Multi-Metals CEMS: A Review of Currently Available Technology

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Why Measure Metals?

- **Significant adverse human health effects (cardiac arrhythmia, neurotoxic, elevated cancer risks)**
- **Developing fetus & children especially susceptible**
- **Metals represent 8 of US EPA's top 33 pollutants of highest concern**
- **Arsenic is one of US EPA's top three priority pollutants of concern**
- **Global concern for metals – As, Cd, Cr, Pb and Hg - RoHS, WEEE and ELV**

•US EPA. Framework for Inorganic Metals Risk Assessment. EPA 120/R-07/001. March 2007.
•US EPA. Health Effects Notebook for Hazardous Air Pollutants. EPA Technology Transfer Network Air Toxics Website. Accessed November 2007.

•Agency for Toxic Substances and Disease Registry. Toxic Substances Portal. Accessed November 2007.

Examples of Contemporary Research

- **1997, Costa and Dreher**: "The lung dose of bioavailable transition metals, **not instilled PM mass**, was the primary determinant of the acute inflammatory response for both the combustion source and ambient PM samples."
- **2002, Magari et al.:** "…Results of this study suggest an association between exposure to airborne metals (vanadium, nickel, chromium, lead, copper, and manganese) and significant alterations in cardiac autonomic function."
- **2009, Chen and Lippmann**: "…Concentrations of nickel and vanadium in ambient air PM were associated with significant differences in mortality rates, **while other measured PM components were not**."
- **2010, Maciejczyk et al**.: "Three metals (nickel, barium, and manganese)… appear to be much more influential on lung cell responses than black carbon and sulfate ions that are present at much higher mass concentrations."
- Metals Are A Significant Contributor to the Health Effects Associated With PM

Multi-Metals CEMS – A Brief History

- 1995 to 1997 EPA/DOE conducts testing of Multi-metals CEMS
- 1996 – EPA Proposes Hazardous Waste Combustor MACT – Multi-metals CEMS would be preferred method for Monitoring Metals
- 1997 Lilly Begins Funding of Xact
- 1997 – EPA Proposes Performance Specification 10
- 1997 – Third in series of EPA Tests Concludes that no currently available multi-metals CEMS can meet performance specification 10
- 1997 -2004 – Continued interest in MM CEMS from Lilly and Army because of potential HWC MACT requirements

Multi-Metals CEMS – A Brief History

- 2001 and 2002 CES' XCEM is Tested at Army Demil Furnaces
- 2004 – Army and Lilly Purchase Xact
- 2005 CES Xact is Method 301 Validated
- 2006 – Lilly's Alternative Monitoring Petition Includes Xact for Metals Compliance
- 2004 to Present - Lilly Xact Operates Passing all Annual RATAs

Overview of Measurement Approaches

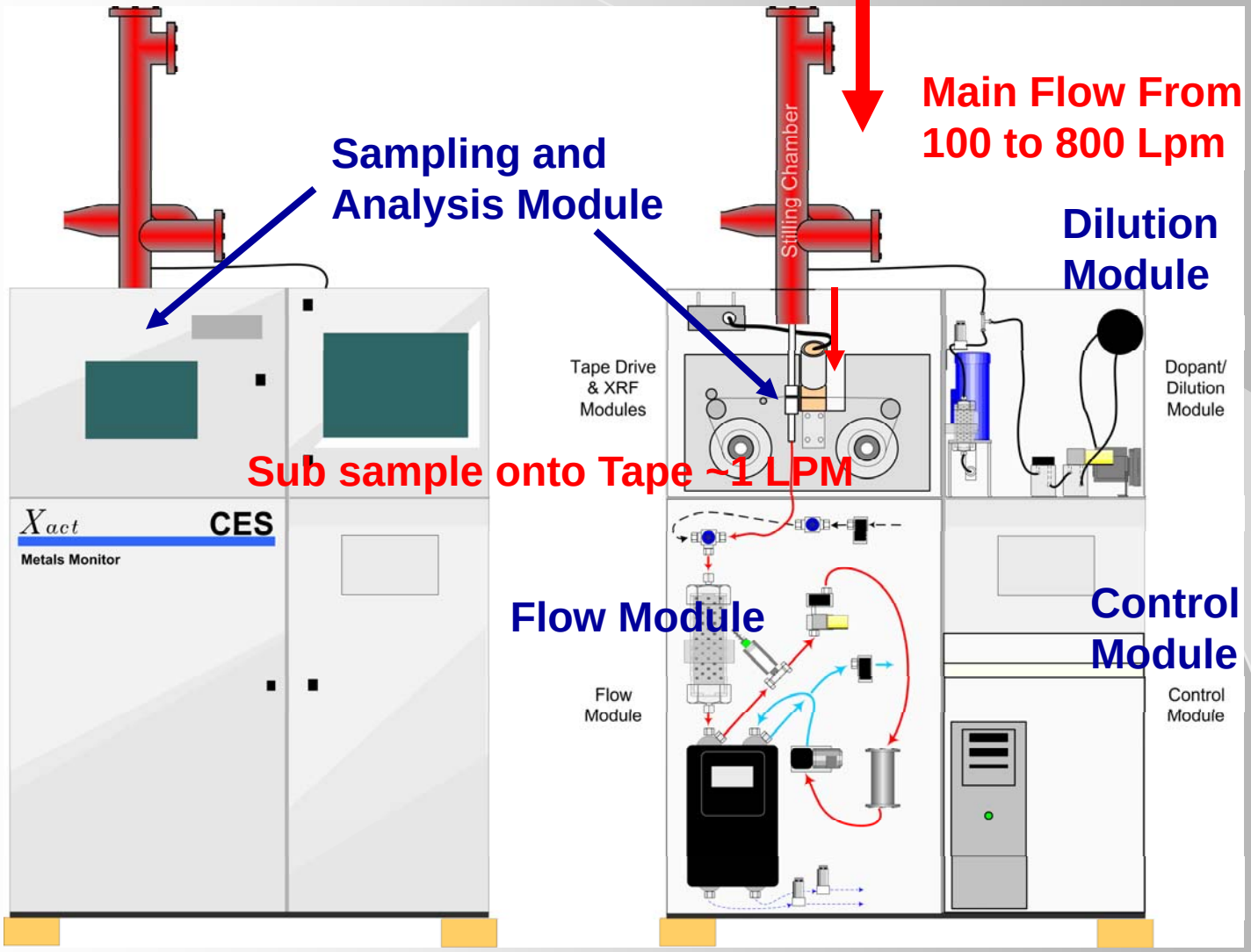
1997 Evaluation Included Eight different MM-CEMS at various stages of development

- Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) – 2 participants (Thermo Jerrell Ash)
- Laser Induced Breakdown Spectroscopy (LIBS) – 2 participants
- Spark Induced Breakdown Spectroscopy - 1 vendor
- Microwave Induced Breakdown Spectroscopy – 1 participant
- High Resolution Interferometric Spectrometer – Vendor
- **Hazardous Element Sampling Train (HEST) + XRF analysis – CES Precursor to Xact**
- **Only CES' XRF Approach is Currently Available**

