Method 301 criteria for alternative method bias.

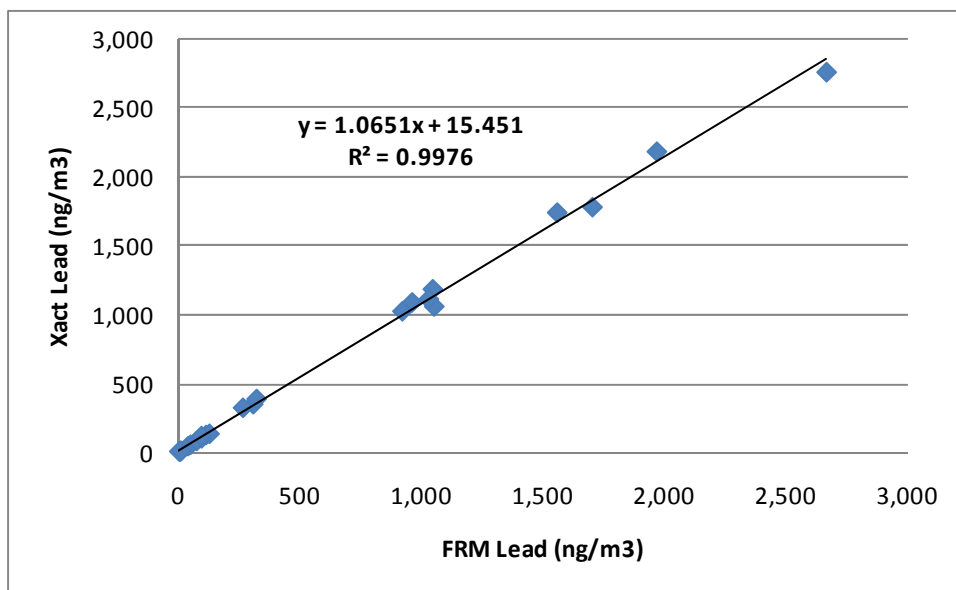


Figure ES 2. Daily Average Xact Lead Concentrations Versus FRM Lead Concentrations Reported by XRF Analysis of FRM Samples

Conclusions and Recommendations

The results of this study demonstrated that a FLM (Xact 620) could provide hourly concentration results for 23 elements with:

- Equal to or better uptime than a FRM sampler
- Stability equal to that expected from laboratory XRF analysis; i.e. about one year between calibrations
- One hour detection limits up to 10 times lower than those attainable with a 24-hour FRM sampler with laboratory XRF analysis
- Relative percent precisions for high concentration elements approaching 2% and equal to or better precisions than attainable with 24 hour FRM samples with laboratory analysis
- Accuracies as represented by bias and regression slopes on the order of 5 to 10% with a positive lead bias of 7% in Herculaneum and 2% in St. Louis.
- Data utility and availability unmatched by any other metals measurement technology with near real time reporting of results on the internet.

In addition, this technology has demonstrated its readiness for deployment by the fact that units similar to those used in Herculaneum and St. Louis (Xact 620s) have been operating for up to two years in such locations as Australia, Canada (2 units) and Korea (4 units). As such, it is the conclusion of this study that FLM as represented by the Xact 620 have demonstrated their potential as a monitoring tool for compliance demonstration, fugitive emission determination, health studies, residual risk assessment, source apportionment and a general tool to improve plant and airshed management.

Further work is needed to assess and correct systematic biases between the Xact and the FRM sampler with laboratory XRF analysis. In addition, specific protocols for acceptance and application of these FLM need to be established as well as modeling protocols for permitting and compliance demonstration.

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1. Introduction

The U.S. Congress amended the federal Clean Air Act (CAA) in 1990 to address a large number of hazardous air pollutants (HAPs) that are known to cause adverse effects to human health. Section 112 of the CAA governs the federal control program for HAPs. National emissions standards for HAPs (NESHAPs) are issued to limit the release of specified HAPs. These standards are “technology-based” meaning that they represent the maximum achievable control technology (MACT). The CAA requires EPA to review and revise MACT standards as necessary every eight years, and directs the EPA to assess the risk remaining (residual risk) after the application of the MACT standards. The EPA is further directed to promulgate additional standards if required to provide an ample margin of safety to protect public health. The EPA is in the process of promulgating residual risk standards for HAPs following its promulgation of MACT standards.

Permitting, monitoring and enforcement of emission limits for HAPs (MACT or residual risk related) are an integral part of managing air quality to protect human health and the environment. Emissions from stacks can be relatively easily permitted, their emissions accurately monitored with continuous emissions monitoring systems (CEMS), and limits enforced based on these measurements. However, it is difficult to permit and enforce fugitive emission limits because of the lack of monitors for fugitive emissions and/or their impacts at a fence line or in the local community. Current permitting and enforcement of fugitive emission sources are based on crude estimates of emissions (uncertainties generally ranging from about 100 to 1,000 percent) and good management practices. This uncertainty and management difficulty is of particular concern because fugitive emissions are often highly variable and may be responsible for the dominate exposure to hazardous pollutants for nearby residents.

Although progress is being made in the development of fugitive emissions monitors for some gaseous pollutants such as ammonia, little progress has been made for other pollutants such as metals. Metals and metal compounds are of particular concern because they are included in EPA’s list of 188 HAPs and represent 8 of the 33 pollutants identified by the EPA as posing the greatest potential health threat in urban areas. Hazardous metals are unique in that they will not biodegrade; once released into the environment, they will always be potentially available for re-introduction into the air, water and food chain. This persistence is particularly important in the context of environmental justice and areas where hand-to-mouth type pathways can represent significant exposure. In these local airsheds, area/fugitive HAP emissions can make a significant contribution to total HAP emissions and impacts in local communities. Perimeter or nearby ambient air monitoring programs to evaluate these contributions have become increasingly valuable. Fence line or nearby ambient monitoring offers the potential to not only greatly increase the accuracy of measurement and enforcement, but also the potential to eliminate the need for costly monitoring of poorly defined emissions from many possible area/fugitive compliance sources within a facility. This

near-real-time monitoring may also provide timely feedback to plant operators to identify sources and minimize their emissions before they become a problem.

Cooper Environmental Services LLC (CES) is currently working on a multi-metal ambient monitoring demonstration program in coordination with MACTEC and EPA sponsorship. The overall objectives of this program are to demonstrate the potential utility of a near-real-time metals monitor for permitting and compliance demonstration, and develop reference procedures for application of this technology in a compliance setting. This program has taken a phased approach to achieving these goals.

The objectives of Phase I were to:

1. Modify CES' existing multi-metal continuous emissions monitor (CEM) to meet the requirements of an ambient metals monitor.
2. Evaluate this modified monitor in CES' laboratory for its potential applicability to ambient metals monitoring.
3. Develop a protocol to demonstrate its practical applicability in the field.

The first two objectives of Phase I were completed in September of 2006. The results of Phase I demonstrated that the CEM technology could be modified to accurately monitor emission impacts at a fence line and achieve detection limits adequate for modeling high impact periods.¹

The overall objective of Phase II was to demonstrate feasibility and availability of a continuous ambient metals monitoring technology for use in permitting and enforcing fugitive emission limits. The specific objectives for Phase II were to:

1. Demonstrate that measurement technology is field ready; i.e. demonstrate it can practically provide accurate and reliable near-real-time measurements of metals in the field.
2. Evaluate the applicability of the field data for models that might be used to quantify either fugitive emission rates and/or impacts at a monitor.
3. If applicable, determine the adequacy of this field data to quantify either source emission rates and/or source impacts to ambient metal concentrations that can be used in permitting and compliance demonstrating situations.
4. Develop procedures for applying this technology in a permitting and compliance demonstration situation.
5. Validate the monitor and procedures developed in the above tasks.

The first three objectives of Phase II were completed in September of 2008.

The current phase of the project (Phase III) has focused on the following two tasks:

1. Creating procedures and criteria for validating the accuracy of fence line metals monitors.
2. Demonstrating the accuracy and precision of the Xact 620.

Whereas previous phases of this program focused on demonstrating the feasibility of metals monitoring using short averaging times, this third phase focused on field demonstration of the validity of the metals fence line monitor results, including precision, accuracy, and detection limits. The accuracy and precision of the fence line monitor were determined during field testing of the unit in an airshed likely to have relatively high concentrations of various metals. The Xact was compared against filter samples acquired using a reference method sampler followed by laboratory metals analysis either by X-ray fluorescence (XRF) or by ICP-MS.

2. Validation Procedures and Criteria

Fence line monitoring falls outside of the current MACT monitoring regime and the current ambient monitoring regime. With the exception of lead there are no applicable federal reference methods for the measurement of metals and no current regulations on their concentration levels. Because of this, there are currently no validation procedures and criteria for multi metals fence line monitors. There are, however, a number of procedures and methods that offer guidance as to the approach to take to validating a fence line monitor and for methods that can be used in comparison studies.

1. Method 301¹ – This method is used to validate alternative stack measurement methods against existing reference methods.
2. Lead National Ambient Air Quality Standard (NAAQS)² – The federal reference method (FRM) for measurement of total suspended particulate (TSP) and PM₁₀ lead are defined by this reference. Additionally, the referenced document outlines procedures by which alternative analytical methods can obtain federal equivalent method (FEM) status.
3. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air³ - This document outlines generally accepted procedures for sampling and measurement of metals in PM₁₀ and PM_{2.5}. These procedures, although generally accepted as scientifically accurate and reliable, do not have the legal stature of a federal reference method.

The procedures and criteria associated with each of these methods are outlined in Sections 2.1 to 2.3

2.1. Method 301

Method 301 outlines procedures for comparing alternative stack emission measurement methods with reference methods. The methods are compared to determine if there is a systematic bias associated with an alternative method and to determine the precision of the alternative method. Method 301 procedures include sampling stack emissions with

at least two collocated reference methods and two collocated alternative methods sampling simultaneously. A bias of 10% is allowed without correction and a bias of up to 30% is allowed with a correction factor. The alternative method must be at least as precise as the validated method at the level of the applicable standard as determined by an F-test.¹ An alternative method is accepted if both the bias and precision criteria are met. For this current study the CES Xact 620 was treated as the alternative method and a Rupprecht & Patashnick Partisol 2025 sampler followed by XRF analysis according to EPA Compendium IO 3.3³ was treated as a pseudo reference or validated method here after referred to as FRM/IO3.3.

Method 301 bias is determined by calculating the difference between the average alternative method measurement and the average of the FRM/IO3.3 measurement according to Equation 1.

$$d_i = \frac{V_{1i} + V_{2i}}{2} - \frac{P_{1i} + P_{2i}}{2} \quad \text{Equation 1}$$

Where:

- d_i = the difference in the mean of the method and the mean of the alternative method
- V_{1i} = First measured value of the FRM/IO3.3 method in the i^{th} sample
- V_{2i} = Second measured value of the FRM/IO3.3 method in the i^{th} sample
- P_{1i} = First measured value of the alternative method in the i^{th} sample
- P_{2i} = Second measured value of the alternative method in the i^{th} sample

The mean, standard deviation, and t-statistic of the differences are determined. The t-statistic is compared to the critical value of the t-statistic to determine if the bias is significant at the 95% confidence level. If the bias is not statistically significant, the data is acceptable. If the bias is statistically significant, the magnitude of the bias is calculated according to Equation 2.

$$B_R = \left| \frac{B}{VS} \right| \quad \text{Equation 2}$$

Where:

- B_R = Method Bias
- B = Mean of difference (d_i) between the FRM/IO3.3 and the alternative method
- VS = Average FRM/IO3.3 method concentration

The precision of the reference method is compared with the precision of the alternative method by comparing the estimated variances (Eq. 3) of each method using an F –test. The F value (Eq. 4) is compared with the critical value for the appropriate number of degrees of freedom. If the value of F is greater than the critical value then the alternative method is not as precise as the reference method.

$$S_p^2 = \frac{\sum_i^n d_i^2}{2n} \quad \text{Equation 3}$$

Where:

- S_p^2 = Variance of the FRM/IO3.3 method or the alternative method
- d_i^2 = difference between the *i*th pair of samples collected with the alternative or the FRM/IO3.3 method
- n = the number of samples and the degrees of freedom

$$F = \frac{S_p^2}{S_v^2} \quad \text{Equation 4}$$

Where:

- F = the F value
- S_p^2 = The estimated variance of the alternative method
- S_v^2 = The estimated variance of the FRM/IO3.3 method

2.2. Lead NAAQS

On November 12, 2008 the US EPA promulgated a new National Ambient Air Quality Standard (NAAQS) for lead (Pb)². This standard reduced the allowed concentration for lead as total suspended particulate (TSP) from 1.5 µg/m³ to 0.15 µg/m³. In addition it outlined a new federal reference method (FRM) for measurement of PM₁₀ lead and new procedures for designating candidate methods as federal equivalent methods (FEM). The new PM₁₀ lead FRM includes sampling PM₁₀ on a Teflon filter using a FRM sampler or officially recognized FEM samplers. Under the new PM₁₀ standard the analytical method for lead is X-ray fluorescence (XRF). The Xact 620 was compared to this new federal reference method for lead using the criteria set forth in the new lead NAAQS. The methods and procedures for determining lead equivalency were written for new analytical equivalent methods and had to be modified somewhat for the Xact 620 continuous monitor which incorporates both sampling and on line analysis.

