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Introduction to the Xact 625i

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Cooper Environmental

The Leader in near real-time elemental speciation of particulate matter

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Presentation Outline

- Xact 625i – Description and Operation
- Accuracy – Comparison Data
- Quality Assurance
- Source Identification

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What is the Xact

- Continuous Metals Monitor Based On
  - X-ray Fluorescence
  - Reel to reel tape drive technology
- Able to measure up to 67 metals simultaneously including Pb, As, and Cd and give near real time analysis results
- Available in Ambient/Fenceline, Stack and water versions

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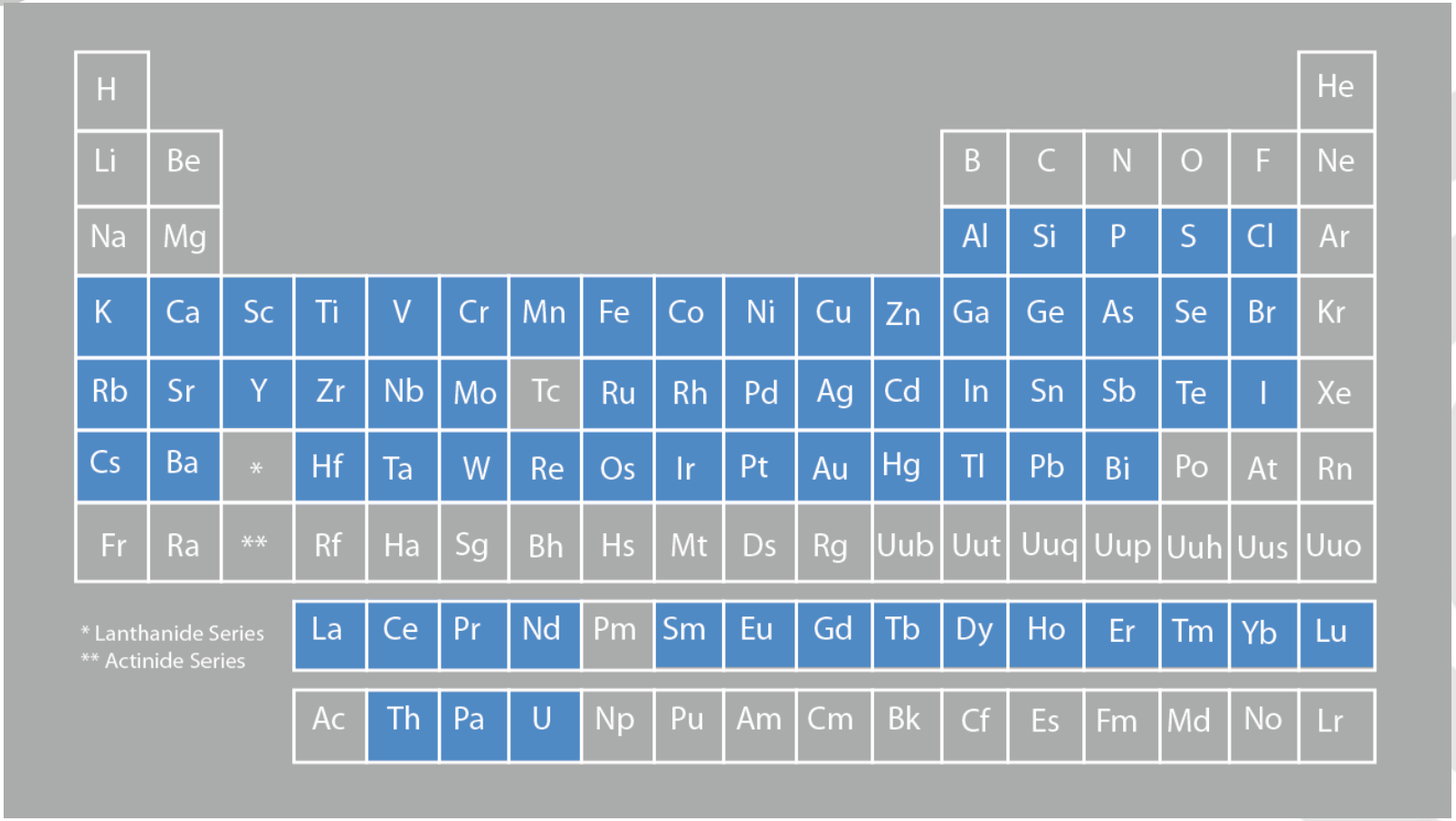
Elements Measured by Xact



- Current Xact 625i can measure up to 67 elements simultaneously
- Standard Configuration is 44 elements

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Measurement Capabilities

Xact 625i Minimum Detection Limits (ng/m³)
68% Confidence Level (C1σ) per US EPA IO 3.3 and Currie *

Element	Atomic Number	15	30	60	120	180	240
Al	13	840	290	100	35	19	12
Si	14	150	51	17.8	6.3	3.4	2.2
P	15	44	15	5.2	1.8	0.99	0.64
S	16	26	9.1	3.16	1.1	0.60	0.39
Cl	17	15	5.0	1.73	0.61	0.33	0.21
K	19	9.8	3.4	1.17	0.41	0.22	0.14
Ca	20	2.5	0.86	0.30	0.10	0.057	0.037
Ti	22	1.3	0.46	0.16	0.056	0.030	0.020
V	23	1.0	0.34	0.12	0.042	0.023	0.015
Cr	24	0.97	0.33	0.12	0.041	0.022	0.014
Mn	25	1.2	0.41	0.14	0.050	0.027	0.018
Fe	26	1.4	0.49	0.17	0.061	0.033	0.021
Co	27	1.1	0.39	0.14	0.049	0.026	0.017
Ni	28	0.78	0.27	0.10	0.034	0.018	0.012
Cu	29	0.65	0.23	0.079	0.028	0.015	0.010
Zn	30	0.55	0.19	0.067	0.023	0.013	0.008
As	33	0.52	0.18	0.063	0.022	0.012	0.008
Se	34	0.66	0.23	0.081	0.029	0.016	0.010
Br	35	0.85	0.30	0.10	0.037	0.020	0.013
Ag	47	16	5.5	1.9	0.68	0.37	0.24
Cd	48	21	7.2	2.5	0.89	0.48	0.31
In	49	26	8.9	3.1	1.1	0.60	0.39
Sn	50	33	12	4.1	1.4	0.78	0.51
Sb	51	42	15	5.2	1.8	0.99	0.64
Ba	56	3.3	1.1	0.39	0.14	0.074	0.048
Hg	80	0.99	0.35	0.12	0.043	0.023	0.015
Tl	81	0.95	0.33	0.12	0.041	0.022	0.014
Pb	82	1.0	0.36	0.13	0.045	0.024	0.016
Bi	83	1.1	0.37	0.13	0.046	0.025	0.016

