# Method 301 Evaluation of Candidate Conditional Methods

# X-Ray Based Filter Method (XFM) Multi-Metals Instrumental Analyzer Procedure (Xact-IAP) Quantitative Reference Aerosol Generator (QAG)

Prepared by:

**Cooper Environmental Services, LLC**
10180 SW Nimbus Blvd Suite J6
Portland, Oregon 97223

**Revision 1.0**
**June, 2005**

# Executive Summary

A new metal emissions measurement and validation system has recently been developed that has the potential to significantly improve our understanding of metal emissions from a wide range of source categories. This system consists of:

- A continuous emission monitoring system (Xact-CEMS)
- An instrumental analyzer procedure (Xact-IAP)
- A sampling and analysis measurement method (XFM)
- A NIST-traceable reference aerosol generator (QAG)

The measurement components of this system are based on collecting a representative sample of stack gas on a chemically reactive filter (solid sorbent) that traps both particulate and vapor phases of metals, followed by non-destructive X-ray fluorescence (XRF) analysis using procedures consistent with ambient measurements. This system is applicable to elements with atomic number ranging from 13 (Al) to 92 (U), and can measure Be after non-destructive XRF analysis if other analytical procedures are used; it can provide detection limits as low as 0.1 µg/dscm with 15 minute turn around times or lower detection limits with longer sampling and analysis times; and has demonstrated accuracies better than five percent and precisions better than three percent. These generation and measurement components are independently traceable to NIST: the QAG through procedural traceability and solution standards, while the measurement methods are analytically traceable through thin film standards and NIST standard reference materials.

A series of laboratory and field tests have been conducted to demonstrate that the QAG, XFM and Xact-IAP components of this new system meet Method 301 accuracy and precision requirements for conditional method status. Each of the methods met the performance criteria outlined in the Method 301 test plan. These criteria included the following:

- **Filter ratios** – percent of Cr and Pb trapped on the XFM front PTFE filter. Although this criterion is not required by Method 301, high percentages assure high particle trapping efficiency.
- **Metal ratios** - ratio of Pb-normalized solution concentration to Pb-normalized aerosol concentration. This criterion is also not required by Method 301[1] but ratios close to one assure high relative generation, transport and sampling efficiencies for all metals including vapors.
- **Efficiency** – percent of NIST-traceable reference aerosol concentration measured. A high percentage assures high absolute generation, transport and sampling efficiencies.
- **Bias correction factor** –ratio of reference to measured aerosol concentration. A value close to one indicates high method accuracy.
- **Precision** – percent relative standard deviation determined from sequential measurements. A low percent value indicates a highly precise and stable system.
- **Linearity** – correlation coefficient (r) based on a regression analysis of a plot of measured versus reference aerosol concentration.

These criteria and their acceptance values are based primarily on those in Method 301 and were defined in the 301 validation test plan (Appendix A). During these tests, five elements (As, Cd, Cr, Pb, and Hg) were spiked at concentrations ranging from blank to about 120 µg/dscm. All three (QAG, XFM, and Xact-IAP) independent approaches showed good agreement over this wide range of concentrations, and all three methods met the required criteria for all five metals. These results are summarized in the following three tables for the QAG reference aerosol generator, and the XFM and Xact-IAP measurement approaches. The Xact-IAP table includes results from all 192 Xact-IAP runs.

**Comparison of QAG laboratory results with criteria acceptance values.**

| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | >25 | Yes |
| Filter Ratio (% Front) | >98 | >99 | Yes |
| Metal Ratio (Sol./Aer.) | 0.9 - 1.1 | 0.95 - 1.01 | Yes[b] |
| Efficiency (%) | >80 | 94 - 100 | Yes |
| Precision (%) | <10 | <4 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]XFM and Xact results for all five elements

[b]Confirmed with independent ICP analysis results

**Comparison of XFM field test results with criteria acceptance values.**

| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | 26 | Yes |
| Bias Corr. Factor | 0.80 - 1.2 | 0.94 - 0.97 | Yes[b] |
| Precision (%) | <10 | <3 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]XFM results for all five elements

[b]Confirmed with independent ICP analysis results

**Comparison of Xact-IAP field test results with criteria acceptance values.**

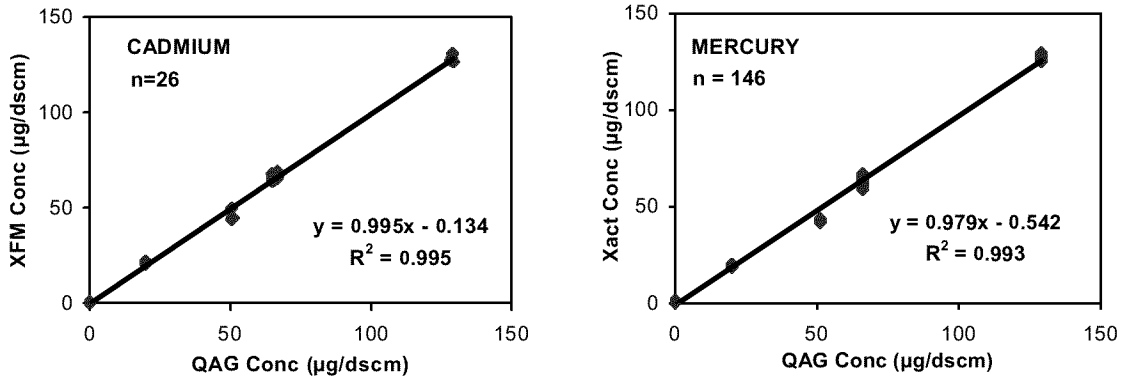
| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | 192 | Yes |
| Bias Corr. Factor | 0.80 - 1.2 | 1.00 - 1.14 | Yes |
| Precision (%) | <10 | <3 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]Xact-IAP results for all five elements

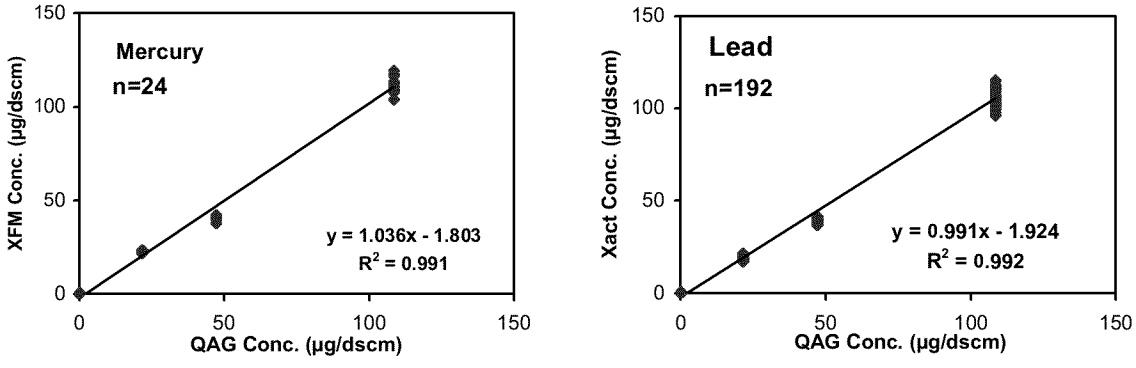
Many more test runs than required by Method 301 were conducted, and all of the data from these runs were included in this evaluation. The QAG and XFM tables shown below include results from all 26 XFM runs.

The filter and metal ratios listed for the QAG are high and indicate that the relative generation, transport and sampling efficiencies for all elements are within the experimental accuracy of 100%. The efficiency, precision and linearity values for the QAG are also all well within the acceptable range. In the case of the XFM and Xact-IAP measurement

methods, all of the criteria were met and the values were substantially within the acceptable range, which in the case of the bias and precision were more restrictive in our test plan than required by Method 301. The high correlation coefficients indicate highly linear methods. This high degree of linearity is illustrated with the following four representative plots of the XFM and Xact-IAP measured values versus the independent QAG reference aerosol concentration during laboratory and field tests at a hazardous waste incinerator.



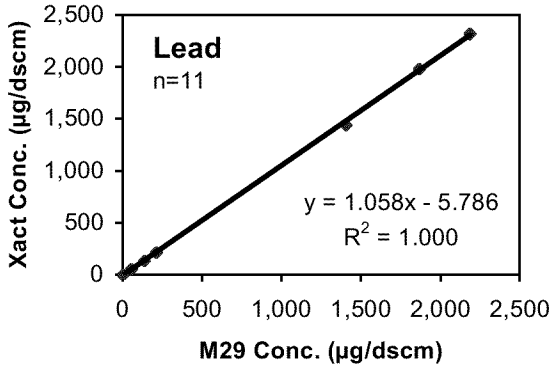

**Representative scatter plots of XFM and Xact-IAP measured concentrations versus QAG reference aerosol concentrations during laboratory validation tests of the QAG.**

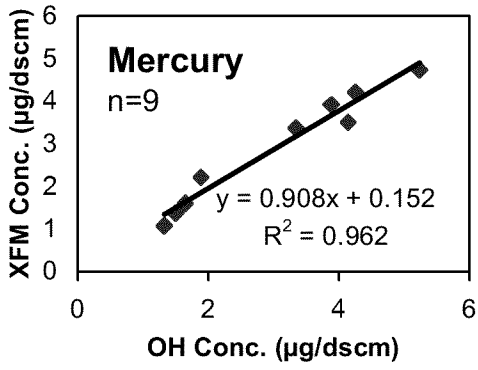



**Representative scatter plots of XFM and Xact-IAP measured concentrations versus QAG reference aerosol concentrations during field validation tests of the XFM and Xact-IAP.**

The XFM and Xact-IAP are rugged and robust methods that are applicable to a wide range of sources and elements. Because these methods include dilution sampling techniques, they are relatively insensitive to most stack gas characteristics (temperature, moisture, PM concentration, and chemistry) and can be optimized for specific stack conditions by adjusting dilution ratios, sampling times, etc... Their range of applicability has been demonstrated by results from these tests as well as other laboratory and field tests over the past five years including relative accuracy testing using both Method 29[2]and Ontario Hydro[3] reference methods. Examples of these field validation test results are illustrated with the following two figures. The plot of lead shows a strong linear relationship between the Xact and Method 29

results up to 2,200 µg/dscm and had a relative accuracy of 4%. The mercury plot shows a similar strong linear relationship between the XFM and Ontario Hydro reference method results at concentrations down to about 1 µg/dscm and had a relative accuracy of 11%.




**Examples of field validation test results at a munitions incinerator[4] (left) and at a coal-fired utility boiler with baghouse and $NO_x$ controls[5] (right).**

These tests have included wet and dry incinerators, and wet and dry coal-fired utility boilers covering a range of controls including electrostatic precipitators, scrubbers and $NO_x$ catalytic reduction controls. The XFM and Xact-IAP are also consistent with ambient measurement methods[6,7]and applicable to most of the elements typically measured in the ambient environment. Thus, the recommended range of source categories for which the XFM and Xact-IAP are applicable includes fugitive and ducted emissions such as those from hazardous, municipal, sewage and other incinerators; cement and lime kilns; smelters and mills; mineral processing, plating and boiler sources using control technologies such as bag house filtration, electrostatic precipitation, scrubbers and $NO_x$ controls.

Also, this technology offers the following additional advantages:

- Significantly shorter reporting times (As short as 15 minutes compared to 3 weeks)
- Precise (<3%), accurate (better than 5%), linear (r>0.99) and verifiable results due to non-destructive analysis
- Minimal operator requirements
- The methods are safe and easy to use and generate no hazardous waste.

The results from these tests as well as results from previous field tests support the following conclusions.

- The QAG candidate reference aerosol generator is independent of its application, met all of the required validation criteria, and should be approved as a NIST-traceable reference aerosol generator for compliance and other regulatory applications such as initial certification and continuing quality assurance audits of multi-metals CEMS as well as calibration and validation of metal measurement methods.

- The XFM and Xact-IAP candidate conditional methods for measuring metal concentrations in emissions from stationary sources met all of the required validation criteria; have demonstrated their applicability to a range of source types, controls and stack conditions; and should be approved for general compliance and other regulatory applications such as initial certification and continuing quality assurance audits of multi-metals CEMS, emission compliance audits, trial burns, and other regulatory applications where stack gas metal emission measurements from stationary sources are required.

# Table of Contents

**Executive Summary** ..... **i**
**Appendices** ..... **viii**
**List of Figures** ..... **ix**
**List of Abbreviations** ..... **xi**
**1.0 Introduction** ..... **1**
What is this report about? ..... 1
Why are we concerned about metal emissions? ..... 1
Why is the current metals measurement system inadequate? ..... 1
What is this new metals measurement system? ..... 2
What are these candidate conditional methods? ..... 2
Why are the XFM and Xact-IAP candidate methods more appropriate than Method 29?. 2
Why are these methods important to the EPA and other stakeholders? ..... 3
How was the performance of these methods evaluated? ..... 3
Where are the results presented in this report? ..... 3
**2.0 Approach** ..... **3**
2.1 Overview ..... 3
2.2 General Approach ..... 4
2.3 Method Independence ..... 5
2.4 QAG Validation (Phase I) ..... 7
2.5 XFM and Xact-IAP Validation (Phase II) ..... 11
2.6 Deviations from Test Plan ..... 12
**3.0 Methods** ..... **14**
3.1 QAG Reference Aerosol Generator ..... 14
3.2 XFM Candidate Conditional Method ..... 18
3.3 Xact Instrumental Analyzer Procedure ..... 21
**4.0 Calculations** ..... **24**
4.1 Overview ..... 24
4.2 List of Symbols and Terms ..... 24
4.3 QAG Reference Aerosol Concentration ..... 26
4.4 XFM Measured Aerosol Concentration ..... 27
4.5 Xact-IAP Measured Aerosol Concentration ..... 28

4.6 Validation Comparison Parameters ..... 28
4.7 Other Comparison Parameters ..... 33
**5.0 Quality Control and Assurance ..... 35**
5.1 Overview ..... 35
5.2 QAG ..... 35
5.3 XFM ..... 37
5.4 Xact-IAP ..... 38
**6.0 Results and Discussion ..... 40**
6.1 Overview ..... 40
6.2 QAG Validation ..... 40
6.3 XFM and Xact-IAP Validation Overview ..... 48
6.4 XFM Validation ..... 50
6.5 Xact-IAP Validation ..... 52
**7.0 Range of Method Application ..... 55**
7.1 Overview ..... 55
7.2 Criteria for Candidate Method Applicability ..... 56
7.3 Key Sampling and Analysis Features ..... 56
7.4 Key Emission Characteristics ..... 57
7.5 Filter Trapping Efficiency for Vapor Phase Metals ..... 58
7.6 Applicable Concentration Range ..... 62
7.7 Deposit Stability ..... 62
7.8 Moisture ..... 63
7.9 Holding Times ..... 64
7.10 Applicable Elements ..... 65
7.11 Other Related Tests ..... 65
7.12 Applicable Source Categories ..... 66
**8.0 Conclusions and Recommendations ..... 67**
**9.0 Glossary ..... 68**
**10.0 References ..... 73**

# Appendices


**Appendix A:** Draft Test Plan for Validating a Reference Procedure for Measuring the Concentration of Metals in Eli Lilly and Company's Hazardous Waste Incinerator Stack Gas

**Appendix B:** Determination of Metal Emissions from Stationary Sources Using Filters and Solid Sorbents with X-Ray Fluorescence Analysis

**Appendix C:** Standard Operating Procedure for Generating a Quantitative Multi-Metals Reference Aerosol with the CES QAG

**Appendix D:** Determination of Metal Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)

**Appendix E:** Performance Specifications for a Quantitative Reference Aerosol Generator

**Appendix F:** Specifications and Test Procedure for X-Ray Fluorescence Based Multi-Metals Continuous Emissions Monitoring Systems at Stationary Sources

Quality Assurance Requirements for X-Ray Fluorescence Based Multi-Metals Continuous Emissions Monitoring Systems at Stationary Sources

**Appendix G:** QA Information during Phase I

**Appendix H:** QA Information during Phase II

**Appendix I:** Phase I Test Data

**Appendix J:** Phase II Test Data

**Appendix K** Calculations Used for Method 301 Validation Tests

**Appendix L:** Additional Data in Support of Service and Range Extension of Candidate Methods

**Appendix M:** Related Reports Produced by Cooper Environmental Services

# List of Figures

Figure 1: Schematic flow diagram illustrating key aspects of the general validation procedure..... 5

Figure 2: Schematic representation of key components of CES' reference aerosol generation system. ..... 6

Figure 3: Flow diagram showing the experimental arrangement used to validate the QAG reference aerosol generator. ..... 8

Figure 4: Schematic representation of the experimental arrangement used in Phase I to validate the QAG reference aerosol generator. ..... 9

Figure 5: A. Schematic of flow through QAG components. B. Overview of the set-up of QAG components..... 15

Figure 6: Schematic flow diagram of the sampling train used in Phase I and II XFM validation tests. ..... 19

Figure 7: Photograph of the assembled port adaptor, extraction assembly and filter holder.. 19

Figure 8: Exploded schematic view of XFM filter holder with filter cassette..... 21

Figure 9: Overview of Xact-IAP components and flow schematic. ..... 23

Figure 10: QAG solution mass loss rate during Phase I testing. ..... 36

Figure 11: QAG solution mass loss rate during Phase II. ..... 37

Figure 12: QAG-generated and XFM- and Xact-IAP-measured aerosol concentrations during Phase I tests..... 41

Figure 13: Ratio of XFM and Xact-IAP measured metal concentrations to the QAG reference aerosol concentration. ..... 42

Figure 14: Phase I QAG linearity plots as determined by the XFM..... 46

Figure 15: Phase I QAG linearity plots as determined with the Xact-IAP ..... 47

Figure 16: Comparison of the XFM and Xact-IAP measured concentrations with the QAG-spiked flue gas concentrations during Phase II testing. ..... 49

Figure 17: Phase II XFM linearity. ..... 51

Figure 18: Phase II Xact linearity. ..... 54

Figure 19. Comparison of Hg concentrations determined by XFM and Ontario Hydro reference method at a coal-fired power plant. ..... 60

Figure 20 Plot of Xact-IAP concentration versus Reference Method 29 measured concentrations showing excellent agreement over two orders of magnitude and at concentrations in excess of 2,000 µg/dscm. ..... 62

Figure 21. Plot of Pb concentrations determined by Reference Method 29 and the Xact..... 63

Figure 22: Comparison of results from laboratory XRF analysis in July, 2002 with Xact field test results from May 2002 relative accuracy tests at a hazardous waste incinerator..... 63

# List of Tables

Table 1: Overview of Phase I validation test schedule. ..... 10
Table 2: Acceptance criteria for QAG. ..... 11
Table 3: Overview of Phase II validation test schedule. ..... 12
Table 4: Acceptance criteria for Phase II validation of the XFM and Xact-IAP. ..... 12
Table 5: Comparison of surrogate and Phase II flue gas characteristics. ..... 14
Table 6: QAG Emission Rates for Phase I and II. ..... 36
Table 7: Flowmeter evaluation during Phase I. ..... 38
Table 8: Flowmeter evaluation during Phase II. ..... 38
Table 9: Upscale and zero drift during Phase I testing. ..... 39
Table 10: Evaluation of NIST thin-film standards by the Xact-IAP. ..... 39
Table 11: Upscale and zero drift during Phase II testing. ..... 40
Table 12: Comparison of Average QAG reference aerosol concentrations with XFM and Xact-IAP average measured concentrations (µg/dscm). ..... 42
Table 13: Lead and chromium measured on the upstream PTFE filter as percent of total XFM lead and chromium (µg/filter). ..... 43
Table 14: QAG efficiencies determined during Phase I laboratory tests (%). ..... 45
Table 15: Summary of QAG Phase I precision (%). ..... 45
Table 16 Summary of Phase I QAG validation results. ..... 47
Table 17: Summary of XFM and Xact-IAP measured concentrations and QAG-spiked flue gas concentrations Phase II (µg/dscm). ..... 49
Table 18: Summary of XFM Phase II bias values for each metal tested (µg/dscm). ..... 50
Table 19: Summary of Phase II XFM validation test criteria and results. ..... 51
Table 20: Comparison of Xact-IAP with QAG reference concentrations and bias (µg/dscm). ..... 53
Table 21: Summary of Phase II Xact results. ..... 54
Table 22: Comparison of Xact Phase II results with proposed PS-10 criteria. ..... 55
Table 23. List of stack conditions for which Xact-IAP and XFM tests have been conducted 58
Table 24. List of test conditions and references used to evaluate method applicability. ..... 61
Table 25: Recent tests of Xact and XFM on wet and dry stacks. ..... 64
Table 26: Xact detection limits determined at Lilly's T149 incinerator ..... 66

# List of Abbreviations

| | |
|---|---|
| µg/m³ | Micro-grams per cubic meter |
| As | Arsenic |
| Cd | Cadmium |
| CEMS | Continuous Emissions Monitoring System |
| CES | Cooper Environmental Services LLC of Portland, OR |
| CFPP | Coal Fired Power Plant. |
| CFR | Code of Federal Regulations. |
| Cr | Chromium |
| DAS | Data Acquisition System |
| DQO | Data Quality Objectives |
| DSCM | Dry Standard Cubic Meters |
| DSLP | Dry Standard Liters Per Minute |
| EPA | United States Environmental Protection Agency |
| Hg | Mercury |
| HWC | Hazardous Waste Combustor |
| IAAP | Iowa Army Ammunition Plant |
| IAP | Instrumental analyzer procedure |
| LVM | Low Volatile Metals (arsenic, beryllium, chromium) |
| M29 | EPA Reference Method 29 |
| M301 | EPA Reference Method 301 |
| MACT | Maximum Achievable Control Technology |
| MFC | Mass Flow Controller |
| MFM | Mass Flow Meter |
| MM-CEM | Multi-metal Continuous Emission Monitor |
| MRI | Midwest Research Institute, Kansas City, MO |
| Pb | Lead |
| PS10 | EPA's proposed Performance Standard 10 for multi-metal CEMS |
| QA | Quality Assurance |
| QAG | Quantitative Aerosol Generator |
| QC | Quality Control |
| RA | Relative Accuracy |

| | |
|---|---|
| RSD | Relative Standard Deviation (% RSD equals precision) |
| slpm | Standard Liters Per Minute |
| SVM | Semi-volatile metals (cadmium, lead) |
| TEAD | Tooele Army Depot |
| USACERL | U.S. Army Construction Engineering Research Library |
| VM | Volatile Metals (mercury) |
| XCEM | X-ray based Continuous Emission Monitor |
| XFM | X-ray based Filter Method |
| XRF | X-Ray Fluorescence |
| Zn | Zinc |

# 1.0 Introduction

*What is this report about?*

This report describes a new multi-metals measurement and validation system. It also presents the results of tests demonstrating that each of the system components meet the U. S. Environmental Protection Agency (EPA) Method 301 criteria for conditional method status. The objectives of this report are to present and discuss these results in support of EPA's evaluation of this system, and obtain EPA acceptance of its components as conditional methods.

*Why are we concerned about metal emissions?*

Air toxic metals have been associated with a wide range of environmental and human health effects including respiratory disorders, pulmonary disorders, and cancer. Recent findings link air toxic metals with in-vivo and in-vitro inflammatory responses[8,9]. As such, there is continuing concern for potential health effects of metal air pollutants including such metals as Sb, As, Cd, Co, Cr, Hg, Mn, Ni, Pb, and Se. The EPA is required to control emissions of toxic and hazardous air pollutants under the Clean Air Act Amendments of 1990[10]. Under Sections 112(k) and 112(c) of the Clean Air Act, the EPA is also required to monitor the ambient air concentrations of these species to evaluate the effectiveness of its reduction strategies. For these reasons, the EPA has developed an air toxics objective that includes an effort to reduce air toxic emissions and implement area specific control strategies to reduce air toxic exposures by 2010[11]. However, our current understanding of metal emissions is relatively poor, primarily because our current measurement technology is inadequate.

*Why is the current metals measurement system inadequate?*

A metals emissions measurement system needs to be capable of meeting a range of practical requirements in addition to meeting such basic requirements as being accurate, precise, reliable and verifiable. Top among practical requirements is that the measurements should be timely and representative; that is the results need to be available within a time frame adequate for decisions (hours to days) and representative of long term emissions (months to years). However, the currently accepted reference measurement system consists of one method capable of only infrequent periodic measurements; i.e. EPA Reference Method 29 (Method 29).

This method is considered inadequate and inappropriate for current applications primarily because it is not a continuous emission monitoring system (CEMS) and therefore may not be adequately representative of long term average emissions; but also because of its long reporting times, which are typically on the order of several weeks or more. For example, to be effective as a quality assurance tool for CEMS validation or trial burn applications, a reference method must provide results within hours of the time of sampling or at least by the next day so as to allow time for adjustments prior to completing these tests. In addition, it is felt that for some metals Method 29 suffers from accuracy and precision limitations[12, 13]. Method 29 is also relatively difficult and dangerous to use, creates large quantities of

hazardous waste, recovered samples are difficult to ship in a post-911 environment, and the method is costly. In addition, Method 29 is not consistent with current ambient metals measurements and as such more likely to have systematic biases relative to these ambient measurements. Because of the above noted limitations of Method 29, candidate alternative methods are being proposed.

*What is this new metals measurement system?*

The currently proposed metals measurement system consists of two candidate conditional measurement methods, a multi-metal CEMS and a quantitative reference aerosol generator. The multi-metals CEMS is not addressed in this report.

*What are these candidate conditional methods?*

The two candidate conditional methods are based on collection of representative samples of particle and vapor phase metals on a reactive filter followed by metal determination using X-ray fluorescence (XRF) analysis. One is a method of collecting periodic samples by drawing stack gas through a series of filters contained in a sealed filter cassette. In this X-ray based filter method (XFM), particulate phase metals are trapped on a non-reactive filter while vapor phase metals including mercury are collected on a chemically reactive filter or solid sorbent. The concentration of metals in the resulting filter deposits are non-destructively determined, either in the field or laboratory using XRF analysis following analytical procedures similar to those listed in EPA's Compendium Method IO-3.3 ("Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy in Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/010a, June 1999.)[14]. The stack gas concentration is calculated by dividing the XRF-determined metal mass by the volume of stack gas that passed through the filters. The other measurement method is an instrumental analyzer procedure (IAP) based on the collection of a representative sample of particles and gas phase metals on a reactive filter tape followed by determination of metals with XRF analysis (Xact-IAP).

The other component in this system is a Quantitative Aerosol Generator (QAG). The QAG generates a NIST-traceable reference aerosol that can be used, in addition to its other applications, to challenge and evaluate the accuracy, precision and linearity of the measurement methods and is applicable to non-metal species as well as metal species.

*Why are the XFM and Xact-IAP candidate methods more appropriate than Method 29?*

These candidate methods are more appropriate than Method 29 primarily because of their rapid analysis turn around times, which can be as short as 15 minutes in the case of the Xact-IAP or two hours in the case of the XFM if a field-portable XRF analyzer is used. Not only do these methods meet the required turn around times, but they also provide better precision and accuracy than Method 29 as the results reported in this document demonstrate, and their results can be independently verified because the analysis is non-destructive. In addition, the methods provide lower detection limits, require fewer resources, are safe and easy to use, generate no hazardous waste and are based on well-established EPA analysis procedures that are consistent with EPA ambient measurement methods.

*Why are these methods important to the EPA and other stakeholders?*

We currently have a poor understanding of metals emitted from the country's smoke stacks because of the absence of metals CEMS, infrequent manual method measurements, and substantial uncertainty in how well these measurements represent emissions, operating conditions and assumptions. The XFM, Xact-IAP, and QAG candidate conditional methods offer the EPA more convenient and reliable tools for measuring and validating metal emissions. This should make it easier for plant operators to make more frequent measurements, which will provide the EPA and other stakeholders with a higher level of understanding of metal emissions. In addition, this technology should make it easier to test and evaluate new measurement and control technologies by reducing cost barriers and by providing more timely results for engineering evaluation and adjustments. Also, more timely results provided by these candidate methods during such tests as trial burns will reduce the need for repeating these tests due to extensive delays in receiving Method 29 results, which are typically not available until after the completion of such tests.

*How was the performance of these methods evaluated?*

A two phased approach was used to evaluate and validate the aerosol generator and the filter based measurement methods. Phase I was a laboratory study in which the accuracy, precision and linearity of the QAG was established and ruggedness test data developed for the XFM and Xact-IAP. Phase II was a field study conducted to validate the measurement methods for applications to stack gases. In Phase II, the validated QAG was used to generate a reference aerosol that was spiked into stack gas, which was subsequently measured with the XFM and the Xact-IAP. All of the valid data generated during these tests were used in these method evaluations, and far more measurements were taken than required by Method 301. That is, no valid results were excluded in our analysis, even though a substantial number of results could have been omitted while still meeting Method 301 requirements.