2.2.1. Precision

Precision as defined by NAAQS procedures is calculated for days when the lead concentration is between 30% (0.045 µg/m³) and 250% (0.375 µg/m³) of the NAAQS limit by analyzing each FRM sample three times and reporting the precision as calculated in Equation 5. For candidate continuous monitors, the precision is calculated using two candidate monitors according to Equation 6. A precision of 15% of the average concentration must be met for both the candidate and the FRM.

$$P_{Ri} = \frac{R_{i\max} - R_{i\min}}{R_{iave}} \quad \text{Equation 5}$$

Where:

- P_{Ri} = The precision of the reference method for the i^{th} sample
- $R_{i\max}$ = the maximum reference method concentration for lead on the i^{th} sample
- $R_{i\min}$ = the minimum reference method concentration for lead on the i^{th} sample
- R_{iave} = the average reference method concentration for lead on the i^{th} sample

$$P_{ci} = \frac{C_{i\max} - C_{i\min}}{C_{iave}} \quad \text{Equation 6}$$

Where:

- P_{ci} = The precision of the candidate method for the i^{th} sample
- $C_{i\max}$ = The maximum reported concentration of the i^{th} sample
- $C_{i\min}$ = the minimum reported concentration of the i^{th} sample
- C_{iave} = The average reported concentration of the i^{th} sample

2.2.2. Comparability

Comparability is the term used in the lead NAAQS rule to describe the accuracy or bias of the candidate method relative to the reference method. At least five days of lead concentration data between $0.045 \mu\text{g}/\text{m}^3$ and $0.375 \mu\text{g}/\text{m}^3$ are required for a valid comparison to be made. For a candidate continuous monitor, a bias comparison must be made between each monitor and each of the three analytical measurements of the reference method, giving a total of six points of comparison. The bias is calculated according to Equation 7 and must be less than 20% for all six points of comparison. During this study there were two reference method samplers used (to meet the M301 procedural requirements) so the comparison was done in this manner with two separate reference method units and between the reference method samplers themselves. Additionally because the Xact 620 reported hourly averages and the reference method gives one sample per day, the comparison was made between each day's reference method sample and each Xact's average of 24 individual one hour samples.

$$D_{ik} = \frac{C_{ik} - R_{ik}}{R_{ik}} \times 100 \quad \text{Equation 7}$$

Where:

- D_{ik} = The percent difference between the reference and the candidate methods

- C_{ik} = The concentration reported by the candidate method for the i^{th} sample and k^{th} measurement
- R_{ik} = The concentration reported by the reference method for the i^{th} sample and k^{th} measurement

2.2.3. Minimum Detection Limits

The minimum detection limit must be determined from the analysis of at least 7 blank filters and must be less than 5% of the lead NAAQS or $0.0075 \mu\text{g}/\text{m}^3$.

2.3. Inorganic Compendium of Methods

For elements other than lead there are no federal reference standards for PM_{10} sample analysis, however, there are several methods set forth in the Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air³ which are widely accepted as accurate and reliable by the scientific community. The filters gathered using the FRM sampler were analyzed using EPA Compendium Method IO 3.3 which outlines procedures for analyzing PM_{10} deposits by X-ray fluorescence (this combined sampling and analysis approach is here in referred to as FRM/IO3.3). Unfortunately, there are no available reference methods with adequate sensitivity with which to compare the individual hourly Xact measurements. Instead, the Xact's daily average was calculated from 24 one hour samples and compared with the daily average as measured by the FRM/IO3.3 method.

3. Experimental

3.1. Field Validation Overview

The field evaluation portion of this study was performed in Herculaneum, Missouri near the fence line of the Doe Run lead smelter. The site was chosen because Herculaneum, Missouri is one of the few airsheds in the country not in attainment under the old lead NAAQS standard of $1.5 \mu\text{g}/\text{m}^3$. Additionally the Missouri Department of Natural Resources owns an Xact 620 which they planned on locating there at the end of July 2009, thus making it possible to determine precision with two collocated Xact's. In addition to the two Xacts, two Rupprecht and Patashnick (R&P) Partisol 2025 reference method PM_{10} samplers were also deployed by the Missouri Department of Natural Resources for this study. The R & P sampler is a recognized federal reference method sampler for PM_{10} . Filters from these samplers were sent to CES for metals analysis by X-ray fluorescence (XRF). Accuracy for the Xact 620 was determined by comparing the concentrations determined from these filters with the Xact daily average concentration levels according to the procedures defined by either Method 301 or by the lead NAAQS.

3.2. Instrument

The Xact 620 ambient multi-metals monitor is a reel-to-reel filter tape sampling system with an integrated metals analyzer based on XRF according to the procedures in EPA's Compendium Method IO 3.3. A schematic of the monitor is illustrated in Figure 1. It

consists of a PM₁₀ inlet and temperature sensor, a sampling and analysis module and a flow control module. It operates by drawing 16.7 lpm through a PM₁₀ size-selective inlet and a filter tape located in the sampling and analysis module. At the end of a sampling interval that can last from 15 minutes to 4 hours (operator defined), the resulting filter tape deposit is advanced approximately 2 inches for analysis. While this sample is being analyzed for metal content, the next sample is being collected. The only dead time in the sampling and analysis system is about 20 seconds required to advance the tape and prepare for the next sample. The average metal concentration for each sampling interval is calculated by dividing the XRF-determined metal mass by the sampled volume. The resulting concentration (ng/m³) is automatically stored in a computer and/or reported to a central monitoring location.

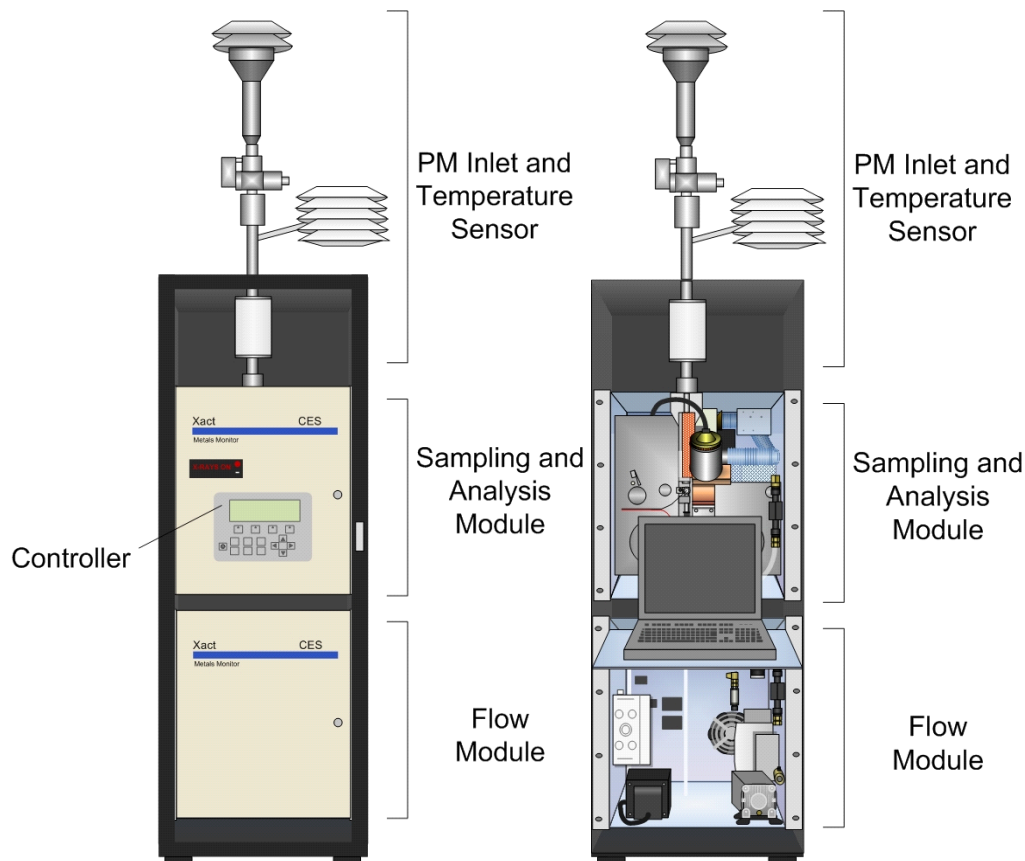


Figure 1. Schematic of the Xact 620

3.3. Pre –field Deployment

Two Xact 620's were used in this study, one owned by the Missouri Department of Natural Resources and the other was manufactured by CES shortly before the field study took place. The Missouri unit had been deployed by the Department of Natural Resources at several locations in and around the greater St. Louis metropolitan area as part of a separate grant funded project. In December of 2008 the Missouri unit had an XRF calibration performed and other than relocation, no major work had been done on the unit since that December 2008 calibration.

The unit deployed by CES for this study was manufactured in July of 2009 and was calibrated in the CES laboratory using a CES owned set of Micromatter⁴ thin film standards according to procedures similar to those found in EPA IO 3.3³. As part of standard CES quality assurance procedures, the unit was challenged with a traceable-to-NIST reference aerosol of iron and zinc using CES' Quantitative Aerosol Generator (QAG). The QAG operates by nebulizing a solution of known concentration at a measured rate into a measured air flow giving a concentration in ng/m³. The QAG has been accepted by the USEPA for the purposes of challenging the Xact CEMS as part of an Alternative Monitoring Plan^{5,6}. In this case, spiking with the QAG serves as an overall quality control check of the Xact 620's operation. Table 1 summarizes the results, which show an average percent difference between the QAG generated aerosol concentration and the Xact measured concentration of less than 2% for iron and zinc.