Typical 1 hour detection limits are less than 1 ng/m^3

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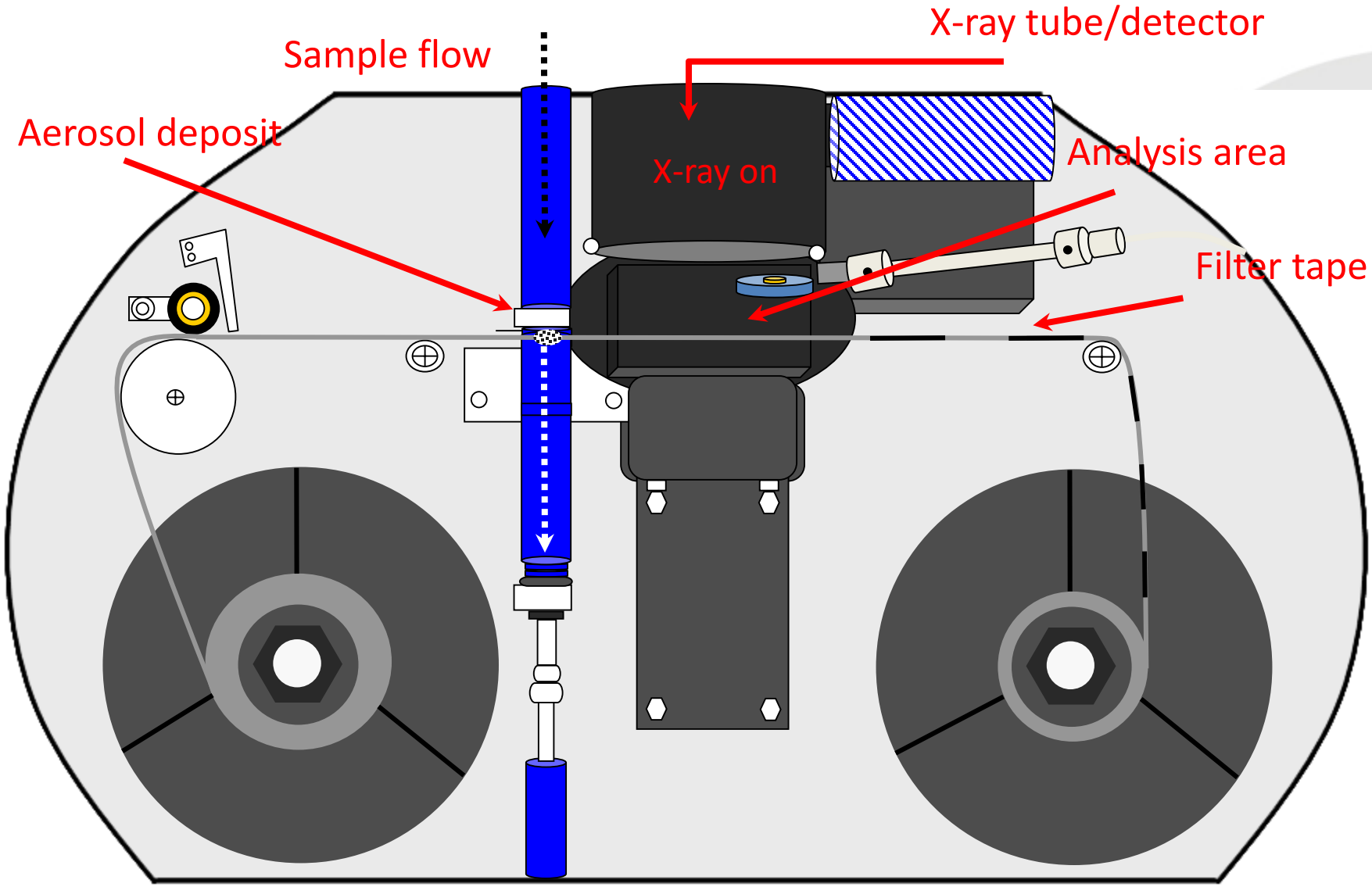
Xact® Sampling and Analysis Module



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Comparison Studies

- U.S. EPA Environmental Technology Verification (ETV)
- At U.S. National Ambient Air Toxics Trends Station
- King's College (London) – Atmospheric Measurement Technology Paper

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Xact® 625 ETV Study

- Data produced by US EPA and Batelle independent of CES
- Xact® 625 daily average compared to reference method PM_{10} sampling followed by metals analysis by ICP-MS
- Xact® and reference sampler operated by Ohio EPA not CES
- Data above Xact® quantitation limit compared to data above reference method detection limit

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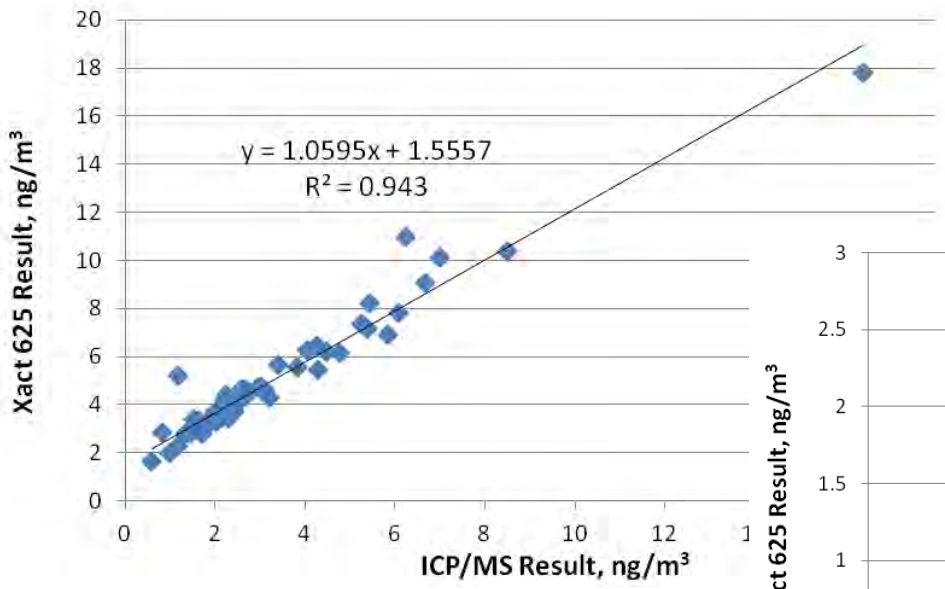
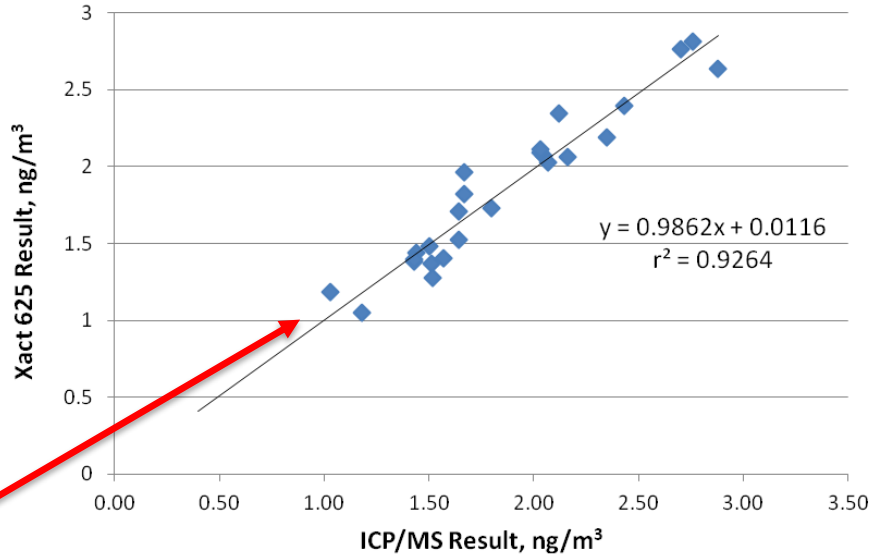
ETV Accuracy Data



Lead (Pb)



Selenium (Se)