*Is this system applicable to other sources and elements?*

This system is applicable to most emissions from stationary sources and all of the hazardous elements as well as all of the elements measured in the ambient environment; including Be if it is measured with other analytical methods after non-destructive XRF analysis.

*Where are the results presented in this report?*

This report presents a summary and discussion of the methods used and test results. The details of the methods and results are presented in the appendices of this report along with field data sheets, NIST-traceable certifications, sample calculations, all unprocessed data, etc.

# 2.0 Approach

## *2.1 Overview*

The primary objectives of these tests were to validate the QAG as a reference aerosol generator and obtain EPA conditional method acceptance for the XFM and Xact-IAP. The

objective of this section is to describe the general approach used to generate the supporting data, and discuss how this approach compares to EPA Method 301 requirements and the approach proposed in CES' test plan (Appendix A).

### *2.2 General Approach*

Neither an appropriate reference method nor performance audit materials were available to evaluate the candidate conditional methods. As such, a new approach was required to demonstrate the precision and accuracy capabilities of the candidate methods. Although there are numerous standard EPA analytical protocols available that are NIST-traceable, the real limitation was in the sample collection part of the sampling and analysis procedure. A key sampling issue in this case was the need to verify sample collection efficiencies to a precision and accuracy consistent with the potential precision (<5%) and accuracy (<5%) believed to be attainable with the candidate methods.

A two-phased approach was used in this case as schematically illustrated in Figure 1. The first phase (Phase I) consisted of laboratory validation of CES' QAG, while Phase II was a field evaluation test of the XFM and Xact-IAP using a reference aerosol generated by the validated QAG. The first step was the development of a QAG capable of emitting a reference aerosol, which could then be validated in the laboratory using independent NIST-traceable aerosol concentration measurements (Phase I). The QAG, thus validated in the laboratory, was then used in the field to spike stack gas with a reference aerosol of NIST-traceable concentration to challenge the candidate conditional measurement methods (Phase II). The success of this approach depended on several key factors including:

- Independence of the NIST-traceable aerosol generation process and the NIST-traceable aerosol measurement methods.
- High level of precision for both the generator and the analytical method (about 2%).
- The resulting small bias between the generator and analytical method (<5%).
- The magnitude of the bias being on the same order of magnitude as the expected uncertainty in the bias established through propagation of errors in both the generator and analytical measurements.

Although under these conditions, the "true" concentration of the generated aerosol was "unknown", its concentration was known at least to an accuracy comparable to the degree of propagated error and independent method agreement or magnitude of the bias; i.e., <5%, which is significantly better than the existing metals reference method. The resulting QAG could thus be used in the field with a high level of confidence that the generated reference aerosol concentration was NIST-traceable to an accuracy of 5% or better.

The general validation procedure used is illustrated in the schematic flow diagram shown in Figure 1. As noted above, a key component of this validation procedure was the fact that the QAG not only generated an accurate, NIST-traceable aerosol of known composition, but the composition of the generated aerosol was stable over periods of several days as documented with the Xact-IAP and XFM performance during evaluation testing. This documented

aerosol stability allowed the determination of precision through the collection of replicate sequential samples instead of collection of simultaneous samples using dual sampling trains.

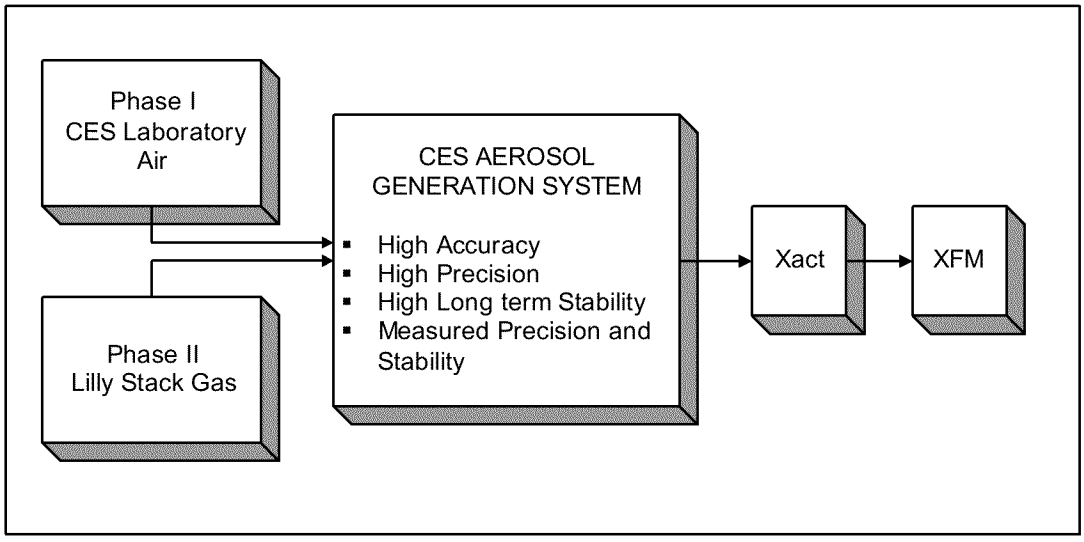



**Figure 1: Schematic flow diagram illustrating key aspects of the general validation procedure.**

### *2.3 Method Independence*

Independence of the aerosol generation and measurement methods is essential to the approach used to validate the QAG and subsequently the XFM and Xact-IAP. This method independence is schematically illustrated in Figure 2. As illustrated in this figure, the QAG generated aerosol concentration is traceable to NIST (Appendix C). In this case, all parameters used in the calculation of the aerosol concentration are NIST-traceable including the concentration of the standard solution and the rate of solution use.

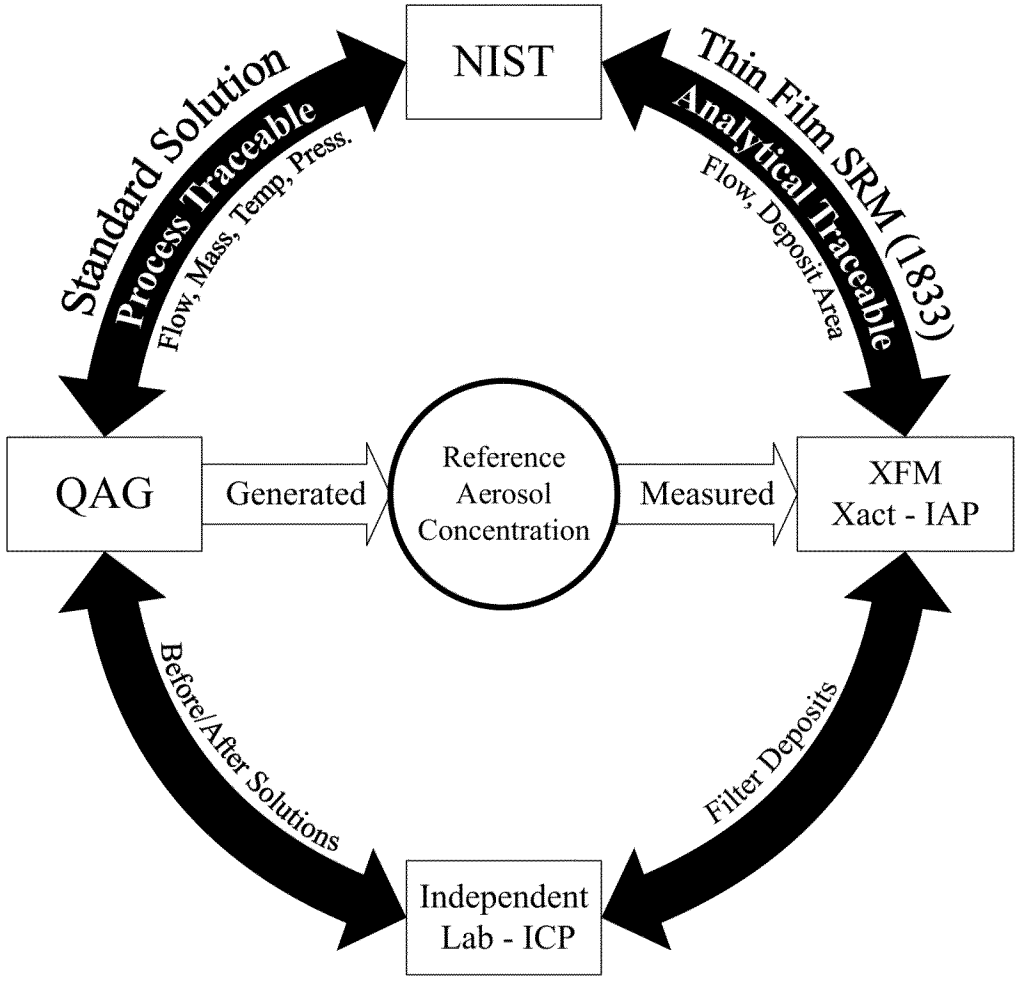



**Figure 2: Schematic representation of key components of CES' reference aerosol generation system.**

The aerosol generation process was evaluated with independent filter samples of the aerosol collected by the XFM and Xact-IAP, which were subsequently analyzed by XRF using two separate X-ray spectrometers. (Appendices B and D) The XFM and Xact-IAP parameters used to determine the volume of aerosol sampled are NIST traceable. (Appendix G) In addition, the XRF parameters used to determine the mass of metal in the filter deposit are traceable to NIST (NIST SRM 1832 and 1833, and gravimetrically NIST traceable thin film standards) and are independent of the aerosol generation process. These generation and measurement methods are clearly independent. Although further traceability or confirming measurements should not be required, additional measurements and routes to traceability were established through independent laboratory inductively coupled plasma analysis (ICP) of solution and filter samples as illustrated in the lower portion of the schematic illustration shown in Figure 2. The resulting independent laboratory-determined elemental concentrations and elemental ratios confirmed the standard solution concentrations used in

the QAG. In addition, selected XFM filter samples were analyzed by ICP using an independent laboratory to confirm the metal deposit measurements made by the XRF analyzer. These independent, third party measurements were also used to confirm the elemental concentrations, their ratios and their NIST traceability (See Appendix G). It should also be noted that the XRF analyzer used to analyze the XFM filter samples was also used in an earlier EPA $PM_{2.5}$ speciation program in which numerous "round robin" type of quality assurance tests were conducted and demonstrated comparable results to two other independent laboratories[15]. Thus, not only are the aerosol generation and measurement methods clearly independent, but there is a reasonable degree of independent quality assurance between the XFM and Xact measurement methods. In addition, since two different Xacts were used in Phase I and Phase II testing (CES and Lilly Xacts) requiring two different calibrations, there is a reasonable degree of independence of these two sets of Xact measurements. As a result, when there is a high degree of agreement between the generated aerosol concentration and the measured concentration, accuracy of both the generator and measurement methods are simultaneously validated within the degree of agreement because of the independence of their NIST traceability.

The test procedures used for this validation report were more rigorous and demanding than the procedures described in EPA Method 301. For example, the Method 301-based evaluation procedures used here include additional linearity requirements as well as the Method 301 precision and bias requirements. In addition, substantially more measurements were made than were required and none of the valid data was excluded from the data analysis. Also, because of the multi-elemental nature of the measurements, inter-elemental ratio requirements were added to acceptability criteria.

### *2.4 QAG Validation (Phase I)*

The experimental arrangement used to validate the QAG during Phase I testing is illustrated in the flow diagrams in Figure 3 and Figure 4 (Details of the test and QAG are discussed in Appendices A and C). The QAG components are illustrated on the right side of Figure 4. It consists of a Collison-type nebulizer[16] maintained at 0°F to minimize water vapor loss from the NIST-traceable spike solution during nebulization and vapor-droplet equilibration. The spiking solution was circulated through a large solution reservoir to minimize the impact on solution concentration due to loss of water from evaporation. The rate of QAG metal emissions was determined by measuring the solution use rate in grams per minute as determined by a NIST-traceable balance and correcting for vapor loss. The resulting nebulizer-produced aerosol (about 15 lpm) passed into a settling chamber where liquid droplets greater than about 20 μm in diameter settled out of the gas flow and were returned to the solution reservoir. The resulting size-selected aerosol was then injected into a drying chamber maintained at about 300 °F where it was dried and diluted with about 30 to 50 lpm of clean, dry laboratory air. The dry salt and metal vapor containing aerosol emerging from the QAG was diluted further with about 20 to 40 lpm of make-up air. The reference aerosol total flow was about 100 to 120 lpm, and was monitored with a NIST-traceable mass flow meter.

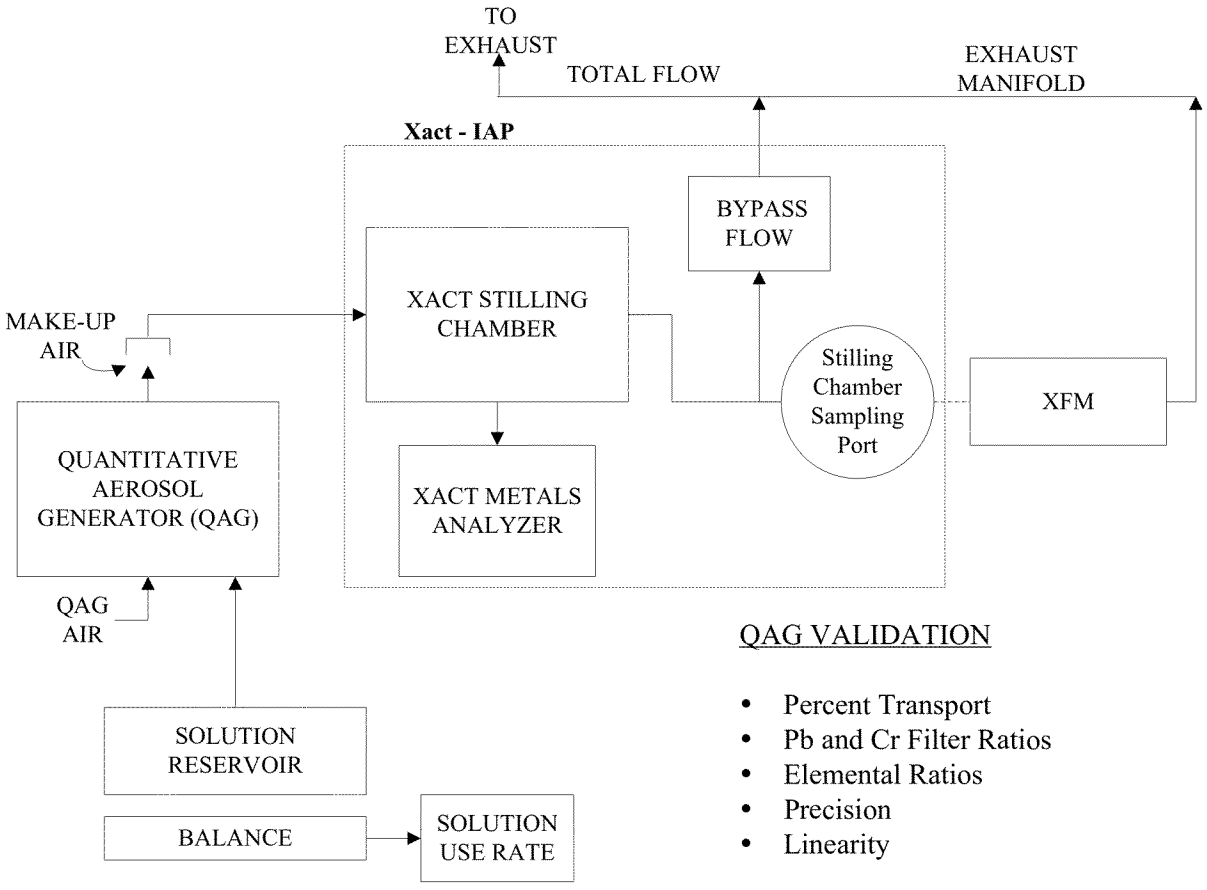



**Figure 3: Flow diagram showing the experimental arrangement used to validate the QAG reference aerosol generator.**

The QAG-generated reference aerosol contained five metals, (As, Cd, Cr, Pb, and Hg) representing the volatile, semi-volatile and low volatility metal categories as defined in the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) rule[17]. Aerosol concentrations ranged from 20 to more than 120 µg/dscm, spanning the range of their MACT emission limits. This reference aerosol was directed from the QAG to the top of the Xact stilling chamber through 2-inch diameter stainless steel (SS) tubing. About 99% of the flow passed through the test apparatus and was filtered prior to flow measurement. Less than 1% of the reference aerosol was sampled from the stilling chamber by the Xact-IAP (about 0.7 slpm). During XFM testing, almost 40% of the sample flow was drawn through the XFM plenum and returned to the exhaust downstream of the stilling chamber. From this subflow, about 1 lpm of the reference aerosol was sampled and drawn through the

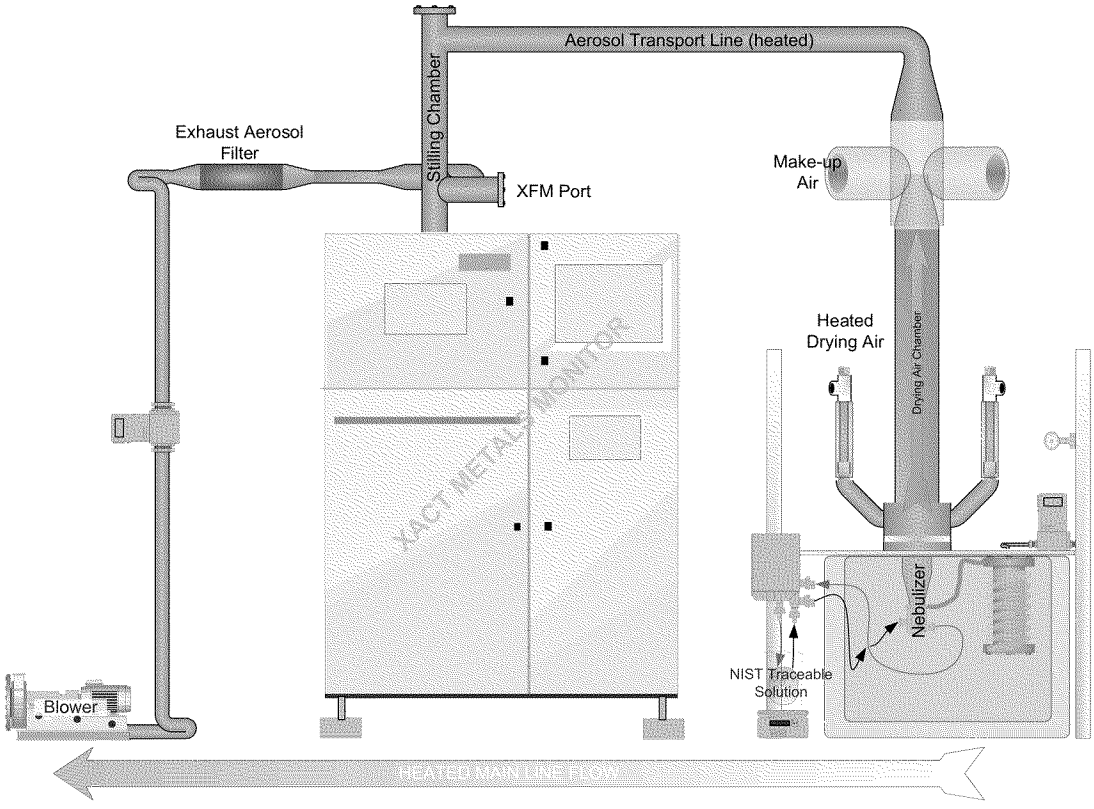



**Figure 4: Schematic representation of the experimental arrangement used in Phase I to validate the QAG reference aerosol generator.**

XFM filter cassette. The resulting XFM filters were analyzed by XRF using EPA Compendium Method IO-3.3 for particle deposits on filters while the CES Xact-IAP automatically reported metal concentrations every 15 minutes for the duration of the test.

Typical test periods consisted of establishing a stable reference aerosol flow through the Xact-IAP stilling chamber and out the exhaust manifold. The concentration of this reference aerosol was stable to within a few percent during each series of test runs as demonstrated by the Xact and QAG combined precision, which was typically on the order of 2 to 4 %. The aerosol metal concentration in the stilling chamber was simultaneously sampled and measured by both the Xact and XFM, which provided independent confirmation of the QAG reference aerosol concentrations. During linearity evaluation tests, the aerosol concentration was increased or decreased by changing the spiking solution concentration.

Phase I validation testing of the QAG was conducted at CES' laboratory using spiked ambient air. During these tests, the QAG spiked five MACT metals (As. Cd, Cr, Pb and Hg) at five concentration levels, including a series of blank runs, which were then compared to the measured concentrations reported by the CES Xact-IAP and the XFM. During Phase I, a total of 26 XFM and 148 Xact runs were compared to the QAG reference concentrations (Table 1).

**Table 1: Summary of QAG validation test schedule.**

| Date | Nominal Level for MACT Metal | Nominal QAG Conc. µg/dscm | No. of XFM Runs | No of Xact Runs |
|---|---|---|---|---|
| Dec. 14-15, 2004 | Mid2 | 65 | 12 | 93 |
| Dec. 16, 2004 | Mid1 | 50 | 4 | 13 |
| Dec. 16, 2004 | Low | 20 | 4 | 12 |
| Dec. 16, 2004 | High | 130 | 4 | 11 |
| Dec. 17, 2004 | Blank | 0 | 2 | 19 |
| **Total Runs** | | | **26** | **148** |

The validation metrics or criteria used to establish the validity of the QAG are listed below:

- **Transport Efficiency:** The calculated transport efficiency shall be greater than 80% for all elements. Since the NIST-traceable reference aerosol concentration is totally independent from the NIST-traceable filter sampling and analysis method, this criterion, if met, might be considered adequate to establish an acceptable efficiency correction factor for the QAG.
- **Lead and Cr Filter Ratios:** To ensure that the filters had adequate particulate trapping efficiency, less than two percent of the Pb and Cr were permitted on the XFM reactive filter downstream of the PTFE filter. This plus the assumed low volatility of these elements will assure a near 100% sample train trapping efficiency for these elements. This criterion plus the following criterion provide additional assurance that the trapping efficiencies for all of the elements are near 100%.
- **Elemental Ratios:** As, Cd, Cr, and Hg concentration ratios to lead measured in the aerosol sample must be within ±10% of the concentration ratios in the QAG solution. Meeting this criterion assures not only high trapping efficiencies but also high generation and transport efficiencies for all of the elements including volatile elements.
- **Precision:** The QAG must have a precision, as measured by percent relative standard deviation (PRSD), of less than 10% for each of the elements. This high precision criterion will enable sequential sampling of the candidate methods at each concentration level.
- **Linearity:** The QAG and both candidate filter-based conditional methods shall have a correlation coefficient (r) that is greater than 0.85. This criterion shows that the QAG is linear over a wide range of concentrations.

These criteria and their acceptable ranges are summarized in Table 2.

**Table 2: Acceptance criteria for QAG.**

| Criteria | Measure | No. Runs | Acceptable Range |
|---|---|---|---|
| **Filter Ratio** | back to front ratio (Cr, PB) | >9 | <0.02 |
| **Metal Ratio** | solution to aerosol ratio | >9 | 0.9 to 1.1 |
| **Efficiency** | t-statistic | >9 | < critical value **or** |
| | efficiency factor | >9 | Between 0.8 and 1.0 |
| **Precision** | percent of spiked conc. | >9 | <10% |
| **Linearity** | correlation coefficient | >9 | > 0.85 |

These criteria include required bias (efficiency) and precision validation parameters from Method 301 (bias or in this case efficiency and precision) and additional validation indicators relevant to these specific tests: i.e., filter ratio, metal ratio and linearity criteria. The acceptability ranges listed in Table 2 were guided by values required by Method 301, Performance Specifications 11 and proposed Performance Specification 10, and are either equal to those listed in these procedures or are more restrictive.

### *2.5 XFM and Xact-IAP Validation (Phase II)*

The primary objective of Phase II testing was to validate the XFM and Xact-IAP while sampling flue gas. The validity of these sampling and analysis methods was evaluated by comparing the Phase I validated QAG reference aerosol concentration with the XFM and Xact-IAP measured concentrations. It is important to note that a different Xact instrument was used in Phase II than was used in Phase I.

Following Phase I testing, the QAG was installed at a hazardous waste incinerator[18] and a series of validation tests were conducted. During these tests, the QAG reference aerosol was spiked into incinerator flue gas at four different concentration levels while an XFM sampling train and Xact-IAP were collecting simultaneous samples from the Xact stilling chamber. The experimental arrangement was similar to that used in the laboratory with the primary difference that the reference aerosol was spiked into stack gas instead of laboratory air. In addition, the Xact used in these field tests was different from the one used during the Phase I tests at CES' laboratory. During Phase II, the QAG spiked five MACT metals at four concentration levels (Table 3) into about 35 slpm of flue gas while the XFM and Xact-IAP concurrently sampled the reference aerosol spiked stack gas. A total of 24 XFM and 192 Xact-IAP runs were completed during Phase II tests while the QAG was operating.

**Table 3: Overview of Phase II validation test schedule.**

| Date | Nominal Level | Nominal QAG Conc. | No. of XFM Runs | No of Xact Runs |
|---|---|---|---|---|
| | | µg/dscm | | |
| March 4-5, 2005 | High | 108 | 12 | 45 |
| March 6, 2005 | Low | 21 | 4 | 46 |
| March 7, 2005 | Mid | 45 | 4 | 37 |
| March 8, 2005 | Blank | 0 | 4 | 64 |
| **Total Runs** | | | **24** | **192** |

Validation criteria used to evaluate the acceptance of the XFM and Xact-IAP were similar to those used for the QAG in Phase I and are listed in Table 4. These criteria include bias, precision and linearity of the measurement methods. The main difference was the omission of the filter and elemental ratio criteria, which were not relevant to Phase II testing. As was the case in Phase I, the acceptability ranges listed in Table 4 were guided by values required by Method 301, Performance Specifications 11[18] and proposed Performance Specification 10[20], and are either equal to those listed in these procedures or are more restrictive.

**Table 4: Acceptance criteria for Phase II validation of the XFM and Xact-IAP.**

| Criteria | Measure | No. Measurements | Acceptable Range |
|---|---|---|---|
| **Bias** | t-statistic | >9 | < critical value **or** |
| | correction factor | >9 | Between 0.8 and 1.2 |
| **Precision** | percent of emission limit | >9 | <10% |
| **Linearity** | correlation coefficient | >9 | > 0.85 |

### *2.6 Deviations from Test Plan*

The original draft Test Plan was developed in the fall of 2004 to organize validation testing of the XFM and can be found in Appendix A. During actual testing, there were five significant deviations from this test plan. Why these deviations occurred and any potential impacts to the resulting data set are discussed below.

- **Evaluation of the Xact-IAP:** The test plan proposed an approach for validating the QAG and XFM, but it did not focus on the Xact-IAP as a separate Instrumental Analyzer Procedure. Following discussions with the EPA, the scope of the test was expanded to include the Xact-IAP, following the same validation criteria as the XFM. Both the XFM and the Xact-IAP are candidate conditional methods, but the Xact-IAP offers end-users more immediate feedback. For this reason, and since the same QAG data set could be applied to both approaches, the test plan was expanded to include validation procedures for the Xact-IAP.
- **Total Capture:** The original test plan proposed using a total capture approach to validate the QAG in Phase I. The total capture approach, however, was technically

problematic and was not used during the validation tests. Instead, the approach used was based on independent measurements of the resulting QAG generated aerosol concentration as described above.

- **Blank Runs:** The original test plan called for injection of water for blank runs to determine XFM detection limits. During the course of testing, it was determined that pure water would freeze in the QAG. For this reason, blank 5% nitric acid was spiked instead of water. These blank tests were conducted during both Phase I (five hours) and II (eight hours). This blank testing resulted in six XFM and about 100 Xact blank test runs. Although all five metals reported blank concentrations of less than one μg/dscm for the XFM and the Xact-IAP, actual detection limits were calculated using a much larger data set (Appendix K) and then compared to the blank runs as discussed in Section 7.11.2.
- **Precision:** The precisions measured for the QAG, XFM, and Xact-IAP were based on the PRSD of the measured metal concentrations when the QAG was spiking at a constant rate. The original test plan called for calculation of precision as a percent of the emission limit, and the results indicate that calculating precision in this manner would have met the test plan precision criteria of 10%. However, since a range of concentrations were used to determine linearity, a more demanding protocol using all of the data including the lowest spiked concentrations was used that divided the standard deviation at each concentration by the mean concentration at each spiked level. This latter approach is consistent with Method 301: Equation 301-6[22].
- **Flue Gas Composition:** Phase II samples were collected when the incinerator was burning natural gas instead of waste. In the week prior to Phase II testing, cracks were observed in a section of incinerator piping that is exposed to pressures of more than 1000 PSI. These cracks precluded the burning of waste during testing and, since it was a two to three month delay before the pipes could be repaired, it was decided to conduct the tests using natural gas rather than delay the tests. A comparison of the flue gas characteristics for Phase II tests relative to flue gas characteristics during surrogate feed stock burns conducted in the Fall of 2004 is shown in Table 5. In general, the incinerator emissions produced while burning natural gas in Phase II were very similar to those observed during the surrogate feed stock burns. Most major flue gas species such as $SO_2$, $H_2O$, CO, and $CO_2$, were found in the same or higher concentrations during Phase II tests than in the surrogate feed stock burn tests in the fall of 2004. The primary difference was a decrease of 64% in particulate concentrations during Phase II tests. However, the impact of this parameter is insignificant at these concentrations (less than 10mg/dcsm @ 7% $O_2$), and would not be significant unless it were well over the permitted PM emission limits.