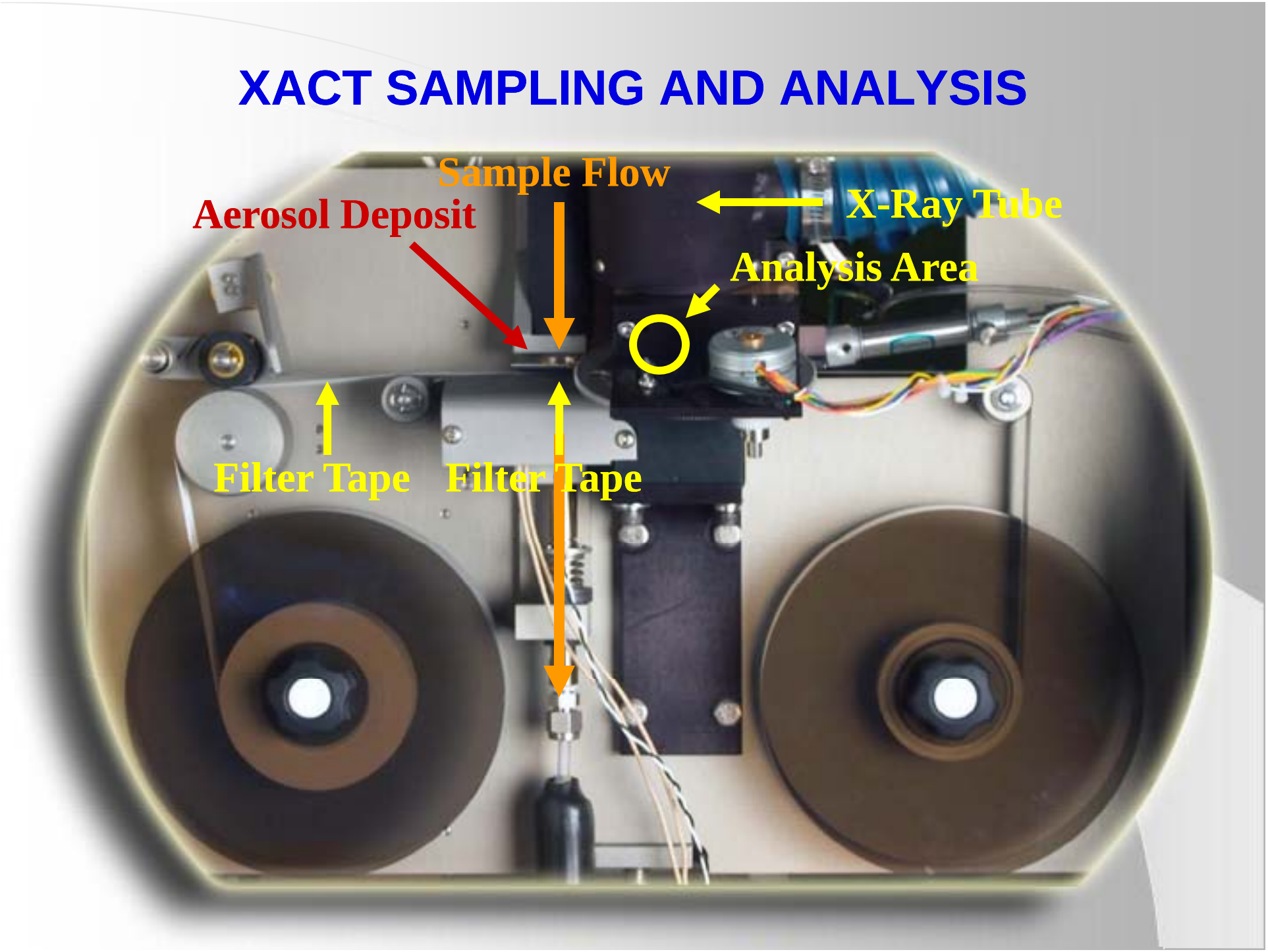
Xact Review

1. How the instrument works
2. M301 Validation
3. QA Procedures and Instrument Performance
4. Compliance Performance Specifications and Procedures
5. Results from other testing

Xact-CEMS


Connect to Probe and Transport Line
Main Flow From Stack 100 to 800 Lpm
Sampling and Analysis Module
Dilution Module
Stilling Chamber
Tape Drive & XRF Modules
Dopant/ Dilution Module
Sub sample onto Tape ~1 LPM
Xact CES
Metals Monitor
Flow Module
Control Module
Flow Module
Control Module

XACT SAMPLING AND ANALYSIS



Determination of Stack Concentration

$$\text{CONC } (\mu g/m^3) = \frac{\text{Mass (XRF)}}{\text{VOLUME (MFM)}}$$

XACT DETECTION LIMITS (µg/m³)*

Element	15 Min.*	60 Min.	Meth. 29**
Cr	0.2	0.03	0.3
As	0.1	0.02	0.4
Cd	2.4	0.3	0.03
Hg	0.3	0.04	0.6
Pb	0.4	0.06	0.3
Mn	0.3	0.04	0.3
Co	0.3	0.04	0.3
Ni	0.3	0.04	5.4
Se	0.1	0.02	0.8
Ag	4.6	0.6	2.6
Sb	6.1	0.7	1.1

*95% confidence based on **3899** blanks

**120 minute samples

Xact Method 301 - Validation

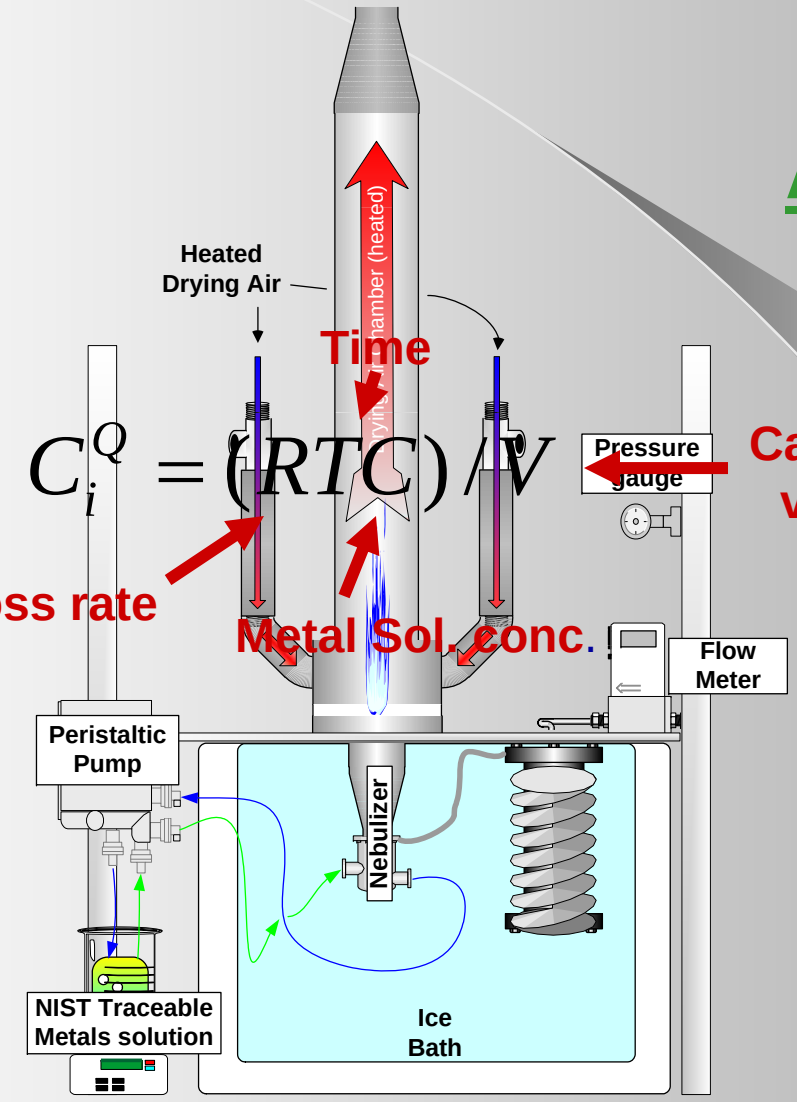
Method 301 is a procedure or guideline for determining the precision and accuracy of candidate methods

The Xact was validated using CES' Quantitative Aerosol Generator or QAG as a Reference Method