Table 1. QAG Audit Test Results for CES Xact 620

Concentration Level	Time	QAG Predicted Fe Conc (ng/m³)	QAG Predicted Zn Conc (ng/m³)	Xact Reported Fe Conc (ng/m³)	Xact Reported Zn Conc (ng/m³)	Percent Error Fe	Percent Error Zn
low	13:15	13,387	18,767	13,633	18,649	1.84	-0.63
	13:30	13,387	18,767	13,707	18,768	2.39	0.00
	13:45	13,387	18,767	14,171	19,469	5.86	3.74
	14:00	13,387	18,767	14,310	19,687	6.89	4.90
	14:15	13,387	18,767	14,857	20,472	10.98	9.08
	14:30	13,387	18,767	14,797	20,415	10.53	8.78
	14:45	13,387	18,767	14,714	20,352	9.91	8.45
	15:00	13,387	18,767	14,740	20,390	10.11	8.65
	15:15	13,387	18,767	14,036	19,226	4.85	2.45
Mid	9:30	25,614	35,907	21,379	29,087	-16.53	-18.99
	9:45	25,614	35,907	22,789	31,088	-11.03	-13.42
	10:00	25,614	35,907	26,325	35,971	2.78	0.18
	10:15	25,614	35,907	25,222	34,538	-1.53	-3.81
	10:30	25,614	35,907	25,696	35,249	0.32	-1.83
	10:45	25,614	35,907	24,827	34,109	-3.07	-5.01
	11:00	25,614	35,907	24,252	33,391	-5.32	-7.01
	11:15	25,614	35,907	23,609	32,431	-7.83	-9.68
High	11:45	42,706	59,869	40,938	56,273	-4.14	-6.01
	12:00	42,706	59,869	39,704	54,692	-7.03	-8.65
	12:15	42,706	59,869	40,242	55,512	-5.77	-7.28
	12:30	42,706	59,869	42,930	59,287	0.52	-0.97
	12:45	42,706	59,869	44,264	61,136	3.65	2.12
	13:00	42,706	59,869	44,798	62,004	4.90	3.57
	13:15	42,706	59,869	44,733	61,885	4.75	3.37
	13:30	42,706	59,869	43,382	60,111	1.58	0.40
	13:45	42,706	59,869	43,382	60,138	1.58	0.45
AVERAGE						0.82	-1.04

3.4. Minimum Detection Limits

XRF minimum detection limits are typically calculated from the analysis of a single blank spectra or a series of blank spectra using the Equation proposed by Lloyd Currie.⁷ Minimum detection limits are usually calculated as one sigma or as 95% confidence detection limits. Equation 8, is for the calculation of 95% confidence detection limits. For one sigma detection limits the 3.29 is replaced by the square root of 2.

$$C_D = \frac{3.29 \frac{\sqrt{R_b t I}}{S_i t I}}{\frac{V}{A}} \quad \text{Equation 8}$$

Where:

- C_D = The concentration at the detection limit (ng/m³)
- R_b = The background count rate (cps/mA)
- t = The acquisition livetime (s)
- I = The X-ray tube current (mA)
- S_i = The sensitivity for the ith element (counts/second/mA/ng/cm²)
- V = The sample volume (m³)
- A = The deposit area (cm²)

Minimum detection limits for the Xact 620 and for the FRM/IO3.3 method analysis have been calculated using Equation 8. For this project, however, Xact 620 detection limits were also determined from 66 blank samples acquired while the instrument was operated in normal run mode. This was done by replacing the PM₁₀ inlet seen in Figure 1 with a high volume filter to remove particulate phase metals. The Xact 620 was then operated under normal run mode in which air was drawn through the high volume filter and the Xact filter tape. Sixty-six one hour samples were acquired in this manner and compared with the single blank calculated 95% confidence detection limits (see Table 2). With a couple of exceptions, the experimental results fall into two categories relative to the calculated 1 hour detection limits. There were either non-detects for the elements (K, Cu, Se, Sn, Hg, Pb) or the experimental value was somewhat higher than the calculated (Equation 8) value. The 66 blank samples acquired for this test exceed the seven required by the lead NAAQS rule for the determination of minimum detection limits. In addition the value of the lead detection limit determined was less than that required by the lead NAAQS (0.0075 µg/m³). The Xact, therefore, met the NAAQS criteria for minimum detection limits. In general the Xact one-hour detection limits are 2 to 20 times lower than the detection limits achieved using 24-hour FRM sampling followed by laboratory XRF analysis (FRM/IO3.3).

Table 2. Comparison of 95% Confidence Minimum Detection Limits (ng/m³)

Element	1-hour Xact 620		24-hour FRM/IO3.3
	66 Blank Measurements	Equation 8 Calculated	Equation 8 Calculated
K	0.00	1.89	4.40
Ca	2.66	0.75	6.30
Ti	0.73	0.41	11.82
V	0.26	0.32	3.70
Cr	0.57	0.25	2.09
Mn	0.31	0.16	0.56
Fe	2.82	0.19	0.49
Co	0.21	0.11	0.28
Ni	0.15	0.08	0.42
Cu	0.15	0.15	0.49
Zn	0.21	0.10	0.70
Ga	0.08	0.06	1.12
As	0.08	0.06	0.56
Se	0.00	0.07	0.49
Ag	2.09	1.91	14.00
Cd	0.00	3.15	15.40
Sn	1.11	5.92	21.36
Sb	1.81	1.55	21.98
Ba	1.55	0.92	36.27
Hg	0.00	0.10	1.05
Tl	0.07	0.11	1.05
Pb	0.00	0.12	1.05

3.5. Field Deployment

3.5.1. Setup and Quality Assurance

Both the CES Xact and the Missouri Xact were installed in a climate controlled shed furnished by the Missouri Department of Natural Resources (MDNR). The CES Xact was installed in the shed during the week of August 3rd, 2009, while the Missouri unit was installed the week prior. Additionally, MDNR installed two R & P Partisol 2025 samplers, one on the roof of the Xact's shed and one on the roof of an adjacent shed. . Figure 2 shows the arrangement of all four sampler inlets.

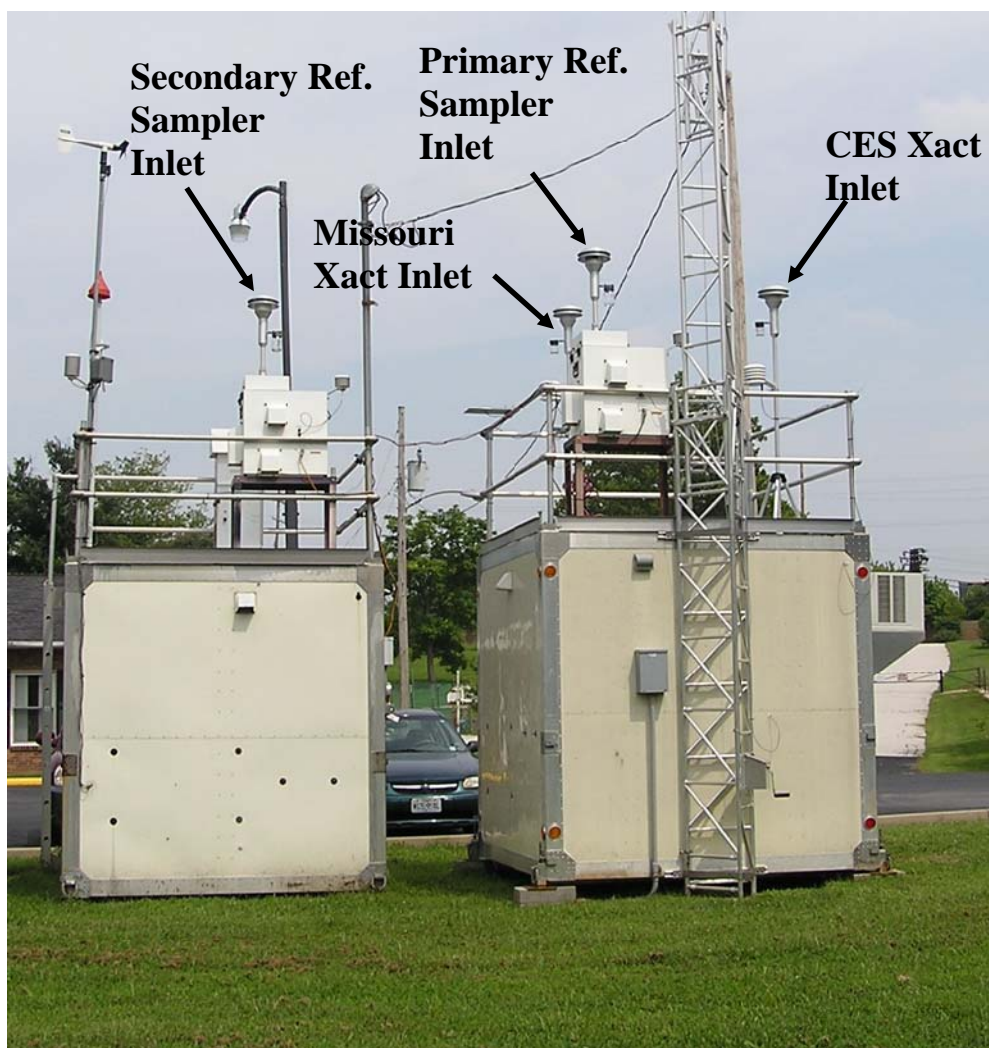


Figure 2. Sampler Inlet Arrangement

All four samplers were outfitted with standard PM₁₀ sampling inlets. The primary reference sampler, the Missouri Xact, and the CES Xact are all more than 1 meter but less than 2 meters apart. The secondary reference sampler was more than 2 meters from any other sampler inlet. All four samplers were calibrated to the same NIST traceable flow meter, a BGI TetraCal, just prior to the start of official testing and recorded volumes in actual cubic meters.

XRF calibration checks were also performed on each Xact prior to testing. The two units were initially calibrated to two independent sets of XRF standards, one owned by the state of Missouri and the other by CES. The initial XRF check revealed a discrepancy of about 5% for lead between the two sets of standards. Because the Missouri unit had a prior history of good comparisons with other reference method samplers, the CES unit was recalibrated in the field using the Missouri standards. Both Xact XRF calibrations were checked again prior to the start of sampling (see Table 3).

Table 3. Pre-Test Xact XRF Calibration Checks

Element of Interest	Standard ID #	Mass (ng)	CES Xact Reported Mass (ng)	CES Xact % Error	Missouri Xact Reported Mass (ng)	Missouri % Error
Fe	18510	34,063	33,092	-2.85	33,796	-0.78
Zn	18514	11,649	11,772	1.05	11,636	-0.11
Pb	18529	31,523	30,956	-1.80	31,063	-1.46

Both Xacts were also equipped prior to sampling with a remote control software and hardware package. This allowed both units to be restarted remotely in the event either one had a malfunction that caused the unit to go into standby.

3.5.2. Testing

Both Xacts operated continuously from August 8th to September 2nd, 2009 without any unscheduled stoppages. The only scheduled stoppage occurred on August 21st when both units did not sample for a five hour period to allow for a tape change, and flow and XRF quality assurance checks. Both units recorded 605 individual hourly data points during the testing period with 23 elemental concentrations recorded for each data point giving a total of 27,830 individual reported concentrations. XRF and flow quality assurance checks were also performed following sampling. For both Xacts on both days (August 21st and September 2nd), the reported flow was within 2% of the flow standard and the XRF reported mass was within 5% of each of the certified standard masses.

Two Rupprecht and Patashnick (R&P) Partisol 2025 reference method PM₁₀ samplers were also operating simultaneously during the sampling period. The primary sampler experienced an unplanned shutdown during the period from 8/23/09 to 8/25/09. The secondary sampler stopped operation on 8/31/09 as planned. Each R & P sampler generates one filter for analysis each day. During the testing period there were 25 days on which at least one reference method sampler was collecting samples and 21 days on which both samplers were producing data. The flows for both samplers were audited prior to testing, on August 21st, and following testing on September 2nd. All flows were within 5% of the reference flow meter.

Following sampling, all filters were shipped to CES for XRF analysis. CES performs XRF analysis of PM₁₀ and PM_{2.5} filters as a standard part of its business and has participated in several major studies involving filter speciation including those sponsored by the USEPA. The filter analysis for this study followed standard CES quality control and assurance procedures. These procedures included the analysis of a quality control standard with every batch, one replicate analysis per day, and the analysis of NIST Standard Reference Materials for XRF once during the analysis period. All quality control and assurance criteria were met for this analysis. In addition a subset of these filters will be shipped to the USEPA to be analyzed by their XRF laboratory⁹ and to Dr. Jay Turner at Washington University to be analyzed by ICP-MS¹⁰.

4. Results of Field Testing

4.1. XRF Data Treatment

One difficulty in making precision and bias comparisons is how to determine what data to compare. Clearly data that falls below the detection limit of either analytical method should not be compared, since the precision of analytical measurements typically get worse as the detection limit is approached. Method 301 deals with this issue by assuming that the data for comparison is at or near the stack emission limit, where, presumably, both the reference and alternative methods have good analytical precision. Similarly the procedures for acquiring lead federal equivalent method status also define a range over which valid comparisons can be made (between 30% and 250% of the lead NAAQS standard). However, with the exception of lead none of the elements measured in this study are regulated in the ambient air or at the fence line. Therefore, there are no defined ranges or concentration levels at which valid comparisons can be made between the reference method and the alternative method.