**Table 5: Comparison of surrogate and Phase II flue gas characteristics.**

| Chemical Species | Surrogate Tests Fall 2004 | | | Phase II March 2005 | | | Phase II Surrogate Ratio |
|---|---|---|---|---|---|---|---|
| **$SO_2$, *dry (ppm)*** | ND | ± | ND | ND | ± | ND | ---------- |
| **HCl, *dry (ppm)*** | 2.3 | ± | 1.2 | 1.9 | ± | 0.6 | 0.8 |
| **$CO_2$, *dry (%)*** | 8.3 | ± | 0.7 | 6.0 | ± | 0.1 | 0.7 |
| **CO, *dry (ppm)*** | 8.4 | ± | 1.9 | 13.8 | ± | 0.7 | 1.7 |
| **$O_2$, *dry (%)*** | 9.1 | ± | 0.9 | 11.4 | ± | 0.1 | 1.3 |
| **$H_2O$ (*%*)** | 9.2 | ± | 3.3 | 10.1 | ± | 0.4 | 1.1 |
| **PM @ 7% $O_2$ (mg/dscm)** | 9.8 | ± | 2.8 | 3.5 | ± | 0.4 | 0.4 |
| **$NO_x$, *dry (ppm)*** | 40.5 | ± | 10.0 | 108.1 | ± | 5.5 | 2.7 |
| **Flow (*dscfm*)** | 14196 | ± | 1096 | 9952 | ± | 423 | 0.7 |

# 3.0 Methods

## *3.1 QAG Reference Aerosol Generator*

The reference aerosol used in these tests was generated with CES' quantitative aerosol generator (QAG). This aerosol was the primary reference source used to determine bias and precision capabilities of the candidate conditional multi-metals methods. The QAG provides a continuous reference aerosol whose analyte concentration is NIST-traceable with documented accuracy and precision. Once validated in the laboratory during Phase I testing, the QAG was used to spike incinerator stack gas in the field during Phase II testing. Although the QAG has the ability to generate a wide range of analyte-containing aerosols, the only type used in the experiments described in this report were metal containing aerosols.

The QAG generates its reference aerosol using the following three basic steps:

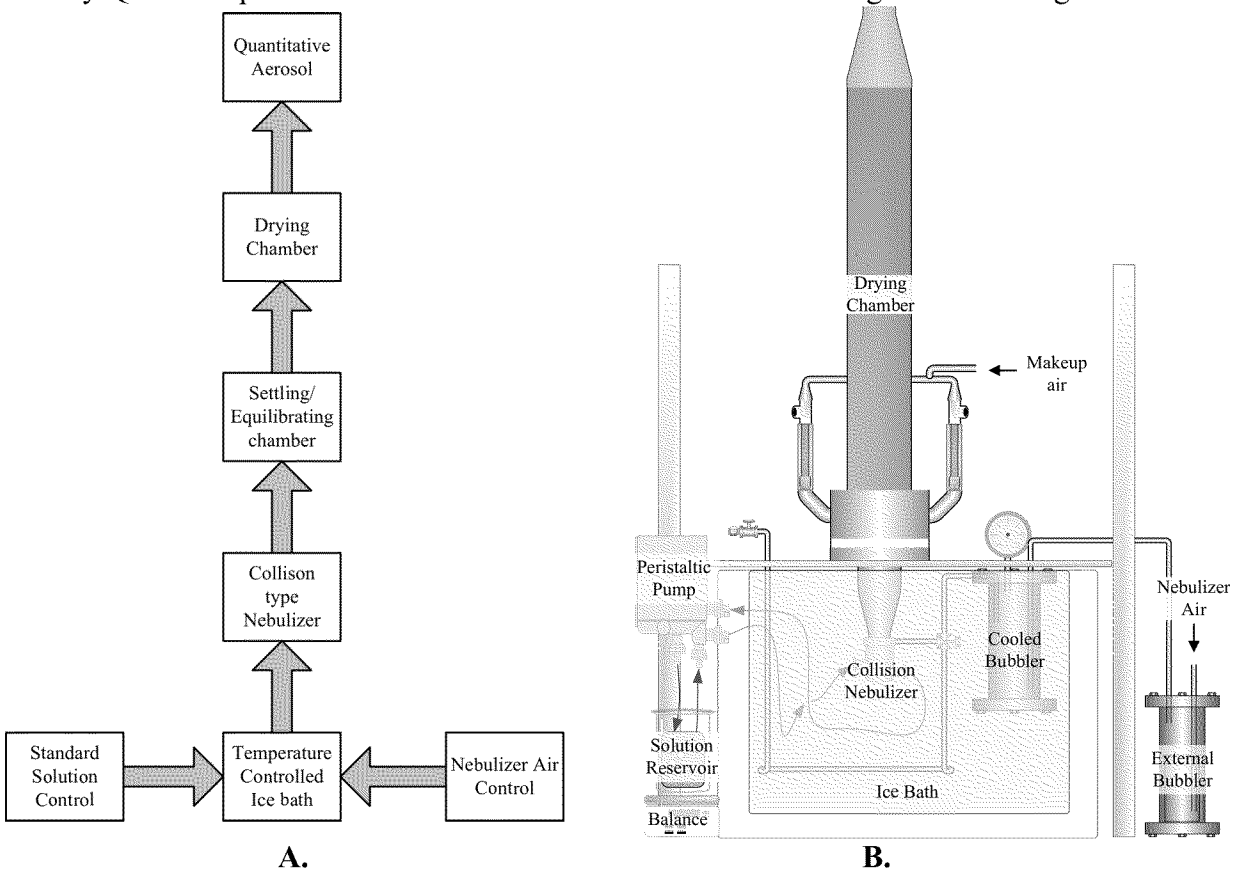
- First, an aerosol of analyte solution droplets is created using a nebulizer[16].
- This is followed by the separation and recirculation of large droplets using a settling chamber where the large droplets are removed while liquid and vapor phases are equilibrated.
- The third step consists of drying droplets smaller than 20μm in diameter.

The dried analyte-containing aerosol emission rate is calculated from the analyte concentration in the nebulized solution, the solution droplet emission rate, and the total volume of nebulizing, drying and dilution gas used to create the resulting aerosol. Use of nebulizers to generate quantitative aerosols is typically limited by three key factors:

- The magnitude and uncertainty of the water vapor emission rate lost during droplet generation and equilibration
- Changing solution concentration due to evaporation of solution
- Generation of large droplets, which can represent a significant fraction of the emitted mass and could have low transport efficiency due to the large size of the resulting dried salt particles.

These potential problems have been effectively either eliminated or minimized in the current model of the QAG by (1) generating the droplet aerosol at 32° F using cooled water-saturated nebulizing air to minimize and quantify the evaporative component, (2) using a large solution reservoir to both minimize the impact of changing concentration due to evaporation and to allow for measurement of total solution use rate, and 3) incorporation of a stilling chamber to separate and recycle large solution droplets.

Key QAG components are illustrated with the schematic drawings shown in Figure 5.




**A.** **B.**

**Figure 5: A. Schematic of flow through QAG components. B. Overview of the set-up of QAG components.**

There are six major components of the QAG:

- A reference solution control component is used to circulate the analyte-containing solution through the nebulizer and measure the total solution use rate. This component consists of a peristaltic pump, solution reservoir, balance, connecting tubing and a laptop used to record the balance reading every 15 seconds.
- A nebulizer air control component used to maintain and measure the flow, temperature, pressure and saturation of air used in the nebulization process. This component uses compressed air at about 20 PSI-gage pressure to force air through the nebulizer. The nebulizing air passes through flow and pressure regulators, an external bubbler to saturate the air at room temperature and then a second bubbler to assure that the nebulizing air is saturated a 32° F prior to entering the nebulizer.
- A temperature control component (ice bath) is used to control the temperature of the nebulizer air, the nebulizer and the settling/equilibrating chamber at 32° F.
- A Collison-type nebulizer[16] component is used to create the solution droplet aerosol. It consists of three major components: the nebulizer cup, the nebulizer and nebulizer nozzle as describe in more detail in Appendix C. The nebulizer cup contains the standard solution. This solution is continuously circulated from the nebulizer cup to an external reservoir to minimize the impact of vapor loss on solution concentration and to allow for determination of the solution use rate.
- A settling/equilibrating chamber component located just above the nebulizer component. The nebulizer-generated aerosol is directed into this chamber where large droplets settle from the gas stream and the remaining droplets equilibrate with water vapor prior to entering the drying chamber. The nebulization process creates a droplet spray containing a wide range of droplet sizes. The largest droplets impact on the walls of the nebulizer cup and are recycled. The smaller droplets are entrained in the nebulizer air flow and pass into the settling-equilibration chamber. The function of the settling-equilibration chamber is to remove and recycle all droplets greater than about 20 µm in diameter as well as to assure droplet-vapor equilibrium at 32°F. Thus, the only droplets emitted into the drying chamber have diameters less than 20 µm and have been equilibrated with water vapor at 32°F.
- A drying chamber component with temperature and flow controls. In this chamber, the size-restricted and vapor equilibrated aerosol from the settling/equilibrating chamber is surrounded by dry air at about 300° F, which is used to dry the reference solution droplets prior to being emitted from the QAG. The aerosol exiting the drying chamber consists of the transport gas (air), water and metal vapor and dried salt particles. The size of the salt particles is controlled by the analyte solution concentration, the design of the settling chamber and the flow rate of nebulizer air. This aerosol is the reference aerosol produced by the QAG. However, in this experiment, the aerosol was further diluted with makeup air prior to being transported to the Xact stilling chamber from which both Xact-IAP and XFM samples were drawn. QAG efficiencies referred to in this report are combination generation

(aerosol emitted from the drying chamber of the QAG) and transport to the Xact stilling chamber.

The QAG's generated aerosol concentration ($C_i^{a\text{-}QAG}$) is process traceable to NIST through the traceability of its components (see Appendix C). As demonstrated in Equation 1 below, the generated concentration is a function of the solution standard concentration of the ($C_i^{s\text{-}QAG}$), total flow rate ($F_t$), rate of mass loss of the solution ($R_m$), and rate of vapor loss ($R_v$). Process traceability to NIST is established by using instruments that are NIST-traceable (e.g., calibrated with NIST standards) to measure these parameters and a solution with NIST-traceable concentrations.

The final product of the QAG is an aerosol containing dried salt particles and vapors of the analyte or analytes. The concentration of the analytes in the aerosol and the concentration uncertainty are calculated from the QAG's recorded operating parameters. The equation for calculating the generated aerosol concentration is as follows:

$$C_i^{a-QAG} = \frac{C_i^{s-QAG}}{F_t}(R_m - R_v)$$ **Equation 1**

Where:

$C_i^{a\text{-}QAG}$ = Concentration of the i[th] element in the reference aerosol generated by the QAG

$C_i^{s\text{-}QAG}$ = Concentration of the i[th] element in the QAG's NIST-traceable solution

$F_t$ = Total combined flow of the nebulizer air, drying air and makeup air or stack gas

$R_m$ = Total rate of solution mass loss for the QAG, determined from the slope of a linear least squares fit of the reservoir mass data over the period of a test or series of tests

$R_v$ = Rate of vapor loss from the reference solution, as calculated using the following equation:

$$R_v = F_e M_v \left[1 - \frac{P_e}{P_c}\right]$$ **Equation 2**

Where:

$F_e$ = Flow of expanded nebulizer air in the QAG

$M_v$ = Mass of water vapor in a liter of saturated air at 32°F

$P_e$ = Absolute pressure of the expanded nebulizer air (atmospheric)

$P_c$ = Absolute pressure of the compressed nebulizer air

Uncertainty in the generated reference aerosol concentration was determined using standard propagation of error techniques relevant to the parameters used in Equation 1 and Equation 2 (See Appendix C). The estimated uncertainties for these parameters during Phase I and II testing are 0.5% for $C_i^{s\text{-}QAG}$, 3% for $F_e$, 1.5% for $F_t$, 7% for $M_v$, 3% for $P_c$, 1% for $P_e$, and 1% for $R_m$. These uncertainty values are based on equipment manufacturer certifications, NIST and/or engineering estimates of nebulization/equilibration temperature uncertainties. Using these uncertainties, the propagated uncertainty during Phase I and II testing was calculated to be about 4% for an aerosol concentration ($C_i^{a\text{-}QAG}$) of about 70 µg/m$^3$.

### *3.2 XFM Candidate Conditional Method*

The current reference method for measuring metal emissions from stationary point sources (Method 29) is based on 30 year old probe, filter and impinger type sampling trains. This method is difficult and dangerous to use, creates large quantities of hazardous waste, recovered samples are difficult to ship, and several weeks are required for an analysis to be completed. The XFM candidate conditional method summarized in this subsection and described in detail in Appendix B is based on a safe, easy to use sampling train that traps both PM and vapor phase metals on stacked filters that a field engineer never touches and can easily be either analyzed by XRF in the field or express mailed to a laboratory for 24 hour turn around times. Although the XFM procedure has been optimized for MACT metal analytes, it is applicable to elements with atomic number ranging from 13 (Al) to 92 (U).

The sampling train used for these Method 301 validation tests is shown schematically in Figure 6. It is composed of five major subcomponents:

- Extraction-stilling chamber interface assembly
- Filter holder
- Sample flow control
- Extraction interface flow control
- Dilution flow control

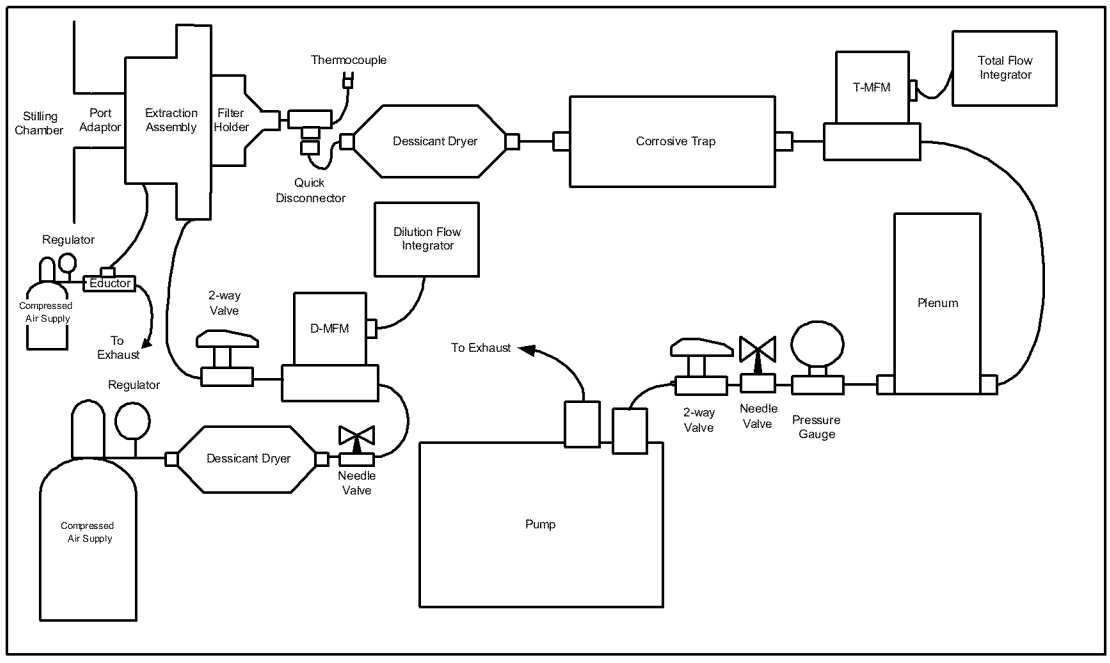



**Figure 6: Schematic flow diagram of the sampling train used in Phase I and II XFM validation tests.**

A photograph of the assembled extraction-interface and filter holder is shown in Figure 7. The port adapter is on the left side in the photograph and consists of PTFE-coated 2-inch diameter stainless steel (SS) tubing with a sanitary flange for attaching the assembly to the stilling chamber. In the case of normal stack sampling, this interface would be attached directly to a large diameter shielded probe type of sample extraction system. This port adapter is followed by an extraction assembly that draws stack gas at the rate of about 20 to 30 lpm into it using an eductor and flow control module. A representative sub-sample of this stack gas is blended with dry dilution gas in this assembly prior to being drawn through the SS sample filter holder assembly shown on the right side of the photograph. The sample and dilution flow rates are on the order of one to two lpm and controlled by the sample and dilution flow control components. All temperatures and flows are controlled, monitored and recorded during sampling.

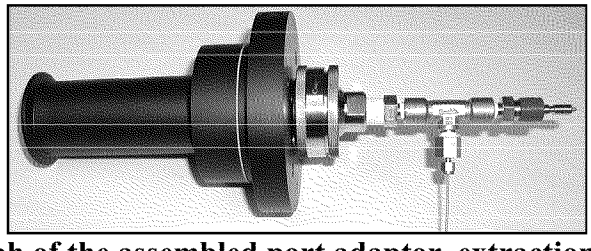


**Figure 7: Photograph of the assembled port adaptor, extraction assembly and filter holder.**

An exploded schematic view of the XFM filter holder with filter cassette is illustrated in Figure 8. The filter cassette shown in the middle contains an off-the-shelf upstream PTFE filter, Teflo™ by Pall Inc.[23] which traps PM and a downstream reactive filter that is used to

trap vapor phase metals. The filters are loaded into the filter cassette in the laboratory and transported to and from the field in plastic Petri dishes. The field engineer simply removes the filter cassette from its Petri dish and places it in the SS filter holder. When sampling is finished, the filter cassette is removed from the filter holder and returned to its Petri dish. In this process, the filters are not touched by the field engineer, which reduces the possibility of contaminating and/or disturbing the deposits.

The analyte mass on each XFM filter deposit is determined by EPA Compendium Method IO-3.3[14]. This method is the same as one used to measure 48 ambient metals for thousands of filters collected by EPA's $PM_{2.5}$ Speciation Program[15].

The aerosol concentration of each metal is calculated using Equation 3.

$$C_i^{e-XFM} = \frac{M_i^{PTFE} + M_i^{REO-7}}{V_t^{XFM} - V_d^{XFM}} \qquad \textbf{Equation 3}$$

Where:

$C_i^{e-XFM}$ = Concentration of the $i^{th}$ analyte in the emissions measured by the XFM

$M_i^{PTFE}$ = XRF-determined mass of the $i^{th}$ analyte on the PTFE filter.

$M_i^{REO-7}$ = XRF-determined mass of the $i^{th}$ analyte on the reactive filter (REO-7[23])

$V_t^{XFM}$ = Total volume (emission plus dilution) sampled by the XFM

$V_d^{XFM}$ = Volume of dilution air drawn through filters of the XFM

Mass and volume measurement uncertainties are typically on the order of one to three percent of the value near the emission limit concentrations. This suggests XFM aerosol concentration uncertainties on the order of three to five percent.

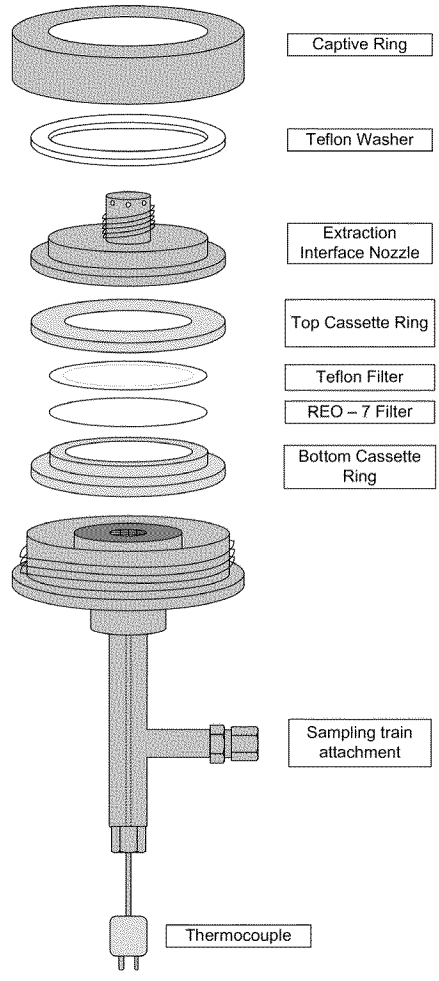



**Figure 8: Exploded schematic view of XFM filter holder with filter cassette.**

### *3.3 Xact Instrumental Analyzer Procedure*

The Xact instrumental analyzer procedure (Xact-IAP) has the ability to provide stack gas metals analysis results for up to 20 metals every 15 minutes. This capability could greatly facilitate trial burn tests, engineering/design studies as well as compliance testing by providing near real time results necessary for rapid evaluation of engineering and/or burn conditions, or compliance success or failure. This candidate conditional reference procedure is based on sampling of PM and vapor phase metals using a reactive filter tape (PRO-11[24]) followed by XRF determination of metal mass in the resulting deposits while the next sample is being collected on a fresh section of filter tape.

The Xact instrumental analyzer draws a continuous representative sample of 25-100 lpm of stack gas through a stilling chamber. A small isokinetic sub-sample (~1 lpm) is extracted from the stilling chamber and blended with about 0.2 lpm of dilution gas. The cooled and diluted stack gas is drawn through the reactive filter tape where the metals are quantitatively trapped. Following collection, the tape is advanced to an XRF analyzer for metal mass determination while another sample is collected. The Xact takes the XRF-determined mass in μg/sample divides this mass by the stack gas volume for the run, and reports concentrations

for up to 20 analyte metals in μg/dscm. Response time depends upon the end-user's required detection limits, but is typically 10 to 30 minutes.

Figure 9 shows key Xact components. The Xact has a two-foot by three-foot footprint and is four-feet tall. Concentrations are determined by the Xact controller, and automatic flow, upscale, and blank checks are available to ensure that calibration is maintained. All data is stored in a personal computer and can be easily imported into a spreadsheet or data acquisition system. XRF calibration is stable over extended periods. Its calibration is checked daily, but rarely needs recalibration more frequently than once or twice a year.

The Xact consists of the following five subsystems (Figure 9):

- **Sample interface:** The sample interface withdraws a representative sample of effluent from the source and delivers it to the sampling module. The Xact sampling probe utilizes a shrouded probe type design to draw a representative sample of effluent from the source. The effluent is then transported from the probe through a heated transport line to the sampling module.

- **Sampling module:** The sampling module consists of all the equipment necessary for extracting all elements of interest from the flue gas. The Xact draws a flow of between 25 and 100 lpm through a stilling chamber where the flow is slowed prior to withdrawing a sub-sample of about 0.50 to 1.0 lpm for analysis. About 0.20 lpm of dilution air is added and drawn through chemically reactive filter tape. The metal analytes of interest are captured quantitatively on this filter tape.

- **Volume measurement module:** After being drawn through the filter tape the flue gas is dried and the total gas flow rate is measured. The sample flow rate is calculated by subtracting the dilution flow from total flow. The flow is totalized over the sampling period to obtain a volume measurement. Because the flue gas has been dried prior to measurement, the volume and reported aerosol concentration are reported in units of dry standard cubic meters (dscm).

- **X-Ray analysis module:** The Xact measures the mass for each metal using XRF analysis in accordance with the procedures listed in EPA's Compendium Method IO-3.3[14].

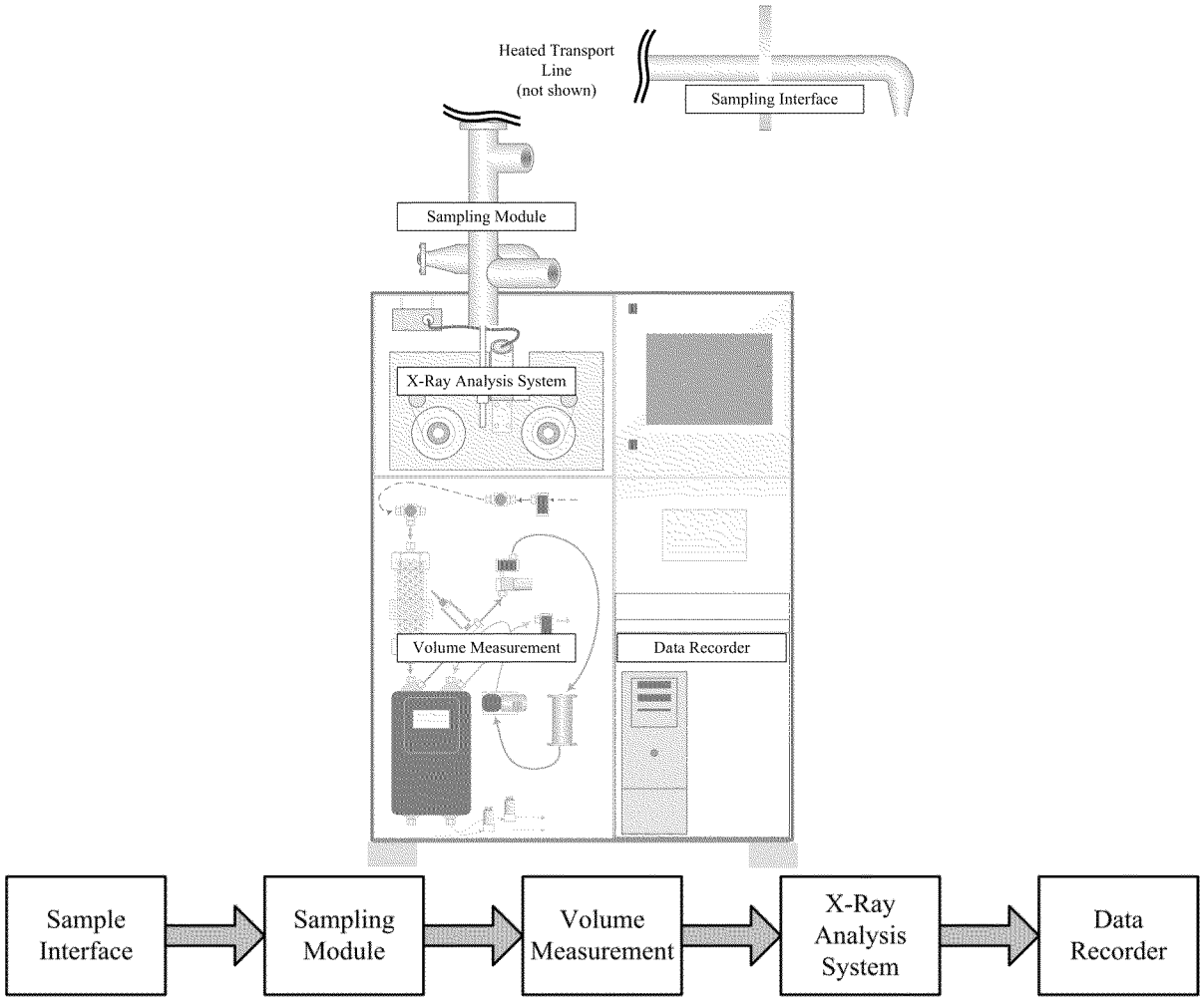



**Figure 9: Overview of Xact-IAP components and flow schematic.**

- **Data recorder:** The mass as determined by XRF is divided by the sample flow rate using Equation 4 and recorded by the Xact controller. The data can then easily be imported into a data acquisition system or can be stored on a personal computer as a text file.

$$C_i^e = \frac{M_i^{e-XACT}}{(V_t^{XACT} - V_d^{XACT})} \qquad \textbf{Equation 4}$$

Where:

$C_i^e$ = Concentration of the i$^{th}$ metal in the emissions measured by the Xact

$M_i^{e-XACT}$ = Mass of the i$^{th}$ metal in the sample as measured by XRF.

$V_t^{XACT}$ = Total volume as measured by the Xact

$V_d^{XACT}$ = Dilution volume as measured by the Xact

The Xact also incorporates a number of procedures to ensure the accuracy and reliability of its data. At least once each day the Xact performs upscale and zero checks. The values reported each day are compared with the original calibration to ensure the accuracy and stability of the XRF analyzer. The Xact also has a palladium rod permanently mounted into the XRF analysis area. The reported concentration of this rod is a known and checked with every sample analyzed on the Xact. The volume measurement is compared at least once a day against another mass flow meter. In addition the calibration of the XRF analysis can be checked for all elements using NIST traceable thin film standards and the accuracy of the flow meters can be verified by checking them with a NIST traceable flow measurement device such as a DryCal® meter[25].