Think Cal Gas for Metals

QUANTITATIVE AEROSOL GENERATOR (QAG)
(Previous Generation Used During M301 Testing)

NIST Traceable Aerosol



$$C_i^Q = (RTC)/V$$

Carrier air volume

Solution loss rate

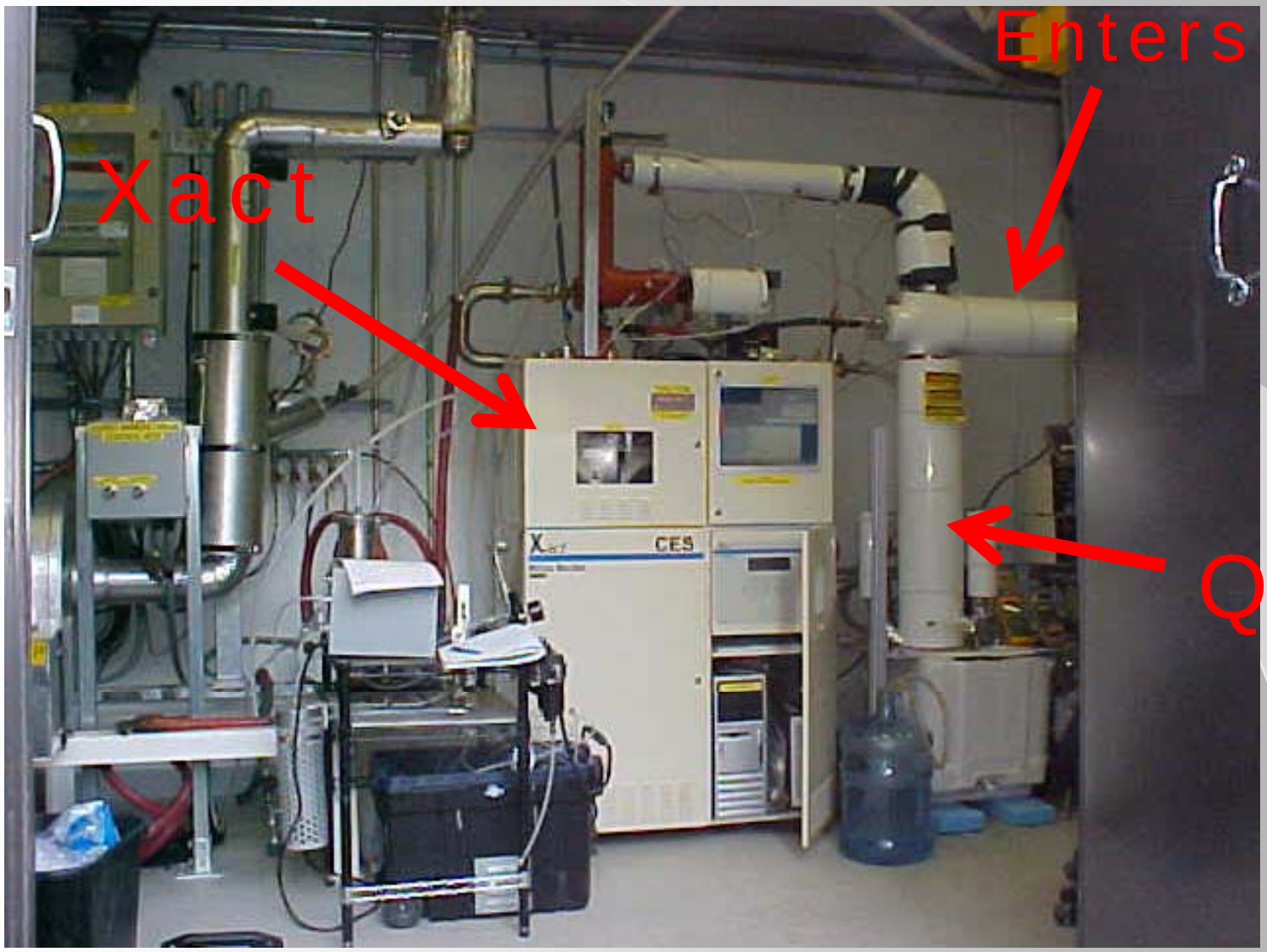
Metal Sol. conc.