Accuracy Demonstrated Down to 1 ng/m³

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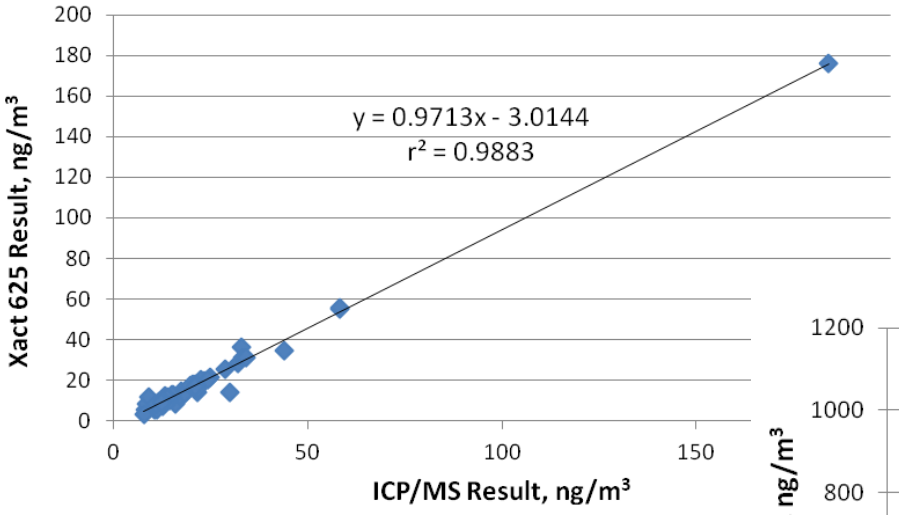
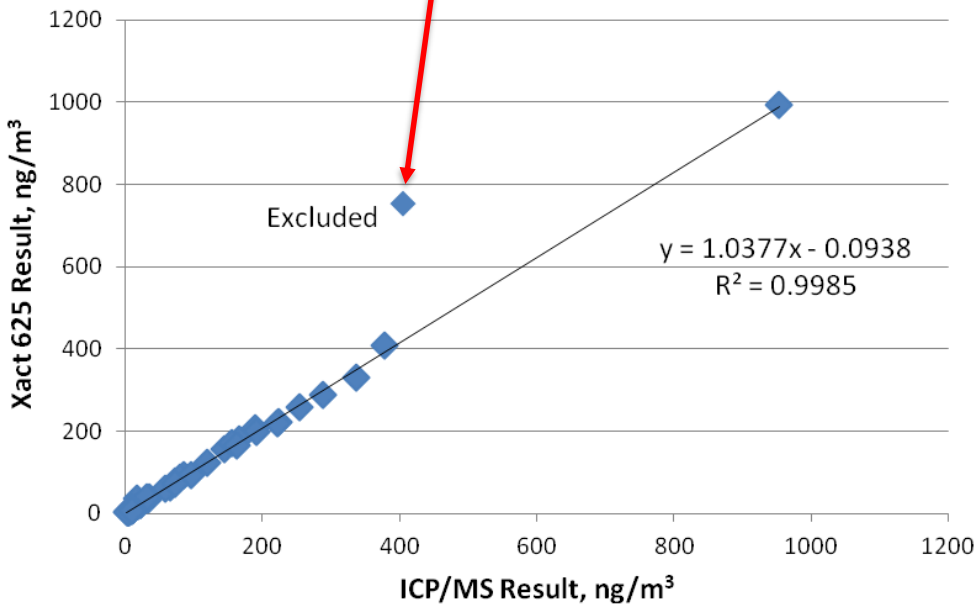
ETV Accuracy Data



Zinc (Zn)

Excluded because Xact® did not sample for 24 hours



Manganese (Mn)

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Xact® 625 at NATTS Site

- Conducted by Missouri Department of Natural Resources at Blair Street NATTS site

  (NATTS = National Air Toxics Trends Station)

  - Station collects Priority and Core HAPs (metals include As, Be, Cd, Cr (total & VI), Pb, Mn, & Ni)
  - Data included metals data collected from November 1, 2012 through March 31, 2014
  - 1-in-6 day samples collected on FRM Sampler
  - Se, Mn and Pb typically observed above quantitation limits

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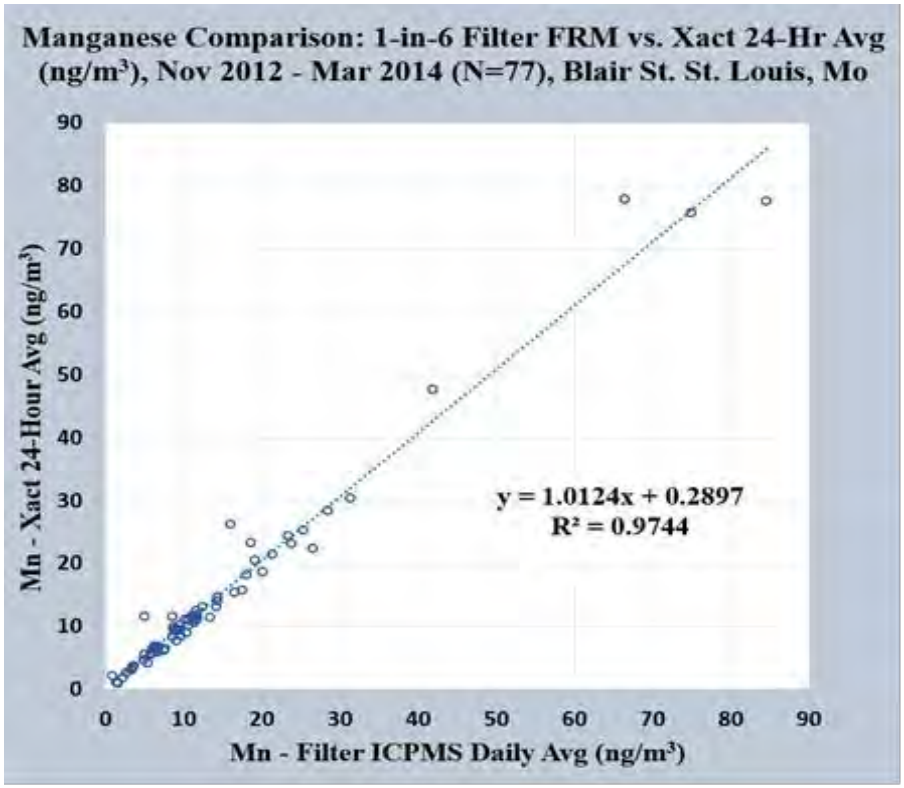
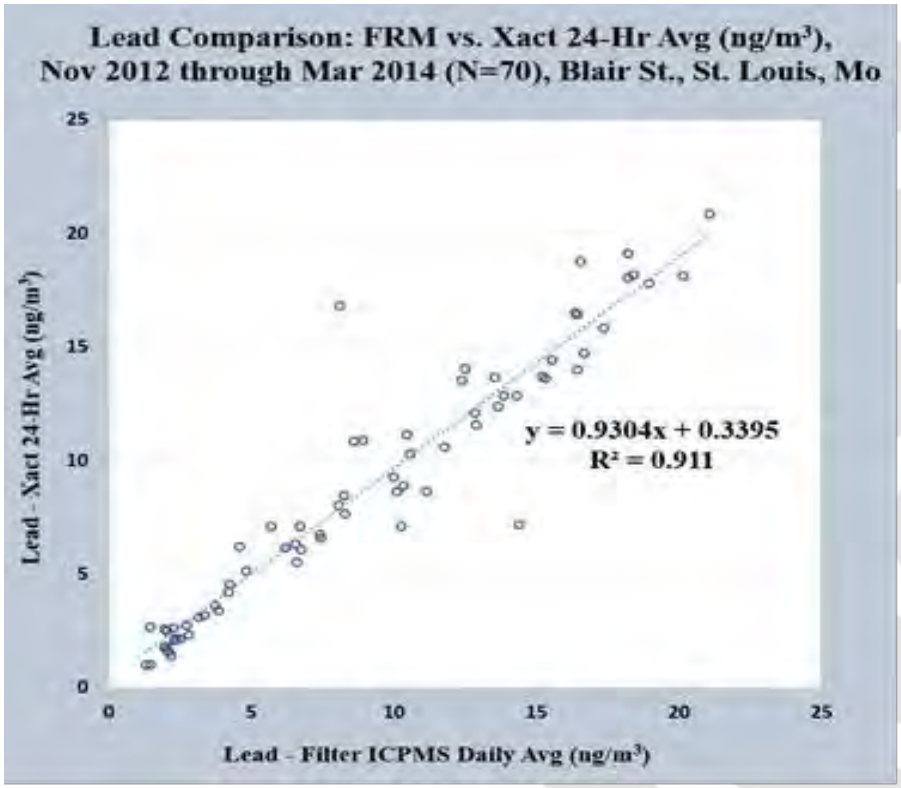
NATTS Results – Mn and Pb





	N	Mean	Mean SE	SD
FRM Daily Mn Avg	77	13.18	1.67	14.62
Xact® Mn Daily Avg	77	13.86	1.72	15.08
Xact® Hourly Mn	10733	16.704	1.2237	126.774

	N	Mean	Mean SE	SD
FRM Daily Pb Avg	70	9.07	0.69	5.79
Xact® Pb Daily Avg	70	8.78	0.67	5.65
Xact® Hourly Pb	11311	9.7	0.23	24.0

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King's College Study

- Three different sampling locations
  - Roadside in downtown London
  - Industrial Area
  - Urban background
- Xact Compared ICP-MS
- Also a Novel Comparison Teom Mass measurement on laboratory aerosol