# 4.0 Calculations

## *4.1 Overview*

This section summarizes key calculations for Phase I and II testing with a more detailed discussion presented in Appendix K. Calculations for the QAG, XFM and Xact-IAP are shown in the next three subsections while Subsection 4.6 presents the calculations of comparison parameters such as bias and precision. The Phase I and II test results show that background concentrations of the five MACT metals in the stack gas and laboratory air were essentially equal to zero, and that the concentration of the spiked reference aerosol was constant to within a few percent. This low background and constant concentration allowed for the determination of bias and precision using replicate sequential measurements instead of paired measurements. This in turn allowed for simpler calculations of validation metrics as discussed in Subsections 4.6 and 4.7.

## *4.2 List of Symbols and Terms*

$b_0$ = $y$ intercept

$b_1$ = slope

$B$ = bias

$|B|$ = absolute value of the bias

$C_D$ = minimum detection limit

$C_i$ = concentration of the i$^{th}$ element

$C_i^a$ = concentration of the i$^{th}$ element in the aerosol

$\overline{C_i}$ = mean concentration of the i$^{th}$ element

$C_{Pb}^a$ = concentration of lead in the aerosol

$C_i^s$ = concentration of the i$^{th}$ element in the solution

$C_{Pb}^s$ = concentration of lead in the solution

$C_{i,j}^u$ = concentration of the i$^{th}$ upscale metal reported for the j$^{th}$ interval

$C_{i,c}^u$ = concentration of the i$^{th}$ upscale metal reported at calibration

$C_i^L$ = Emission limit of the i$^{th}$ metal

$C_{i,j}^z$ = Blank concentration of the i$^{th}$ metal reported for the j$^{th}$ interval

$C_{i,c}^z$ = Reference value of the low level calibration standard for the i$^{th}$ metal

$\overline{C}_i^M$ = mean metal concentration

$C_i^{a-M}$ = concentration of the i$^{th}$ element in the aerosol as measured by the candidate method

$\overline{C}_i^{a-M}$ = mean concentration of the i$^{th}$ element in the aerosol as measured by candidate method

$C_i^{a-QAG}$ = concentration of the i$^{th}$ element in the reference aerosol generated by the QAG

$C_i^{a-XACT}$ = concentration of the i$^{th}$ element in the aerosol reported by the Xact

$C_i^{a-XFM}$ = concentration of the i$^{th}$ element in the aerosol measured by the XFM

$C_i^{s-QAG}$ = concentration of the i$^{th}$ element in the standard solution used for the QAG

$C_i^{REO-7}$ = concentration of the i$^{th}$ analyte on the XFM reactive filter[23]

$C_i^{PTFE}$ = concentration of the i$^{th}$ analyte on the PTFE filter

$C_i^{PRO-11}$ = concentration of the i$^{th}$ analyte on the Xact reactive filter

$CD_i$ = i$^{th}$ element calibration drift

$CF_i$ = correction factor for the i$^{th}$ element

$\overline{d}$ = average of differences

$E_i$ = efficiency of the i$^{th}$ element

$F_e$ = flow of expanded nebulizer air in the QAG

$F_t$ = total spiked flow

$M_v$ = mass of water vapor in a liter of saturated air

$M_i^{PTFE}$ = XRF-determined mass of the i$^{th}$ analyte on the PTFE filter

$M_i^{PRO-11}$ = XRF-determined mass of the i$^{th}$ analyte on the Xact reactive filter[23]

$M_i^{REO-7}$ = XRF-determined mass of the i$^{th}$ analyte on the XFM reactive filter

$M_i^{e-XACT}$ = XRF reported metal mass on the filter (µg/filter)

$n$ = number of measurements

$p^i$ = precision for the i$^{th}$ element

$P_c$ = absolute pressure of the compressed nebulizer air in the QAG

$P_e$ = pressure of the expanded nebulizer air in the QAG

$PRB_i$ = percent relative bias for the i$^{th}$ element

PRSD = percent relative standard deviation

$r$ = correlation coefficient

$r^2$ = Square of the correlation coefficient

$R_f$ = filter ratio to confirm total metal trapping efficiency with the XFM filters

$R_i^{Pb}$ = relative ratio for the for the i$^{th}$ element divided by the concentration of lead

$R_m$ = total rate of solution mass loss for the QAG

$\overline{R_{RM}}$ = average of the RM data set
$R_v$ = rate of vapor loss of the QAG standard solution
$RA$ = relative accuracy
$RSD$ = relative standard deviation
$SD$ = standard deviation
$SDM$ = standard deviation of the means
$SDM_i^M$ = standard deviation of the mean of a series of concentration measurements of the i$^{th}$ element
$t$ = t-statistic
$V_t$ = total volume sampled
$V_d$ = volume of dilution air drawn through the XFM
$V_t^{XFM}$ = total volume sampled through the XFM filters
$V_d^{XFM}$ = volume of dilution air drawn through the XFM filters
$V_t^{XACT}$ = total volume sampled during Xact run (dscm)
$V_d^{XACT}$ = volume of dilution air during Xact run (dscm)
$U_i^B$ = Uncertainty in the i$^{th}$ element bias
$U_i^{a-QAG}$ = Uncertainty in the i$^{th}$ element reference aerosol concentration
$x_i$ = value of the i$^{th}$ data point for data set $x$
$\bar{x}$ = average of the values in data set $x$
$y_i$ = value of the i$^{th}$ data point for set of data $y$
$\bar{y}$ = average of the values in data set $y$
$ZD_i$ = i$^{th}$ element zero drift

### *4.3 QAG Reference Aerosol Concentration*

Calculation of the QAG generated reference aerosol concentration was based on a measurement of the nebulization rate of analyte-containing solution and a measurement of the rate of flow of gas into which the nebulized solution droplets were injected. The concentration of this reference aerosol was calculated using the following equation:

$$C_i^{a-QAG} = \frac{C_i^{s-QAG}}{F_t}(R_m - R_v)$$ **Equation 1 (see Section 3.1)**

Where:

$C_i^{a-QAG}$ = QAG reference aerosol concentration of the i$^{th}$ element (µg/dscm)
$C_i^{s-QAG}$ = Concentration of the i$^{th}$ element in the solution (µg/g)
$F_t$ = Total spiked reference aerosol gas flow rate (dscm/min)
$R_m$ = Measured rate of solution mass loss from a reservoir (g/min)

$R_v$ = Reservoir mass loss rate due to water vapor loss (g/min)

The total solution use rate ($R_m$) was determined by measuring the mass of the solution reservoir every 15 seconds and determining the slope of a scatter plot of this measured mass versus time. The rate of water vapor loss was calculated using to the following equation:

$$R_v = F_e M_v \left[ 1 - \frac{P_e}{P_c} \right]$$

**Equation 2 (see Section 3.1)**

Where:

$F_e$ = Expanded nebulization air flow rate as measured by the flow meter on the nebulizing air line.

$M_v$ = Mass of water vapor contained in a liter of water vapor saturated air at 32 °F. This value has been well defined and is listed as 4.84 mg/liter[26]

$P_e$ = Pressure of the expanded gas outside the nebulizer nozzle. Since the droplet generating chamber and the droplet size selector are open to the atmosphere, $P_e$ is the atmospheric pressure recorded from a field barometer during Phase II testing and was assumed to be 14.7 psi for Phase I testing that was conducted at near sea level.

$P_c$ = The absolute pressure of the compressed air upstream of the nebulizer aspiration nozzle, recorded from the precision pressure gauge located on the nebulizer air line (psi).

### *4.4 XFM Measured Aerosol Concentration*

The XFM determined concentration of the five MACT metals in the QAG-generated reference aerosol is based on a measurement of the metal mass deposited on the XFM filters and the sample volume that passed through the filters. The total volume that passed through the XFM filter cassette and the volume of dilution air were recorded with flow integrators and an operator during each XFM run. Sample volume was calculated by subtracting the dilution volume from the total volume. Metal mass concentrations in micrograms per spot were determined using a CES XRF analyzer and procedures defined in EPA's Inorganic *Compendium Method 3.3 "Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectroscopy"*[14] The XFM determined concentrations were calculated using the following equation:

$$C_i^{a-XFM} = \frac{M_i^{PTFE} + M_i^{REO-7}}{V_t^{XFM} - V_d^{XFM}}$$

**Equation 3 (see section 3.2)**

Where:

$C_i^{a\text{-}XFM}$ = XFM measured concentration of the i[th] element in the aerosol (µg/dscm)

$M_i^{PTFE}$ = XRF-determined mass of the i[th] analyte on the PTFE filter

$M_i^{REO-7}$ = XRF-determined mass of the i[th] analyte on the reactive filter (REO-7)[23]

$V_t^{XFM}$ = Total volume sampled during XFM run (dscm)

$V_d^{XFM}$ = Volume of dilution air drawn through filters XFM run (dscm)

### *4.5 Xact-IAP Measured Aerosol Concentration*

During a sample run, the Xact recorded the total dry volume of gas that passed through the filter tape. Following the sampling period, the tape was advanced to the XRF analysis region where each metal's mass was determined in micrograms per spot. The mass was then divided by the total dry volume for a given sample run to produce concentrations in µg/dscm. Xact concentrations for these tests were calculated using the following equation:

$$C_i^{a-Xact} = \frac{M_i^{XACT}}{(V_t^{XACT} - V_d^{XACT})}$$ **Equation 4 (see Section 3.3)**

Where:

$C_i^{a-Xact}$ = Xact reported concentration of i[th] element in the aerosol (µg/dscm)

$M_i^{XACT}$ = XRF reported metal mass on the filter (µg/filter)

$V_t^{XACT}$ = Total volume sampled during Xact run (dscm)

$V_d^{XACT}$ = Volume of dilution air during Xact run (dscm)

### *4.6 Validation Comparison Parameters*

#### *4.6.1 Bias*

The proposed candidate conditional method bias was determined by comparing the candidate method's mean measured concentration ($\overline{C}_i^{a-M}$) to the calculated reference aerosol analyte concentration ($C_i^{a-QAG}$). The bias (*B*) of the proposed candidate conditional method is defined as the difference between the mean candidate method measured aerosol concentration and the calculated reference aerosol concentration over a common measurement interval; i.e.,

$$B_i = \overline{C}_i^{a-M} - C_i^{a-QAG}$$ **Equation 5**

*4.6.2 Bias Significance Test*

The test for significance of bias used in this report is different from that used in Method 301 primarily because sequential measurements were used in these tests instead of paired measurements, but also because the uncertainty in the reference aerosol concentration was significant relative to the standard deviation of the mean of the measurements. In this case, the criteria for bias significance is whether or not the bias is greater than two times (95% confidence level) the uncertainty in the bias. The uncertainty in the bias for the i$^{th}$ element ($U_i^B$) is given by the following equation when a reference aerosol spike is used:

$$U_i^B = \sqrt{\left(U_i^{a-QAG}\right)^2 + \left(SDM_i^M\right)^2} \qquad \textbf{Equation 6}$$

Where:

$U_i^B$ = Uncertainty in the i$^{th}$ element bias

$U_i^{a-QAG}$ = Uncertainty in the i$^{th}$ element reference aerosol concentration

$SDM_i^M$ = Standard deviation of the mean of a series of concentration measurements of the i$^{th}$ element

Thus, the bias is significant at the 95% confidence level if $B_i > 2U_i^B$.

*4.6.3 Correction Factor*

The correction factor is a factor used to correct for significant differences between measured and reference concentration; i.e., efficiency difference in the case of the QAG or bias in the case of the XFM and Xact. If the efficiency or bias is determined to be significant, a correction factor for the i$^{th}$ element ($CF_i$) can be calculated using the following equation and applied to future measurements to compensate for the method's bias or inefficiencies.

$$CF_i = \frac{C_i^{a-QAG}}{C_i^{a-M}} \qquad \textbf{Equation 7}$$

*4.6.4 Drift*

Drift is generally defined as a percent change in a mean value measured over an extended period of time. It is primarily applicable to the Xact CEMS and Xact-IAP and based on a comparison of zero and upscale measurements with those made when the instrument was last calibrated. These measurements are indicators of instrument calibration drift ($CD_i$) and zero drift ($ZD_i$). These drift values are calculated using the following two equations, which are based on equations used in proposed performance specification 10 for multi-metal CEMS.

$$CD_i = \frac{\left(C_{i,j}^{u} - C_{i,c}^{u}\right)}{C_{i,c}^{u}} 100\% \qquad \textbf{Equation 8}$$

Where:

$CD_i$ = i[th] element calibration drift

$C_{i,j}^{u}$ = Concentration of the i[th] upscale metal reported for the j[th] interval

$C_{i,c}^{u}$ = Concentration of the i[th] upscale metal reported at calibration

$$ZD_i = \frac{\left(C_{i,j}^{z} - C_{i,c}^{z}\right)}{C_i^{L}} 100\% \qquad \textbf{Equation 9}$$

Where:

$ZD_i$ = i[th] element zero drift

$C_{i,j}^{z}$ = Blank concentration of the i[th] metal reported for the jth interval

$C_{i,c}^{z}$ = Reference value of the low level calibration standard for the i[th] metal

$C_i^{L}$ = Emission limit of the i[th] metal

### *4.6.5 Efficiency*

Efficiency as used in this document is defined as the ratio of a measured concentration to a reference concentration expressed as a percent. In the case of the QAG, for example, it is the ratio of the aerosol concentration measured in the Xact stilling chamber to the calculated reference aerosol concentration. Efficiencies other than 100% are due to generation and transport inefficiencies and/or errors associated with the generation and measurement of the aerosol concentration. The efficiency ($E_i$) of the i[th] element is calculated using the following equation:

$$E_i = \frac{\overline{C}_i^{a-M}}{C_i^{a-QAG}} 100\% \qquad \textbf{Equation 10}$$

### *4.6.6 Efficiency Significance Test*

The criteria for efficiency significance is whether or not the difference between the measured efficiency and 100% is greater than two times (95% confidence level) the uncertainty in this

difference. The uncertainty in the efficiency for the i[th] element ($U_i^E$) is given by the following equation when a reference aerosol spike is used:

$$U_i^E = E_i \sqrt{\left(\frac{U_i^{a-QAG}}{C_i^{a-QAG}}\right)^2 + \left(\frac{SDM_i^{a-M}}{\overline{C}_i^{a-M}}\right)^2}$$

**Equation 11**
**(See Section 4.6.2)**

Thus, the efficiency is significant at the 95% confidence level if

$$E_i - 100 > 2U_i^E$$

**Equation 12**

*4.6.7 Filter Ratio*

A validation parameter called filter ratio ($R_f$) was used as an indicator to confirm total metal trapping efficiency with the XFM filters. The mass of the low volatility metals Pb and Cr as measured on the XFM PTFE filter ($M_i^{PTFE}$) and the following reactive filter ($M_i^{REO-7}$) were used in this calculation. The filter ratio is calculated using the following equation:

$$R_f = \frac{M_i^{PTFE}}{M_i^{PTFE} + M_i^{REO-7}} 100\%$$

**Equation 13**

*4.6.8 Linearity*

Evaluation of linearity of the QAG and the candidate conditional methods was based on four parameters derived from a linear least squares fit of the measured concentration plotted against the reference concentration; i.e., slope, intercept, correlation coefficient and variance. Given a general set of data $(x_i, y_i)$ with $n$ data points, the slope ($b_1$), y-intercept ($b_0$), correlation coefficient ($r$), and the variance ($r^2$) are defined by the following equations:

$$b_1 = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2}$$

**Equation 14**

$$b_0 = \bar{y} - b_1 \bar{x}$$

**Equation 15**

$$r^2 = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})^2}{\sum (x_i - \bar{x}) \sum (y_i - \bar{y})}$$ **Equation 16**

*4.6.9 Mean Concentration*

The mean metal concentration ($\overline{C}_i^M$) measured by a candidate conditional method is equal to the sum of the individual measured concentrations ($C_i$) divided by the number of measured concentrations ($n$).

$$\overline{C}_i^M = \frac{\sum C_i}{n}$$ **Equation 17**

*4.6.10 Metal Ratio*

As used in this report, the metal ratio ($R_i^{Pb}$) is the ratio of the i$^{th}$ metal aerosol concentration normalized to the Pb aerosol concentration divided by the i$^{th}$ metal solution concentration normalized to the Pb solution concentration; i.e.,

$$R_i^{Pb} = \frac{\left[\frac{C_i^a}{C_{Pb}^a}\right]}{\left[\frac{C_i^s}{C_{Pb}^s}\right]}$$ **Equation 18**

*4.6.11 Percent Relative Bias*

The percent relative bias for the i$^{th}$ element ($PRB_i$) is the i$^{th}$ element bias ($B_i$) divided by the reference aerosol concentration for the i$^{th}$ element ($C_i^{a-QAG}$) time 100%, i.e.,

$$PRB_i = \frac{100 B_i}{C_i^{a-QAG}} \%$$ **Equation 19**

*4.6.12 Precision*

Precision is an indicator of the degree of mutual agreement between individual measurements of a parameter having the same value. In this report it is defined as the percent relative standard deviation (PRSD) of a series of measurements of the same aerosol concentration held constant over a relative short test period in contrast to stability, which is the PRSD of a series of measurements determined over an extended period of time. The precision for the i$^{th}$ element ($P_i$) is given by the following equation:

$$P_i = PRSD = \frac{SD}{C_i}100\%$$ **Equation 20**

Because there is random variability associated with both the reference aerosol concentration as well as the measured aerosol concentration, the measured precision is an indicator of the variability introduced by all components of the generation-measurement system; i.e., QAG and candidate conditional method. For this series of tests, the magnitude of the QAG precision is considered to be similar to the candidate conditional method. As such, the precision of the QAG or candidate conditional method is defined as the measured precision divided by the square root of 2.

*4.6.13 Standard Deviation*

The standard deviation (*SD*) in the concentration is equal to the square root of the sum of the differences between the mean concentration and individual concentration measurements squared, divided by the number of measurements less one.

$$SD_i = \sqrt{\frac{\sum\left(\overline{C_i} - C_i\right)^2}{n-1}}$$ **Equation 21**

*4.6.14 Standard Deviation of the Mean*

The standard deviation of the mean (*SDM*) is equal to the *SD* divided by the square root of the number of measurements (*n*).

$$SDM_i = \frac{SD_i}{\sqrt{n}}$$ **Equation 22**

*4.6.15 t-statistic*

$$t = \frac{|B|}{SDM}$$ **Equation 23**

*4.7 Other Comparison Parameters*

*4.7.1 Detection Limits*

The minimum detection limit, $C_D$, is defined as the smallest concentration that a particular measurement can detect. Using the definition developed by Currie[27] detection may be

considered reliable when the probability of detecting a concentration $C_D$ is sufficiently large (95%), while the probability of incorrectly detecting a blank is sufficiently small (5%). Using this definition of detection and the selected probabilities (95% and 5%), it can be shown that:

$$C_D = 3.29SD \qquad \textbf{Equation 24}$$

where *SD* is the standard deviation of observed results when the true concentration is zero; i.e., standard deviation of a series of blank measurements. The minimum detection limit of a candidate conditional method will be the analytical detection limit as defined above using a blank filter, divided by the typical volume of stack gas sampled; i.e., about 0.012 dscm for the Xact-IAP and 0.03 dscm for the XFM.

*4.7.2 EPA Relative Accuracy*

The EPA has defined a figure-of-merit to evaluate candidate measurement methods relative to current reference methods or standards. This figure-of-merit, called relative accuracy, includes both a component for bias and a component for precision, which is designed to exclude imprecise methods with low bias as well as precise methods with high bias. However, it does not take into consideration uncertainties in reference method measurements nor can it be related to a statistically defined level of confidence. Although this EPA-defined relative accuracy term has proved useful in some cases, it is neither required nor is it considered appropriate for this evaluation. It is defined here because it is discussed in this report.

$$RA_i = \frac{\bar{d} + \frac{t_{0.975}}{\sqrt{n}} SD}{\overline{R_{RM}}} \qquad \textbf{Equation 25}$$

Where:

| | | |
|---|---|---|
| $RA_i$ | = | Relative accuracy for the $i^{th}$ element |
| $\bar{d}$ | = | Arithmetic mean of the difference, *d*, of paired CEMS and reference method (RM) data set |
| $SD$ | = | Standard deviation |
| $\overline{R_{RM}}$ | = | Average of the RM data set |

# 5.0 Quality Control and Assurance

## *5.1 Overview*

The overall objectives of Quality Control (QC) and Assurance (QA) for these tests were to assure and document that the accuracy of the measurements were 1) NIST traceable and 2) supportive of the method validation goals stated in the test plan (Appendix A). It is clear that these goals were met as evidenced by the high level of agreement between the QAG generated reference aerosol concentration and the independently measured XFM and Xact-IAP aerosol concentrations (±5%) as discussed in the following section. Overall, the QAG and candidate methods showed good QA/QC and all 240 Xact-IAP and 50 XFM runs taken during QAG operations were considered to be valid. Mass, temperature, pressure, XRF standards check, Xact-IAP upscale, Xact-IAP blank, and Xact-IAP thin film measurements, etc. met the test plan objectives. The complete QA/QC database and calculations are presented in Appendices G and H, and the original QA/QC data sheets are provided in Appendices I and J. This section provides a summary of key QA/QC results and issues for the QAG, XFM, and Xact-IAP Phase I and II tests.

## *5.2 QAG*

Generating an aerosol with an accurate NIST-traceable concentration with the QAG required control of such parameters as mass, flow, temperature, and pressure. The primary measurements for these parameters all met the test plan objectives. One key parameter, standard solution use rate ($R_m$, Equation 5), was a calculated parameter based on the slope of a plot of reservoir mass versus time. Although the balance used for the reservoir mass measurement was NIST traceable to better than 1%, the uncertainty in the slope (use rate, g/min.) for any particular period was on the order of a few percent. The QAG solution use rates during Phase I and II test periods are listed in Table 6. The plots from which these rates were determined are shown in Figure 10 and Figure 11. For both phases, the total mass consumption was reasonably stable with an average correlation ($r$) of better than 0.99 and an average standard solution consumption rate of 0.112 ± 0.009 g/min.

The total consumption rate depends upon the rate of solution droplet generation and evaporation. Since the nebulizer emits at a constant rate as soon as it begins operation, the QAG metal emission rate is stable after only a few minutes. The evaporation rate; however, is dependent upon the temperature of solution reaching a steady state, which typically requires several hours of operation if the solution has not been pre-cooled. QAG evaporation rates are typically 20-30% of the total solution consumption rate. For both phases, the temperature of the flow was controlled to 32ºF using an ice water bath and bubbler, pressure was maintained between 17 and 19 PSI, and flow was kept constant at 10.1 slpm. The ambient pressure is also used to determine evaporation rate and was assumed to be 14.7 PSI for Portland, OR and 14.3 PSI for Lafayette, IN[28]. Uncertainty in the evaporation rate is on the order of 10% resulting in a 2-3% uncertainty in the total solution consumption rate.

**Table 6: QAG Emission Rates for Phase I and II.**

| Test Phase | Date | Run | Corr Coeff. | QAG Rate |
|---|---|---|---|---|
| I | 15-Dec-04 | 1-12 | 0.999 | 0.105 |
| I | 16-Dec-04 | 13-16 | 0.992 | 0.121 |
| I | 16-Dec-04 | 17-20 | 0.989 | 0.105 |
| I | 16-Dec-04 | 21-24 | 0.973 | 0.105 |
| I | 17-Dec-04 | 25-26 | 0.926 | 0.110 |
| II | 4-Mar-05 | 1-12 | 0.997 | 0.130 |
| II | 6-Mar-05 | 15-18 | 0.976 | 0.108 |
| II | 7-Mar-05 | 19-22 | 0.995 | 0.114 |
| II | 8-Mar-05 | 23-26 | 0.997 | 0.110 |
| **Avg.** | | | **0.983** | **0.112** |
| **SD** | | | **0.023** | **0.009** |
| **PRSD** | | | **2.4** | **7.6** |

On March 5th, the QAG experienced problems with freezing in the nebulization chamber. Although the chamber and the tubing leading to it were maintained at 32ºF, it is believed that the expanding gas and solution evaporation in the chamber lowered the solution to below its freezing point. The stainless steel tubing leading to the nebulizer was replaced with Tygon™ tubing which helped maintain the temperature above freezing. Two XFM runs, 13 and 14, were taken during this time and were in good agreement with the Xact-IAP (less than 10% difference). These two XFM runs, however, were disregarded since they could not be compared to the predicted QAG concentration because of the above noted QAG freezing problem.

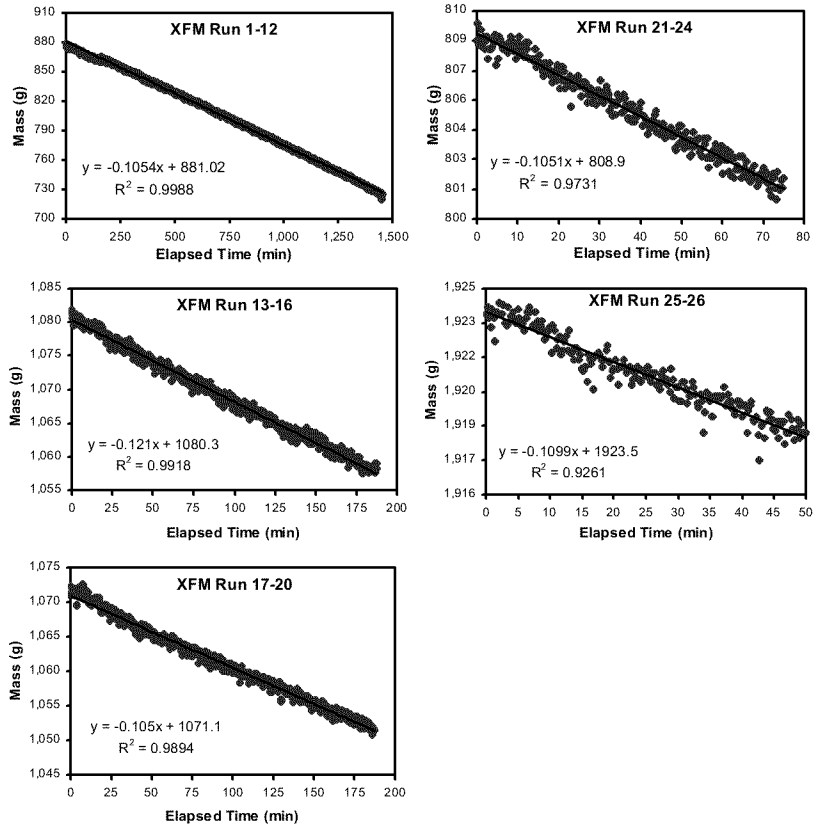



**Figure 10: QAG solution mass loss rate during Phase I testing.**

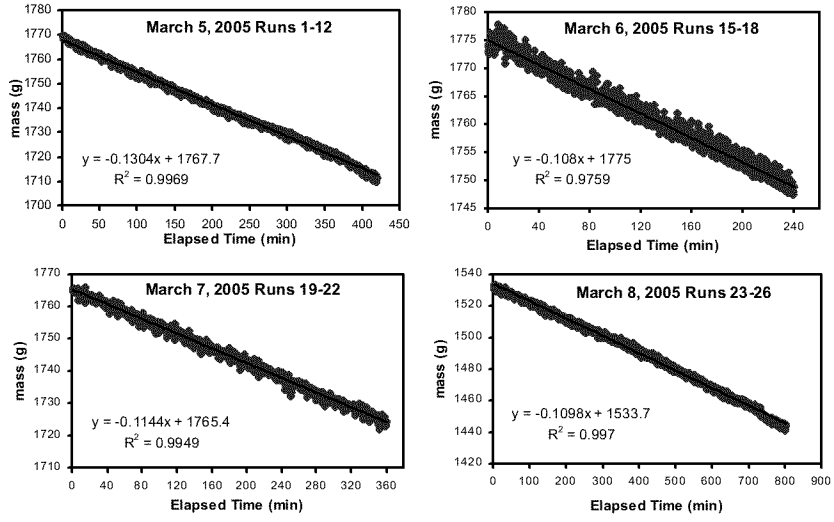



**Figure 11: QAG solution mass loss rate during Phase II.**

## *5.3 XFM*

The XFM was operated for 26 runs during each test phase. Other than the two runs that could not be compared to the QAG because of solution freezing, all XFM runs were considered valid and were used in calculating QAG efficiency and XFM bias and precision. The XFM reports concentrations in mass per volume. As part of the QA procedures for these tests, the XFM mass and volume measurements were evaluated for accuracy using NIST-traceable standards. For these tests, the XRF reported concentrations within 5% of the NIST standards (SRM 1832 and 1833) for all elements measured during calibration, and all of the daily XRF QA measurements were within 5% of the values obtained immediately after calibration. For this reason, no changes were made to any of the reported XRF metal mass concentrations.