Aerosol Types

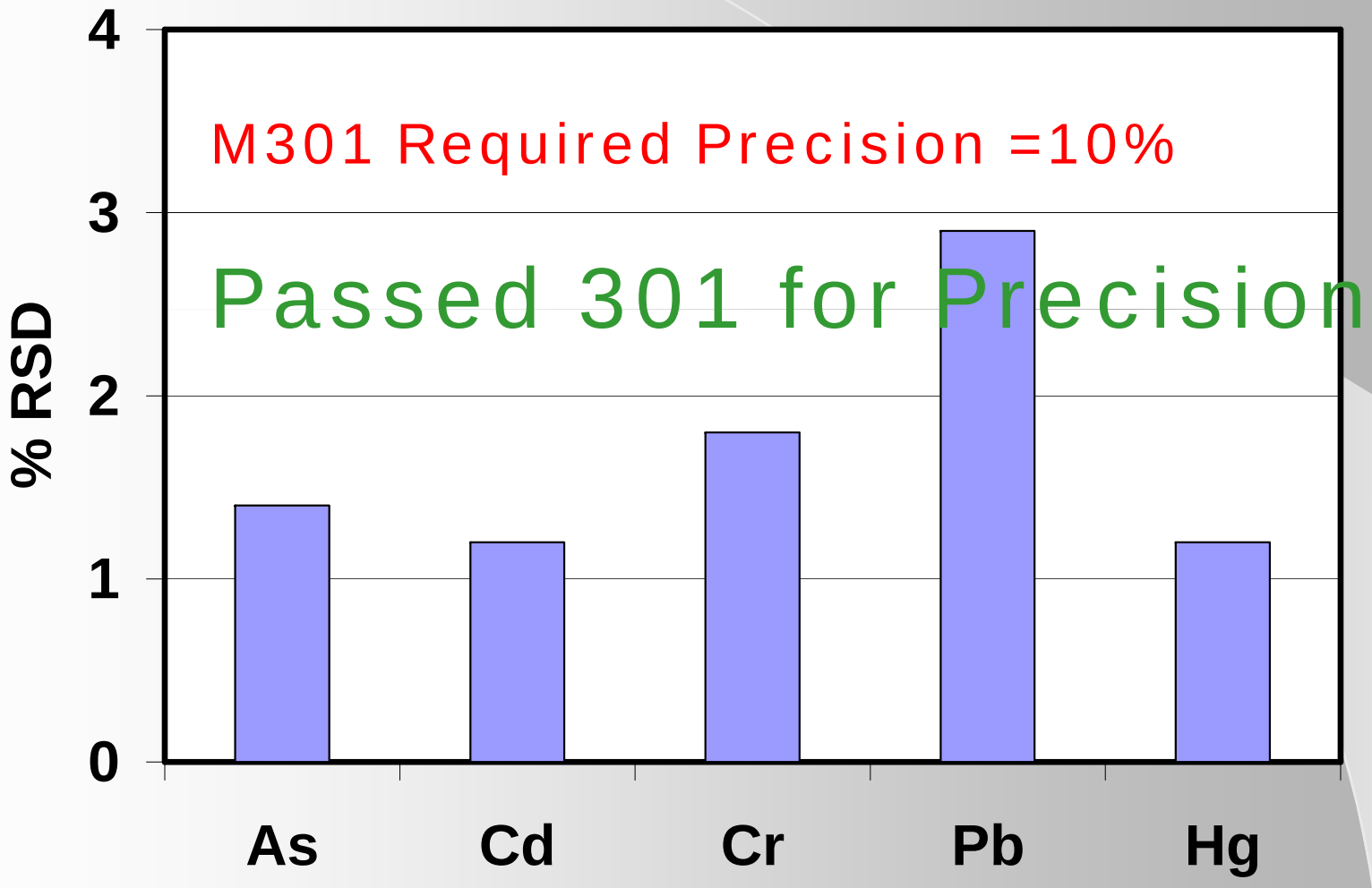
-Metals

-PM

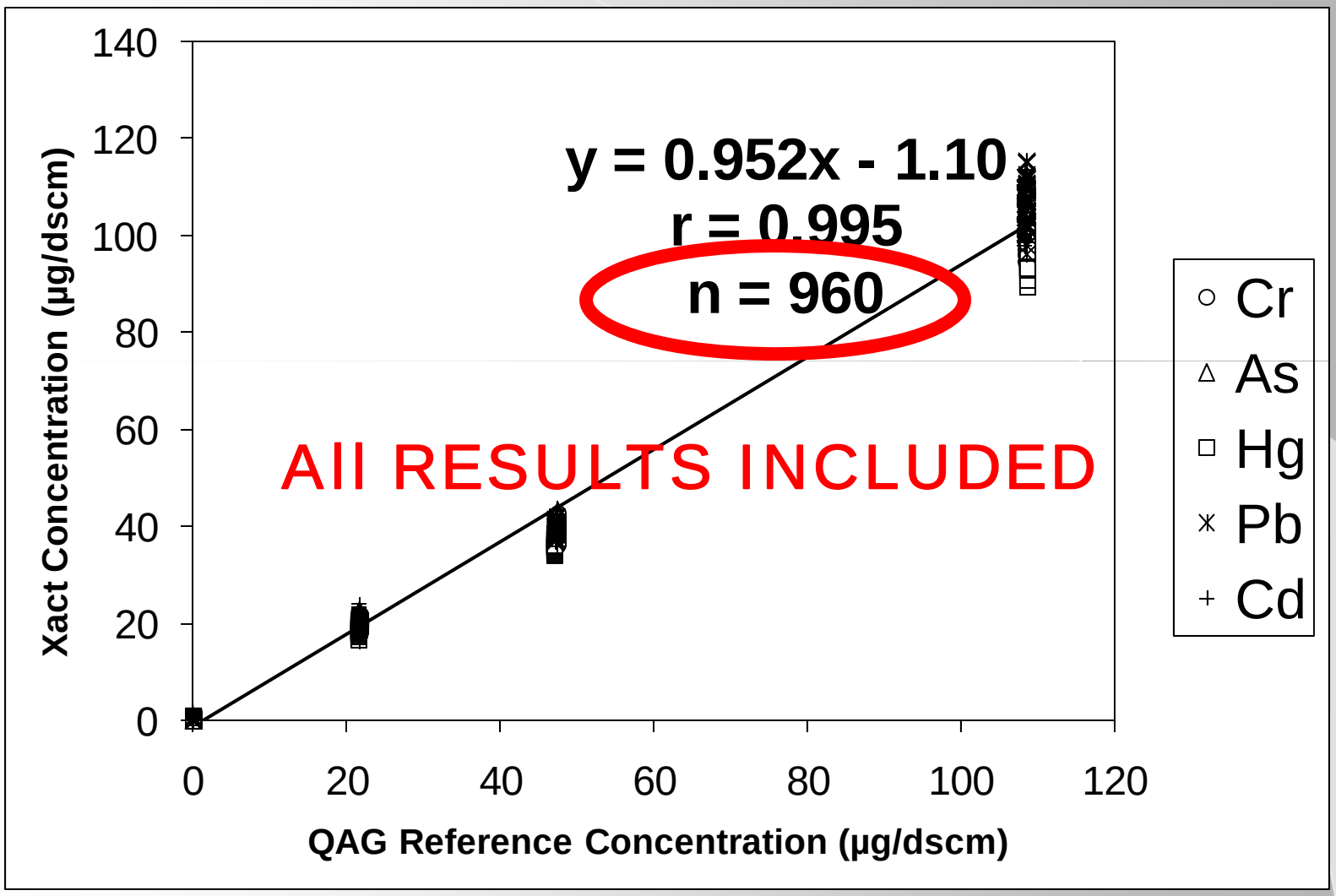
M301 Arrangement (March 2005)



Xact Method 301 - Precision



Xact - Linearity



Method 301 Xact Validation Summary

	Goal	Test Result	Pass?
Number of Runs	9	192	Pass
Precision (RSD)	<10%	<3%	Pass
Bias	<20%	<7%	Pass
Corr. Coeff. (R)	>0.85	>0.99	Pass
NIST traceable	Yes	Yes	Pass
Slope	ND	0.95	ND
Intercept	ND	1.10	ND

All measurement results included

ND: Not Defined

Automated Quality Assurance

1. Every Sample

- **Calibration stability check**
- **Reactant level Check**
- **Leak test**

2. Daily

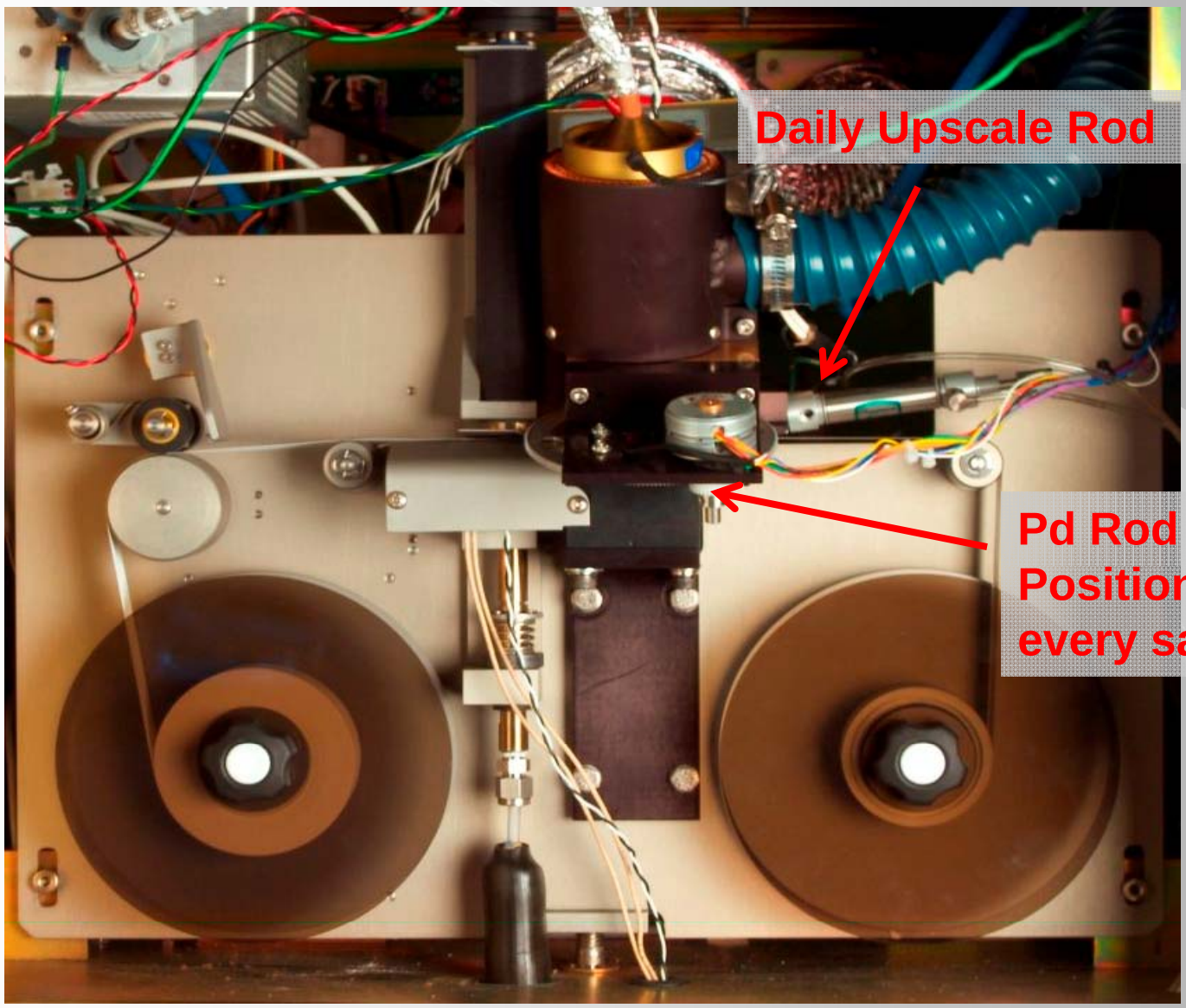
- **Upscale error check**
- **Flow calibration check**
- **Zero level check**