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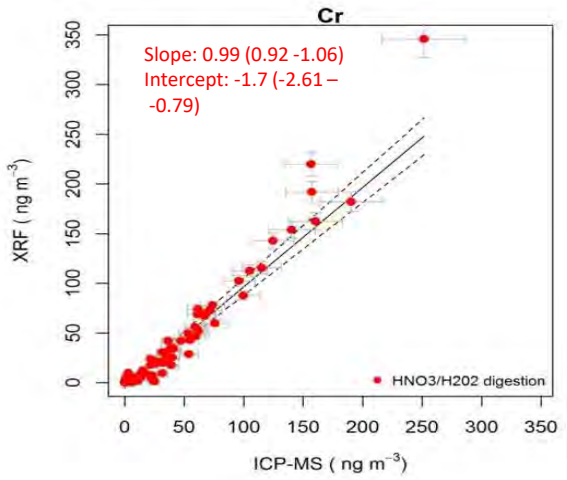
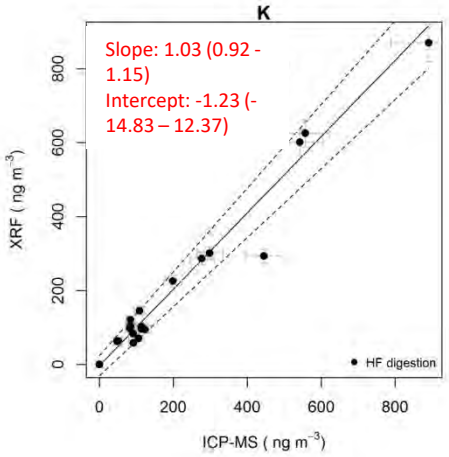
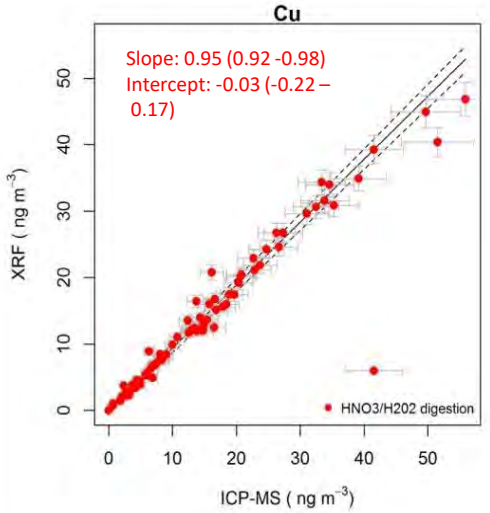
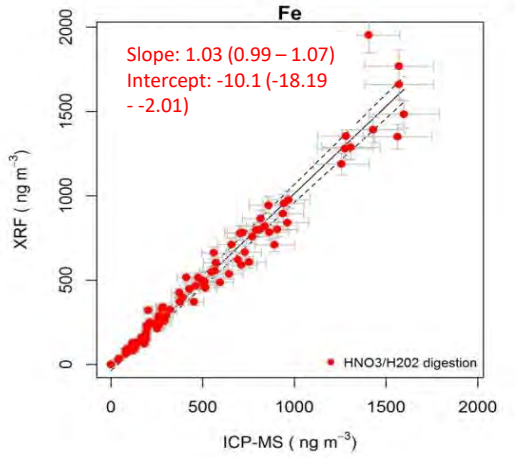
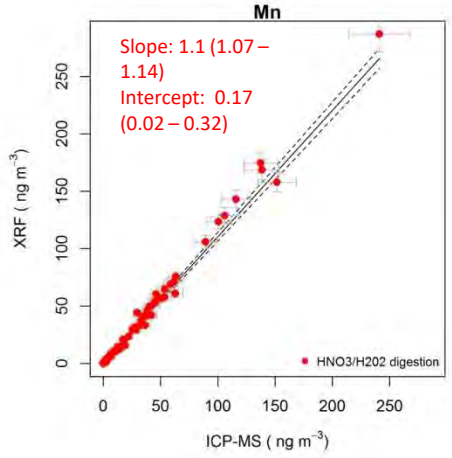
Results for Selected Elements











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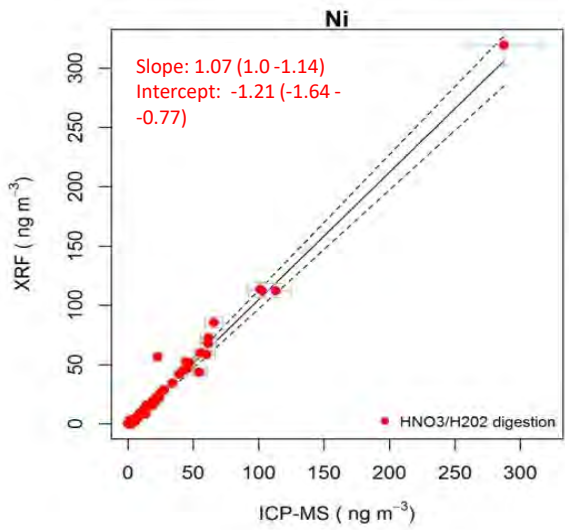
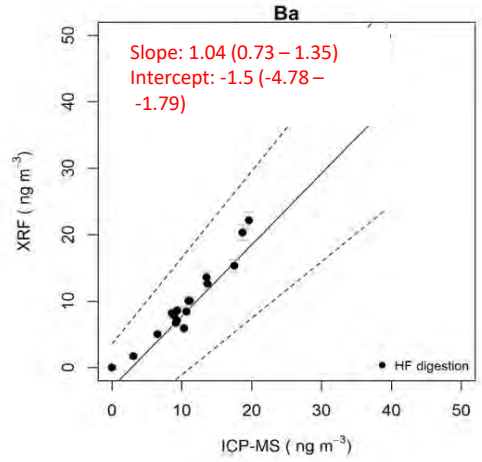
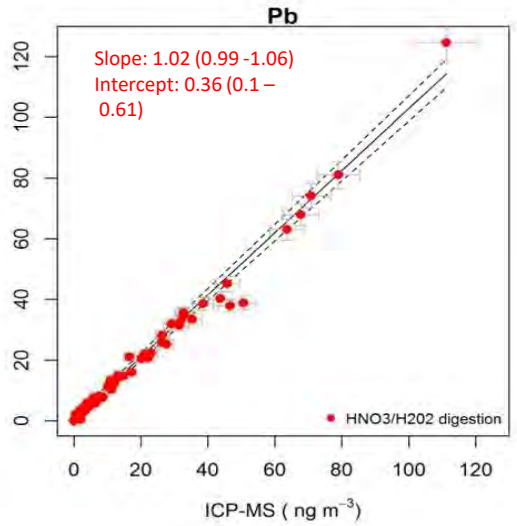
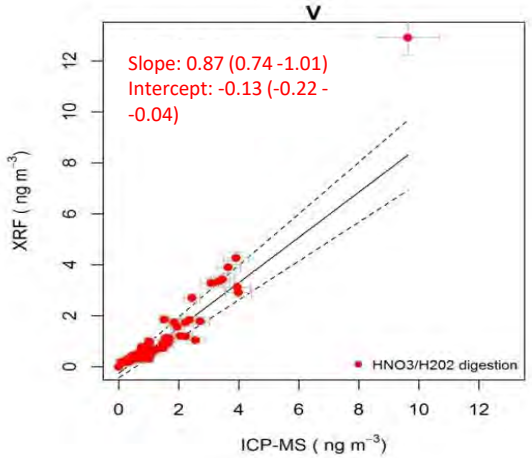
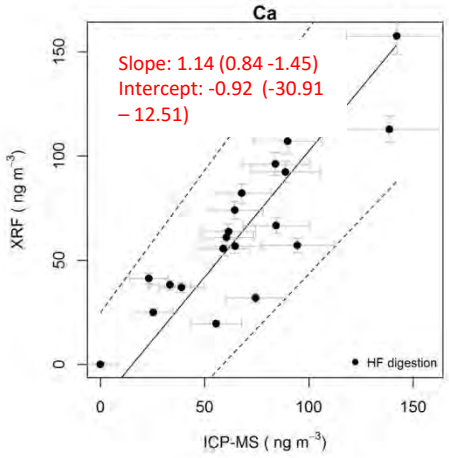
Results for Selected Elements