The XFM dilution and total flow meters were found to be biased during Phase I tests by about 5% as indicated below in Table 7. In addition, the XFM dilution flow meter was found to be biased by about 6% during Phase II tests (Table 8). These flow meter bias determinations were made using a NIST traceable DryCal™ primary flow sensor. Following Phase II, the DryCal™ was reevaluated by the manufacturer and was found to be within 0.1% of the NIST standard. If a meter exhibited an average bias of more than 5%, a correction factor was applied to the recorded flows and subsequent calculations. Thus, correction factors of 5 to 7 % were applied only to the biased XFM flows as noted above.

**Table 7: Flowmeter evaluation during Phase I.**

| Meter | | Flow Check | | | | Flow Corr. for M301 | Flows Corr. Factor |
|---|---|---|---|---|---|---|---|
| | | Date | MFM slpm | DryCal slpm | % Diff. | | |
| A | QAG Neb Air[1] | 01/03/05 | 10.7 | 10.8 | -0.8 | No | -- |
| B | XFM Total | 10/20/04 | 1.32 | 1.25 | 5.6 | Yes | 0.95 |
| C | XFM Dilution | 10/20/04 | 0.75 | 0.71 | 5.0 | Yes | 0.95 |
| D | XFM Extract | 12/16/04 | 18.8 | 18.5 | 1.1 | No | -- |
| E | Overall Flow | 12/16/04 | 110.4 | 113.3 | -2.6 | No | -- |
| F | Xact (Samp, Dop) | 03/03/05 | 0.71 | 0.70 | 0.8 | No | -- |
| G | Xact Dopant | 03/03/05 | 0.20 | 0.20 | -0.4 | No | -- |

**Table 8: Flowmeter evaluation during Phase II.**

| Meter | | Pre-test | | | | Post-test | | | | Avg. % Diff. | Flow Corr. for M301 | Flows Corr. Factor |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Date | MFM slpm | DryCal slpm | % Diff. | Date | MFM slpm | DryCal slpm | % Diff. | | | |
| A | QAG Neb Air[1] | 01/03/05 | 10.7 | 10.8 | -0.8 | 3/9/2005 | 10.7 | 10.4 | 2.7 | 0.9 | No | -- |
| B | XFM Total | 10/20/04 | 1.32 | 1.25 | 5.6 | 3/8/2005 | 1.60 | 1.57 | 1.9 | 3.8 | No | -- |
| C | XFM Dilution | 10/20/04 | 0.75 | 0.71 | 5.0 | 3/8/2005 | 0.75 | 0.70 | 7.9 | 6.5 | Yes | 0.94 |
| D | XFM Extract | 12/16/04 | 18.8 | 18.5 | 1.1 | 3/8/2005 | 16.8 | 16.2 | 3.2 | 2.2 | No | -- |
| E | Overall Flow | 12/16/04 | 110.4 | 113.3 | -2.6 | 3/25/2005 | 104.2 | 103.6 | 0.6 | -1.0 | No | -- |
| F | Xact (Samp, Dop) | 03/03/05 | 0.71 | 0.70 | 0.8 | 3/8/2005 | 0.71 | 0.70 | 1.1 | 0.9 | No | -- |
| G | Xact Dopant | 03/03/05 | 0.20 | 0.20 | -0.4 | 3/8/2005 | 0.20 | 0.21 | -5.8 | -3.1 | No | -- |

### *5.4 Xact-IAP*

The Xact-IAP was turned on prior to a test and continued operation until the test was completed. During Phase I and II tests, the Xact-IAP completed more than 730 runs and 9 daily upscale/blank checks. Since no outliers were reported for the Xact-IAP and all flows met test plan objectives, all Xact-IAP data was accepted as reported.

The CES Xact-IAP was calibrated on October 8, 2004, two months before the Phase I evaluation. Upscale and blank concentrations (Table 9) were determined in December 2004. Upscale concentrations were determined automatically by the Xact-IAP while blank concentrations were calculated based on measurements taken when spiking was not occurring and flue gas/ambient air was being measured. Overall, the Xact-IAP upscale concentrations were within 1% of the original calibration and the blank concentrations were below 2 μg/dscm for all elements.

**Table 9: Upscale and zero drift during Phase I testing.**

| Parameter | Date | UPSCALE | | | | BLANK | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cr | Cd | Hg | Pb | Cr | Cd | Hg | Pb |
| | | Effective mass/region | | | | µg/dscm | | | |
| Original Calibration | 11/11/2005 | 3260 | 4300 | 2789 | 1983 | 0.00 | 0.00 | 0.00 | 0.00 |
| Avg. Conc. Pre-Test | 12/7/05 to 12/14/05 | 3250 | 4270 | 2784 | 1981 | 0.09 | 0.56 | 1.67 | 0.09 |
| Avg. Conc. During Test | 12/15/05 to 12/17/05 | 3270 | 4274 | 2789 | 1988 | 0.32 | 0.69 | 1.13 | 0.39 |
| Pre-Test/Orig Cal. | 12/8/05 to 12/14/05 | 1.00 | 0.99 | 1.00 | 1.00 | -- | -- | -- | -- |
| Test/Original Cal. | 12/15/05 to 12/17/05 | 1.00 | 0.99 | 1.00 | 1.00 | -- | -- | -- | -- |

The Xact-IAP XRF was calibrated using thin-film standards with NIST-traceable metal concentrations. These same standards were analyzed following Phase I and II tests with the results shown in Table 10. Overall, the concentrations for the metals remained within 5% of the original calibration for all metals. The two independent Xacts, CES' Xact for Phase I and Lilly's Xact for Phase II, were also in good agreement, with concentrations within 5% of each other.

For Phase II testing, the Lilly Xact-IAP was calibrated on January 28, 2005, one month prior to the field evaluation. Upscale and zero/blank drifts were determined in February 2005 and during the March tests with a summary shown in Table 11. Upscale concentrations were determined automatically by the Xact-IAP while blank concentrations were calculated based on measurements taken when spiking was not occurring and flue gas/ambient air was being measured. Overall, the Xact-IAP showed upscale and blank drifts below 4%, meeting the criteria found in proposed Performance Specification 10[20].

All mass and flow checks met QA precision requirements and no Xact-IAP outliers were present during the 460 runs of Phase II testing. No changes were made to the reported Xact-IAP concentrations and no Xact-IAP data was removed from the original data set.

**Table 10: Evaluation of NIST thin-film standards by the Xact-IAP.**

| Elem | NIST-Traceable Std No. | PHASE I: CES Xact | | | PHASE II: Lilly Xact | | | PHASE I VS. PHASE II | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Pre-Test 10/8/2004 µg/cm² | Post-Test 3/28/2005 µg/cm² | Post/ Pre Ratio | Pre-Test 1/28/2005 µg/cm² | Post-Test 3/9/2005 µg/cm² | Ratio Post-Test/ Calib. | Avg Phase I | Avg. Phase II | PI/PII |
| As | 15207 | 12.50 | 12.17 | 0.97 | 11.92 | 12.52 | 1.05 | 12.33 | 12.22 | 1.01 |
| Cd | 15207 | 8.25 | 8.14 | 0.99 | 8.27 | 8.32 | 1.01 | 8.20 | 8.30 | 0.99 |
| Cr | 15090 | 12.16 | 12.08 | 0.99 | 12.23 | 13.20 | 1.08 | 12.12 | 12.72 | 0.95 |
| Co | 15207 | 14.39 | 14.34 | 1.00 | 13.71 | 14.31 | 1.04 | 14.36 | 14.01 | 1.02 |
| Se | 15207 | 18.55 | 17.70 | 0.95 | 19.41 | 20.44 | 1.05 | 18.12 | 19.92 | 0.91 |
| Hg | 15102 | 16.50 | 16.00 | 0.97 | 15.73 | 16.18 | 1.03 | 16.25 | 15.96 | 1.02 |
| Ni | 15090 | 10.66 | 10.47 | 0.98 | 10.16 | 10.71 | 1.05 | 10.56 | 10.44 | 1.01 |
| Tl | 15090 | 11.36 | 11.17 | 0.98 | 10.84 | 11.49 | 1.06 | 11.27 | 11.16 | 1.01 |
| Sn | 15090 | 14.41 | 14.32 | 0.99 | 13.86 | 13.92 | 1.00 | 14.36 | 13.89 | 1.03 |
| Mn | 15091 | 12.93 | 12.98 | 1.00 | NM | NM | NM | 12.96 | NM | NM |
| Cu | 15091 | 11.77 | 11.79 | 1.00 | NM | NM | NM | 11.78 | NM | NM |
| Br | 15091 | 4.82 | 4.76 | 0.99 | NM | NM | NM | 4.79 | NM | NM |
| Ba | 15091 | 11.16 | 11.27 | 1.01 | NM | NM | NM | 11.21 | NM | NM |
| Ag | 15091 | 12.39 | 12.65 | 1.02 | NM | NM | NM | 12.52 | NM | NM |
| Fe | 15092 | 14.05 | 13.62 | 0.97 | 13.39 | 13.80 | 1.03 | 13.83 | 13.59 | 1.02 |
| Zn | 15092 | 7.82 | 7.60 | 0.97 | 7.45 | 7.64 | 1.03 | 7.71 | 7.55 | 1.02 |
| Sb | 15092 | 14.16 | 13.44 | 0.95 | 13.63 | 13.53 | 0.99 | 13.80 | 13.58 | 1.02 |
| Pb | 15092 | 13.36 | 12.93 | 0.97 | 12.73 | 13.13 | 1.03 | 13.14 | 12.93 | 1.02 |
| Sr | 15092 | 9.41 | 9.17 | 0.97 | 8.96 | 9.20 | 1.03 | 9.29 | 9.08 | 1.02 |

NM: Not Measured

**Table 11: Upscale and zero drift during Phase II testing.**

| Parameter | Date | UPSCALE | | | | BLANK | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cr | Cd | Hg | Pb | Cr | Cd | Hg | Pb |
| | | Effective µg/region | | | | µg/dscm | | | |
| Conc. During Calibration | 1/28/2005 | 1812 | 430 | 334 | 475 | 0.00 | 0.00 | 0.00 | 0.00 |
| Avg. Conc. Pre-Test[1] | 1/29/05 to 3/1/05 | 1855 | 429 | 346 | 488 | 0.23 | 0.60 | 0.05 | 0.09 |
| Avg. Conc. During Test[2] | 3/4/05 to 3/8/05 | 1857 | 427 | 346 | 493 | 0.42 | 0.71 | 0.71 | 0.71 |
| PreTest Avg. Cal. Drift (%)[1] | 1/29/05 to 3/1/05 | 2.4 | -0.1 | 3.5 | 2.9 | 0.2 | 0.5 | 0.1 | 0.1 |
| Test Avg. Cal Drift (%)[2] | 3/3/05 to 3/8/05 | 2.4 | -0.6 | 3.5 | 3.8 | 0.3 | 0.6 | 1.2 | 0.2 |

1) Upscale avg. of 26 days. Blank avg. of 2078 runs. One blank run (2/15/05 16:30:00) removed due to possible stainless steel contamination from stack operations.
2) Upscale avg. of 5 days. Blank avg. of 210 runs.

# 6.0 Results and Discussion

## *6.1 Overview*

This section summarizes the QAG, XFM, and Xact-IAP results from Phase I and II tests. In Phase I, the QAG was validated by demonstrating that it met all of the criteria required in Method 301 and the study plan. It generated a reference aerosol whose concentration for the five test metals was linearly related to the measured concentration over the range from zero to120 µg/dscm. The QAG demonstrated a precision and stability of about 2% and an efficiency of 100% within the experimental accuracy of the tests. These QAG validation results are summarized in Subsection 6.2 and discussed relative to the validation criteria in Subsection 6.2.2.

In Phase II, the XFM and Xact-IAP were evaluated for accuracy, precision, and linearity while sampling flue gas spiked with a metals-containing reference aerosol from the QAG. The XFM and Xact-IAP met all Method 301 and test plan criteria, with precisions of better than 3% and a high linear correlation with the reference aerosol concentration. Phase II results for the XFM and Xact-IAP are summarized in Subsection 6.3 and discussed as they pertain to the validation criteria in Subsections 6.4 and 6.5.

The complete set of test data and results is listed in Appendices I and J. Sample calculations are presented in Appendix K.

## *6.2 QAG Validation*

### *6.2.1 Summary*

The primary objective of this phase was to validate the QAG by demonstrating that it met the criteria in Method 301 and those established in the test plan. During these tests, five metals (As, Cd, Cr, Pb, and Hg) were spiked at five concentration levels ranging from zero to over 120 µg/dscm. The QAG reference concentrations were verified by 146 Xact-IAP and 26 XFM analyses, with the three independent approaches in good agreement for all five metals

(Figure 12 and Table 12). All three independent approaches showed very good agreement over the wide range of concentrations and for all five metals. Overall, the XFM to QAG and the Xact-IAP to QAG ratios were both 0.98 ± 0.07 (Figure 13). This good agreement between the QAG reference concentration and the XFM and Xact-IAP measured concentrations indicates that the aerosol generation, transport and collection efficiencies were all essentially 100% within the uncertainty.

The average XFM to QAG ratio for each of the five elements ranged from 0.94 to 1.00, while the Xact-IAP to QAG elemental ratios ranged from 0.96 to 1.01. The consistency of the XFM/QAG and Xact-IAP/QAG ratios for individual elements confirms the quantitative generation, transport and collection efficiency for each element. This suggests that no significant fractionation of metals took place during these tests. This is particularly important because the metals represent both particle and vapor phases. Independent inductively-couple plasma (ICP) analyses of the solutions conducted by Chester LabNet[21] of Tigard, OR confirmed the inter-element concentration ratios. It is important to note that in all Phase I and II tests, the two measurement methods were totally independent from the QAG reference aerosol generator as illustrated in Figure 2.

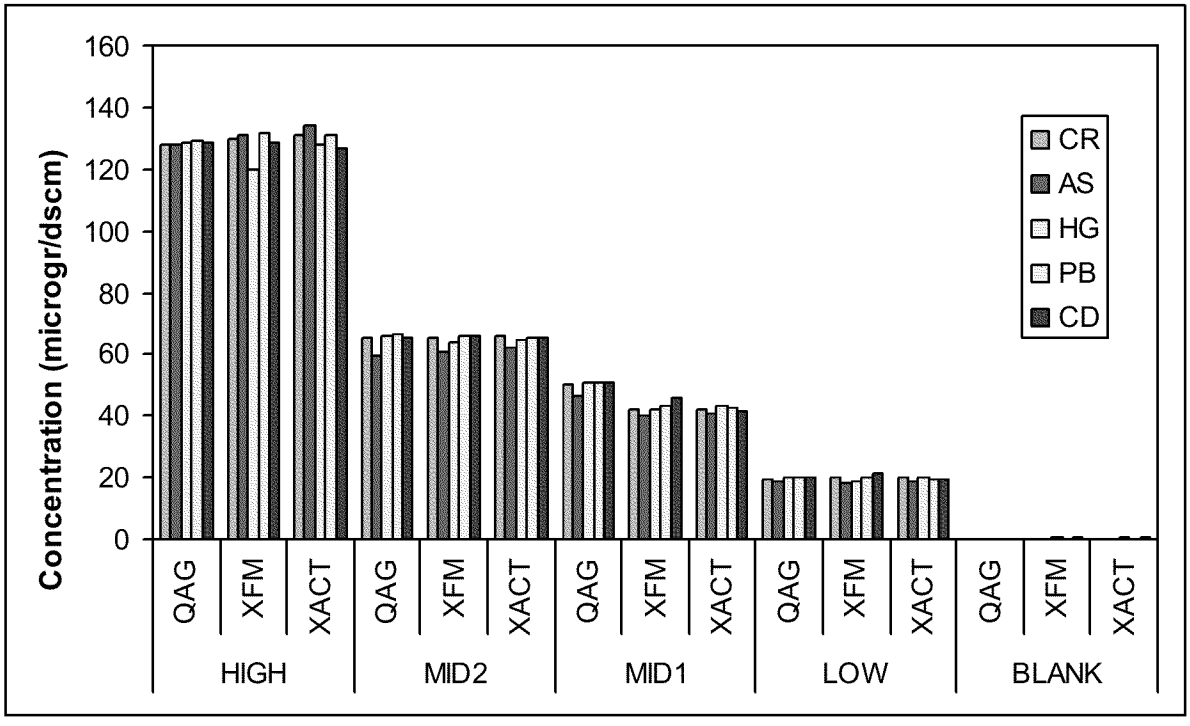



**Figure 12: QAG-generated and XFM- and Xact-IAP-measured aerosol concentrations during Phase I tests.**

**Table 12: Comparison of Average QAG reference aerosol concentrations with XFM and Xact-IAP average measured concentrations (µg/dscm).**

| Approach | Metal | Blank | Low | Mid 1 | Mid 2 | High |
|---|---|---|---|---|---|---|
| QAG | CR | 0.0 | 19.8 | 50.3 | 65.0 | 128 |
| | AS | 0.0 | 18.7 | 46.5 | 59.6 | 128 |
| | HG | 0.0 | 20.0 | 50.9 | 65.7 | 129 |
| | PB | 0.0 | 19.9 | 50.8 | 66.2 | 129 |
| | CD | 0.0 | 19.9 | 50.7 | 65.4 | 129 |
| XFM | No. | 2 | 4 | 4 | 12 | 4 |
| | CR | 0.1 | 20.2 | 42.2 | 65.5 | 130 |
| | AS | 0.0 | 18.4 | 39.9 | 61.1 | 131 |
| | HG | 0.7 | 18.7 | 42.3 | 63.7 | 120 |
| | PB | 0.2 | 20.3 | 43.5 | 66.1 | 132 |
| | CD | 0.5 | 21.1 | 46.0 | 65.7 | 128 |
| XACT-IAP | No. | 11 | 23 | 22 | 67 | 23 |
| | CR | 0.1 | 19.8 | 42.0 | 65.7 | 131 |
| | AS | 0.0 | 18.6 | 40.7 | 62.1 | 134 |
| | HG | 0.7 | 19.8 | 43.1 | 64.9 | 128 |
| | PB | 0.2 | 19.5 | 42.8 | 65.5 | 131 |
| | CD | 0.6 | 19.6 | 41.7 | 65.2 | 126 |

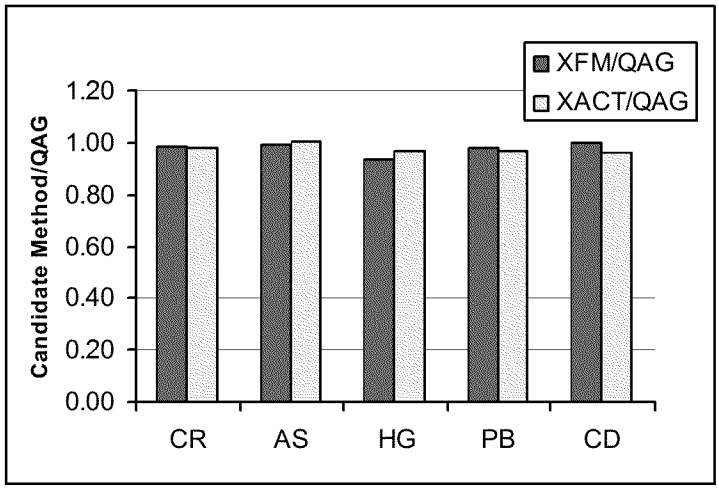



**Figure 13: Ratio of XFM and Xact-IAP measured metal concentrations to the QAG reference aerosol concentration.**

*6.2.2 Validation Criteria*

The QAG was validated by comparing the QAG-generated reference aerosol concentration to the aerosol concentration measured with the independent, analytically NIST-traceable XFM and Xact-IAP methods. The first step in this validation process was to demonstrate high relative transport and sampling efficiency for all test metals using metal concentration ratios. The second step was to demonstrate high absolute generation efficiency by comparing the QAG predicted reference aerosol concentration with the analytically measured aerosol concentration. The criteria used to demonstrate high relative transport and sampling efficiency were:

- **Filter Ratio:** More than 98% of two representative particulate metals (Cr and Pb) were required to be on the XFM's front filter to demonstrate high particulate capture efficiency.
- **Metal Ratio:** A high transport and sampling efficiency for vapor phase metals was assured by requiring the measured metal ratios be within 10% of the predicted QAG ratios.

High absolute efficiency was then demonstrated by showing that the following criteria were met:

- **Efficiency:** The overall (generation, transport, and sampling) QAG efficiency was required to be better than 80% for each metal as measured by the XFM and Xact-IAP.
- **Precision:** The combined QAG and filter measurement method were required to have a precision of better than 10%.
- **Linearity:** The QAG was required to be linearly related to the two candidate methods with a correlation of better than 0.85.

### *6.2.3 Filter Ratio*

The objective of this criterion was to demonstrate that essentially all (>98%) of the Cr (low volatility metal) and Pb (semi-volatile metal) were captured on the upstream PTFE XFM filter. Meeting this objective demonstrates >98% trapping efficiency for these two MACT metal categories. The high concentration XFM runs (21 – 24) were the most sensitive tests for this evaluation. The results for these runs are summarized in Table 13. The average percent lead on the first filter for these high concentration runs was 99.9%, with no measurable Pb or Cr found above their detection limit on the downstream filter. Similar results were observed in Phase II where none of the Cr was measured on the downstream filter and the average Pb on the upstream filter was more than 99%. These high trapping efficiencies indicate that all of the Pb and Cr were captured by the XFM's PTFE filter and that this test plan criterion was met.

**Table 13: Lead and chromium measured on the upstream PTFE filter as percent of total XFM lead and chromium (µg/filter).**

| | Lead | | | Chromium | | |
|---|---|---|---|---|---|---|
| Run No. | Upstream µg/filter | Downstream µg/filter | % Upstream µg/filter | Upstream µg/filter | Downstream µg/filter | % Upstream µg/filter |
| 21 | 3.83 | 0.017 | 99.6 | 3.69 | 0.000 | 100.0 |
| 22 | 3.63 | 0.000 | 100.0 | 3.62 | 0.000 | 100.0 |
| 23 | 3.61 | 0.000 | 100.0 | 3.57 | 0.000 | 100.0 |
| 24 | 3.76 | 0.000 | 100.0 | 3.72 | 0.000 | 100.0 |
| AVE | 3.71 | 0.004 | 99.9 | 3.65 | 0.000 | 100.0 |

### *6.2.4 Metal Ratio*

The objective of this criterion was to demonstrate quantitative transport and sampling efficiency for the other three MACT metals (As, Cd and Hg) with the XFM and XACT-IAP. The metric for this comparison was defined as the ratio of the Pb-normalized solution concentration to the

Pb-normalized aerosol concentration for these metals. The reasoning is, if the Pb and Cr are quantitatively trapped by physical filtration as demonstrated above, and if the ratio of the other elements to Pb for the XFM and Xact-IAP is the same as in the nebulized solution, then the total sampling and transport efficiency for these metals as measured with the XFM filter cassette is the same as that for Pb, i.e., 100%. The acceptable range for this ratio was defined in the test plan as 0.9 to 1.1.

The average metal ratios ranged from 0.99 to 1.05 for the XFM and 0.96 to 1.01 for the Xact-IAP. These metal ratio values are clearly within the range defined in the test plan. As such, this criterion was met. Meeting this and the preceding filter ratio criteria demonstrates that these metals do not fractionate during generation, transport and measurement of the reference aerosol.

### *6.2.5 Efficiency*

Efficiency is defined as the ratio of the measured aerosol concentration to the QAG-predicted reference aerosol concentration expressed as a percent. This efficiency includes the QAG generation efficiency as well as the transport and measurement efficiencies. This total system efficiency for five metals measured at four concentration levels during Phase I QAG validation testing are listed in Table 14. The average QAG efficiency over all five metals and all four concentration levels was 97.8±2.3% and 97.7±1.8% as measured by the XFM and Xact-IAP, respectively. This represents all 24 XFM and 142 Xact-IAP individual efficiency determinations. The average QAG efficiency for each metal as measured with the XFM ranged from a low of 94% for Hg to a high of 100% for Cd. The average QAG efficiency for each metal as determined with the Xact-IAP ranged from a low of 96% for Cd to a high of 101% for As. In addition, the QAG efficiencies at low and high concentrations as determined with both candidate analytical methods were greater than 99%, which demonstrates that efficiency is independent of aerosol concentration in the range from 20 to 125 µg/dscm. Thus, the average total system efficiency (generation, transport and measurement) is 98 ± 2%. However, the uncertainty in the reference aerosol concentration was about 4%. As such, the test plan criterion was met, the measured efficiency was essentially 100% within the uncertainty, and no efficiency correction factor is required. A complete set of results and sample calculations used for these efficiency determinations are presented in Appendices I and K.

### *6.2.6 Precision*

QAG precision measurements are summarized in Table 15. This table lists the precision for each element as determined for each concentration level, and are based on sequential measurements. The average QAG precision over all elements and all concentration levels was better than 2.5%, significantly better than the required 10% criteria value. The high precision at each level demonstrates the ability of the QAG to maintain a constant concentration over extended periods of time. These precision results are based on data listed in Appendix I with sample calculations provided in Appendix K.

**Table 14: QAG efficiencies determined during Phase I laboratory tests (%).**

| | Xact Determined QAG Efficiency | | | | | XFM Determined QAG Efficiency | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RUN | CR | HG | AS | CD | PB | CR | HG | AS | CD | PB |
| 1 | 100 | 97 | 103 | 100 | 98 | 102 | 101 | 101 | 98 | 100 |
| 2 | 100 | 99 | 102 | 98 | 98 | 93 | 99 | 100 | 99 | 93 |
| 3 | 101 | 97 | 103 | 98 | 98 | 98 | 94 | 101 | 104 | 99 |
| 4 | 99 | 98 | 104 | 103 | 97 | 99 | 97 | 100 | 98 | 100 |
| 5 | 101 | 100 | 107 | 101 | 99 | 101 | 100 | 105 | 99 | 98 |
| 6 | 103 | 99 | 103 | 98 | 101 | 101 | 100 | 103 | 104 | 101 |
| 7 | 103 | 99 | 107 | 102 | 101 | 102 | 98 | 101 | 98 | 102 |
| 8 | 104 | 101 | 107 | 100 | 100 | 101 | 97 | 104 | 99 | 99 |
| 9 | 100 | 99 | 103 | 98 | 99 | 102 | 90 | 103 | 100 | 102 |
| 10 | 101 | 99 | 104 | 97 | 98 | 103 | 96 | 104 | 102 | 98 |
| 11 | 103 | 99 | 103 | 98 | 101 | 109 | 102 | 111 | 105 | 109 |
| 12 | 100 | 99 | 104 | 102 | 99 | 98 | 92 | 97 | 98 | 98 |
| 13 | 83 | 86 | 88 | 76 | 83 | 83 | 80 | 83 | 89 | 87 |
| 14 | 84 | 84 | 87 | 84 | 85 | 85 | 84 | 88 | 87 | 87 |
| 15 | 82 | 85 | 87 | 84 | 85 | 83 | 86 | 85 | 99 | 85 |
| 16 | 84 | 84 | 88 | 85 | 85 | 84 | 83 | 87 | 88 | 84 |
| 17 | 98 | 101 | 100 | 96 | 96 | 102 | 95 | 96 | 105 | 100 |
| 18 | 103 | 98 | 102 | 103 | 95 | 104 | 93 | 102 | 106 | 99 |
| 19 | 101 | 102 | 101 | 100 | 99 | 100 | 93 | 98 | 103 | 105 |
| 20 | 99 | 96 | 96 | 96 | 101 | 104 | 94 | 98 | 111 | 104 |
| 21 | 103 | 100 | 106 | 97 | 100 | 101 | 100 | 101 | 99 | 104 |
| 22 | 102 | 99 | 104 | 100 | 102 | 103 | 95 | 104 | 100 | 103 |
| 23 | 102 | 100 | 104 | 96 | 103 | 100 | 88 | 102 | 98 | 100 |
| 24 | 103 | 100 | 106 | 99 | 102 | 102 | 90 | 103 | 101 | 102 |
| **Avg.** | **98.2** | **96.7** | **100.8** | **96.3** | **96.7** | **98.4** | **93.6** | **99.0** | **99.6** | **98.2** |
| SD | 7.0 | 5.6 | 6.5 | 6.9 | 6.0 | 7.3 | 6.0 | 6.8 | 5.5 | 6.5 |
| %SD | 7.1 | 5.8 | 6.5 | 7.2 | 6.2 | 7.4 | 6.4 | 6.9 | 5.5 | 6.6 |

**Table 15: Summary of QAG Phase I precision (%).**

| ELEM | XFM | | | | | XACT | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Low Runs 17-20 (%) | Mid 1 Runs 13-16 (%) | Mid 2 Runs 1-12 (%) | High Runs 21-24 (%) | AVG. (%) | Low Runs 17-20 (%) | Mid 1 Runs 13-16 (%) | Mid 2 Runs 1-12 (%) | High Runs 21-24 (%) | AVG. (%) |
| CR | 1.3 | 1.0 | 2.3 | 0.9 | **1.4** | 1.7 | 1.0 | 1.1 | 0.3 | **1.0** |
| AS | 1.8 | 2.0 | 2.2 | 1.1 | **1.8** | 2.0 | 0.6 | 1.0 | 0.7 | **1.1** |
| HG | 0.8 | 2.1 | 2.8 | 3.7 | **2.3** | 2.0 | 1.0 | 0.7 | 0.6 | **1.1** |
| PB | 1.7 | 1.3 | 2.2 | 0.8 | **1.5** | 2.0 | 0.8 | 0.8 | 1.1 | **1.2** |
| CD | 2.3 | 4.1 | 1.9 | 1.0 | **2.3** | 2.5 | 3.4 | 1.5 | 1.2 | **2.1** |
| **AVG** | **1.6** | **2.1** | **2.3** | **1.5** | **1.9** | **2.0** | **1.4** | **1.0** | **0.8** | **1.3** |

### *6.2.7 Linearity*

The test plan linearity criterion for validation acceptance was a correlation coefficient ($r$) value greater than 0.85. The QAG linearity was determined from a regression analysis for a plot of the measured aerosol concentration versus the QAG-predicted reference concentration over four concentration levels and a blank level. These plots for both the XFM and the Xact-IAP are illustrated in Figure 14 and Figure 15 (Note that only $r^2$, coefficient of determination, values are listed in these plots). Since all of the $r^2$ values are greater than 0.99, the r values are also greater than 0.99 and thus clearly meet the test plan acceptability requirement for r.