3. Quarterly and annual audits

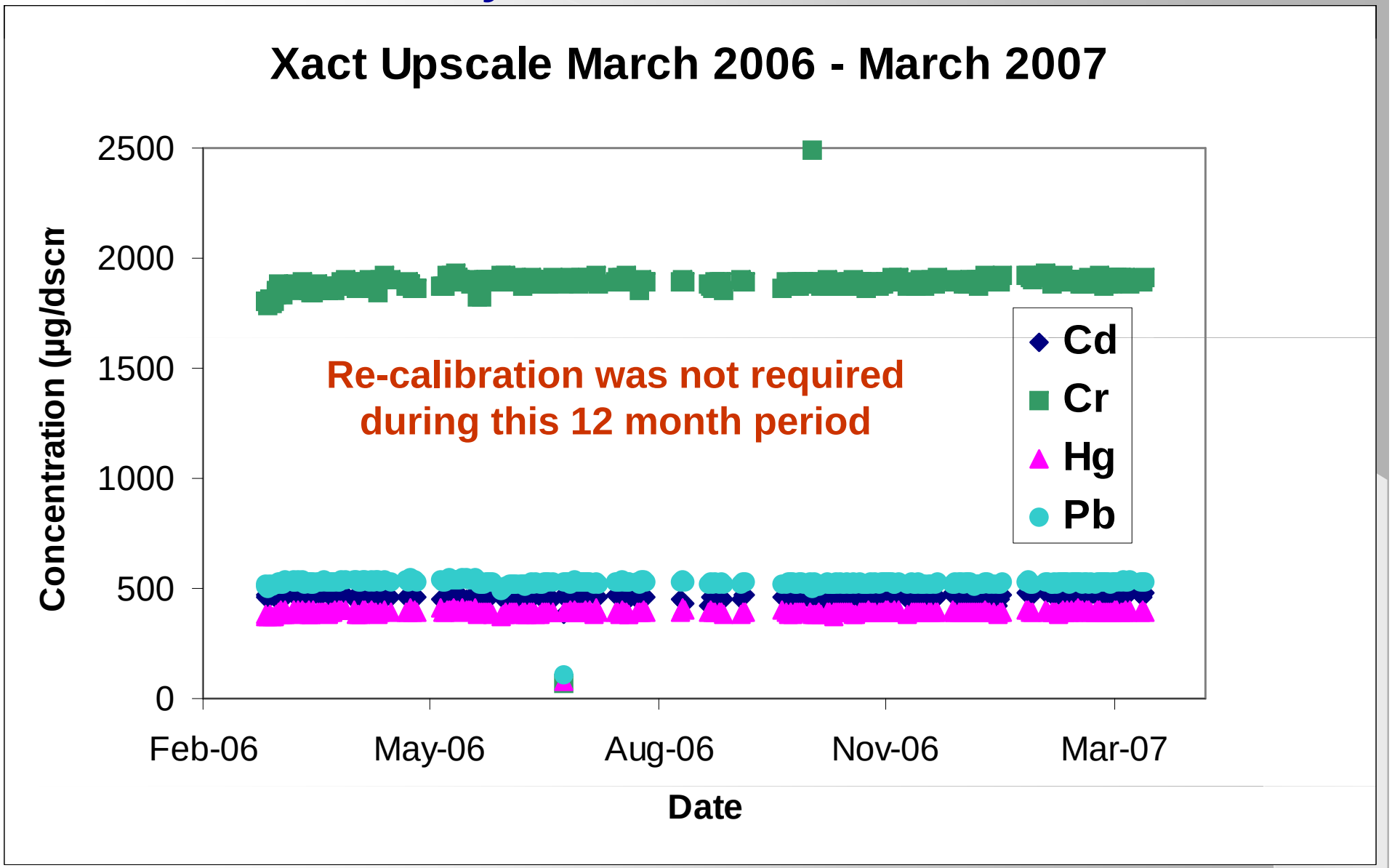
- **Linearity**
- **Annual RATA - check of the whole system**