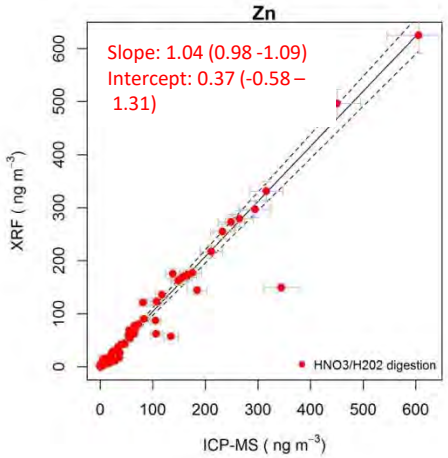












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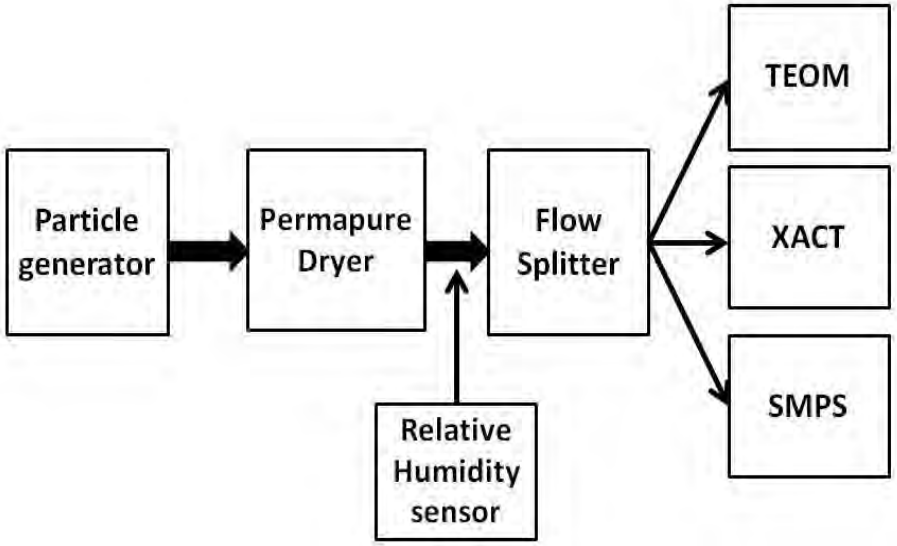
TEOM Comparison

- Xact reported mass compared to the mass reported for Teom for several laboratory generated aerosols
- Potassium Chloride (KCl), Zinc Acetate $Zn(O_2CCH_3)_2$ and ammonium sulfate
- $(NH_4)_2SO_4$
- Teom mass calculated based on stoichometry and compared to the Xact
- Direct Mass comparison – no digestion or spectral interference considerations



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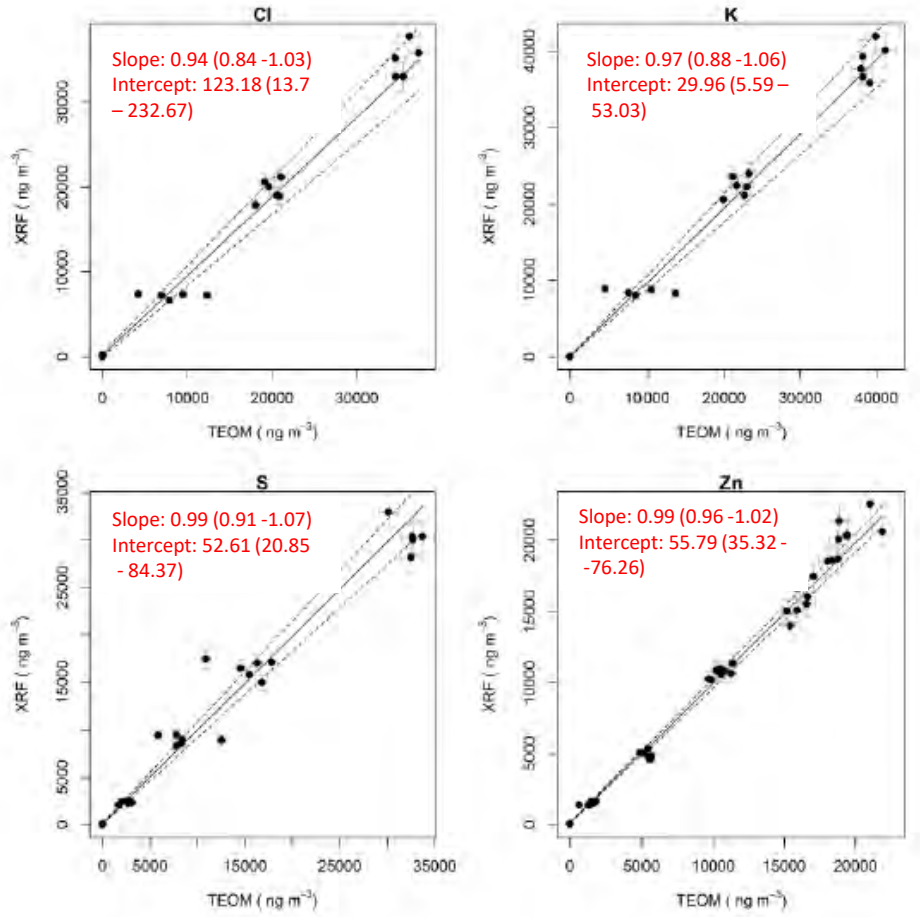
TEOM Comparison Results



- All Slopes nearly 1.0 – indicated great comparison between the Xact and TEOM measured mass

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Quality Assurance and Traceability to NIST

- XRF Calibration Standards
- Factory Acceptance Testing with a Traceable to NIST Reference Aerosol
- Automatic Daily Quality Assurance

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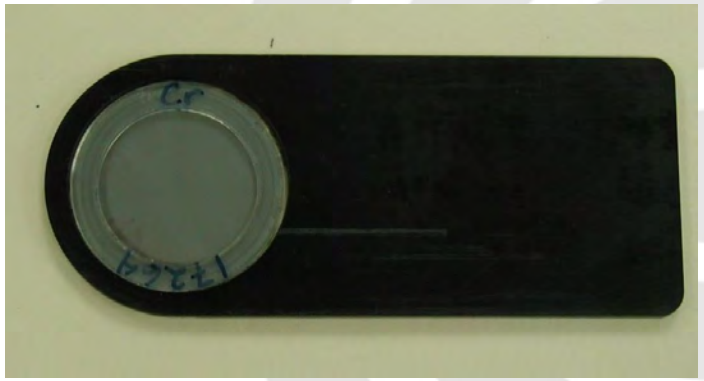
Calibration with NIST Traceable Standards

- Aerosol Concentration measured by dividing the XRF determined metal mass by volume
- XRF Standards
  - Gravimetrically NIST Traceable
  - Recommended in EPA IO 3.3
- NIST Traceable flow standards



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Factory Acceptance Test

- Xact Challenged with a reference aerosol to validate the entire system
- Aerosol Generated using CES' Quantitative Aerosol Generator (QAG)
- QAG is traceable to NIST Standards
- EPA Method 301 Validated