To eliminate some of the lower concentrations at which the precision of either the Xact 620 or the XRF analysis of the FRM sampled filters is expected to be poor, any data falling below the limit of quantitation was removed from the comparison data set. For XRF a generally accepted definition of the limit of quantitation is given in Equation 9 which is very similar to the calculation for minimum detection limit (Equation 8) except that 3.29 has been replaced by 10^7 . In an interference free sample an element present at the limit of quantitation would be expected to have a 10 percent relative standard deviation if repeated measurements were acquired. Although, the samples acquired for this study are not likely to be interference free, the limit of quantitation gives a starting point for eliminating data likely to have poor precision due to the limitations of the analytical method.

$$C_Q = \frac{10 \frac{\sqrt{R_b t I}}{S_i I}}{\frac{V}{A}} \quad \text{Equation 9}$$

Where

C_Q	=	The concentration at the limit of quantitation (ng/m ³)
R_b	=	The background count rate (cps/mA)
t	=	The acquisition livetime (s)
I	=	The X-ray tube current (mA)
S_i	=	The sensitivity for the i th element (counts/sec/mA/ng/cm ²)
V	=	The sample volume (m ³)
A	=	The deposit area (cm ²)

Concentrations below the limits of quantitation were removed from both the Xact 620 and the XRF analysis of the federal reference method. The limit of quantitation, for the Xact 620 was either determined by using the calculated limit of quantitation as defined in Equation 9 or by applying a ratio 10/3.29 (the ratio of the limit of quantitation to the detection limit) to the empirically determined detection limit (section 3.4). Table 4 shows that the limits of quantitation are very similar for the two methods with one important difference being that the Xact is a 1 hour sample while the FRM is a 24 hour sample.

Table 4. Xact and FRM Limits of Quantitation (ng/m³)

Element	Xact (1-hour)	FRM/IO3.3 (24-hour)
K	5.74	2.42
Ca	8.08	1.31
Ti	2.23	0.83
V	0.97	0.79
Cr	1.74	0.86
Mn	0.94	1.16
Fe	8.56	1.08
Co	0.64	0.68
Ni	0.47	0.71
Cu	0.45	0.99
Zn	0.62	1.25
Ga	0.24	1.46
As	0.23	0.69
Se	0.23	0.65
Br	0.11	0.71
Ag	6.36	6.97
Cd	9.57	12.81
Sn	17.98	14.27
Sb	5.49	19.95
Ba	4.70	2.14
Hg	0.31	1.31
Tl	0.33	-
Pb	0.38	1.19

4.2. Daily Averages and Data Range

Tables 5 and 6 show the reported concentrations for each day for both the primary and secondary FRM samplers. Tables 7 and 8 show the daily averages for the CES Xact and the Missouri Xact respectively. The Xact daily average represents an arithmetic average of 24 hourly concentrations. Data was not reported (NR) if the daily average was below the limit of quantitation.

Table 5. Primary FRM Daily Reported Concentration (ng/m³)

Date	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br	Ag	Cd	Sn	Sb	Ba	Hg	Pb
8/8/2009	204	892	29.5	2.2	NR	8.4	346	1.4	1.7	13.9	65.0	NR	NR	NR	4.7	NR	54	NR	NR	NR	NR	1034
8/9/2009	143	351	22.2	NR	NR	6.3	218	0.9	NR	2.8	16.4	NR	NR	NR	2.8	NR	NR	NR	NR	10	NR	108
8/10/2009	130	498	11.6	NR	1.3	6.0	175	NR	NR	2.5	20.0	NR	NR	NR	2.1	NR	NR	NR	NR	18	NR	118
8/11/2009	114	415	7.3	NR	3.2	4.4	116	NR	2.8	6.5	14.6	NR	1.3	NR	2.1	NR	NR	NR	NR	3	NR	45
8/12/2009	119	674	7.6	NR	0.9	7.7	235	1.0	1.9	5.5	25.7	NR	1.6	NR	3.2	NR	NR	NR	NR	10	NR	35
8/13/2009	121	772	9.6	NR	NR	5.1	203	NR	1.5	11.0	74.6	NR	NR	1.0	5.1	NR	25	NR	NR	10	NR	302
8/14/2009	135	1552	16.6	1.5	NR	6.7	284	1.9	3.4	31.0	217.1	NR	NR	1.1	5.2	NR	118	NR	NR	NR	NR	1053
8/15/2009	160	1029	20.6	2.8	NR	7.7	275	1.4	1.1	14.1	101.9	NR	NR	NR	5.1	NR	80	NR	NR	NR	NR	954
8/16/2009	133	735	15.7	5.5	NR	6.8	198	0.9	1.2	13.9	202.7	NR	NR	2.3	5.3	NR	294	NR	NR	NR	NR	2004
8/17/2009	155	511	13.8	2.3	NR	6.3	166	0.8	1.3	6.9	186.7	NR	NR	NR	4.3	NR	131	NR	NR	4	NR	988
8/18/2009	120	252	8.5	1.0	1.2	2.0	112	NR	1.1	4.4	32.0	NR	NR	0.7	2.0	NR	NR	NR	NR	7	NR	90
8/19/2009	127	285	9.6	1.2	NR	4.0	111	0.8	NR	3.3	89.5	NR	NR	NR	2.2	NR	23	NR	NR	NR	NR	268
8/20/2009	85	120	3.5	NR	NR	3.2	53	NR	NR	2.2	2.9	NR	NR	NR	NR	NR	NR	NR	NR	3	1.9	2
8/21/2009	92	279	3.5	NR	NR	3.9	75	NR	NR	2.3	3.7	NR	0.9	NR	1.6	NR	NR	NR	NR	5	NR	2
8/22/2009	91	258	7.2	NR	NR	3.1	126	NR	NR	2.7	6.8	NR	NR	NR	19.8	NR	NR	NR	NR	5	NR	73
8/23/2009	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/24/2009	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/25/2009	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/26/2009	126	1392	20.2	1.4	NR	7.9	254	0.7	1.3	12.5	239.7	NR	NR	NR	2.9	NR	107	NR	NR	NR	NR	1643
8/27/2009	129	960	20.4	1.7	NR	7.9	297	NR	0.9	12.5	905.6	NR	NR	NR	4.1	NR	141	NR	NR	9	NR	2744
8/28/2009	77	274	6.8	NR	NR	3.7	77	NR	NR	2.1	9.8	NR	1.1	NR	1.5	NR	NR	NR	NR	NR	NR	6
8/29/2009	120	364	5.9	NR	NR	4.6	95	NR	NR	2.1	6.4	NR	2.4	NR	2.7	NR	NR	NR	NR	7	NR	NR
8/30/2009	68	309	6.8	NR	NR	2.4	91	NR	NR	3.1	8.0	NR	1.1	0.7	1.7	NR	NR	NR	NR	NR	NR	6
8/31/2009	65	505	5.9	NR	NR	4.2	122	NR	NR	3.5	11.7	NR	NR	1.0	3.1	NR	NR	NR	NR	NR	NR	8
9/1/2009	72	632	6.2	NR	2.3	5.1	205	NR	3.2	6.5	39.7	NR	NR	NR	2.1	NR	NR	NR	NR	8	1.4	91

NA – Not available – sampler was not operating; NR – Not Recorded – concentration is below the limit of quantitation

Table 6. Secondary FRM Daily Reported Concentration (ng/m³)

Date	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br	Ag	Cd	Sn	Sb	Ba	Hg	Pb
8/8/2009	214	921	32.5	1.8	1.5	8.5	359	1.7	2.0	14.0	69.3	NR	NR	NR	4.1	NR	58	NR	NR	NR	NR	1066
8/9/2009	143	363	21.8	0.8	NR	6.4	219	0.8	NR	2.5	16.8	NR	NR	NR	2.4	NR	NR	NR	NR	9	NR	112
8/10/2009	130	521	10.8	1.0	NR	4.8	176	NR	NR	2.5	22.5	NR	NR	NR	2.2	NR	NR	NR	NR	20	NR	131
8/11/2009	114	427	6.8	0.8	3.0	4.8	116	NR	2.4	7.2	15.5	NR	NR	NR	3.1	NR	NR	NR	NR	8	NR	48
8/12/2009	127	731	9.6	NR	1.9	7.3	245	1.1	1.7	6.0	26.8	NR	1.2	NR	3.4	NR	NR	NR	NR	6	NR	37
8/13/2009	139	811	9.6	NR	3.7	5.8	231	0.7	2.1	11.3	78.1	NR	NR	0.7	4.8	NR	26	NR	NR	10	NR	307
8/14/2009	134	1527	16.5	2.5	1.8	7.0	273	1.7	2.8	30.1	217.3	NR	NR	0.7	5.3	NR	111	NR	NR	5	NR	1035
8/15/2009	145	946	18.4	2.6	NR	7.5	249	1.5	1.2	12.8	93.4	NR	NR	NR	3.9	NR	76	NR	NR	NR	NR	883
8/16/2009	125	691	12.9	3.9	NR	6.2	187	1.7	1.4	13.2	196.8	NR	NR	NR	5.7	NR	285	NR	NR	NR	NR	1929
8/17/2009	160	529	12.9	2.4	1.0	5.9	179	0.7	1.8	7.0	209.9	NR	NR	NR	4.6	NR	145	NR	NR	3	NR	1067
8/18/2009	117	249	6.3	NR	NR	3.3	114	NR	0.8	4.9	32.4	NR	NR	NR	1.9	NR	NR	16	NR	8	NR	94
8/19/2009	119	271	9.0	1.4	NR	4.1	106	0.7	NR	2.9	85.8	NR	NR	NR	1.6	NR	25	NR	NR	NR	NR	257
8/20/2009	89	121	3.7	NR	NR	2.4	55	NR	NR	2.0	2.9	NR	0.9	NR	0.8	NR	NR	NR	NR	4	NR	4
8/21/2009	84	248	4.7	NR	NR	3.7	67	NR	NR	2.2	4.4	NR	1.1	NR	1.1	NR	NR	NR	NR	3	NR	2
8/22/2009	90	277	6.1	NR	NR	3.2	126	NR	NR	3.6	7.5	NR	NR	NR	21.5	NR	NR	NR	NR	NR	NR	70
8/23/2009	97	248	5.1	NR	NR	3.1	114	NR	NR	5.0	49.0	NR	NR	NR	2.0	NR	23	NR	NR	NR	NR	319
8/24/2009	101	667	8.2	3.5	NR	4.9	216	1.1	1.0	18.9	130.1	NR	NR	NR	5.0	NR	125	NR	NR	5	NR	1556
8/25/2009	98	1256	11.7	0.9	0.9	4.4	198	1.3	3.0	14.2	102.8	NR	NR	NR	2.7	NR	65	NR	NR	NR	NR	959
8/26/2009	137	1428	17.8	1.8	1.0	7.3	269	2.0	1.4	13.1	258.5	NR	NR	1.3	2.9	NR	116	NR	NR	7	NR	1760
8/27/2009	124	882	20.5	1.1	1.1	10.0	282	0.7	1.2	10.7	864.5	NR	NR	NR	3.5	NR	138	NR	NR	NR	NR	2587
8/28/2009	79	262	6.1	NR	NR	2.2	75	NR	NR	2.1	8.8	NR	NR	NR	1.4	NR	NR	16	NR	NR	1.7	7
8/29/2009	112	344	6.4	NR	NR	3.6	89	NR	NR	2.5	6.2	NR	2.0	NR	2.4	NR	NR	NR	NR	5	NR	NR
8/30/2009	65	296	5.2	NR	NR	3.1	88	NR	NR	3.8	7.8	NR	0.8	NR	1.8	NR	NR	NR	NR	3	NR	5
8/31/2009	75	545	7.3	NR	NR	3.6	135	0.8	NR	3.6	11.6	NR	1.6	NR	3.5	NR	NR	NR	NR	NR	NR	6
9/1/2009	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

NA – Not available – sampler was not operating; NR – Not Recorded – concentration is below the limit of quantitation

Table 7. CES Xact Daily Average Concentrations (ng/m³)