Other linearity defining factors such as slope and intercept were also determined and are supportive. As can be seen from the plots in these two figures, the slopes ranged from a low

of 0.94 for Hg as measured with the XFM to a high of 1.05 for As measured with the Xact-IAP. The overall average slope was close to 1.00 verifying the strong agreement between these independent approaches. In addition, the intercepts were all below 2% of the full scale indicating a low blank bias.

It is also important to note that none of the data was excluded in these linearity plots. In the case of the XFM, results from all 26 runs are included. The Xact-IAP ran continuously during the three days of Phase I tests and completed more than 270 runs, of which 146 were conducted while the QAG was in operation. All 146 Xact-IAP runs that corresponded to QAG runs are included in the plots shown in Figure 15. The Xact reported no outliers, experienced no mechanical problems, and had an effective uptime of 100% during Phase I. This strong linear relationship between the concentrations measured with the candidate methods and the independent QAG-generated reference aerosol concentration demonstrates the ability of the QAG to spike quantitatively over a wide range of concentrations.

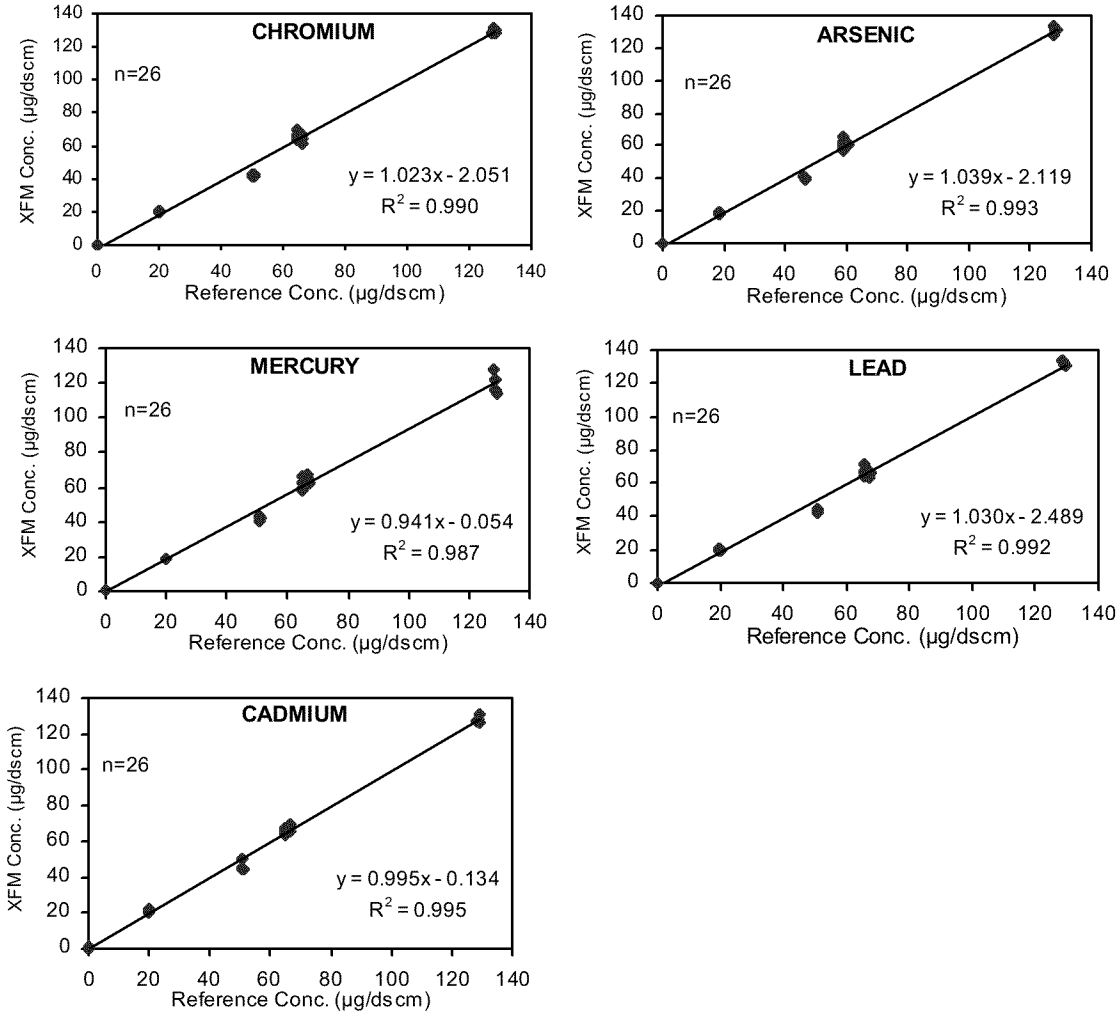



**Figure 14: Phase I QAG linearity plots as determined by the XFM.**

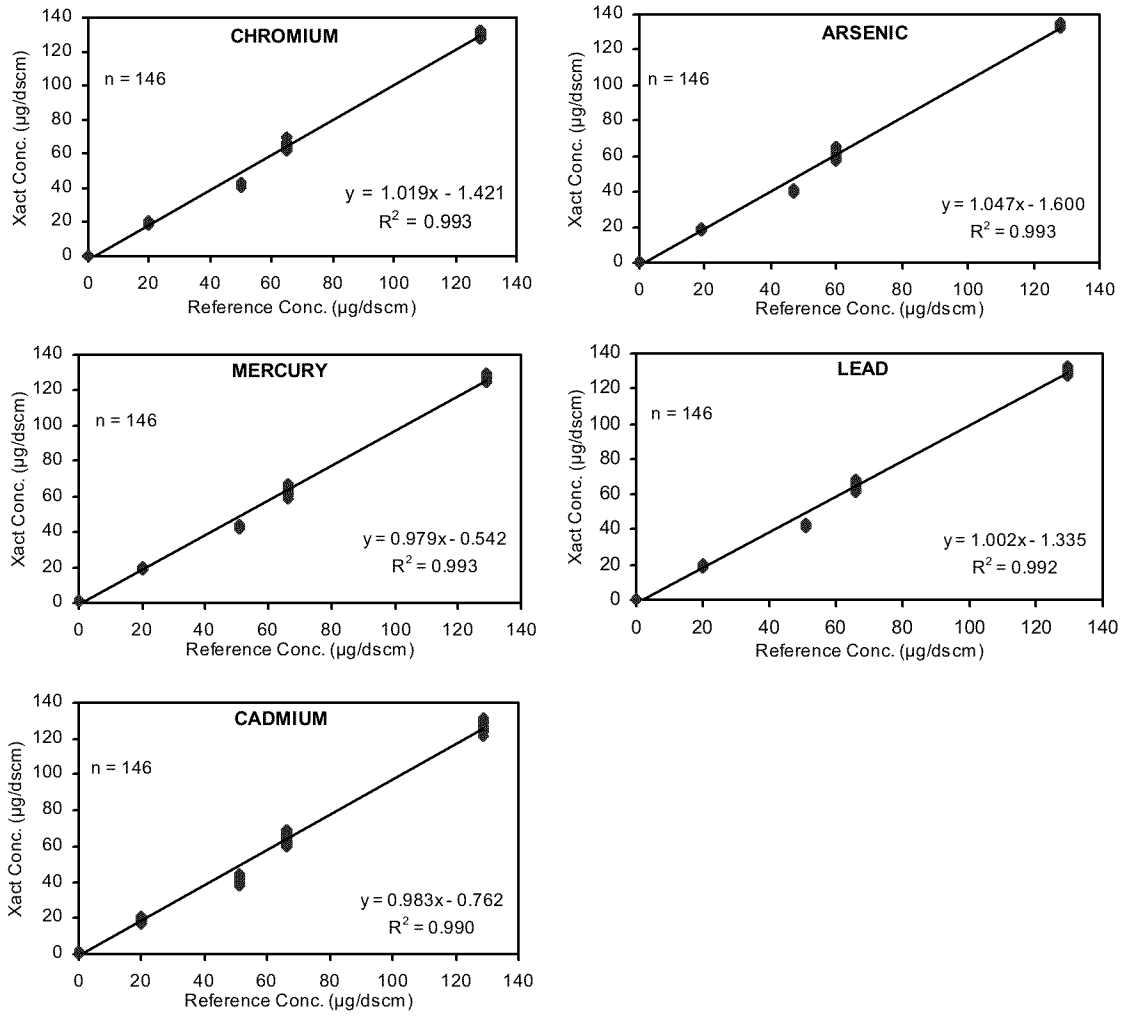



**Figure 15: Phase I QAG linearity plots as determined with the Xact-IAP**

### *6.2.8 QAG Validation Summary and Recommendation*

Phase I results as they pertain to the QAG validation criteria are summarized below in Table 16. It is clear from this summary that all QAG validation criteria established in the test plan were met. As such, the QAG should be approved as a reference aerosol generator that can be used for validating emission measurement instruments and methods including CEMS, IAP, alternatives to reference methods and conditional methods.

**Table 16 Summary of Phase I QAG validation results.**

| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | >25 | Yes |
| Filter Ratio (% Front) | >98 | >99 | Yes |
| Metal Ratio (Sol./Aer.) | 0.9 - 1.1 | 0.95 - 1.01 | Yes[b] |
| Efficiency (%) | >80 | 94 - 100 | Yes |
| Precision (%) | <10 | <4 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]XFM and Xact results for all five elements

[b]Confirmed with independent ICP analysis results

### *6.3 XFM and Xact-IAP Validation Overview*

The primary objective of Phase II testing was to validate the XFM and Xact-IAP by demonstrating that they met the conditional method criteria established in the test plan. The QAG, validated in Phase I, was used in this phase to spike a NIST-traceable reference aerosol into incinerator flue gas. As such, it is assumed that the characteristics of the QAG reference aerosol generator are those demonstrated in Phase I; i.e., 100% generation and transmission efficiency. Validation criteria and acceptance values are the same for both the XFM and the Xact-IAP, and include bias, precision and linearity. Phase II results and test conditions are listed in Appendix J and sample calculations are provided in Appendix K. The general results from Phase II testing for both the XFM and Xact-IAP are summarized below. The detailed XFM results as they pertain to the specific validation criteria are presented in Subsection 6.4 while the results for the Xact-IAP are presented in Subsection 6.5.
It needs to be emphasized that:

- The QAG, XFM and Xact-IAP were independent of each other in Phase II as they were in Phase I. That is, the QAG was not used to calibrate the XFM and the Xact as is commonly accepted practice in EPA instrumental analyzer procedures such as Methods 6C and 7E where the same gas standard used to calibrate the instrument is used to spike the stack gas. The XFM and Xact-IAP results are based on NIST-traceable thin film standards.
- The Xact instrument used in Phase II was not the same one used in Phase I. As such, the Xact used in Phase II was calibrated independently of the Phase I Xact.
- Results from all of the runs were used for the data analysis. In some cases, data from some runs could have been excluded, which would have resulted in a significant improvement in the agreement between the methods. However, even when all the data is included, all of the validation criteria are still met.

Phase II testing consisted of spiking stack gas with a QAG-generated reference aerosol containing five elements (As, Cd, Cr, Hg, and Pb) at three concentrations ranging from about 20 to 120 µg/dscm and at a blank level. The concentration of the QAG-spiked stack gas and the measured XFM and Xact concentrations are summarized in Table 17 and Figure 16. Concentrations reported by the XFM and the Xact-IAP were in good agreement with each other and with the reference aerosol concentration at all three spiked concentrations and the blank. Overall, the XFM to reference aerosol concentration ratio was 1.02 ± 0.07 while the Xact-IAP ratio was 0.93 ± 0.07.

**Table 17: Summary of XFM and Xact-IAP measured concentrations and QAG-spiked flue gas concentrations Phase II (µg/dscm).**

| Approach | | Avg. Blank | Avg. Low | Avg. Mid | Avg. High |
|---|---|---|---|---|---|
| Number | | 4 | 4 | 6 | 12 |
| QAG | CR | 0.0 | 21.3 | 46.2 | 108 |
| | AS | 0.0 | 21.2 | 46.2 | 108 |
| | HG | 0.0 | 21.2 | 45.9 | 108 |
| | PB | 0.0 | 21.2 | 45.9 | 108 |
| | CD | 0.0 | 21.2 | 46.2 | 107 |
| XFM | CR | 0.2 | 22.9 | 41.8 | 112 |
| | AS | 0.0 | 21.7 | 41.0 | 114 |
| | HG | 0.3 | 22.7 | 40.2 | 111 |
| | PB | 0.9 | 22.6 | 40.6 | 115 |
| | CD | 0.3 | 22.3 | 43.1 | 113 |
| XACT | CR | 0.0 | 20.0 | 37.8 | 103 |
| | AS | 0.1 | 21.0 | 39.9 | 107 |
| | HG | 0.2 | 18.5 | 35.2 | 95 |
| | PB | 0.0 | 18.8 | 37.9 | 108 |
| | CD | 0.3 | 21.5 | 39.9 | 106 |

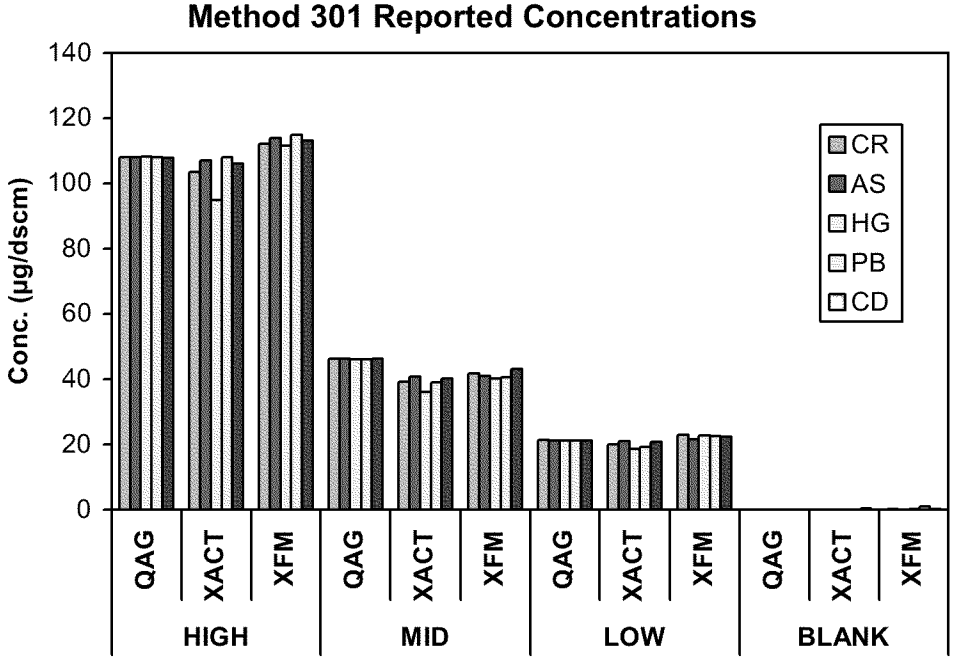



**Figure 16: Comparison of the XFM and Xact-IAP measured concentrations with the QAG-spiked flue gas concentrations during Phase II testing.**

## 6.4 XFM Validation

### 6.4.1 Bias

The twelve high concentration runs were used to calculate bias with results shown in Table 18. Overall, there is very good agreement between the XFM measured concentration and the reference aerosol concentration with an average bias over all metals of 4.8±1.3%. Mercury exhibited the lowest bias at 3.1% and Pb the highest at 6.3%, which are all below the 10% acceptance criterion.Thus, the XFM meets the required bias criteria for all metals tested.

**Table 18: Summary of XFM Phase II bias values for each metal tested (µg/dscm).**

| Run | Reference Concentration | XFM | | | | | XFM Bias (XFM-Reference) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CR | AS | HG | PB | CD | CR | AS | HG | PB | CD |
| 1 | 108 | 113 | 112 | 109 | 114 | 113 | 5.36 | 4.40 | 1.38 | 5.80 | 5.22 |
| 2 | 108 | 114 | 117 | 108 | 118 | 118 | 6.54 | 9.00 | -0.21 | 9.57 | 10.46 |
| 3 | 108 | 111 | 113 | 114 | 110 | 110 | 2.66 | 5.29 | 5.52 | 2.20 | 2.48 |
| 4 | 108 | 112 | 113 | 104 | 113 | 113 | 3.80 | 4.75 | -3.97 | 4.63 | 4.79 |
| 5 | 108 | 111 | 112 | 109 | 120 | 114 | 3.38 | 3.76 | 0.67 | 11.58 | 5.91 |
| 6 | 108 | 114 | 116 | 117 | 116 | 112 | 5.63 | 8.17 | 8.66 | 8.29 | 4.40 |
| 7 | 108 | 110 | 112 | 113 | 111 | 112 | 2.30 | 4.39 | 4.52 | 3.34 | 4.37 |
| 8 | 108 | 104 | 110 | 117 | 112 | 104 | -3.63 | 2.15 | 9.13 | 3.89 | -3.58 |
| 9 | 108 | 109 | 110 | 109 | 109 | 113 | 0.70 | 2.49 | 0.69 | 0.61 | 4.96 |
| 10 | 108 | 116 | 114 | 108 | 124 | 113 | 8.50 | 6.40 | 0.09 | 15.90 | 5.23 |
| 11 | 108 | 117 | 121 | 120 | 117 | 119 | 9.58 | 13.06 | 11.44 | 9.20 | 11.16 |
| 12 | 108 | 113 | 116 | 111 | 115 | 117 | 5.30 | 7.70 | 2.84 | 6.86 | 8.87 |
| **AVG** | **108** | **112** | **114** | **111** | **115** | **113** | **4.18** | **5.96** | **3.40** | **6.82** | **5.35** |
| SD | | 3.5 | 3.1 | 4.6 | 4.3 | 3.8 | 3.54 | 3.10 | 4.56 | 4.34 | 3.85 |
| XFM SD | | 2.50 | 2.20 | 3.22 | 3.07 | 2.72 | 2.50 | 2.20 | 3.22 | 3.07 | 2.72 |
| XFM SDM | | 0.72 | 0.63 | 0.93 | 0.89 | 0.79 | 0.72 | 0.63 | 0.93 | 0.89 | 0.79 |
| % Bias | | | | | | | **3.87** | **5.52** | **3.14** | **6.32** | **4.96** |

### 6.4.2 Precision

The average XFM precision (PRSD) based on the XFM standard deviations (XFM SD) listed above in Table 18 was 2.5±0.4% and ranged from a low of 2.0% for As to a high of 3.0% for Hg. This represents a significant improvement over the currently accepted precision for Reference Method 29 and well within the 10% criterion acceptance value required for validation.

### 6.4.3 Linearity

The key linearity criterion for the XFM is a correlation coefficient ($r$) value greater than 0.85. To test the linearity of the XFM, the flue gas was spiked with all five metals at four reference aerosol concentrations using the QAG. The results from these five tests are plotted in Figure 17. A least-squares regression analysis of all 26 data points provided the correlation coefficient as well as the slope and intercept for each metal. All of the correlation coefficients were greater than 0.99, easily exceeding the requirement to be greater than 0.85. The slopes averaged 1.06±2 and ranged from a low of 1.04 for Hg to a high of 1.07 for As and Pb. The intercepts were less than 3% of the full scale indicating low blank values.

### *6.4.4 XFM Summary*

Phase II XFM results are summarized in Table 19. This table shows that all the acceptance criteria were met for all of the five MACT metals tested. As such, it is recommended that the XFM be approved as a conditional method.

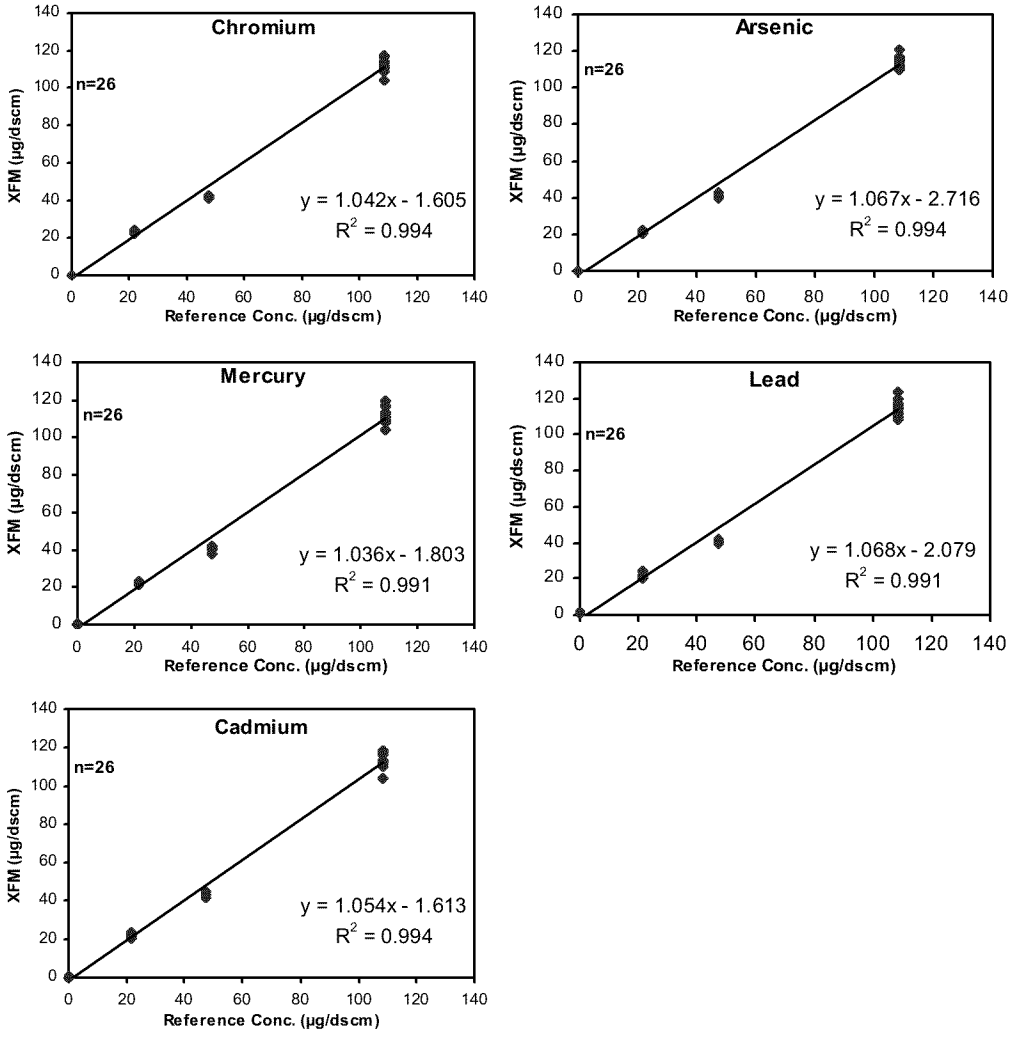



**Figure 17: Phase II XFM linearity.**

**Table 19: Summary of Phase II XFM validation test criteria and results.**

| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | 26 | Yes |
| Bias Corr. Factor | 0.80 - 1.2 | 0.94 - 0.97 | Yes[b] |
| Precision (%) | <10 | <3 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]XFM results for all five elements

[b]Confirmed with independent ICP analysis results

## *6.5 Xact-IAP Validation*

### *6.5.1 Xact-IAP Overview*

The Xact multi-metals analyzer, when permanently installed, acts as a CEMS, whereas if it is installed for short term emission measurements (days to weeks), it is part of an IAP. It is this latter application that is the focus of this subsection. Two different Xact instruments were used during Phase I (CES Xact) and Phase II (Lilly Xact) tests, requiring two independent calibrations using NIST traceable thin-film standards.

All of the validation criteria were met for all of the elements. However, as discussed below, a key issue is whether or not to apply a bias correction factor if a significant bias is observed.

### *6.5.2 Bias*

The twelve high concentration runs (nominal concentration of 110 μg/dscm) were used to calculate bias. These bias results along with the measured Xact-IAP results and the reference aerosol concentration are listed in Table 20 along with standard deviations and percent bias. As can be seen from this table, there is very good agreement between the Xact-IAP measured concentrations and the reference aerosol concentration for all the elements.

Method 301 requires an evaluation for bias in the candidate method in order to determine if a correction factor is required[1]. For Phase II tests, bias was determined by evaluating the systematic differences between the reference aerosol method and candidate method relative to the uncertainty in the methods. Bias was considered to be significant when it exceeded two times the combined uncertainty in the reference generation and candidate measurement method at the 95% confidence level. Since the combined Xact-IAP and QAG uncertainty is on the order of 5%, the significance criteria resulted in a 10% threshold for determining the significance of bias. Four of the elements measured by the Xact-IAP – As, Cd, Cr, and Pb – had biases of less than 2%, well within the uncertainty of the methods and below the threshold of significance. For this reason, no correction factor is required for As, Cr, Cd, or Pb. The average percent bias for Hg was 12.3±1.0%. This bias is clearly above the 10% level of significance for the QAG/Xact-IAP, but well within the acceptable range of 30% specified in Method 301; particularly with the high precision (±1%) observed for this bias. Although a correction might be considered necessary, it is not recommended in this case as is discussed in detail in the following subsection.

### *6.5.3 Mercury Bias Correction Factors*

As noted above, a significant, systematic bias greater than 10% was observed in the Hg results from Phase II tests of the Xact-IAP. However, even though the percent bias (12.3%) was greater than 10%, it is recommended the Xact-IAP be approved without the requirement of a bias correction factor, since half of the bias was due to a post-test identified calibration error. This error was identified by evaluating the Hg/Pb sensitivity (calibration) ratio, which is used to obtain NIST traceability through the Pb concentration in NIST SRM 1833. This ratio should have been 0.93, but was instead 0.99. If this 6% error had not existed, the Xact-IAP Hg results would have been 6% higher and the Hg percent bias would have been about 6%, well within the required 10%.