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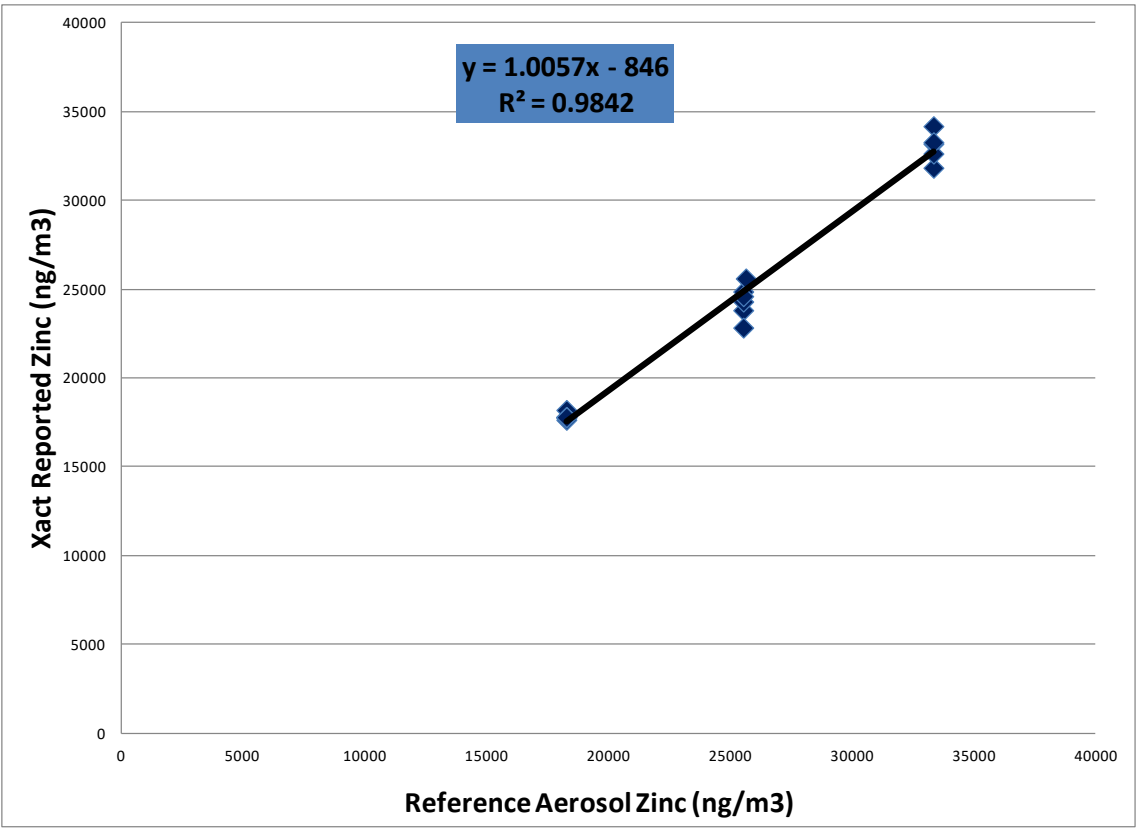
Example Factory Acceptance Test Results



- Xact challenged with a reference aerosol
- Concentration of aerosol is independent of Xact measurement
- Slope of 1.0 indicates perfect agreement between reference aerosol and the Xact
- High R^2 indicates good precision

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Xact 625 Quality Assurance

- Automatic
  - XRF Stability with every sample – Pd or Nb rod
  - Upscale – Stable response to three different elements once each
- Manual
  - Quarterly Flow Check – Check with NIST traceable reference flow meter
  - Quarterly XRF Check – Check Xact response to thin film standards
  - Quarterly Blank Check

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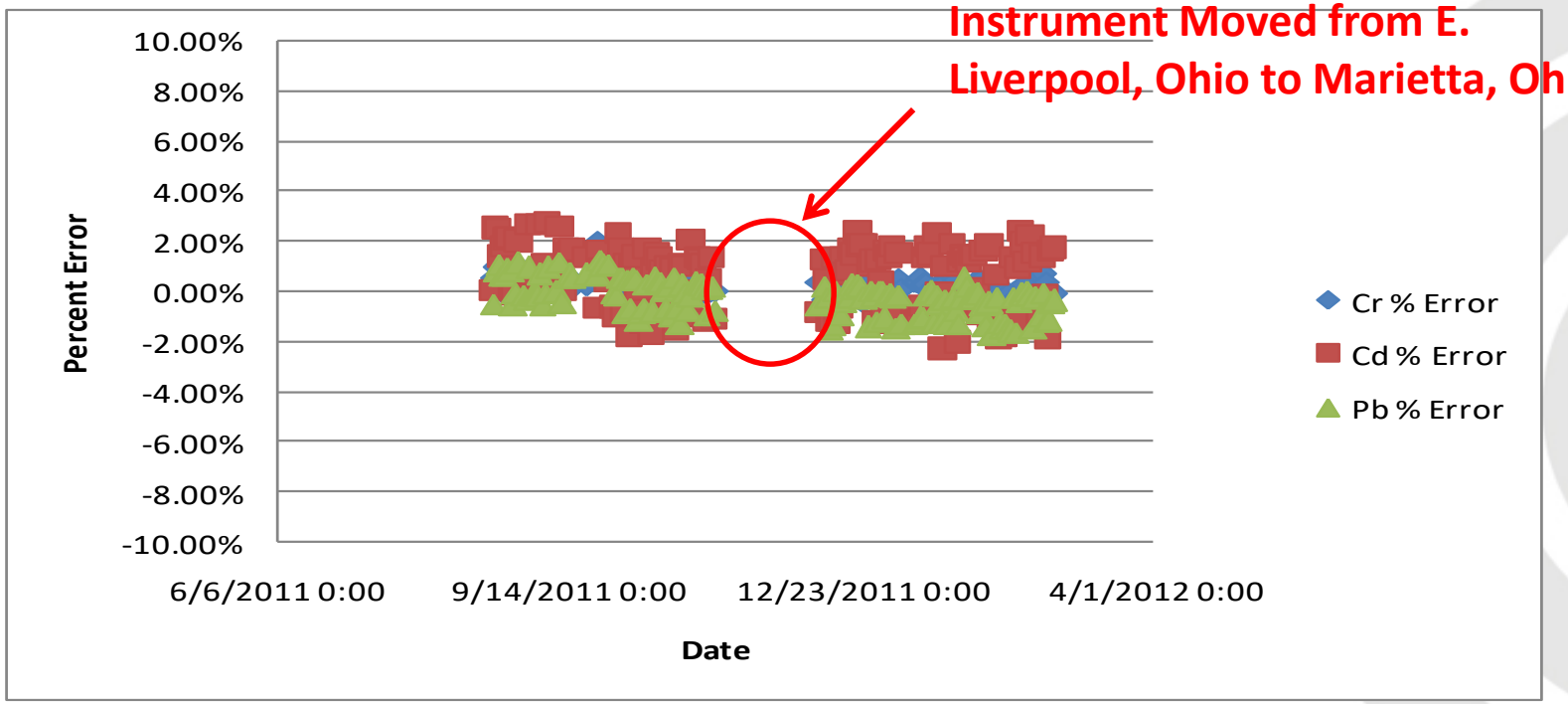
Example QA Data From Field Study



XRF Upscale Check never exceeds 3.0% error for 145 days and a move from one site to another

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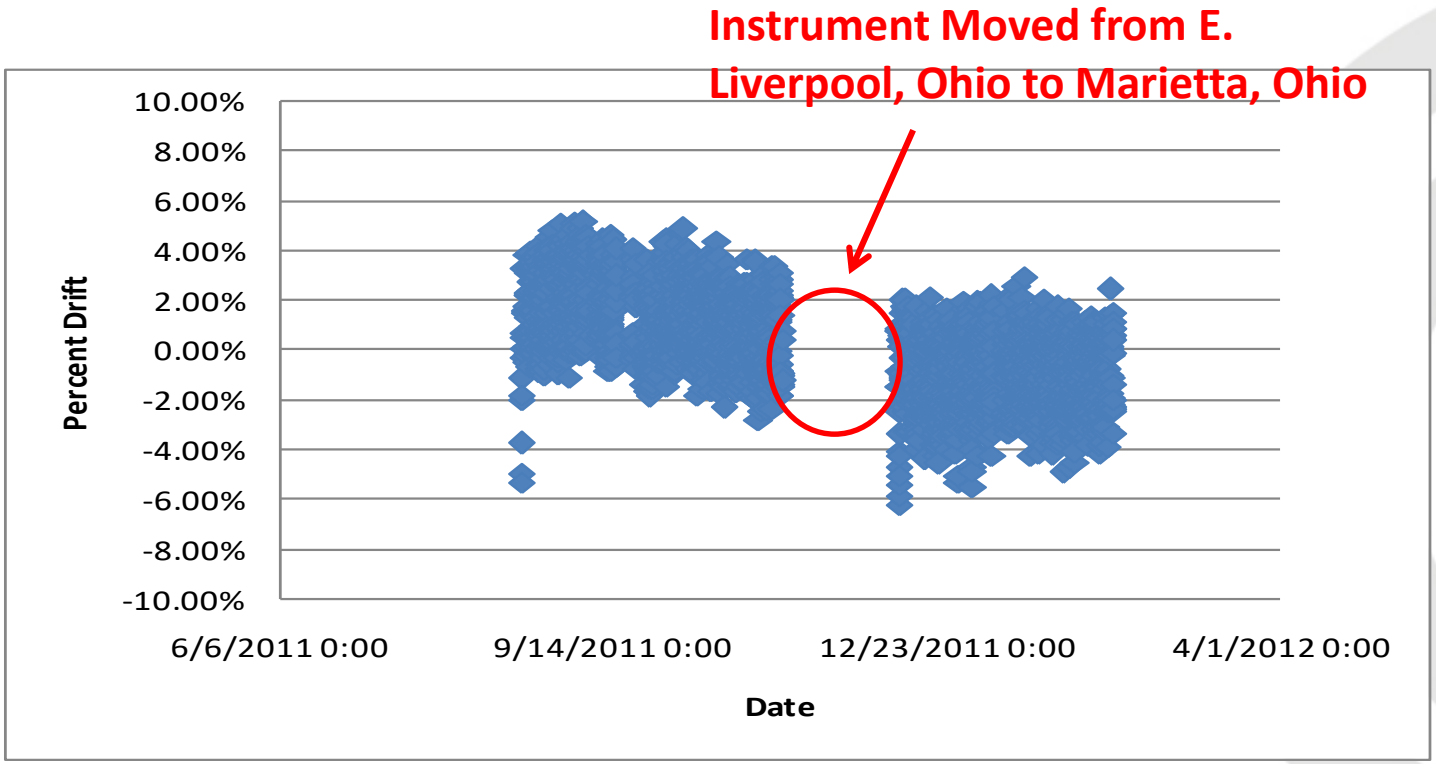
Field Quality Assurance Data – XRF Stability