Date	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br	Ag	Cd	Sn	Sb	Ba	Hg	Tl	Pb
8/8/2009	276	989	33.6	3.8	5.3	11.1	419	3.6	3.5	16.9	73.8	0.4	0.3	0.8	3.7	10.5	205	133	40	27	NR	NR	1064
8/9/2009	164	406	26.8	1.8	1.8	6.2	259	NR	0.9	3.1	18.2	NR	0.4	0.9	2.9	NR	20	NR	NR	10	NR	NR	123
8/10/2009	149	562	13.7	1.2	2.2	5.8	203	NR	1.0	4.1	24.0	NR	0.6	0.4	2.2	NR	27	34	8	22	NR	NR	134
8/11/2009	136	501	7.6	NR	4.6	4.4	138	NR	3.1	8.7	18.0	NR	1.4	0.6	3.0	NR	NR	33	9	11	NR	NR	54
8/12/2009	144	880	9.9	NR	3.6	7.7	298	0.7	2.5	7.3	33.5	NR	1.2	0.8	4.1	NR	16	31	9	17	NR	NR	44
8/13/2009	165	905	11.0	1.4	3.3	5.7	242	1.4	2.9	13.3	91.6	0.3	0.9	0.9	7.4	NR	43	36	26	21	NR	NR	347
8/14/2009	228	1759	14.8	4.5	5.3	8.9	326	3.4	5.8	35.7	251.9	0.7	0.6	1.0	6.4	7.7	191	65	59	30	NR	NR	1168
8/15/2009	248	1175	20.7	4.7	4.4	10.1	329	2.7	3.2	16.7	109.1	0.7	0.5	0.8	3.8	6.8	154	56	45	23	NR	NR	1017
8/16/2009	351	804	11.8	8.6	6.7	9.6	230	4.6	4.9	18.5	224.8	1.7	NR	0.3	5.9	10.6	467	133	85	33	NR	NR	2197
8/17/2009	262	557	13.2	4.2	4.2	7.0	194	2.4	3.0	8.7	211.1	0.8	0.4	0.5	3.0	NR	224	72	42	20	NR	NR	1094
8/18/2009	138	276	7.3	NR	2.6	3.2	132	NR	1.3	5.6	35.4	NR	1.3	1.1	2.5	NR	16	37	12	15	NR	NR	97
8/19/2009	157	320	9.0	2.1	2.1	4.7	132	1.0	1.2	4.0	116.9	0.3	0.4	0.5	2.1	NR	44	32	17	12	NR	NR	321
8/20/2009	107	140	3.5	NR	NR	2.0	68	NR	NR	2.6	5.0	NR	0.6	NR	1.2	NR	NR	29	NR	7	NR	NR	6
8/21/2009	103	329	4.7	NR	NR	3.7	93	NR	0.6	2.6	5.6	NR	0.8	0.4	0.7	NR	NR	NR	NR	7	NR	NR	6
8/22/2009	112	298	6.2	NR	NR	3.1	143	NR	NR	4.1	8.4	NR	0.7	0.2	31.9	NR	NR	36	10	9	NR	NR	81
8/23/2009	130	281	2.8	NR	1.8	3.3	137	1.0	1.2	6.6	60.9	0.3	2.3	0.4	3.0	NR	51	36	19	12	NR	NR	385
8/24/2009	218	758	5.0	5.3	5.8	6.6	261	4.0	4.4	24.0	149.7	1.2	0.4	0.3	3.5	9.5	286	133	74	32	NR	NR	1752
8/25/2009	178	1425	9.2	3.4	4.5	7.0	242	3.0	5.5	18.9	120.2	0.7	0.3	0.8	2.4	NR	128	61	63	23	NR	NR	1073
8/26/2009	244	1514	15.9	4.7	6.3	10.3	300	4.0	4.5	15.1	270.3	1.2	0.7	1.1	2.5	16.5	321	177	90	35	NR	NR	1773
8/27/2009	286	1018	16.9	5.9	9.4	13.7	352	6.7	6.6	15.0	959.4	2.5	1.8	1.5	2.9	68.7	723	411	108	50	NR	NR	2752
8/28/2009	87	276	5.0	NR	NR	2.2	83	NR	NR	2.3	10.6	NR	0.7	0.6	1.8	NR	NR	NR	7	5	NR	NR	8
8/29/2009	131	409	6.9	NR	NR	4.3	113	NR	NR	2.9	7.2	NR	0.9	0.9	2.0	NR	NR	22	13	8	NR	NR	5
8/30/2009	80	333	5.6	NR	NR	2.2	109	NR	NR	3.8	9.5	NR	1.1	0.5	1.9	NR	NR	NR	9	7	NR	NR	7
8/31/2009	82	572	5.4	NR	NR	3.4	147	NR	NR	4.0	13.8	NR	1.3	0.6	4.9	NR	NR	21	19	8	NR	NR	10
9/1/2009	94	737	7.1	1.0	4.4	6.6	242	0.9	3.4	9.7	51.1	NR	1.6	0.8	4.7	NR	20	32	30	17	NR	NR	113

NR – Not Recorded – concentration is below the limit of quantitation

Table 8. Missouri Xact Daily Average Concentrations (ng/m³)

Date	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br	Ag	Cd	Sn	Sb	Ba	Hg	Tl	Pb
8/8/2009	280	933	32.7	4.4	6.0	11.2	405	3.8	4.0	16.7	71.0	0.5	0.3	0.8	3.6	13.2	190	161	53	31	NR	NR	1054
8/9/2009	178	404	26.8	2.5	2.9	6.9	259	0.8	1.0	3.7	18.5	0.3	0.4	0.9	2.9	NR	22	57	20	17	NR	NR	128
8/10/2009	158	543	13.5	1.7	2.8	6.0	198	0.7	1.1	4.0	23.1	NR	0.5	0.4	2.1	NR	31	67	19	26	NR	NR	133
8/11/2009	144	480	7.3	NR	5.1	4.6	132	NR	3.2	8.6	17.0	NR	1.5	0.6	2.7	NR	15	78	17	14	NR	NR	53
8/12/2009	154	856	9.6	1.6	4.4	7.9	292	0.7	2.5	7.6	32.0	NR	1.1	0.8	3.9	NR	18	64	19	20	NR	NR	44
8/13/2009	172	861	11.1	2.0	4.0	6.0	237	1.5	2.8	13.4	88.9	0.4	0.9	0.9	7.1	NR	43	64	34	24	NR	NR	350
8/14/2009	237	1710	14.6	5.4	6.5	9.5	329	3.8	6.4	36.7	255.3	0.9	0.8	0.9	6.1	11.6	196	121	69	35	NR	NR	1200
8/15/2009	258	1145	20.8	5.6	5.7	10.9	329	3.0	3.6	17.5	108.5	0.9	0.5	0.9	3.8	9.5	152	102	55	29	NR	NR	1030
8/16/2009	343	782	12.6	9.1	7.4	10.0	231	4.9	5.2	18.4	214.8	1.8	NR	0.4	5.9	13.4	445	158	88	37	NR	NR	2173
8/17/2009	270	568	13.8	5.0	5.5	7.8	202	2.9	4.0	9.8	215.4	0.9	0.5	0.6	3.1	9.8	227	120	52	26	NR	NR	1130
8/18/2009	147	268	7.4	1.1	3.2	3.5	131	NR	1.4	5.9	36.4	NR	1.4	1.1	2.3	NR	21	80	16	17	NR	NR	105
8/19/2009	168	315	8.9	2.7	2.9	5.1	130	1.1	1.3	4.3	111.4	0.3	0.5	0.5	2.1	NR	46	70	22	15	NR	NR	324
8/20/2009	112	135	3.3	NR	NR	2.3	67	NR	NR	2.6	3.8	NR	0.5	NR	1.2	NR	NR	56	10	10	NR	NR	5
8/21/2009	117	332	4.3	NR	NR	4.0	90	NR	NR	3.1	6.2	NR	1.1	0.3	0.5	NR	11	73	11	11	NR	NR	8
8/22/2009	122	301	6.4	NR	2.0	3.6	141	NR	0.5	4.2	8.5	NR	1.1	0.2	30.2	NR	12	70	15	12	NR	NR	82
8/23/2009	139	279	3.0	1.2	2.7	3.8	137	1.2	1.4	7.0	59.8	0.3	2.5	0.4	2.9	NR	53	78	25	15	NR	NR	388
8/24/2009	234	758	5.7	6.1	6.6	7.2	258	4.1	4.7	24.0	146.8	1.6	0.4	0.2	3.3	11.5	263	156	74	36	NR	NR	1729
8/25/2009	189	1425	9.9	4.1	5.5	7.6	246	3.3	6.1	20.2	121.5	1.1	0.3	0.7	2.3	8.6	127	93	59	28	NR	NR	1105
8/26/2009	256	1486	16.6	5.5	7.7	10.8	298	4.3	5.1	16.1	265.4	1.8	0.6	1.0	2.4	18.2	292	199	84	41	NR	NR	1788
8/27/2009	296	1022	17.9	7.0	11.2	14.8	360	7.3	7.4	16.8	918.2	2.6	2.2	1.5	2.7	67.6	685	436	112	58	NR	NR	2771
8/28/2009	98	276	4.9	NR	NR	2.6	82	NR	0.5	3.0	10.4	NR	1.0	0.6	1.8	NR	10	68	12	10	NR	NR	7
8/29/2009	143	419	7.5	NR	NR	5.0	114	NR	NR	3.3	6.9	NR	1.1	0.9	1.9	NR	10	65	14	12	NR	NR	4
8/30/2009	93	330	5.8	NR	NR	2.8	109	NR	NR	4.5	9.3	NR	1.4	0.5	1.6	NR	10	70	13	12	NR	NR	7
8/31/2009	95	584	5.9	1.1	2.0	3.8	147	NR	NR	4.6	13.5	NR	1.2	0.6	4.6	NR	10	54	15	12	NR	NR	11
9/1/2009	109	767	7.7	1.6	5.4	7.2	242	0.9	3.6	10.4	51.0	NR	1.5	0.8	4.4	NR	22	63	23	21	NR	NR	121

NR – Not Recorded – concentration is below the limit of quantitation

4.3. Precision

4.3.1. Xact and FRM Percent Difference

Average percent difference of all data greater than the level of quantitation was used as a general indicator of precision. The average percent difference was calculated using Equation 10.

$$\bar{P} = \sum_1^n P_i = \sum_1^n \left| \frac{C_i^1 - C_i^2}{(C_i^1 + C_i^2)/2} \right| \quad \text{Equation 10}$$

Where:

- \bar{P} = Average percent difference
- P_i = The percent difference for the i^{th} element
- C_i^1 = The concentration of the i^{th} element as reported by the first Xact or the first FRM sampler
- C_i^2 = The concentration of the i^{th} element as reported by the second Xact or the second FRM sampler

Table 9 summarizes the calculated precisions for each element. The percent difference for the Xact was calculated for each hourly data point as well as for the daily average. Concentrations below the limit of quantitation for either method were not included in the calculation. In general the precision of the two methods is fairly comparable. The Xact's daily average is somewhat more precise than the FRM/IO3.3 method, and the hourly average is about as precise as the 24 hour integrated FRM/IO3.3 method. It is important to note that the Xact numbers represent the precision of two different samplers and two different analyzers while the FRM/IO3.3 numbers represent the precision of two different samplers and one analyzer.

It also needs to be emphasized that this precision indicator is strongly influenced by the concentration of the elements in the specific airshed. As such it is an indicator of precision that can be expected when using the specified sampling and analysis procedure in this specific airshed. However, it is not a good indicator of the potential method precision that can be expected at higher concentrations such as those at or above fugitive source emission limits.

Table 9. Xact and FRM Percent Difference Indicator of Precision

Element	Xact				FRM Daily Average Precision	
	Hourly		Daily Average			
	N	% Difference	N	% Difference	N	% Difference
K	605	9.3%	25	7.2%	21	5.3%
Ca	605	5.9%	25	2.2%	21	5.0%
Ti	526	10.6%	25	4.5%	21	12.1%
V	307	25.4%	14	21.9%	8	24.2%
Cr	304	22.1%	18	22.0%	2	36.0%
Mn	599	11.4%	25	9.0%	21	14.5%
Fe	605	5.0%	25	1.5%	21	5.0%
Co	188	13.2%	14	9.6%	9	25.6%
Ni	351	19.6%	18	10.0%	11	20.7%
Cu	605	13.6%	25	7.4%	21	8.8%
Zn	605	7.9%	25	3.9%	21	5.7%
Ga	156	28.3%	12	22.0%	0	NR
As	314	32.4%	24	14.7%	4	23.5%
Se	426	16.8%	24	7.1%	2	37.6%
Br	593	13.0%	25	5.8%	20	13.6%
Ag	76	20.5%	7	21.4%	0	NR
Cd	335	14.9%	17	7.5%	9	5.7%
Sn	418	55.8%	21	55.0%	0	NR
Sb	462	33.2%	22	28.1%	0	NR
Ba	541	27.1%	25	26.7%	10	34.2%
Hg	18	19.2%	0	NR	0	NR
Tl	0	NR	0	NR	0	NR
Pb	587	20.2%	25	4.7%	20	10.4%

4.3.2. Xact Linearity

Linearity can also be a useful indicator of precision. Figures 3 through 6 are plots of the reported Missouri Xact concentration for calcium (Ca), iron (Fe), copper (Cu), and lead (Pb) versus the reported CES Xact concentration for the same elements. These points were fit using linear least squares regression – a slope and an R^2 value close to one indicate good precision. In general, the slopes of linear least squares regression fits are dominated by the high concentration values. The average percent difference in contrast, is more likely to be driven by the more numerous lower concentration data points. As might be expected, given the greater importance of high concentration values, the linear slope data indicates significantly better precision than average percent difference. For lead, the slope of a line containing all the data points is 0.99 indicating about a 1% difference between the two Xacts. The average percent difference for lead from the same data set is 20.2%. However, it is important to note that these higher concentration data points for which this precision indicator is more representative can dominate average lead concentration over a regulated period. For example, the highest one-hour lead concentration illustrated in Figure 6, when averaged over a month, represents 40% of the new monthly average NAAQS lead standard of $0.15 \mu\text{g}/\text{m}^3$.