**Table 20: Comparison of Xact-IAP with QAG reference concentrations and bias (µg/dscm).**

| Run | Ref. Conc. | Xact | | | | | XACT-QAG | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CR | AS | HG | PB | CD | CR | AS | HG | PB | CD |
| 1 | 108 | 105 | 106 | 94 | 102 | 106 | -3.07 | -2.11 | -14.44 | -5.65 | -1.57 |
| 2 | 108 | 103 | 106 | 96 | 104 | 105 | -5.26 | -2.01 | -12.44 | -3.84 | -2.51 |
| 3 | 108 | 102 | 106 | 95 | 105 | 106 | -6.14 | -1.88 | -12.74 | -3.17 | -1.93 |
| 4 | 108 | 102 | 105 | 94 | 107 | 105 | -5.77 | -2.75 | -14.24 | -1.02 | -2.78 |
| 5 | 108 | 100 | 106 | 94 | 105 | 105 | -7.94 | -2.06 | -14.22 | -2.55 | -2.62 |
| 6 | 108 | 103 | 107 | 94 | 110 | 105 | -4.92 | -1.45 | -14.19 | 1.76 | -2.26 |
| 7 | 108 | 103 | 107 | 95 | 111 | 109 | -5.08 | -1.33 | -13.18 | 2.98 | 1.61 |
| 8 | 108 | 103 | 107 | 94 | 109 | 107 | -4.64 | -1.28 | -13.68 | 1.44 | -0.54 |
| 9 | 108 | 105 | 108 | 95 | 110 | 106 | -2.54 | 0.05 | -13.08 | 1.65 | -1.41 |
| 10 | 108 | 104 | 107 | 94 | 109 | 105 | -4.10 | -1.02 | -14.12 | 1.37 | -2.89 |
| 11 | 108 | 107 | 110 | 97 | 111 | 107 | -1.07 | 2.27 | -11.29 | 2.99 | -1.13 |
| 12 | 108 | 105 | 109 | 97 | 112 | 106 | -2.44 | 1.43 | -11.32 | 3.74 | -1.30 |
| **AVG** | **108** | **103** | **107** | **95** | **108** | **106** | **-4.41** | **-1.01** | **-13.25** | **-0.02** | **-1.61** |
| SD | | 1.9 | 1.5 | 1.1 | 3.1 | 1.3 | 1.89 | 1.52 | 1.12 | 3.10 | 1.25 |
| Xact SD | | 1.34 | 1.07 | 0.79 | 2.19 | 0.89 | 1.34 | 1.07 | 0.79 | 2.19 | 0.89 |
| Xact SDM | | 0.39 | 0.31 | 0.23 | 0.63 | 0.26 | 0.39 | 0.31 | 0.23 | 0.63 | 0.26 |
| % Bias | | | | | | | **-4.09** | **-0.93** | **-12.27** | **-0.02** | **-1.49** |

This type of error did not appear in Phase I testing using CES' Xact which had been calibrated with the appropriate Hg/Pb sensitivity ratio. For Phase I, the Hg bias was less than 2% for the 12 runs near the emission limit and was less than 4% averaged over all of the 146 Xact-IAP measurements.

This error is readily correctable within the Xact software and should not be present in future tests. As such, it is recommended that no correction factor be made to future Xact-IAP mercury measurements.

### *6.5.4 Precision*

The average Xact-IAP precision (PRSD) based on the Xact-IAP standard deviations (Xact SD) listed above in Table 20 was 1.3 ± 0.6% and ranged from a low of 0.8% for Hg to a high of 2.0% for Pb. This represents a significant improvement over the currently accepted precision for Reference Method 29 and substantially less than the required validation acceptance limit of 10%.

### *6.5.5 Linearity*

The Xact-IAP ran continuously during the five days of Phase II tests and completed more than 450 runs, of which 192 were conducted while the QAG was operated. The Xact-IAP experienced no mechanical problems during Phase II testing and had an effective uptime of 100%. To test the linearity of the Xact-IAP, the incinerator flue gas was spiked with all five metals at four reference aerosol concentrations using the QAG. The results from these tests, including a series of blank runs, are plotted in Figure 18. A least-squares regression analysis of all 192 data points provided the correlation coefficient as well as the slope and intercept for each metal (The coefficient of determination, $r^2$, is listed on the figures.) All of the correlation coefficients ® were greater than 0.99, easily exceeding the required lower limit value of 0.85.

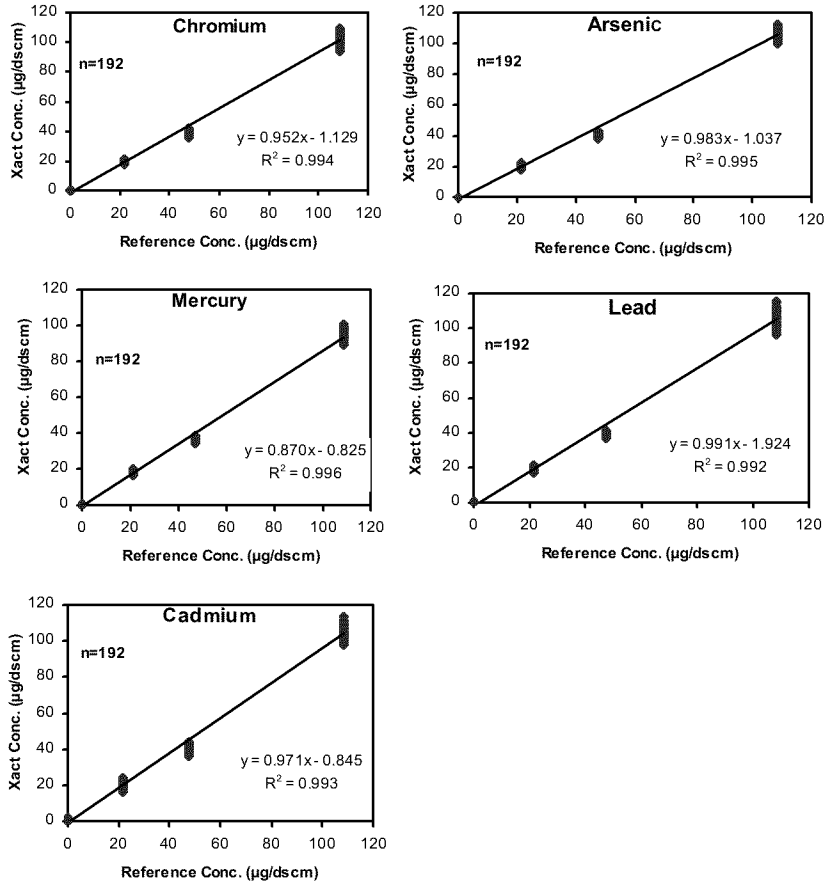



**Figure 18: Phase II Xact linearity.**

### *6.5.6 Xact-IAP Summary and Recommendations*

The Phase II Xact-IAP results are summarized in Table 21 and Table 22. Table 21 shows that all the acceptance criteria were met for all of the five MACT metals tested. Only one metal, Hg, might have required a bias correction factor. However, it is recommended that the procedure be approved without a correction factor because, as discussed in Subsection 6.5.3, the significant bias observed was due to a calibration error, was not observed in Phase I, and should not happen in future applications because of changes made to the software and SOP.

Table 22 compares the Xact-IAP results from Phase II with proposed Performance Specification 10 for multi-metals CEMS. It is clear from the comparison, that all of the criteria in this proposed performance specification were met.

**Table 21: Summary of Phase II Xact results.**

| Criteria | Acceptable | Results[a] | Met Criteria |
|---|---|---|---|
| No. Runs | >9 | 192 | Yes |
| Bias Corr. Factor | 0.80 - 1.2 | 1.00 - 1.14 | Yes |
| Precision (%) | <10 | <3 | Yes |
| Linearity - Corr. Coef. ( r ) | >0.85 | >0.99 | Yes |

[a]Xact-IAP results for all five elements

**Table 22: Comparison of Xact Phase II results with proposed PS-10 criteria.**

| CRITERIA | UNITS | XACT | PS-10 Criteria | MET PS-10 Criteria |
|---|---|---|---|---|
| Uptime | % | 100 | NA | Yes |
| Metals Measured During Testing | -- | 5 | 2 | Yes |
| Response Time | min. | 45 | 240 | Yes |
| Reporting Time | min. | 15 | 60 | Yes |
| Upscale/Calibration Drift | % | <4 | 5 | Yes |
| Zero/Blank Drift | % | <2 | 5 | Yes |
| Precision (PRSD) | % | <4 | 15 | Yes |
| No. of Measurements | -- | 20 | 9 | Yes |
| Relative Accuracy | % | 2-16 | 20 | Yes |

* Comparison to EPA Method 29's typical precision of 15%.

# 7.0 Range of Method Application

## *7.1 Overview*

The results from the preceding section clearly demonstrate the ability of the XFM and Xact-IAP to accurately and precisely quantify metals in stack emissions over a broad range of concentrations, and that these methods are applicable to the quantitative measurement of the five validated metals in hazardous waste incinerators. The question then arises as to

*What other source categories and elements is this technology applicable?*

The answer to this question lies in how key features of the sampling and analysis procedures depend on and respond to changes in emission characteristics associated with different source categories. The EPA suggests in Method 301 that this might be addressed in part by conducting a series of ruggedness tests, which are laboratory tests of a method's sensitivity to key method variables[1,29,30]. This type of evaluation of the XFM and Xact-IAP was conducted during Phase I laboratory testing. In addition, a substantial body of previous laboratory and field test data on this reactive-filter based technology is also available that supports the general applicability of these methods to most sources and elements.

The above tests and data are summarized in this section along with key aspects of the XFM and Xact-IAP methods, and relative characteristics of emissions. The objective of this review is to demonstrate that these methods should be considered generally applicable to a wide range of emissions and elements including those from regulated sources. This review is presented in the following subsections:

- Method Applicability (7.2)
- Key Sampling and Analysis Features (7.3)
- Key Emission Characteristics (7.4)
- Filter Trapping Efficiency for Vapor Phase Metals (7.5)
- Applicable Concentration Range (7.6)

- Deposit Stability (7.7)
- Moisture (7.8)
- Holding Times (7.9)
- Other Related Tests (7.10)
- Applicable Elements (7.11)
- Sensitivity to Reactive Stack Gases (7.12)

The details of this review are presented in Appendix L and supporting reports are provided in Appendix M. The conclusion of this review is that there is a substantial body of information about the chemistry and physics of the methods and emissions as well as specific test data covering some of the more challenging of conditions that strongly supports the extension of these methods to other regulated source categories and elements.

### *7.2 Criteria for Candidate Method Applicability*

It is clear that when a candidate method meets the requirements of Method 301, it is valid for the source tested, and may be applicable to the specific source category. Method 301 recommends that additional test data be submitted to extend the applicability of the candidate method to other source categories. This recommendation, however, does not specify criteria that can be used to evaluate possible extension of a method's applicability when direct test data is not available. For the following discussion, it will be assumed that the candidate methods will be applicable to an untested source category if differences in emission characteristics between sources tested and candidate source emissions are such that they are unlikely to contribute significantly to imprecision and bias in measured metal concentrations.

### *7.3 Key Sampling and Analysis Features*

Both the XFM and Xact-IAP draw a representative sample of stack gas through a filter matrix where metals are concentrated prior to analysis. The XFM draws the stack gas through an upstream PTFE filter that removes PM from a gas stream and then through a downstream reactive filter that traps vapor phase metals. The Xact-IAP, on the other hand, uses a single reactive filter to trap both the PM and vapor phase metals. Both methods measure the mass of each metal deposited on the filter(s) using XRF analysis procedures based on EPA's IO Compendium Method 3.3[14]. The concentration of metal in stack gas (C) is calculated by dividing the mass of metal in the filter(s) deposit (M) by the volume of stack gas (V) that passed through the filter(s). That is;

$$C = M/V \qquad \textbf{Equation 26}$$

Key sampling and analysis features are thus those that contribute to the quantitative accuracy of the metal mass and volume determinations. Consequently, a method will likely be applicable to a particular source emissions category if the differences in stack gas characteristics are such that they do not significantly contribute to inaccuracies in volume and mass measurements.

In the case of volume determination, both methods dilute, cool, filter, and dry the stack gas as well as denude the gas of corrosive species such as acids, $SO_2$, etc. prior to volume determination. This dilution and extensive conditioning of the stack gas prior to volume determination makes it relatively insensitive to differences in stack gas characteristics. Thus, if differences in stack gas characteristics are to significantly impact the accuracy of the measured aerosol concentration, it must be through the metal mass determination.

Accurate determination of metal mass depends on two key factors, which may depend on stack gas characteristics:

- XRF analytical determination of metal mass in the filter deposit
- Filter trapping efficiency

Again, it is important to note that both methods use dilution to maintain and control such sampling conditions as temperature, dew point, and PM concentration in their optimal range. As such, the method's sensitivity to specific stack gas characteristics is significantly reduced even for these two factors. For example, when applying these methods, the applications engineer is directed to adjust non-critical parameters within specified limits such as dilution ratio and sampling time to optimize the method for a particular application. Furthermore, since there is no direct interaction between stack gas and the analysis, the XRF determination of metal mass in the filter deposit is only indirectly dependent on the characteristics of the stack gas through how the stack gas impacts the characteristics of the deposit on the filter. Other than the analyte metals of interest, the only species deposited on the filter are non-analyte PM species, the total mass of which is controlled through the method application by selecting optimal sampling times and dilution ratios. None of the major components of stack gas are trapped on the filters and cannot therefore interfere with the XRF analysis.

For this reason, the only factor that might be sensitive to stack gas characteristics is the filter trapping efficiency for PM and vapor phase metals. Filter trapping efficiencies for PM are well established and generally accepted to be greater than 99%[23,31] are not expected to be dependent on differences in stack gas characteristics. As such, filter trapping efficiency for vapor phase metals is the key factor that might be impacted by stack gas characteristics. The primary focus of the next two sections is on the potential dependence of vapor phase metal trapping efficiency on flue gas conditions and the available data showing the range within which the method has demonstrated acceptable quantitation.

### *7.4 Key Emission Characteristics*

Characterization of emissions depends on such factors as source type (combustion, process, fuel type, etc.), type of emissions (ducted or fugitive) and type of controls (filtration, electrostatic precipitators, scrubbers, absorbers, reactive, etc.). However, from the method applicability evaluation perspective, the characteristics of emissions that are most relevant are those defined in terms of their physical (primarily temperature) and chemical (composition) characteristics. Emissions are generally composed of varying amounts of air ($N_2$, $O_2$), combustion products ($NO_x$, $SO_x$, $CO_2$, CO, $H_2O$, etc.), contributions from controls (Na, Ca, $H_2O$, $NH_3$, etc.) and various process species, and can be further divided into categories such as PM, reactive and non-reactive gases, acid vapors, etc.

As discussed above, the filters used by the XFM and Xact-IAP have a high PM metals trapping efficiency regardless of the stack gas physical and chemical characteristics when sampling within the conditions specified by their SOPs. Some potential exists, however, for the vapor phase collection efficiency to be impacted by the stack gas physical parameters and chemical composition. For both the XFM and Xact-IAP, the sampling temperature, flow rate, and pressures are controlled by the operator within the bounds of the SOP and are independent of the source type. Thus, the key characteristics of emissions that might impact the reactive filter's trapping efficiency are the sampling interferences caused by reactive gases such as $NO_x$, $SO_x$, $NH_3$, $Cl_2$, HCl, $HNO_3$, and $H_2SO_4$. Although this list is not complete, it does represent the more abundant and more reactive species likely to be present at varying concentrations in most stacks of regulatory interest. Oxygen was not listed, since it is expected to be present in most emissions at ambient concentrations (21%) or less, and laboratory tests in Phase I demonstrated high trapping efficiency at the highest likely $O_2$ concentration. Potentially interfering reactive gases are listed below in Table 23 along with measured stack gas concentrations during supplemental testing discussed below and in Appendix L. Although this list is incomplete, the concentrations and conditions are representative of these sources and cover a broad range of concentrations and temperatures.

**Table 23. List of stack conditions for which Xact-IAP and XFM tests have been conducted**

| Species | | Phase II Tippe, IN | CFPP-CES Boardman, OR | CFPP-EPA Midwest | HWC - TEAD Tooele, UT |
|---|---|---|---|---|---|
| CO, dry | ppm | 14 | < 10 | NA | 10 |
| $O_2$, dry | % | 11 | 4.5 | 12-15 | 14-15 |
| $CO_2$, dry | % | 6 | 12.5 | 4-8 | 5 |
| $NO_x$, dry | ppm | 110 | 200 | 70 | 1200 |
| $SO_2$, dry | ppm | ND | 225 | 20-35 | 10 |
| HCl (equiv.), dry | ppm | 2 | NA | NA | 50 |
| $H_2O$ | % | 9 | 10 | 15-20% | 5 |
| PM @ 7% O2 | mg/dscm | 4 | 27 | NA | 10 |
| Temp | °F | 170 | 300 | 160 | 450 |

NA: Not Available
ND: Not Detected

CFPP-CES: CES sponsored collection efficiency test at PGE CFPP
CFPP-EPA: EPA sponsored test of Hg monitors
HWC-TEAD: US Army sponsored tests at demiliterization HWC

### *7.5 Filter Trapping Efficiency for Vapor Phase Metals*

The Clean Air Act lists 11 metals as air toxics: Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni and Se[10]. Of these metals, Hg is the only one that is predominately in the vapor phase at the operating temperature of the Xact-IAP and XFM (180°F). For this reason, Hg is the most challenging to trap by filtration and most sensitive indicator of vapor phase metal trapping efficiency. Over the past several years, three series of Hg trapping and relative accuracy tests have been conducted in addition to Phase I and II tests described in the first part of this report. Whereas Phase II tests demonstrated high Hg trapping efficiencies under conditions more representative of emissions from modern hazardous waste incinerators, these additional tests focused on emissions from coal-fired boilers. The supplemental tests were more challenging in part because of their lower Hg concentrations (<10 µg/dscm) but also because of the presence of higher concentrations (Table 23) of potentially interfering species such as

$NO_x$, $SO_2$, $SO_3$, $NH_3$, PM, etc. The first series of tests discussed below were sponsored by CES and were conducted both in the laboratory and at a coal-fired utility boiler to define the concentration range of applicability for the reactive filters. The second and third series of tests were sponsored by the EPA and the army, and focused on relative accuracy of the measurements at coal-fired boiler emissions. In the following summaries, an acceptable relative accuracy when compared to an EPA authorized reference method will be taken to imply an acceptable vapor phase trapping efficiency. The supplemental tests summarized below are discussed in more detail in Appendix L and supporting reports are provided in Appendix M.

### *7.5.1 CES Sponsored Trapping Efficiency Tests*

A series of tests were conducted at CES and a coal-fired power plant in Boardman, OR to evaluate the Hg trapping efficiency of reactive filters under a variety of sampling conditions. For these tests, mercury was injected into either laboratory air or stack effluent and the trapping efficiency evaluated with the XFM using two reactive filters in series. The mercury trapping efficiency was determined by comparing the Hg trapped on the upstream filter with the total mercury collected on both filters. Mercuric chloride laboratory tests in the temperature range between 100 and 212°F exhibited capture efficiencies greater than 99% for concentrations ranging in excess of 800 µg/dscm with sampling times up to one hour. Similar tests were conducted at the coal-fired power plant using elemental Hg spiked into the stack gas. In this case, the elemental Hg trapping efficiency was greater than 99% for concentrations ranging up to 300 µg/dscm.

### *7.5.2 EPA Sponsored Relative Accuracy Tests*

CES tested the XFM filter approach during an EPA sponsored evaluation of mercury measurement methods at a Midwest coal-fired power plant5. These tests, conducted in July 2003, compared simultaneous XFM and Ontario-Hydro Reference Method (OH) measured mercury concentrations between 1 and 6 µg/dscm. The accuracy of the reactive filter based methods at low concentrations was demonstrated using an in-stack version of the XFM. A total of 12 two-hour OH runs were conducted. For each OH run, two simultaneous 50 minute, in-stack XFM samples were collected by CES. For these tests, the XFM and the OH results were in good agreement with a relative accuracy of 11% for the nine valid runs, well within the 20% criteria for conditional methods specified by EPA's proposed Performance Specification 12[32]. Three of the 12 OH test runs were omitted from comparison by the EPA contractors. Two were omitted because of poor OH replication (>40% difference) and one was omitted due to a plant upset. The remaining nine runs were used for comparison, the results of which are plotted in Figure 19. The high correlation of these results and low relative accuracy demonstrates the effectiveness of the reactive filter approach for trapping and quantifying Hg concentrations between 1 and 6 µg/dscm.

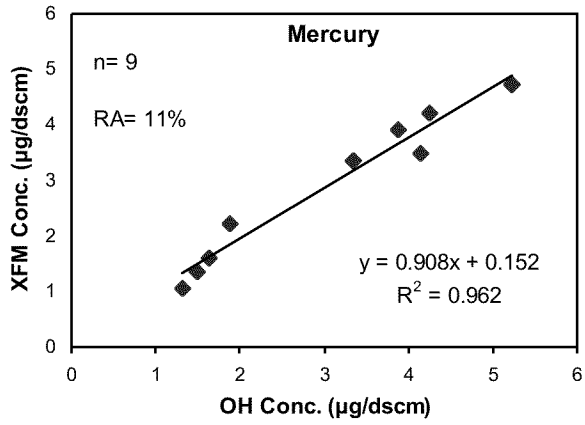



**Figure 19. Comparison of Hg concentrations determined by XFM and Ontario Hydro reference method at a coal-fired power plant.**

*7.5.3 US Army Sponsored Relative Accuracy Tests*

The U.S. Army sponsored a series of tests in January 2005 to evaluate a mercury-optimized Xact at a coal-fired power plant[33]. For these tests, mercury and arsenic were spiked into stack gas followed by simultaneous Hg and As measurements using the Xact and Reference Method 29. The results from these tests demonstrated relative accuracies of 17% for these two elements, meeting the proposed 20% criteria proposed for Performance Specification 10.

*7.5.4 Summary of Trapping Efficiency Sensitivity to Reactive Stack Gases*

Unlike the physical filtration mechanism used to collect particulate metals, vapor phase metals react with the chemically treated filter and bind to the filter substrate. Some stack gas constituents could potentially interfere with this process. However, the more abundant stack gas species such as $N_2$, $O_2$, $CO_2$, CO, and vapor phase $H_2O$ are relatively inert, are not trapped on the reactive filter, and test results indicate that they do not influence the filter trapping efficiency. Oxidants within the gas stream such as $Cl_2$ have been shown to improve the vapor phase collection efficiency for Hg. Other minor stack gas components such as $NO_x$, $SO_x$, and $NH_3$, have the potential to interfere with vapor phase Hg trapping efficiency. However, this potential to interfere has not been observed in the extensive testing that has been conducted to date. For example, the possibility of $NH_3$ interference was evaluated during EPA's test of mercury measurement approaches at a Midwest coal-fired power plant with state-of-the-art ammonia injection and selective catalytic reduction $NO_x$ control equipment[34]. Despite the use of ammonia, the XFM reactive filter demonstrated an 11% relative accuracy when compared to the Ontario-Hydro Hg reference method concentrations, which ranged from 1 to 6 µg/dscm. Similarly, minor reactive components such as $NO_x$, and $SO_x$ have the potential to impact vapor phase collection efficiency. However, there is no indication that these species affected the Hg trapping efficiency at the concentrations listed in Table 22. Indeed, the 99+% trapping efficiency for elemental Hg at the Boardman site was completed with measured $NO_x$ concentrations of 200 PPM and $SO_x$ concentrations of about 225 PPM. In addition, there is no indication that high acidic concentrations affect the trapping efficiency since nitric acid concentrations during Phase I and II testing was greater

than 50 PPM. The tests conducted to date and the range of key test parameters are summarized below in Table 24.

**Table 24. List of test conditions and references used to evaluate method applicability.**

| Parameter | Test Summary | Test |
|---|---|---|
| **Concentration Range** | | |
| Particulate Metals | 3-2200 µg/dscm | 1, 2 |
| Elemental Mercury | 1-314 µg/dscm | 3, 4 |
| Oxidized Mercury | 1-880 µg/dscm | 3, 5 |
| **Holding Time** | | |
| XFM: Particulate Filter | 12 Months | 6, 7 |
| XFM: Vapor Phase Filter | 24 Months[a] | 8 |
| Xact | 12 Months | 6, 7, 8, 9 |
| **Stack Type & Conditions** | | |
| Moisture | Filters acceptable for Wet Stacks | 3, 10, 11 |
| | Filters acceptable for Dry Stacks | 1, 2, 4, 9 |
| HWC | Filters acceptable for HWC applications | 1, 2, 9, 11 |
| CFPP | Filters acceptable for CFPP applications | 3, 4, 10 |
| **Stack Temperature** | 450°F | 1, 2 |
| **Filter Temperature** | | |
| XFM Particulate Filter | 400°F | 12 |
| XFM Vapor Phase Filter | 185°F | 4, 5 |
| Xact Particulate/Vapor Phase Filter | 185°F | |
| **Sampling Time** | | |
| XFM | 60 min | 4, 5 |
| Xact | 30 min | 10 |
| **Sampling Flow Rate** | | |
| XFM | 4.5 lpm/cm² | 4, 12 |
| Xact | 2.4 lpm/cm² | 12 |
| **Field Blank** | Det. Limits less than 2 µg/dscm[b] | 11 |

a) Correction factor of 0.5%/month required after six months.
b) One-sigma limits based upon analysis of 3899 filters measurements at Lilly's T149 Incinerator

1 HWC at TEAD production furnace (Section 2.3).
2 HWC at TEAD research furnace (Section 2.3).
3 EPA test at Midwest CFPP (Section 2.3).
4 CES Test at Oregon CFPP (Section 2.3).
5 CES Laboratory Tests (Section 2.3).
6 Reevaluation of Phase I Filters (Section 2.3).
7 EPA $PM_{2.5}$ Speciation Program[7]; Reevaluation of Phase I Filters (Section 2.3).
8 CES Laboratory Evaluation of XFM Filters (Section 2.3).
9 CES Reanalysis of Xact Filter Tape from TEAD tests (Section 2.3).
10 Xact Test at IAAP CFPP (Section 2.3).
11 Evaluation of Blank Filters at Lilly's T149 Incinerator (Section 2.3).
12 Manufacturers Specifications
13 Phase II Tests at Lilly's T149 Incinerator

### *7.6 Applicable Concentration Range*

The applicable concentration range for these reactive filter based methods was extended to over 2000 µg/dscm during Xact and Reference Method 29 relative accuracy tests conducted in 2002 at an Army hazardous waste test incinerator[34]. Twelve Reference Method 29 test runs were conducted while the stack gas Pb concentrations ranged from a low of about 10 µg/dscm to over 2200 µg/dscm. The results from these twelve tests are compared to the corresponding Xact results in Figure 20. These results show a high degree of linearity over this broad range of concentrations and a high relative accuracy of 4% when compared to the Method 29 results. If these results are combined with those in the preceding subsection where the Hg results were in good agreement with the reference method down to almost 1 µg/dscm, it is clear that the method is quantitative over at least three orders of magnitude and at concentrations greater than 2200 µg/dscm.

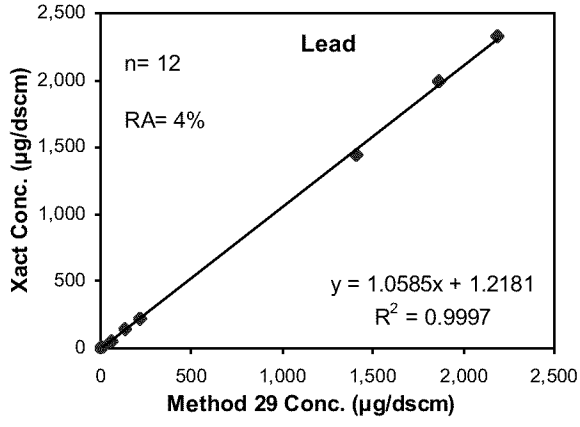



**Figure 20 Plot of Xact-IAP concentration versus Reference Method 29 measured concentrations showing excellent agreement over two orders of magnitude and at concentrations in excess of 2,000 µg/dscm.**

### *7.7 Deposit Stability*

The Xact-IAP uses a reel-to-reel tape system to collect stack gas metal samples, which are then transported to a position for XRF analysis. After analysis, the tape is drawn over a take up spool where the exposed filter deposits come into contact with following tape as it wraps over the previously exposed tape. Some potential exists for transfer of metals from their original deposit to the tape covering the deposit. If this transfer were significant, it would reduce the potential to post-test validate Xact-IAP results with independent analysis of the deposits. As such, post test analyses were conducted on 72 deposits collected during relative accuracy tests conducted in May 2002 at a US Army hazardous waste production incinerator at the Tooele Army Depot (TEAD) in Tooele, UT[34]. During these tests, the Xact monitored emissions in an instrument shed about 40 feet from the incinerator stack while EPA Reference Method 29 samples were collected at the stack. Twelve Method 29 test runs were conducted with concentrations varying from 5 to 300 µg/dscm. There was very good agreement with the reference method as illustrated in Figure 21. The relative accuracy was 4% and the results exhibited a high degree of linearity.

Following these tests, the exposed filter tape was stored at room temperature at CES. Two months after the field tests were completed, the tape was removed from the spool exposing the previously collected deposits. These deposits were cut from the tape and analyzed with CES' laboratory XRF analyzer. These laboratory results are compared to the original concentrations reported by the Xact in Figure 22. Clearly, there is a high degree of agreement between the original Xact Pb results and the laboratory results. The slope and correlation suggests that there was not a significant transfer of Pb from the deposit to the covering tape at the level of a few percent.