4. Optional independent analytical audit of archived Samples

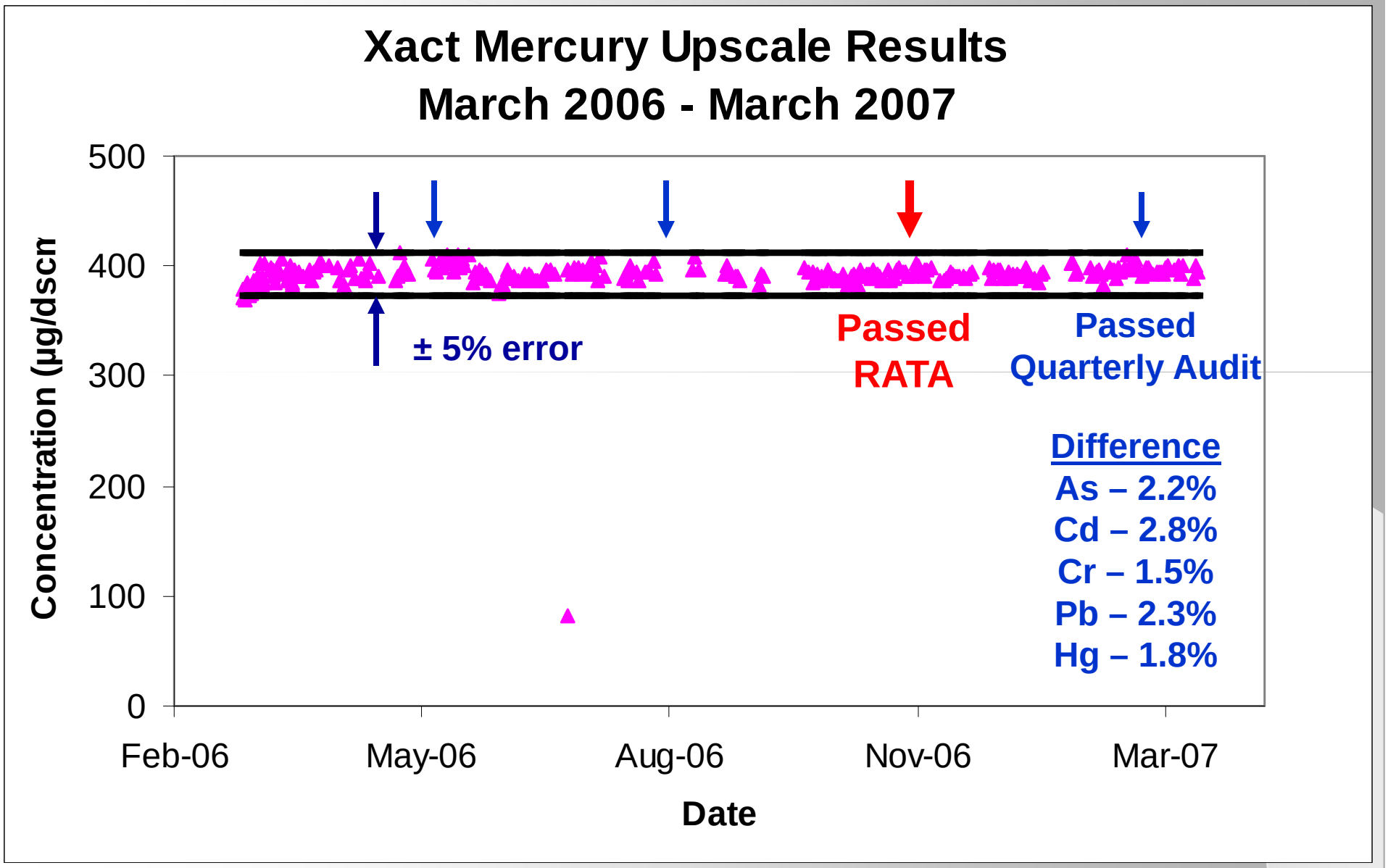
XRF QA


Daily Upscale Rod
Pd Rod – Fixed Position – checks every sample

12 Month Daily Calibration Error Check



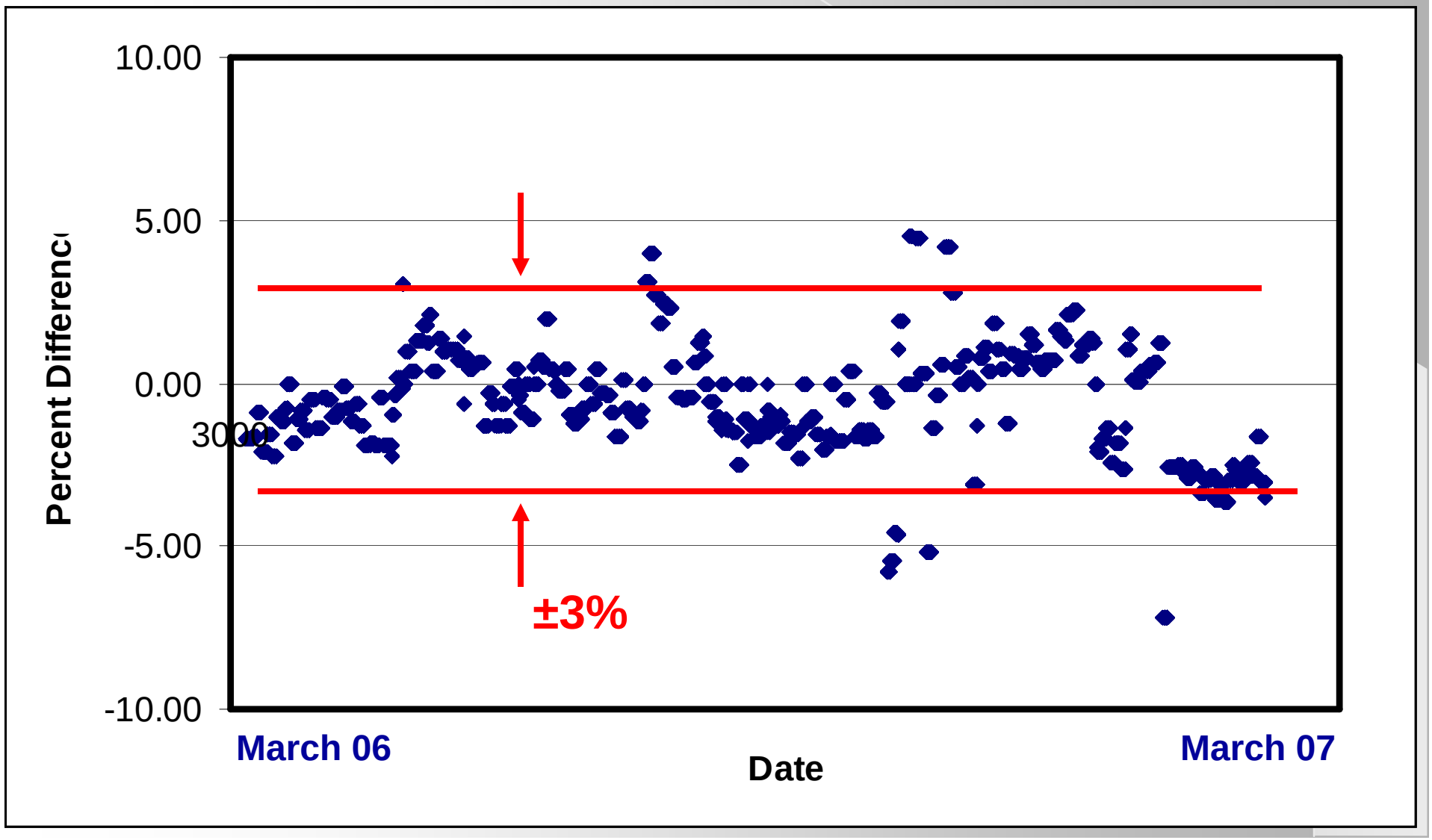
12 Month Daily Calibration Error Check



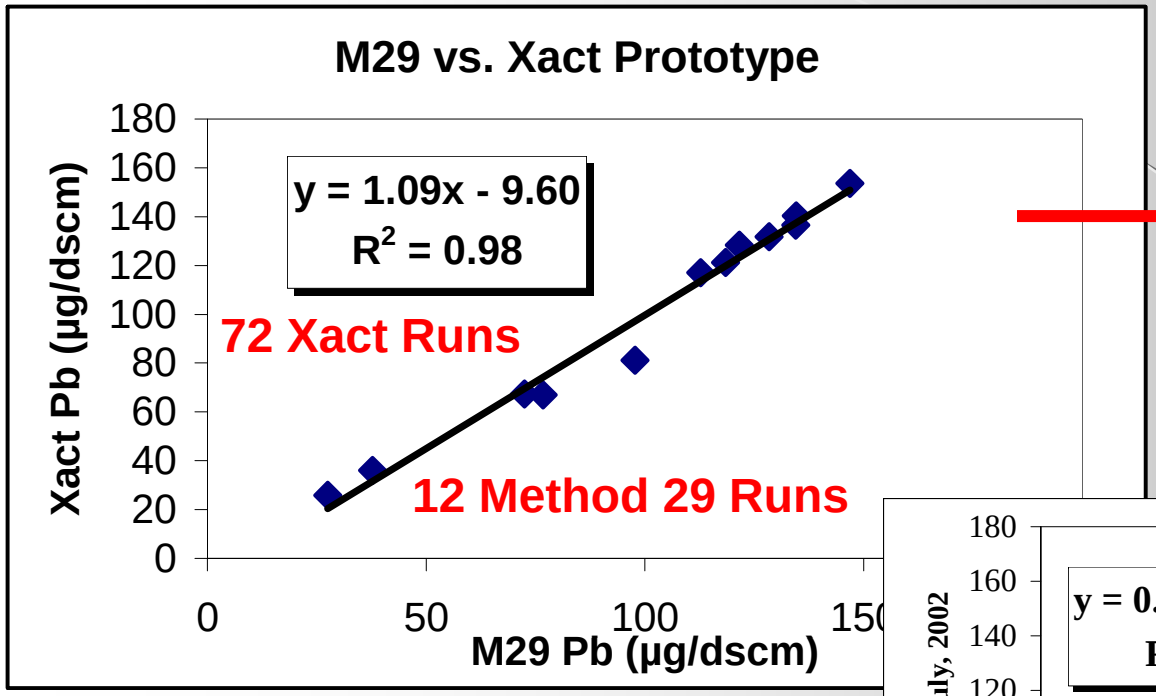
Micromatter Standards

- Used to calibrate the Xact
- Used to perform XRF audits on the Xact (Quarterly)
- Recommended by IO 3.3 for calibration of XRF instruments
- Gravimetrically NIST traceable