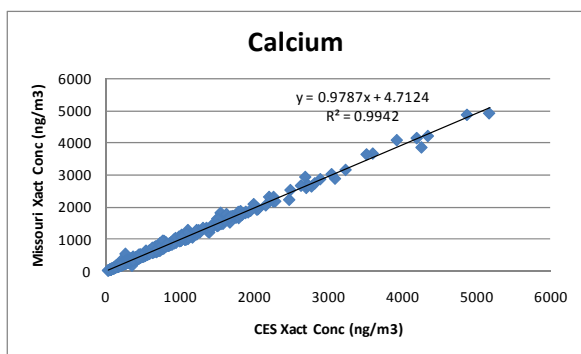


Figure 3. Xact Precision for Calcium

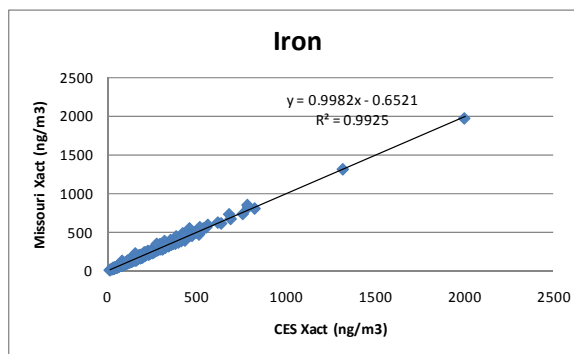


Figure 4. Xact Precision for Iron

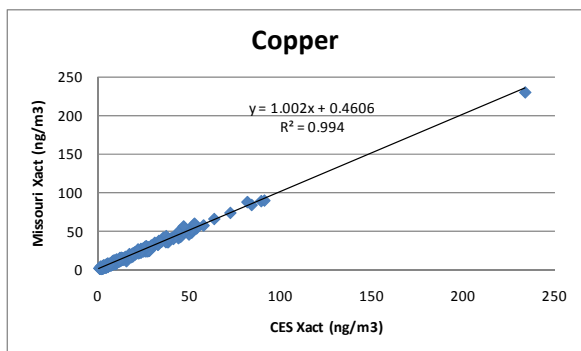


Figure 5. Xact Precision for Copper

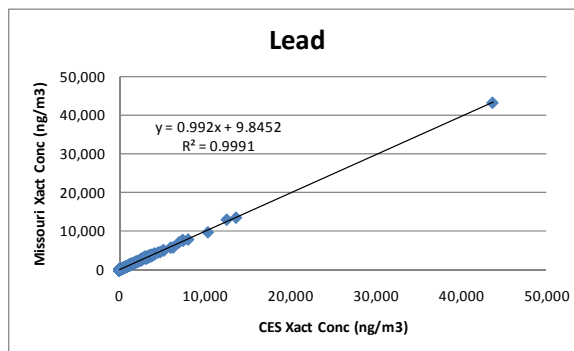


Figure 6. Xact Precision for Lead

4.3.3. Reference Method Linearity

Figures 7 through 10 are plots of the concentrations reported by the secondary FRM sampler versus those from the primary FRM/IO3.3 for calcium, iron, copper and lead. As is the case for the Xact, the slopes indicate a somewhat better precision than is indicated by the percent difference. For lead, the relative percent difference for the FRM/IO3.3 is 10.4% while the slope of the line is 0.97 indicating about a 3% difference for the two samplers.

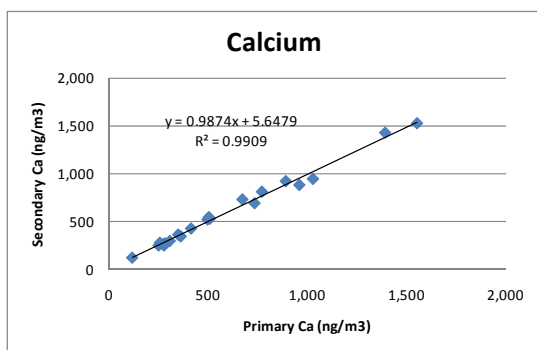


Figure 7. FRM/IO3.3 Calcium Precision

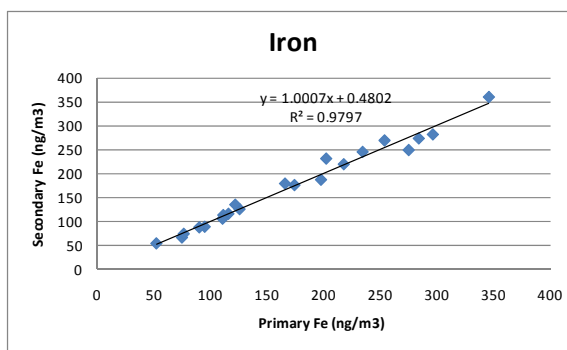


Figure 8. FRM/IO3.3 Iron Precision

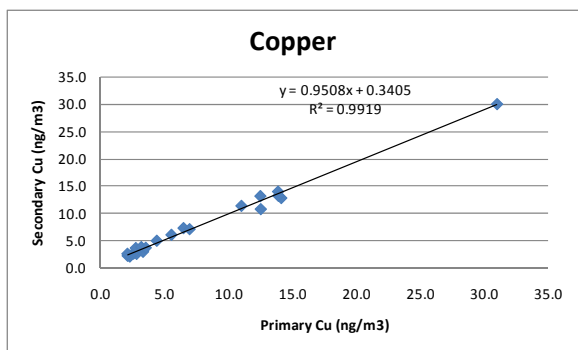


Figure 9. FRM/IO3.3 Copper Precision

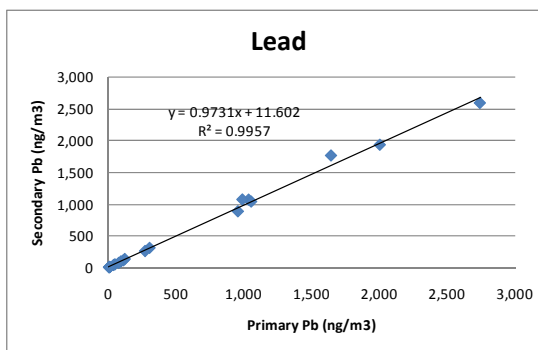


Figure 10. FRM/IO3.3 Lead Precision

4.4. Xact vs FRM/IO3.3 Linearity

Figures 11 to 16 show linear regression curves for several of the elements measured during field testing including calcium, titanium, iron, copper, zinc, and lead. These elements were present at relatively high concentrations and demonstrated good precision for both the Xact and FRM data. A slope of one for a linear regression curve would indicate perfect agreement between the Xact 620 and the federal reference method data. The slopes range from a low of 1.05 for titanium to a high of 1.21 for copper. With the exception of titanium, the Xact was biased high relative to the FRM/IO3.3.

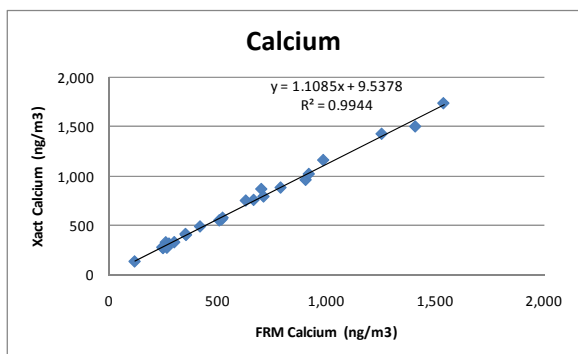


Figure 11. Xact vs FRM/IO3.3 for Ca

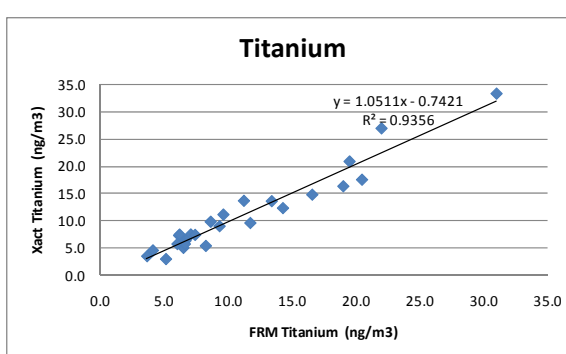


Figure 12. Xact vs FRM/IO3.3 for Ti

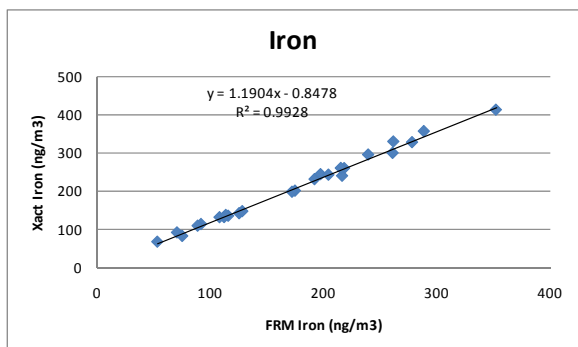


Figure 13. Xact vs. FRM/IO3.3 for Fe

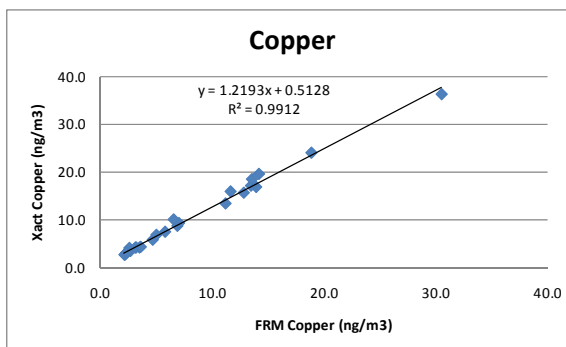


Figure 14. Xact vs FRM/IO3.3 for Cu

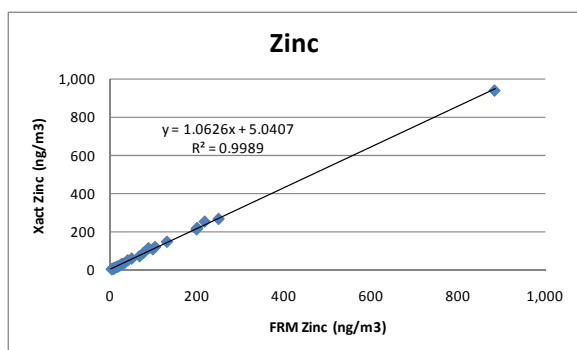


Figure 15. Xact vs FRM/IO3.3 for Zn

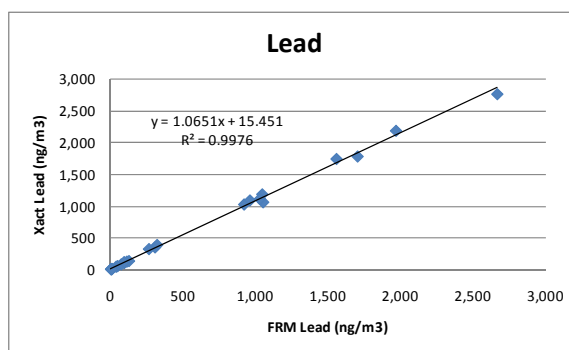


Figure 16. Xact vs. FRM/IO3.3 for Pb

4.5. Method 301 Comparison

4.5.1. Bias

Bias was calculated according to the procedures described in EPA Method 301, a method designed for comparing candidate stack testing methods with established reference methods at or near emission limits. The results of applying this Method 301 bias determination to our ambient data set can be found in Table 10. The Xact 620's bias relative to the federal reference method was found to be statistically significant for the following elements: K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Cd, Ba, and Pb. This bias was over 100% for V, Cr, Co, Ni, and Ba. However, the concentrations for these latter five elements are low relative to the analytical sensitivity of either method and the precisions are poor (See Table 9 in Section 4.3.1). In all fairness, Method 301 was designed to compare two sampling and analysis procedures on a stack when both methods are measuring concentrations near the required emission limits. It was not designed to compare two methods operating near the limits of quantitation.