- XRF Stability Checked with Each and Every Sample acquired over 145 days
- Includes **3,442** samples
- Less than 6% drift at every data point

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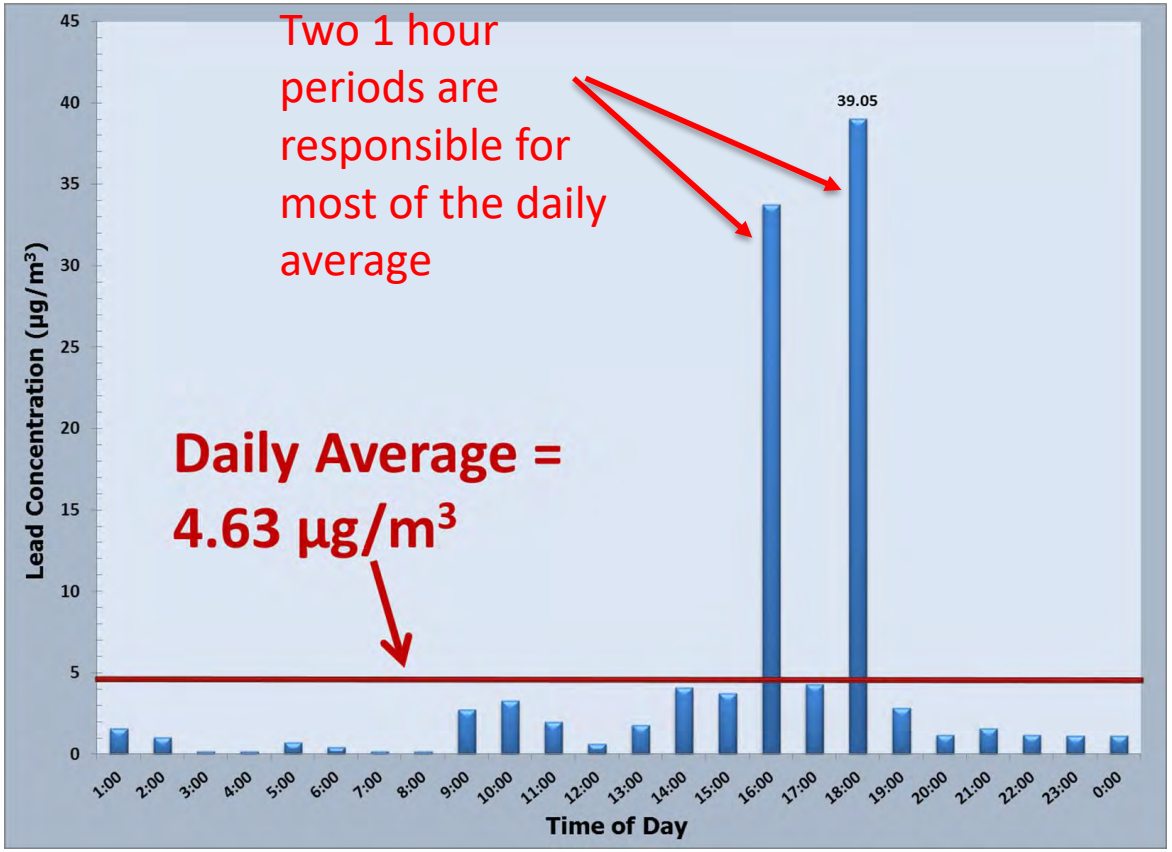
Xact 625 for Identification of Emissions

- Time Resolution
  - Correlate high concentrations with local activities
- Chemistry – compare chemistry measured by the Xact with plant operational chemistry
- Correlation with Wind Direction
- Highly Time Resolved Factor Analysis (Hong Kong University of Science and Technology and Shanghai Academy of Environmental Sciences)

Emission Identification– Time Resolution



- Monitoring on Fenceline of a Pb Smelter
- Variability in concentration is lost when using 24 hour sampling
- Time resolution can allow for a correlation of the measurement with plant activities
- Real time feed back from the monitor may allow for process control

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Emission Identification- Chemistry

- Sources may be identified based on their unique ratio of elements – their chemical fingerprint
- Data can be used for Chemical Mass Balance Source Apportionment or for Factor Analysis (e.g. PMF, PCA)

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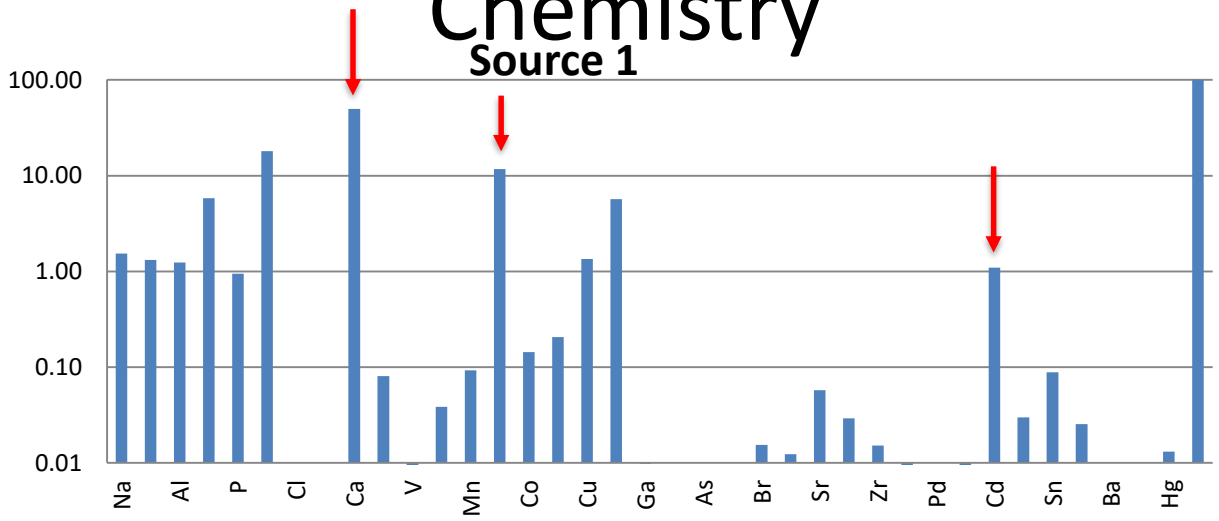
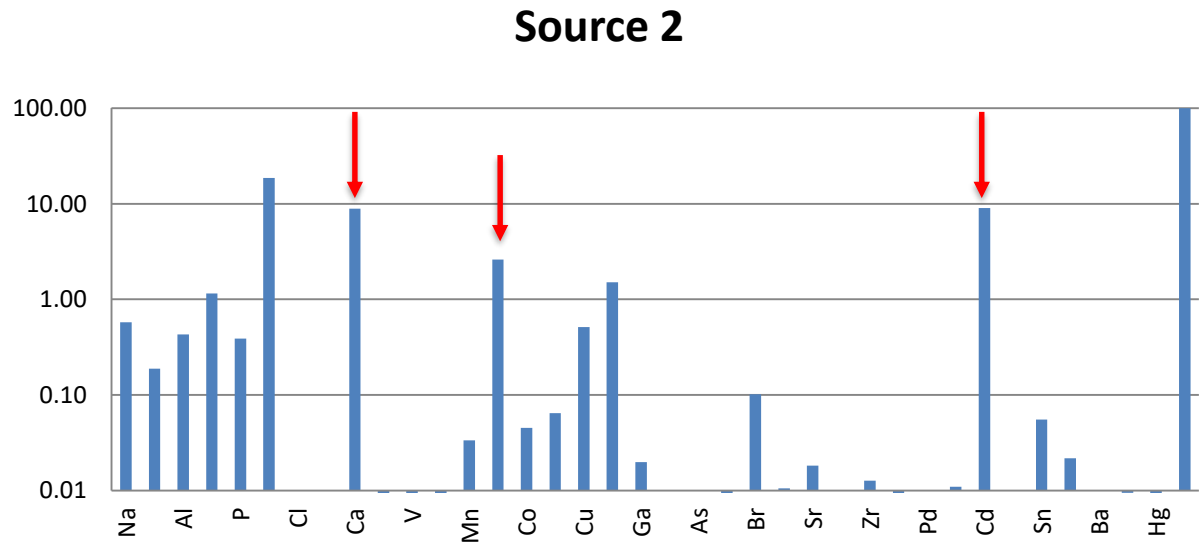
Emission Identification- Chemistry