Daily Flow QA/QC Check - Percent Difference

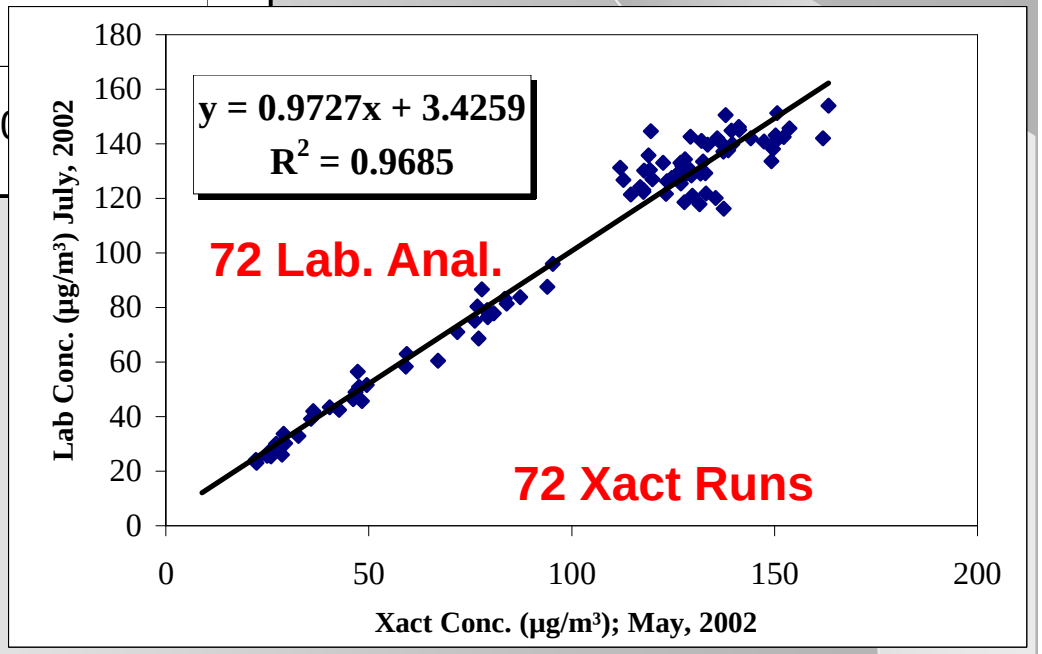


Independent Verification of Xact Results



72 Xact spots cut from tape and re-analyzed in the lab

Independent Verification



Lilly HWI Alternative Monitoring Plan

- **Xact Used for Compliance**
- **Pass Performance Specification**
- **On-going QA Requirements**
  - **Daily**
  - **Quarterly**
  - **Annually**

Lilly HWI Alternative Monitoring Plan Performance Specifications

- **7 Day Stability Test – Meet Criteria Every Day for 7 Days**
  - **Upscale Drift < 15% Drift – Checks XRF Drift**
  - **Zero Drift < 20% Drift – Checks XRF Drift in Background**
  - **Flow Drift < 20% Drift – Checks Stability of Xact Flow Measurement**
- **XRF Calibration Audit – <10% Error**
  - **Checks Calibration Against NIST Traceable Standards**
- **Flow Calibration Audit - <10% Error**
  - **Flow Audit with NIST Traceable flow meter**
- **Linearity RATA**
  - **Spiking with the QAG – Three Concentration Levels**
  - **Slope between 0.80 and 1.20**
  - **Intercept less than 20% of emission limit**
  - **Correlation Coefficient > 0.90**

Lilly HWI Alternative Monitoring Plan On-Going QA Requirements

- **Daily**
  - **Upscale**
  - **Zero**
  - **Flow**
- **Quarterly**
  - **XRF**
  - **Flow**
- **Annually**
  - **QAG Linearity**

Lilly QAG Audit Results Since 2006

Year	Slope					
	Cr	As	Cd	Hg	Pb	Average
2006	0.83	0.90	0.85	0.82	0.85	0.85
2006 (Quarterly)	0.91	0.77	0.95	0.92	0.93	0.89
2007	0.84	0.82	0.88	0.84	0.81	0.84
2008	0.96	0.71	0.98	0.99	0.97	0.92
2009	0.96	0.99	0.99	1.10	1.00	1.01
2010	0.97	1.06	1.11	1.02	1.04	1.04
Average	**0.91**	**0.87**	**0.96**	**0.95**	**0.93**	**0.93**

HAS Passed All Required Annual and Quarterly Audits Since Start of AMP

Xact CEMS

EPA Method 301 Validated

AMP EPA Approved

EPA Site Certified

~6 Years On-Stack Operations

May 2007 – EPA Clean Air Excellence Award

Over View of Other Testing

- **XCEM (Xact Predecessor) Comparison with M29 on Army Incinerator**
- **Army Xact Comparison with M29 for As and Hg on a Coal Fired Boiler**
- **Small Business Innovative Research Grant – Spiking with QAG on Coal Fired Test Furnace**
- **Hg Measurement on Coal-fired Power Plant – Comparison with Method 30B and Thermo Hg Freedom**

XCEM Tests (2002)

- **Comparison of XCEM to Method 29**
- **Metals Spike at Army Munitions Incinerator**
- **Spiked Concentration Measured by M29 and Xact**
- **Sponsored by US Army Engineer Research and Development Center Construction Engineering Research Laboratory (EDRC/CERL)**
- **M29 gathered and analyzed by independent laboratory group**