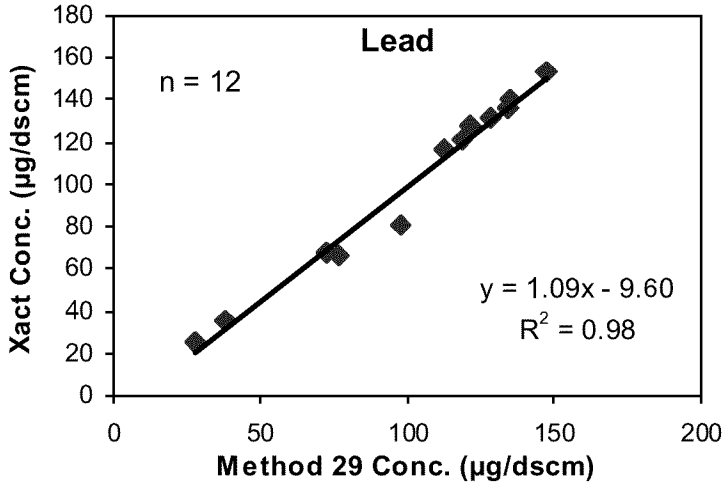



**Figure 21. Plot of Pb concentrations determined by Reference Method 29 and the Xact.**

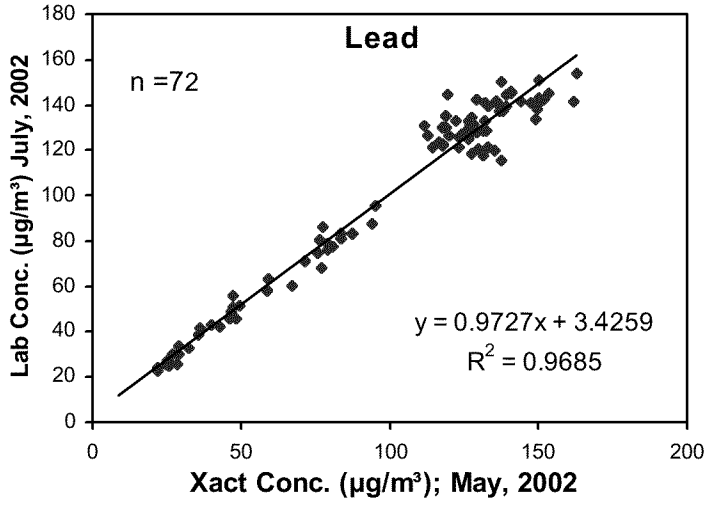



**Figure 22: Comparison of results from laboratory XRF analysis in July, 2002 with Xact field test results from May 2002 relative accuracy tests at a hazardous waste incinerator**

### *7.8 Moisture*

Over the last three years, the Xact-IAP and XFM have been evaluated on both wet and dry stacks (Table 25) using Method 29, Ontario-Hydro and the QAG reference aerosols. In all

cases, the Xact-IAP and XFM showed good relative accuracy and trapping efficiencies. For this reason, it is believed that the candidate measurement methods are valid for both wet and dry stacks as long as the probe and filter temperature remain above the water vapor dew point, which are controlled primarily with dilution.

**Table 25: Recent tests of Xact and XFM on wet and dry stacks.**

| Date | Test Location | Inc. Type | Air Pollution Control Technology | Wet or Dry Stack | Elements Analyzed | Results |
|---|---|---|---|---|---|---|
| March 2005 | Eli Lilly Lafayette, IN | HWC | Scrubber | Wet | As, Cr, Cd, Hg, Pb | Xact and XFM within 15% of QAG predicted for As, Cr, Cd, Hg, Pb |
| Jan. 2005 | IAAP Ames, IA | CFPP | Scrubber | Wet | As, Hg | Xact RA of 17% vs. M29 for As, Hg |
| Sept. 2003 | TEAD Tooele, UT | HWC | High Temp. Baghouse | Dry | Pb | Xact RA of 4% vs. M29 for Pb |
| May 2003 | Midwest | CFPP | Ammonia injection, SCR, baghouse | Dry | Hg | XFM RA of 11% vs. OH for Hg |
| Aug 2002 | Boardman, OR | CFPP | Scrubber | Wet | $Hg^o$ | Trapping efficiency of 99% for $Hg^o$ |

### *7.9 Holding Times*

Tests were also conducted to evaluate the holding times for the XFM and Xact-IAP filters. These tests included both the XFM PTFE filter and the reactive filter. During the December 2004 Phase I tests, the PTFE filter had collected particulate As, Cd, Cr, Hg, and Pb at concentrations ranging from 20 µg/dscm to 125 µg/dscm. In order to determine PTFE filter holding times, CES reanalyzed filters from seven of these tests (Runs 1-4 and 21-24) in April 2005. During the five months between the initial and second XRF analysis, the filters were stored at room temperature in plastic petrie dishes. Both analyses were conducted using XRF following the IO Compendium Method 3.3[14]. Overall, the average metal concentrations measured in April 2005 were within one percent of the concentrations determined five months earlier. All measurements were within 4% of their original concentration, with no significant bias. The good replication of the metal mass demonstrates the ability of the PTFE filters to retain metal concentrations over a five month period.

Reactive filter tests were conducted to determine retention efficiencies and estimated holding times for vapor phase metals using Hg as an indicator species. These tests are based on filters exposed to both elemental mercury and mercuric chloride vapors during tests conducted in June and August 2002 and filters from coal-fired power plant flue gas tests. All filters were kept at room temperature and analyzed using IO Compendium Method 3.3[14]. These filters were reanalyzed periodically over the past two years and were found to have lost on average about 10% of the original mercury over this period. This finding was

independent of laboratory or field application, or oxidation state of Hg trapped. A linear model was developed which assumes the mercury loss from the reactive filter to be constant over time. This model showed that, when using a correction factor that assumes a loss of about 0.5% per month, the mercury concentrations measured after two years were, on average, within 10% of the original mercury concentrations. The good agreement for all of these tests supports the use of a correction factor of 0.5% per month for filters that have been archived for more than six months. This would allow the holding time to extend to at least two years.

### *7.10 Applicable Elements*

The XRF analysis determination of metals in the filter deposit is based on EPA IO Compendium Method 3.3, which is generally applicable to elements with atomic numbers ranging from about 13 (Al) through 92 (U). This range of elemental applicability is expected to apply to the XFM PTFE filter but not to the reactive filter. In the case of the reactive filter, the lowest atomic number element quantifiable with XRF analysis is Cr (24) because of significant impurities in the filter matrix.

The elements of primary regulatory interest are those the Clean Air Act Amendments classify as Air Toxics: i.e. Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), and Selenium (Se). These eleven elements have been sorted by volatility in the Maximum Achievable Control Technology (MACT) rules[17] as follows:

- Non-enumerated metal compounds (N): Sb, Co, Mn, Ni, Se; equated to particulate matter in the MACT
- Low volatile metal compounds (L): As, Be, Cr
- Semi-volatile metal compounds (S): Pb, Cd
- High volatile metals (V): Hg

The metals tested in Phase I and II represented particulate matter as well as all of the metals in the three volatility categories except the low volatility element Be. The other elements not tested are non-enumerated metals, which the EPA has equated to particulate matter in the MACT rules. Although these eleven elements represent the primary focus of this discussion, it is important to note that these filter based methods are expected to be applicable to most of the elements listed in EPA IO Compendium Methods 3.3[14] and Be by IO Compendium Method 3.4[35].

### *7.11 Other Related Tests*

#### *7.11.1 Sample Collection Times*

The theoretical sampling time for the XFM and Xact-IAP is primarily limited by filter loading with PM since XRF correction factors may be required for high particulate deposit densities. However, the filter loading can be controlled in sources with high particulate levels by adjusting the sampling times and dilution ratios up to 4:1. For this reason, it is believed

that, these filter-based methods can sample for periods up to four times greater than has currently been demonstrated; i.e. four hours for the XFM and two hours for the Xact-IAP.

### *7.11.2 Xact Blank Concentrations*

The Lilly Xact, was installed on the T149 hazardous waste incinerator in May 2004 and operated throughout the summer of 2004. During this time, the Xact completed about 4000 runs while the stack was not burning hazardous waste. These runs were treated as field blanks and were used to statistically determine Xact-IAP detection limits. These statistically determined detection limits were in good agreement with those calculated from the analysis of a few filters.

**Table 26: Xact detection limits determined at Lilly's T149 incinerator**

| Elem | DETECTION LIMITS | |
|---|---|---|
| | XFM[1] | Xact[2] |
| | µg/dscm | µg/dscm |
| CR | 0.08 | 0.3 |
| AS | 0.08 | 0.1 |
| CD | 0.80 | 2.4 |
| HG | 0.14 | 0.3 |
| PB | 0.12 | 0.6 |
| MN | 0.08 | 0.2 |
| CO | 0.08 | 0.3 |
| NI | 0.06 | 0.3 |
| SE | 0.08 | 0.1 |
| AG | 0.60 | 4.2 |
| SB | 1.60 | 6.2 |
| CU | 0.08 | 0.5 |
| FE | 0.12 | 0.9 |
| ZN | 0.06 | 0.2 |
| BR | 0.20 | 0.4 |
| SR | 0.18 | 0.3 |
| TL | 0.14 | 0.3 |

1) 95% Confidence, Interference free, 30 minute sample.
2) 95% of 3899 Xact blank measurements at T149 Incinerator

## *7.12 Applicable Source Categories*

As discussed earlier, the filter-based sampling approach has been successfully tested in the laboratory and on two hazardous waste incinerators as well as three coal-fired boilers. Each of these tests showed good relative accuracy and trapping efficiencies. Source emissions can be divided into two categories: fugitive and ducted emissions. Fugitive sources include emissions from processes such as field-burning, slag-pouring, emissions from buildings, demolition activities, forest fires, etc. in addition to passive fugitive emissions from sources such as wind-blown dust and dust suspended by vehicular traffic. These fugitive emissions are typically characterized by substantially lower concentrations of possible reactive species

than the concentrations in the ducted emissions already successfully tested. As such, the XFM and Xact-IAP should be applicable, in general, to these fugitive emission sources because the characteristics of their emissions are less challenging than the ducted sources already tested.

Ducted sources, on the other hand, can have emission characteristics similar to those already tested, and in some cases may exceed the values for some parameters that may be more challenging than those already tested. As discussed earlier, the filter-based approach has shown consistent success over the past few years while sampling at two hazardous waste incinerators and three coal-fired boilers with a wide range of controls (wet scrubbers, ESPs, high temperature ceramic baghouses, ammonia injection, selective catalytic reduction, lime spray dryer absorber for $SO_2$ control, and a fabric filter for particulate control). In each case the relative accuracy in comparison to the QAG, Ontario Hydro, and Method 29 was better than the EPA required 20% for conditional method consideration. In general, the filter-based approaches have been accurate regardless of source category, emission control technology used, moisture content and stack chemistry. As such, the Xact-IAP and XFM methods should be applicable to a wide range of source categories including incinerators, boilers, kilns, smelters, plating operations, foundries, mineral processing and other industrial processes using a wide range of pollution control technologies.

## 8.0 Conclusions and Recommendations

The results from Phase I and II tests and the preceding discussion, as well as results from previous tests, support the following conclusions.

1. The QAG candidate reference aerosol generator met all of the required validation criteria and should be approved as a NIST-traceable reference aerosol generator for initial certification and continuing quality assurance audits for multi-metal sampling and analysis methods.
2. The XFM candidate conditional method for measuring metal concentrations in emissions from stationary sources met all of the required validation criteria and should be approved for initial certification and continuing quality assurance audits of multi-metals CEMS.
3. The Xact-IAP candidate conditional method for measuring metal concentrations in emissions from stationary sources met all of the required validation criteria and should be approved for use at incinerators for initial certification and continuing quality assurance audits of multi-metals CEMS.
4. The QAG candidate reference aerosol generator is independent of its application and should be approved as a generally applicable reference aerosol generator for research, method certification, and audit validation.
5. The XFM and Xact-IAP candidate conditional methods have demonstrated their applicability to a wide range of source types, controls and stack conditions; and because of their use of dilution techniques and the resulting insensitivity to stack gas characteristics; these methods should be approved as conditional reference methods

for use in regulatory applications where stack gas metal emission measurements for fugitive or stationary sources are required.

## 9.0 Glossary

**Accuracy:** The closeness of agreement between a measured value and the true value. Accuracy involves a combination of random error components and a systematic bias component.

**Aerosol:** A dispersion of solid or liquid particles in gaseous media.

**Analyte:** Element of interest in an analytical measurement.

**Analytical NIST Traceable:** Procedure in which NIST-traceability is achieved by calibrating the measurement instrument with NIST standard reference materials (SRM) or standards which are themselves traceable to NIST. To ensure continuing accuracy the calibration of the measuring instrument should be checked against the NIST standard reference materials or NIST traceable materials on a regular basis.

**Approved alternative method:** A procedure that is an approved alternative to a method required by 40 CFR Parts 60, 61 and 63 as described by the General Provisions of the corresponding Parts. As such, it may be used by sources for determining compliance with the requirements of these Parts per their specified applicability provisions without further EPA approval.

**Aspiration:** The process by which a liquid is drawn from a reservoir through a narrow tube by creating a vacuum above the tube with fast moving air.

**Atomization:** The process of converting a liquid into small suspended droplets.

**Attenuation:** Reduction of amplitude or change in wave form due to energy dissipation or distance.

**Audit:** A methodical examination and review.

**Bias:** The difference between a measured mean and the true value. Bias represents systematic difference.

**Blank: A** sample known to have a parametric value of zero.

**Calibration Drift (CD):** The difference in measured output readings from a calibrated reference value after a stated period of operation during which no scheduled maintenance, repair, or adjustment took place.

**Calibration:** The process of comparing a sampling or instrumental response with a known parametric value for the purpose of obtaining a quantitative relationship between the response and the parametric value. This relationship can then be used to determine the parametric value for an unknown sample.

**Candidate method:** The sampling and analytical procedure selected for validation by the method described herein.

**Certification:** To attest to being true or as represented or as meeting a standard.

**Compendium method:** A collection of approved EPA methods for the determination of inorganic (IO) or organic (TO) compounds in ambient air.

**Conditional test method:** Methods that have been evaluated by the EPA and may be applicable to one or more categories of stationary sources. These method's QA/QC procedures are required as a condition of applicability and must be approved as alternatives before a source may use them to meet Federal requirements under 40 CFR Parts 60, 61, and 63. They may be used by State and local programs in conjunction with federally enforceable programs (e.g., Title V permits, State Implementation Plans (SIP)) provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice and opportunity for comment.

**Correction factor:** A quantity applied to a measurement to adjust the value of that measurement to the true value.

**Correlation coefficient:** A number or function that indicates the degree of correlation between two sets of data or between two variables and that is equal to their covariance divided by the product of their standard deviations.

**Detection Limit:** The lowest concentration of a chemical that can reliably be distinguished from a zero concentration.

**Drift**: Percent change in a mean value measured over period of time.

**Elemental ratios:** The relationship in quantity, or mass between two or more elements trapped during a single sampling period.

**Emissions:** The total of substances discharged into the air from a stack, vent, or other discrete source.

**Error:** The difference between an observed or calculated value and a true value; *specifically*: variation in measurements, calculations, or observations of a quantity due to unsystematic factors.

**Filter:** A porous medium for collecting particulate matter.

**Filter ratio:** The relationship in quantity, or mass of an element trapped on two or more filters used in combination during a single sampling period.

**Holding Time:** The maximum amount of time a sample may be stored before analysis.

**Impaction:** A forcible collision of particles of matter with an object.

**Impactor:** **A** device that employs the principle of impaction.

**Intercept:** The distance from the origin to a point where a line crosses a coordinate axis.

**Interferent:** A substance that causes systematic errors in the measurement of another substance.

**Isokinetic sampling:** Emissions sampling in which the linear velocity of the gas entering the sampling nozzle is equal to that of the undisturbed gas stream at the sample point.

**Linearity**:A check of the degree to which the candidate reference method response is linear relative to a change in concentration of a reference aerosol a change in concentration reported by a reference method. .

**Low-volatile metals (LVM)**: Any metal that does not volatilize readily (e.g., arsenic (As), beryllium (Be), and chromium (Cr)).

**Metal ratio**: The relationship in quantity, or mass of two or more metals trapped on a filter or series of filters used in combination during a single sampling period.

**Method 29**: An EPA reference method to determine the metals emissions from stationary sources it is contained in 40 CFR 60 Appendix A.

**Method 301**: An EPA protocol for the field validation of candidate pollutant measurement methods from various waste media.

**Negative bias:** Bias when the measured result is less than the "true" or reference value.

**NIST:** U. S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899

**Non-destructive:** Not causing destruction of material being investigated or treated

**Ontario Hydro Method** A method for determining the concentration of elemental, oxidized, particle-bound and total mercury in flue gas generated from coal-fired stationary sources.

**Outlier**: Extreme measurements that stand out from the rest of the sample and may be faulty.

**Particle**: A small discrete mass of solid or liquid matter.

**Particulate**: Solids or liquids existing in the form of separate particles.

**Performance audit material:** EPA-approved material of known composition that can be used to simulate an unknown sample to test the candidate procedure.

**Performance Specifications:** Performance specifications are used for evaluating the acceptability of the CEMS at the time of or soon after installation and whenever specified in the regulations. Quality assurance procedures in 40 CFR Part 60 Appendix F are used to evaluate the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by any CEMS that is used for determining compliance with the emission standards on a continuous basis as specified in the applicable regulation.

**Positive bias:** Bias when the measured result is greater than the "true" or reference value.

**Practical limit of quantitation (PLQ):** The lowest level above which quantitative results may be obtained with an acceptable degree of confidence. The PLQ is defined as 10 times the standard deviation, $S_o$, at the blank level with an uncertainty of ±30% at the 99% confidence level.

**Precision:** The degree of mutual agreement between individual measurements of a parameter having the same value,. In this report it is defined as the percent relative standard deviation (PRSD) of a series of measurements over a relative short test period in contrast to stability, which is a determined measurement over an extended period of time.

**Process NIST Traceable:** A parameter whose value is traceable to NIST through a procedure, the steps of which are each NIST traceable[1]

**Quality Assurance/Quality Control:** A system of procedures, checks, audits, and corrective actions to ensure that all EPA research design and performance, environmental monitoring and sampling, and other technical and reporting activities are of the highest achievable quality.

**Quantitative Aerosol Generator (QAG)**: An aerosol generator system that uses analytes of known concentrations in aqueous solution to create aerosol emissions of known metal concentrations.

**Quantitative:** Of, relating to, or involving the measurement of quantity or amount.

**QuanX** ®:A Spectrace Instruments energy-dispersive x-ray fluorescence spectrometer.

**R**: Correlation coefficient, an indicator of how well the data fits a linear relationship.

**$R^2$ 1**: proportion of the total sum of squares that can be accounted for by the linear regression of y on x **2**: a statistic that indicates the strength of the relationship between x and y.

**Reference aerosol:** An aerosol that contains a known concentration or concentrations of analytes.

**Reporting time**: The time interval for which the report is representative.

**Representative sample:** A portion of material that is as nearly identical in content and consistency as possible to that in the larger body of material being sampled.

**Response time:** The time interval from a step change in pollution concentration at the input to the continuous monitoring system to the time at which 95 % of the corresponding final value is reached as displayed on the continuous monitoring systems data recorder.

**Ruggedness test**: A laboratory study to determine the sensitivity of a method to parameters such as sample collection rate, interferent concentration, collecting medium temperature, and sample recovery temperature by changing several variables at a time.

**Sampling system:** The system which extracts a sample of effluent gas from a source and and delivers it to point where collection or measurement of the analytes in the source can occur.

**Secondary Particles (or Secondary Aerosols)**: Aerosols that form in a gaseous matrix as a result of chemical reactions.

**Semi-volatile metals**: Lead (Pb), cadmium (Cd).

**Slope:** For a line described by the equation $y = mx + b$, $m$ is the slope of the line. The slope expresses the amount of change that will occur in y due to changes in x.

**Spectral Interferent:** An interfering element or species that's absorption or emission characteristics overlap or lie so close to the analytes absorption or emission characteristics that resolution becomes impossible.

**SRM:** Standard Reference Materials.

**Stability:** The consistency in the measurement of a constant value over an extended period of time.

**Standard:** An item with a value for a parameter that has been established by authority, custom, or agreement to serve as a model or rule in the measurement of quantity or the establishment of a practice or procedure.

**Surrogate Data:** Data from studies of test substance or substances that are used to estimate the characteristics or effects on another substances.

**Thin film standard reference material**: A NIST traceable standard reference material comprised of either an element(s) or compound(s) of a known and stable concentration. The thin film standards are used to calibrate X-ray fluorescence instruments.

**Traceable to NIST:** A documented procedure by which a measured response is related to a standard with an accuracy defined by and certified by the National Institute of Standards Technology (NIST).

**Transport efficiency**: The percentage of a known concentration of analyte or analytes that can be conveyed to an analysis instrument from their source.

**Uncertainty:** A statistically defined value associated with a single measurement or a value associated with a group of measurements that defines the range and probability of additional measurements falling within the defined range, and can include allowance for both systematic and random sources of error.

**Unknown:** A sample submitted for analysis whose elemental concentration is not known.

**Upscale drift:** The difference in an instrument's output readings from the established upscale reference value after a stated period of operation during which no scheduled maintenance, repair or adjustment took place.

**Validation**: The determination of the degree of validity of a measuring device

**Verifiable**: Capable of being confirmed for precision and accuracy.

**Verification**: Confirming the precision and accuracy of an instrument.

**Volatile metal**: Any metal substance that evaporates readily at low temperature (e.g., mercury).

**Xact**: Cooper Environmental Service's X-ray fluorescence based emissions monitor capable of measuring metals found in flue gas emissions.

**Xact-CEMS:** Cooper Environmental Service's X-ray fluorescence based continuous metal emissions monitor.

**XACT-IAP:** An instrumental analyzer procedure utilizing Cooper Environmental Service's XACT to measure metal emissions from stationary sources.

**XFM:** Cooper Environmental Service's X-ray based filter method to measure metal emissions from stationary sources.

**Xact-IM**: Cooper Environmental Service's X-ray fluorescence based continuous emissions monitor primarily focused on the detection of mercury in flue gas emissions.

**XRF:** X-ray fluorescence – An analytical technique used to determine the concentration of an element or elements.

**Zero Drift:** The difference in an instrument's output readings for zero input after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

## 10.0 References


1. EPA Test Method 301, Field Validation of Pollution Measurement Methods for Various Media, 40 CFR 56, 27370-27374. June 13, 1991.
2. EPA Test Method 29, Determination of Metals Emissions from Stationary Sources, 40 CFR 60, Revised July 1, 1996.
3. ASTM D6784-02. Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method), 2002.
4. Cooper, J.A, B.E. Johnsen, S.C. Fry, May 2003. Installation and Use of an X-ray Based Continuous Emissions Monitor for AED Treatability Study. Submitted to US Army Equipment Directorate, Tooele Army Depot. Contract No. DAAA14-02-P-0216.
5. Hosenfeld, J., Sept. 2003. Long-Term Field Evaluation of Mercury (Hg) Continuous Emission Monitoring Systems: Coal-Fired Power Plant Equipped With Dry Flue Gas Desulfurization/Fabric Filtration Emission ControlsPhase III (Field Work Performed May-July 2003). Final Report for U.S. Environmental Protection Agency. EPA Contract 68-D2-01-002 Work Assignment 3-04. MRI Project No. 110130.3.004.
6. EPA. May 03, 2005. List of Designated Reference and Equivalent Methods (Ambient Methods). Found on EPA website at http://www.epa.gov/ttn/amtic/criteria.html.
7. EPA. April 1994. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume II: Ambient Air Specific Methods (Interim Edition). EPA/600/R-94/038b.
8. Prieditis, H. IYR Adamson 2002. Comparative Pulmonary Toxicity of Various Soluble Metals Found in Urban Particulate Dust. Exp. Lung. Res 28: 563-576.
9. Monn C, Becker S. 1999. Cytotoxicity and induction of proinflammatory cytokines from human monocytes exposed to fine ($PM_{2.5}$) and coarse particles ($PM_{10-2.5}$) in outdoor and indoor air. Toxicol Appl Pharmacol 155:245-252.
10. Clean Air Act Amendments of 1990 (CAAA), Pub.L. No. 104-549, 104 Stat. 2399 (1990).
11. EPA, 2005. Rules and Implementations for Toxic Air Pollutants. Found at EPA's Technology Transfer Network Air Toxics Website. http://www.epa.gov/ttn/atw/eparules.html.

12. EPA 450/4-92-013 Vol. 1 December 9, 1991. Evaluation of Two Methods for the Measurement of Mercury Emissions in Exhaust Gases from a Municipal Waste Combustor.

13. Rigo, H.G., A.J. Chandler. Quantiation Limits for Reference Methods 23, 26, and 29. J. Air & Waste Manage. Assoc. 49:399-411.

14. 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.

15. Jayanty, RKM. 2002. PM2.5 Chemical Speciation Nationwide Network and its Challenges. Symposium on Air Quality Measurement Methods and Technology – 2002. San Francisco, CA.

16. May K.R. (1973) The Collison Nebulizer. Description, Performance & Application J. of Aerosol Science, Vol. 4, #3, p. 235

17. US EPA. NESHAPS Standards for Air Pollutants for Hazardous Waste Combustors Final Rule. FR67 No. 31 pp. 6967-6996. February 14, 2002.

18. Eli Lilly and Company T149 Liquids and Solid Waste Incinerator. Tippe, IN.

19. US EPA PS-11. Performance Specification 11 – Specifications and Test Procedures for Particulate Matter Continuous Emissions Monitoring Systems at Stationary Sources. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emissions Measurement Center, FR69 vol. 7. pp. 1785-1821. January 12, 2004.

20. US EPA PS-10. Proposed Performance Specification 10 – Specifications and Test Procedures for Multi-Metals Continuous Monitoring Systems at Stationary Sources. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emissions Measurement Center, August 1997.

21. Chester LabNet. 12242 SW Garden Place Tigard, Oregon 97223 ph. 503.624.2183

22. EPA Test Method 301, Field Validation of Pollution Measurement Methods for Various Media, 40 CFR 56, 27371. June 13, 1991.

23. Pall Life Sciences. 2003. Laboratory Filtration and Separation Catalog. pp.30-31.

24. CES. 2005. Pro-11 Filter used by CES' Xact Multi-Metals Continuous Emissions Monitor. http://www.cooperenvironmental.com/products.html.

25. Dry Cal DC Lite Primary Flow Calibrators. Found on the web at http://www.drycal.com/drycal/index.htm.

26. Handbook of Chemistry and Physics. 65th Edition. Weight in Grams of a Cubic Meter of a Saturated Aqueous Vapor (From Smithsonian Tables). p. E-37.

27. Currie, L.A. 1978. "Detection and Quantitation in X-ray Fluorescence Spectrometry. in X-ray Fluorescence Analysis of Environmental Samples. T. G. Dzubay (ed). Ann Arbor Science Publishers, Inc. pp. 289-306.

28. Seinfeld, J.H., S.N. Pandis. 1998. Atmospheric Chemistry and Physics. Page 10. Elevation of incinerator is about 630 ft.

29. Paule, R.C., G. Marinenko, M. Knoerdel, and W.F. Koch. Jan 1986. Ruggedness Testing – Part I: Ignoring Interactions. Journal of Research of the National Bureau of Standards. Vol. 91. No. 1. pp. 3-8.

30. Paule, R.C., G. Marinenko, M. Knoerdel, and W.F. Koch. Jan 1986. Ruggedness Testing – Part II – Recognizing Interactions. Journal of Research of the National Bureau of Standards. Vol. 91. No. 1. pp. 9-16.

31. Ahmed, K. of Pall Corporation personal communication to CES' B.E. Johnsen June 3, 2005. Results of Air Techniques TDA-100A standard DOP Test.

32. US EPA PS-11. Performance Specification 12a – Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Emissions Monitoring Systems in Stationary Sources. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emissions Measurement Center, FR69. pp. 4701-4750. Appendix B Part 60 Jan. 30 2004.

33. Cooper, J.A., B.E. Johnsen, P. Ginochio. April 2005. Re-design and Field Testing of an X-Ray Fluorescence Multi-Metals Monitor at the Iowa Army Ammunition Plant, Middleton, Iowa Coal Fired Boiler. Submitted to US Army Corp of Engineers: Engineer Research and Development Center under contract no. W9132T-04-P-0065.

34. Hay, K.J., V.M. Boddu, B.E. Johnsen, J.A. Cooper. January 2005. Report No. ERDC/CERL-TR-05-3. X-Ray Fluorescence-Based Multi-Metal Continuous Emission Monitor Technology Demonstration. US Army Corps of Engineers: Engineer Research and Development Center.

35. EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. June, 1999. Compendium Method IO-3.4 Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy. EPA/625/R-96/010a.

36. Scott Specialty Gases. Scott Gas Mixtures Data: Gas and Liquid Mixture Basics. Plumsteadville, PA: Scott Specialty Gases; 2004.