Cadmium, however, is present at high enough concentration levels for fair comparisons of the two methods to be made. The precision data for both the FRM (RPD = 5.6%) and the Xact 620 (RPD = 7.8%) support this assertion. The observed cadmium bias was due to an XRF spectral phenomenon known as sum peaks. Essentially, the Xact used for this study was designed to minimize detection limits for monitoring at remote locations with low concentrations and was optimized to measure lead, mercury and arsenic. When high concentrations of lead are present, as they were in this study, they cause an interference with cadmium and the report of falsely high cadmium concentrations. This problem was well understood before the outset of this study and can easily be corrected in fence-line versions of the Xact by adding analysis conditions similar to those used for the XRF analysis of the FRM filters.

Even though the cadmium reported by the Xact was too high some of the cadmium is, in fact, real. The presence of cadmium was responsible for the problems with potassium bias (52% relative to the reference method). Cadmium L peaks interfere with the potassium K lines used for analysis on the Xact. The cadmium L lines were not included in the peak shape reference library used on either Xact. Again, this problem

can be alleviated by incorporating analysis conditions similar to those used for the analysis of the FRM filters on a fence line version of the Xact.

Calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), and lead (Pb) all exhibit statistically significant bias. All of these elements except lead have a bias of between 10 and 30% and would require a correction factor according to Method 301. Lead with a bias of 9% would not require a correction factor. Finally, there is no statistically significant bias between the Xact 620 and the FRM/IO3.3 for titanium. In this case the difference between the two methods was only 2%.

Table 10. Method 301 Bias

Element	N	Measured Mean		Difference in Means (ng/m ³)	SD of the Differences (ng/m ³)	T-stat	T-Stat at 95% Confidence Level	Statistically Significant?	M301 Bias (%)
		FRM/IO3.3 (ng/m ³)	Xact (ng/m ³)						
K	25	115.5	175.6	-60.2	53.6	5.61	2.06	YES	52%
Ca	25	608.4	684.0	-75.5	52.6	7.18	2.06	YES	12%
Ti	25	11.2	11.0	0.2	1.9	0.45	2.06	NO	2%
V	10	2.2	4.1	-2.9	1.1	7.99	2.23	YES	128%
Cr	4	1.9	4.8	-2.8	1.0	5.74	2.78	YES	143%
Mn	25	5.2	6.4	-1.2	1.5	3.98	2.06	YES	23%
Fe	25	174.7	207.1	-32.4	17.1	9.47	2.06	YES	19%
Co	10	1.2	2.9	-1.8	1.2	4.89	2.23	YES	150%
Ni	14	1.8	3.4	-2.3	1.6	5.21	2.14	YES	123%
Cu	25	8.1	10.4	-2.3	1.7	6.79	2.06	YES	28%
Zn	25	102.4	113.9	-11.5	12.8	4.46	2.06	YES	11%
Ga	0	NR	1.0	NR	NR	NR	NR	NO	NR
As	4	1.4	0.9	0.3	0.7	1.02	2.78	NO	24%
Se	2	0.9	0.7	-0.1	0.0	2.23	4.30	NO	7%
Br	24	3.9	4.3	-0.6	2.3	1.18	2.06	NO	14%
Ag	0	NR	19.7	NR	NR	NR	NR	NO	NR
Cd	12	99.2	169.7	-132.3	148.2	3.09	2.18	YES	133%
Sn	0	NR	94.6	NR	NR	NR	NR	NO	NR
Sb	0	NR	38.4	NR	NR	NR	NR	NO	NR
Ba	12	7.5	20.6	-10.0	7.6	4.59	2.18	YES	134%
Hg	0	NR	NR	NR	NR	NR	NR	NO	NR
Tl	0	NR	NR	NR	NR	NR	NR	NO	NR
Pb	24	598.7	627.7	-54.9	62.9	4.27	2.06	YES	9%

4.5.2. Precision

Method 301 requires that the alternative method be at least as precise as the reference method as determined by an F-test (see section 2.1). The results of the F-test are presented in Table 11. According to this criterion, the Xact is at least as precise as the reference method for every element except potassium (K), chromium (Cr), cadmium (Cd), and barium (Ba). The precision problems with cadmium and potassium are likely due to the sum peak issues discussed in Section 4.5.1. For chromium there are only four reference method samples above the limit of quantitation, so the imprecision of the Xact 620 relative to the reference method may very well be a statistical anomaly. Finally, for barium at least some of the imprecision of the Xact 620 relative to the FRM/IO 3.3 may be due to the fact that barium is one of the few elements where the Xact one hour limit of quantitation is worse than that for FRM IO/3.3 (see Table 4).

Table 11. M301 Precision

Element	F-Test Critical Value	F	Is the Xact At Least As Precise as the FRM
K	2.05	4.18	NO
Ca	2.05	0.17	YES
Ti	2.05	0.01	YES
V	3.24	1.72	YES
Cr	19.4	43.70	NO
Mn	2.05	0.24	YES
Fe	2.05	0.02	YES
Co	3.03	0.18	YES
Ni	2.67	2.48	YES
Cu	2.05	1.18	YES
Zn	2.05	0.41	YES
Ga	NR	NR	NR
As	5.77	0.62	YES
Se	19.5	0.01	YES
Br	2.07	0.20	YES
Ag		NR	NR
Cd	2.97	35.37	NO
Sn		NR	NR
Sb		NR	NR
Ba	2.77	34.51	NO
Hg		NR	NR
Tl		NR	NR
Pb	2.07	0.01	YES

4.6. Lead FEM Comparison Results

The Xact 620 was also evaluated for precision and reliability using the procedures for achieving FEM status outlined in new lead NAAQS. The acceptable concentration range for data comparisons in this approach is a daily average of between 30% and 250% of the lead concentration standard or between 45 and 375 ng/m³. Nine days met these criteria during the 25 day testing period. For each of these dates, each FRM filter sample was analyzed three times and the analytical precision was calculated using Equation 10. The Xact precision on each of these days was also calculated by determining the percent difference between the two Xacts. The concentrations reported from each analysis and from the two Xacts along with the calculated precisions are found in Table 12. In general the Xact's inter-instrument (sampling and analysis) precision is better than the analytical precision obtained with the FRM sampler and EPA Method IO 3.3.

Table 12. Calculated Lead NAAQS Precision

Date	Primary FRM Conc (ng/m ³)			Secondary FRM Conc (ng/m ³)			CES Xact (ng/m ³)	Missouri Xact (ng/m ³)	Xact Precision	Primary FRM Precision	Secondary FRM Precision
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3					
8/9/2009	108	103	104	112	108	114	123	128	4.33%	5.27%	4.80%
8/10/2009	118	117	115	131	129	135	134	133	0.71%	2.80%	4.63%
8/11/2009	45	43	41	48	44	48	54	53	2.09%	8.66%	7.66%
8/13/2009	302	294	286	307	299	312	347	350	0.66%	5.32%	4.35%
8/18/2009	90	89	85	94	89	95	97	105	7.91%	5.21%	6.50%
8/19/2009	268	263	265	257	252	259	321	324	0.81%	2.02%	2.76%
8/22/2009	73	67	68	70	68	71	81	82	0.36%	9.31%	3.85%
8/23/2009	NA	NA	NA	319	310	318	385	388	0.80%	NA	2.75%
9/1/2009	91	89	90	NA	NA	NA	113	121	6.25%	2.50%	NA
AVERAGE									2.66%	5.14%	4.66%

Data from each Xact unit was compared with each of the three measurements of the primary and the secondary FRM samples using Equation 7. The result is six comparisons per reference method sampler. All six comparisons must be less than 20% to meet the NAAQS comparability criteria. Table 13 summarizes the comparability data, including the number of comparisons, meeting criteria and the average difference between the Xacts and each sampler. The Xact met the 20% criteria for all six points on only two of the nine days when compared with the primary sampler, but met on five of the nine days when compared with the secondary sampler. In general the results indicate that the Xact is biased by about 15 to 20% high over the NAAQS defined concentration range. That value, however, drops to about 7% for days on which the average concentration was greater than 1000 ng/m³, the days which contribute most heavily to lead concentrations in excess of the NAAQS standard.

Table 13. Lead NAAQS Comparability (Xact Versus Primary and Secondary FRM)

Date	No. Meeting Criteria		Average (%)		Met NAAQS Criteria?	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
8/9/2009	4	6	19.3	12.6	NO	YES
8/10/2009	6	6	14.9	1.5	YES	YES
8/11/2009	1	4	25.3	16.3	NO	NO
8/13/2009	4	6	18.6	14.0	NO	YES
8/18/2009	5	6	15.4	9.1	YES	YES
8/19/2009	1	0	21.6	26.0	NO	NO
8/22/2009	2	6	17.6	17.0	NO	YES
8/23/2009	NA	0	NA	22.5	NA	NO
9/1/2009	0	NA	29.7	NA	NO	NA

The two reference method samplers were also compared to each other using the same criteria for comparability as was used for the Xact 620 (see Table 14). Although the calculated percent difference never exceeded 20%, several measurement comparisons do approach and even exceed 15%. This level of comparability was achieved using the same analyzer for both units – if filters from the two samplers were analyzed using different instruments it is quite possible that the 20% criteria would also have been exceeded. The intercomparison of the two samplers highlights the fact that criteria for achieving FEM status for lead are written primarily for approving different analytical

techniques – not methods that include both sampling and analysis. In general the 20% criteria for comparability would be for different methods of analyzing the very same filter. If two different samplers are used, even the FRM itself may have difficulty meeting FEM criteria.

Table 14. Comparability of Results for Primary (P) and Secondary (S) FRM Samplers

P 1 vs S 1 (%)	P1 vs S2 (%)	P 1 vs S 3 (%)	P 2 vs S 1 (%)	P 2 vs S 2 (%)	P 2 vs S 3 (%)	P 3 vs S 1 (%)	P 3 vs S 2 (%)	P 3 vs S 3 (%)	Ave %
-3.19	0.06	-4.87	-8.75	-5.33	-10.52	-7.59	-4.21	-9.34	-5.97
-11.23	-9.49	-14.67	-12.46	-10.71	-15.94	-14.39	-12.61	-17.93	-13.27
-5.22	2.59	-5.27	-11.89	-3.59	-11.95	-14.67	-6.17	-14.74	-7.88
-1.78	1.07	-3.33	-4.55	-1.62	-6.14	-7.33	-4.33	-8.97	-4.11
-4.65	0.33	-6.40	-5.96	-0.92	-7.73	-10.27	-5.02	-12.11	-5.86
4.19	6.01	3.38	2.23	4.10	1.41	3.14	4.98	2.32	3.53
4.05	6.98	3.32	-5.24	-2.03	-6.05	-2.85	0.29	-3.64	-0.57
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

4.7 Review of Other Xact 620 Field Comparison Data

The Missouri-owned Xact 620 was used in the St. Louis, Missouri metropolitan area as part of a separate grant program prior to being used in our Herculanum field demonstration.⁸ This St. Louis program was a joint effort between the Missouri Department of Natural Resources and Dr. Jay Turner at Washington University in St. Louis. One component of this independent program was a series of comparisons between the Xact 620 measurements and results from collocated simultaneous FRM samples analyzed in the laboratory. Comparisons were made with two separate samplers and two independent analyses as indicated below:

- Medium volume FRM PM₁₀ samples analyzed by the US EPA XRF laboratory using EPA Method IO 3.3 (FRM/IO 3.3)⁹
- High volume FRM PM₁₀ samples analyzed by Washington University⁸ using ICP/MS based on EPA IO 3.5 methods (FRM/IO 3.5).