2002 XCEM Testing Results

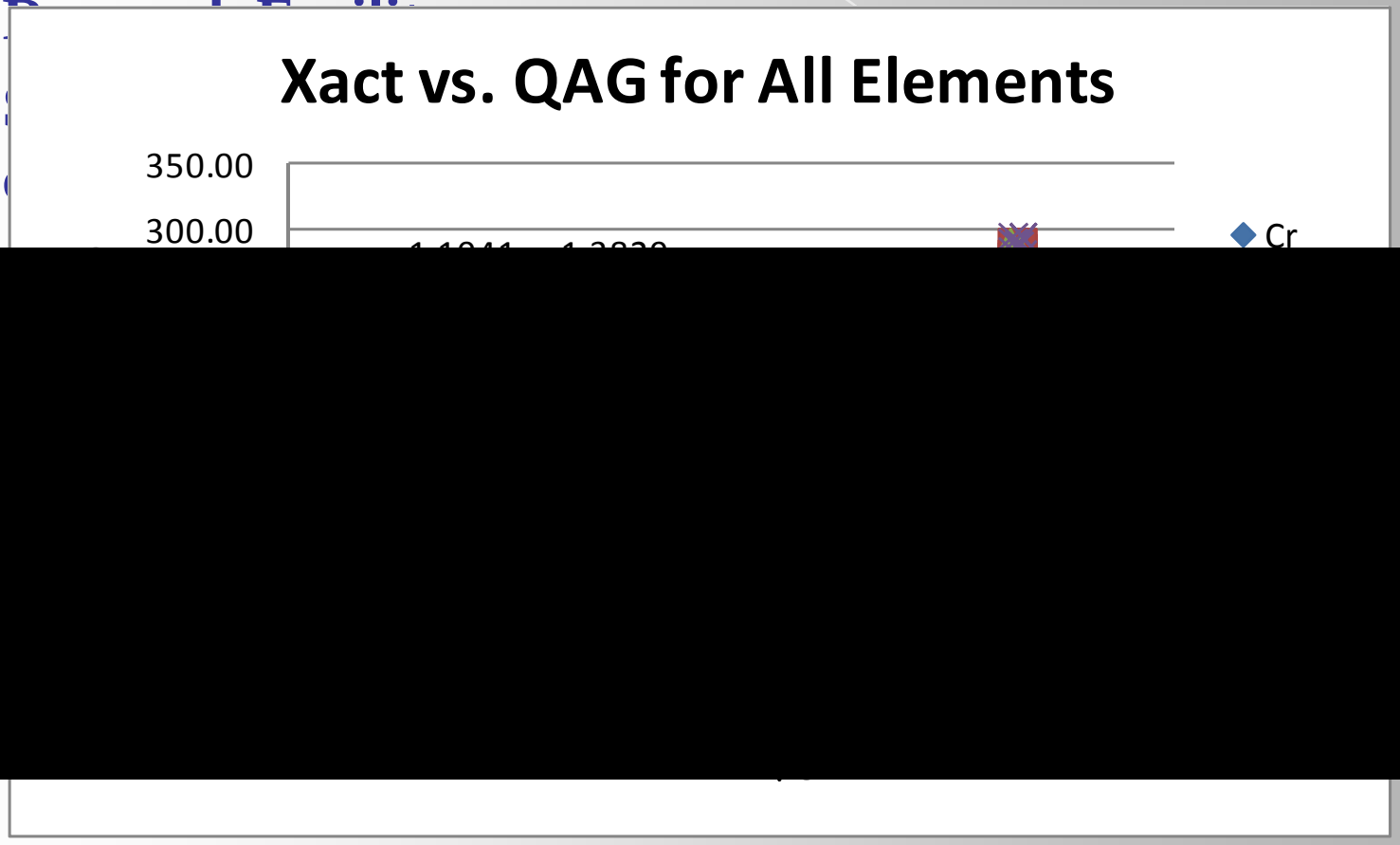
Element	% Relative Accuracy	Met PS-10 Criteria
Pb	**4.4%**	**Yes**
Cd	**17%**	**Yes**
Cr	**15%**	**Yes**
Ba	**4%**	**Yes**

Army Xact Comparison to M29

- **Later Version of Xact**
- **Hg and As spiked into a subsample of Coal fired boiler Effluent**
- **Hg and As Measured by M29 and Xact**
- **Results % Relative Accuracy**
  - **Hg – 17%**
  - **As 16%**

EPA Sponsored Small Business Innovative Research Grant

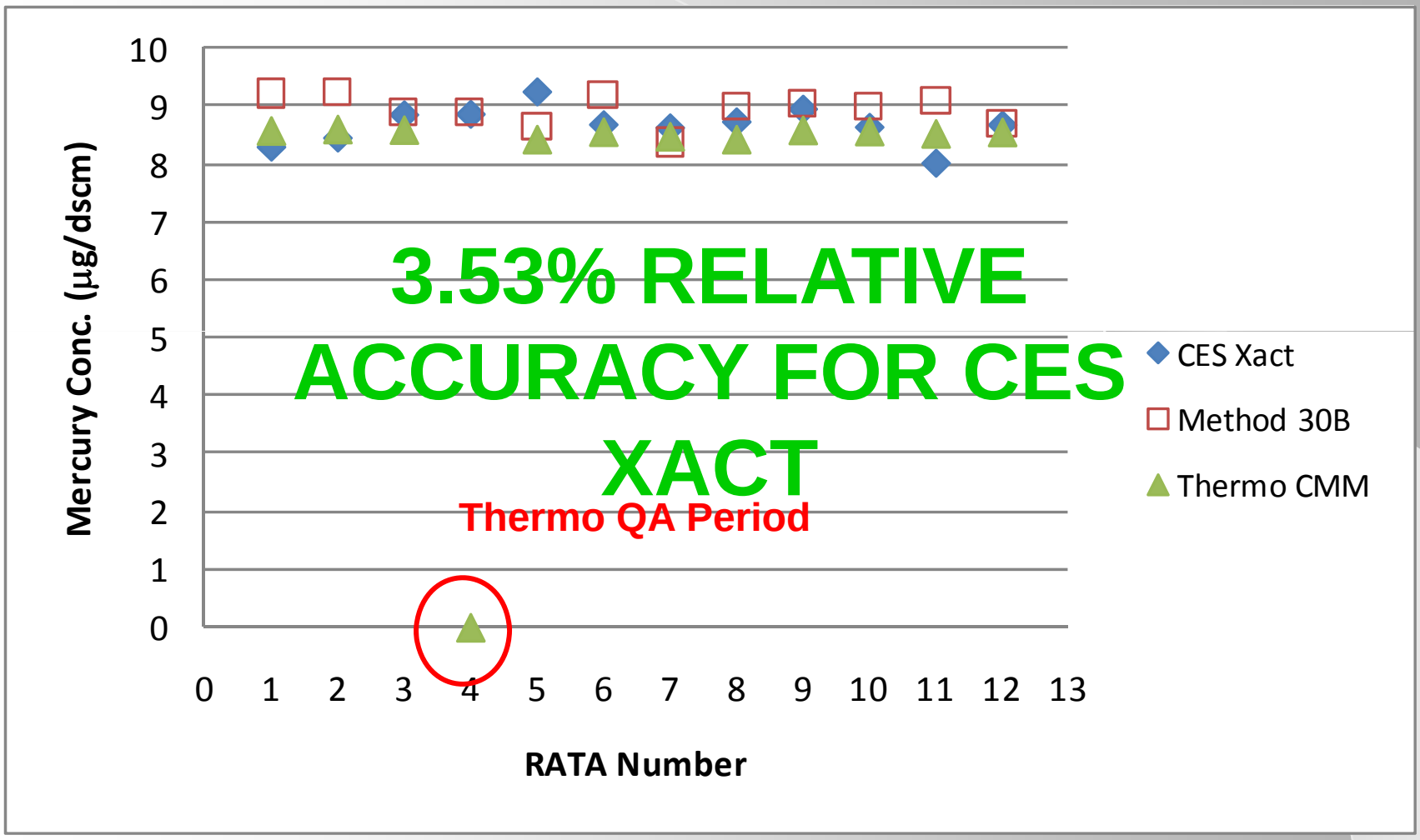
- **Coal Fired furnace - EPA's Multi-Pollutant Control**



Hg Measurement on Coal Fired Power Plant

- **585 Mwatt Coal Fired Power Plant**
- **Downstream of Electrostatic Precipitator**
- **Measurement of Stack Concentrations of Hg**
- **Comparison with Method 30B and an on-site operating Thermo Mercury Freedom Unit**
- **Xact was installed and operating within 2 days**

Hg Measurement on a Coal Fired Power Plant



Applicable Sources?

- Incinerators (Tested and installed)
- Coal-fired Boilers (Tested)
- Wet and Dry Stacks (Tested)
- 50 PPM Acid Gases (Tested)
- Smelters and Mills
- Cement and Lime Kilns
- Mineral Processing
- Plating and Welding

What Next?

- **EPA Asked for Comment on the use of multi-metals CEMS as a part of CISWI MACT (August 2010)**
- **EPA Asked for Comment on the use of multi-metals CEMS for Sewage Sludge Incinerators (September 2010).**
- **Why is EPA regulating with Surrogate (PM) instead of MM-CEMS?**
- **MM-CEMS as an alternative to Hg CEMS + PM CEMS for PC MACT, Boiler MACT, CISWI MACT and Utility MACT?**

QUESTIONS?

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