It needs to be emphasized in these comparisons that the Missouri Xact 620 used in this grant program and our Herculanum demonstration study was calibrated in December 2008 and was not recalibrated during either of these studies. As such, the Xact 620 results reported for the St. Louis and Herculanum studies are based on the same calibration performed months earlier.

Examples of the comparison results between the Xact 620 and the FRM/IO 3.3 method are illustrated in Figures 17 through 20. Figures 17 and 18 show comparisons of measured concentrations for titanium and lead which are generally well above detection limits for both methods. In these figures, the solid line represents a 1:1 ratio. As can be seen from these comparisons, the agreement of the best fit line (dashed) with the 1:1 solid line is quite good. The titanium best fit line has a slope of 1.05 while the slope of the best fit lead line is 1.02 at concentrations ranging from a few ng/m³ to about 20 ng/m³. On the other hand, there is no apparent correlation for elements like selenium

and arsenic whose concentrations ($<3 \text{ ng/m}^3$) are at or near the FRM/IO 3.3 method detection limits as illustrated with the scatter plots shown in Figures 19 and 20.

However, there is a strong correlation when these same Xact 620 arsenic and selenium results are compared to results from simultaneously collected high volume samples analyzed with laboratory ICP/MS methods (FRM/IO 3.5) as illustrated with the plots shown in Figures 21 and 22. In this case, both the Xact 620 and the FRM/IO 3.5 method measured concentrations are above the detection limits for both methods. These comparisons show good agreement with the 1:1 solid line down to a couple of tenths of a ng/m^3 . In addition, these comparisons represent data collected at two different monitoring sites; Blair Street (solid circles) and Arnold Street (open circles). These St. Louis comparisons are consistent with the Herculaneum results in general, and more specifically strongly supportive of the Xact 620 lead measurements. This independent St. Louis comparison with the FRM/IO 3.3 lead comparison showing a regression slope of 1.02 in the concentration range from a few ng/m^3 to about 20 ng/m^3 is consistent with the Herculaneum field study results showing a regression slope of 1.07 when compared to the FRM/IO 3.3 over a 24-hour concentration range that exceeded $2,500 \text{ ng/m}^3$ and individual hourly averages that exceeded $40,000 \text{ ng/m}^3$. These combined and independent results demonstrate excellent comparability over a lead concentration range spanning more than five orders of magnitude; i.e. tenths of ng/m^3 to over tens of thousands of ng/m^3 .

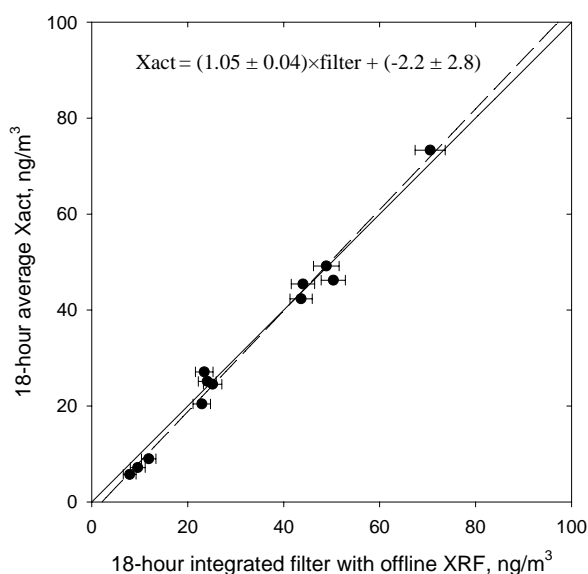


Figure 17. Xact vs. FRM Titanium

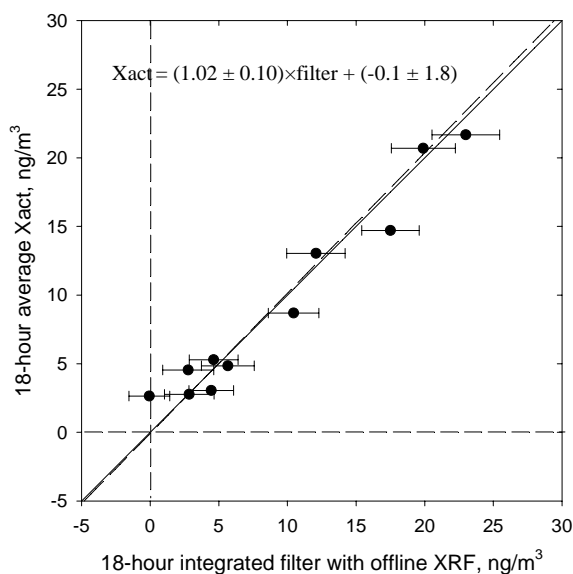


Figure 18. Xact vs. FRM Lead

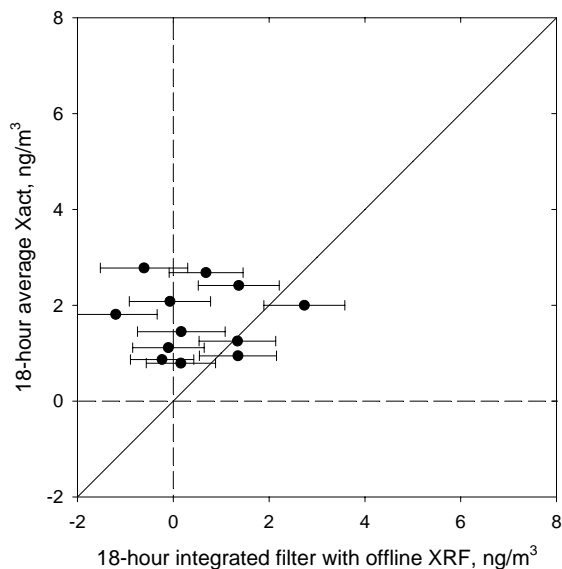


Figure 19. Selenium Low Volume PM₁₀ vs Xact 620

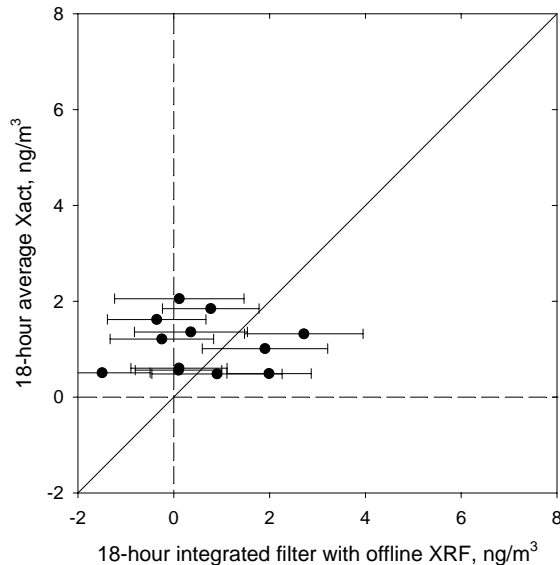


Figure 20. Arsenic Low Volume vs. Xact 620

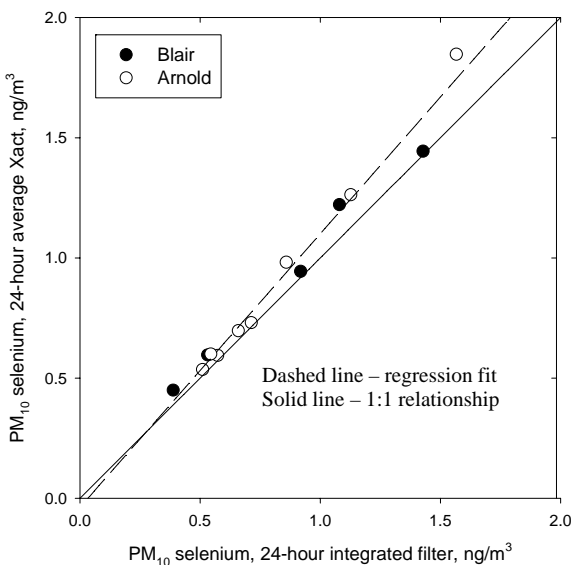


Figure 21. Selenium Xact vs High Volume With Lab ICP MS

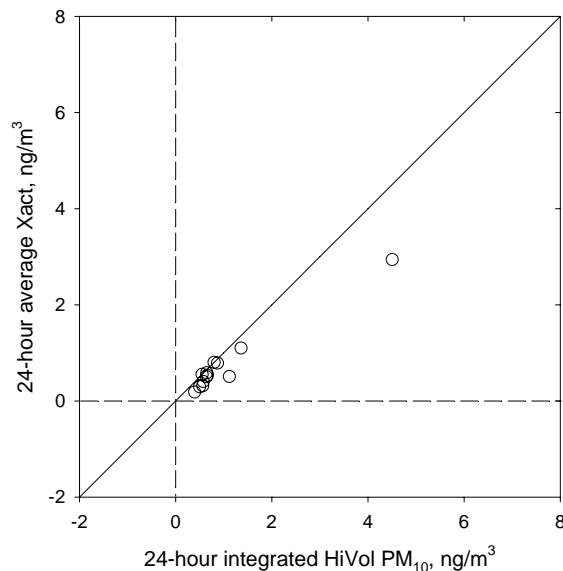


Figure 22. Arsenic: Xact vs. High With Lab ICP MS

4.8 Monitor Utility

The foundation of any candidate FLM is based on its precision, accuracy and comparability with reference methods as demonstrated and discussed in the preceding

sub-section. However, it must also be able to provide timely data required for estimating fugitive emissions and other possible FLM data applications. For example, the 24-hour FRM/IO 3.3 method typically integrates emissions from a wide range of wind directions and sources, the results of which become available weeks to months later. On the other hand, the Xact 620 with its significantly superior sensitivity (lower detection limits) integrates emissions from a well defined wind direction and speed over its 15 minute to 4 hour sampling interval and can provide results in near real time to regulators, plant personnel and the general public through the internet as demonstrated with the Missouri Xact 620. These unique capabilities give the Xact 620 the potential to meet the requirements of applications like FLM and quantifying fugitive emissions. In addition, these capabilities have the potential to improve analytical and source impact signal to noise ratios during periods of high concentrations that can represent significant portions of emission limits; as well as improve source apportionment and exposure modeling, and plant and airshed management.

5. Summary and Further Work

In general these field test data indicate the Xact 620 is more precise for most elements than the federal reference method followed by XRF analysis (FRM/IO3.3). This was true for precision as indicated by percent difference as calculated according to Method 301 and as calculated using the lead NAAQS rule. The Xact, however, seems to be somewhat biased relative to the FRMIO3.3. For elements, present at high enough concentrations to have good measurement precision when measured by both methods the Xact was biased by about 10% to 20% high relative to the reference method.

Further work should be done to understand the reason behind these differences. These include:

1. Potential errors in deposit area – Both the FRM/IO3.3 method and Xact incorporate the deposit area in the calculation of metal concentration. The Xact is much more likely to be impacted by this potential error since its deposit area is about a tenth of the deposit area of the FRM sampler. For the Xact a small change in the diameter measurement will translates into a larger systematic bias as a percent of the area.
2. FRM sample non-uniformity – Many of the FRM filters had a darkened ring around the outer edge of the filter. The X-ray fluorescence analysis used on these filters assumes a uniform deposit and deviations from this uniform deposit assumption may cause errors in the overall measurement.
3. XRF calibration differences – In general the uncertainty in the XRF calibration is on the order of plus or minus five percent. This would give a potential error range of about 10%.

CES will follow-up with the area measurements of the Xact deposits. Potential calibration errors will be checked by follow up analysis by XRF at the USEPA and further analysis by ICP-MS at Washington University. The ICP-MS data may also shed

light on the importance of sample uniformity. Also CES will spike both the Xact and the reference method sampler with the Quantitative Aerosol Generator. This comparison against a third standard may help identify how big an issue sample uniformity is and help assess if there are any other potential reasons for the observed bias.

In addition to the above tests to resolve the source of bias, further work on the project should focus on the following items:

- Develop protocol for using an FLM in a permitting and compliance demonstration application.
- Develop performance specifications for a FLM
- Develop on-going QA/QC procedures for a FLM
- Develop and demonstrate modeling protocol including automated differential data filtration using latest Herculanum, Mo database
- Demonstrate viability of a FLM-integrate modeling protocol

6. References

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10. Dr. Jay Turner, Washington University, School of Engineering and Applied Science, St. Louis, MO, 63130.

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