- All elements normalized to lead
- This ratio is the source's "fingerprint"
- Chemistry allows for the resolution of these two sources
- Note the different ratios for the highlighted elements

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Industrial Processes Tracers

• Coal, Oil, and Wood Combustion	• As, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn
• Non-Ferrous Metal Industry	• As, Cd, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Zn
• Waste Incineration	• As, Cd, Cr, Cu, Hg, Mn, Sb, Se, Sn, V, Zn
• Cement Production	• As, Cr, Hg, Se
• Glass Production	• As, Cd, Cr, Pb, Ni, Se, V, Zn

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Emission Identification– Wind Direction

- With high time resolution it is possible to correlate wind direction and concentrations
- For some areas it may be possible to orient the monitor so that the sources can be located based on wind direction

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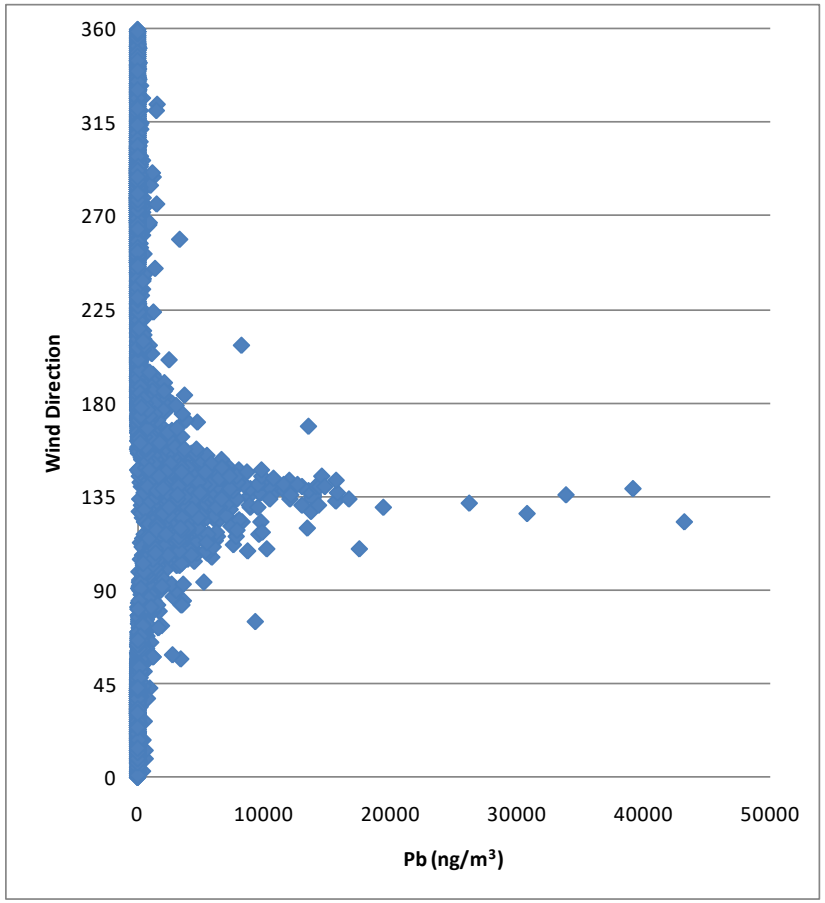
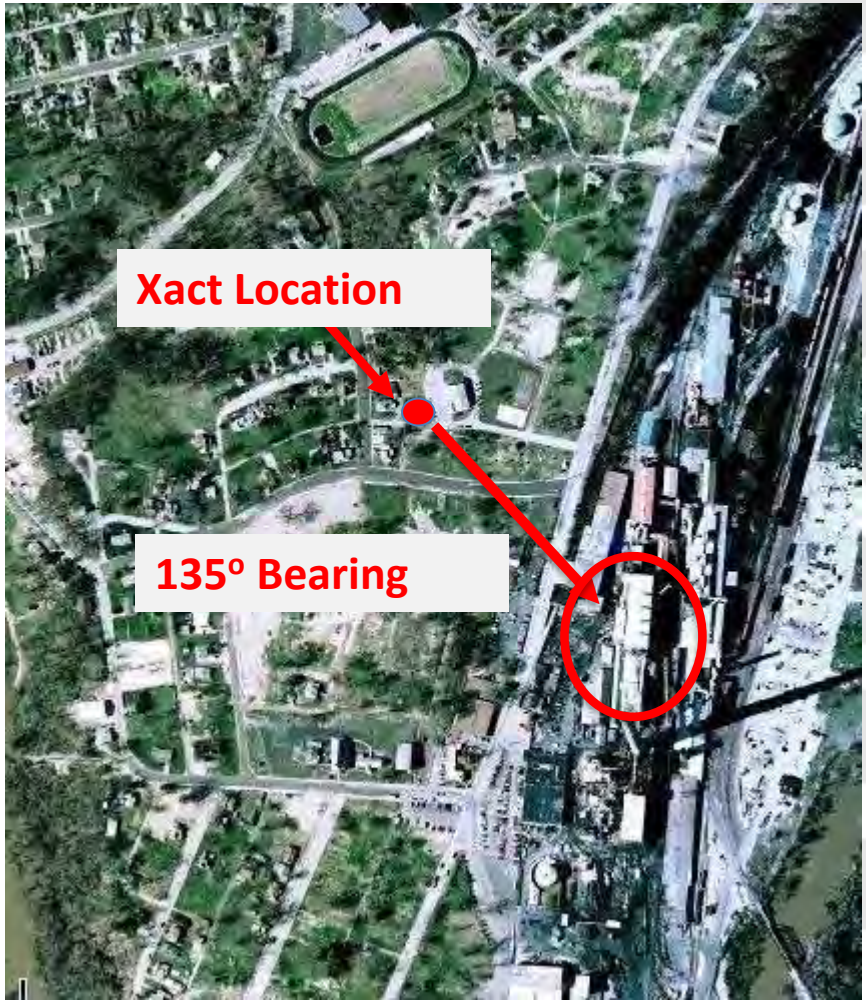
Process Control – Wind Direction





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Source Identification with Multiple Xact 625's

- Upwind and downwind – takes advantage of both time resolution and correlation with wind direction
- Can help identify if a source is local or regional
- Triangulation of data from multiple monitoring locations can help identify the location of a source

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Multiple Xact Sampling Sites to Determine Area Contribution

- Sampling at an industrial plant in a river valley
- Wind direction is either up or down the valley
- Monitor can be useful in identify what is from the plant and what isn’t
- As a first approximation subtract upwind concentration from downwind location to get plant contribution

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Multiple Xact Sampling Sites to Determine Area Contribution

Site contribution = Concentration at Site 1 – Concentration at Site 2

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Emission Source Triangulation

- Data from Xact 625's monitoring at multiple locations can be used to triangulate a sources location
- Individual elements can be triangulated
- Or alternatively factors (combinations of different elements) can be triagulated

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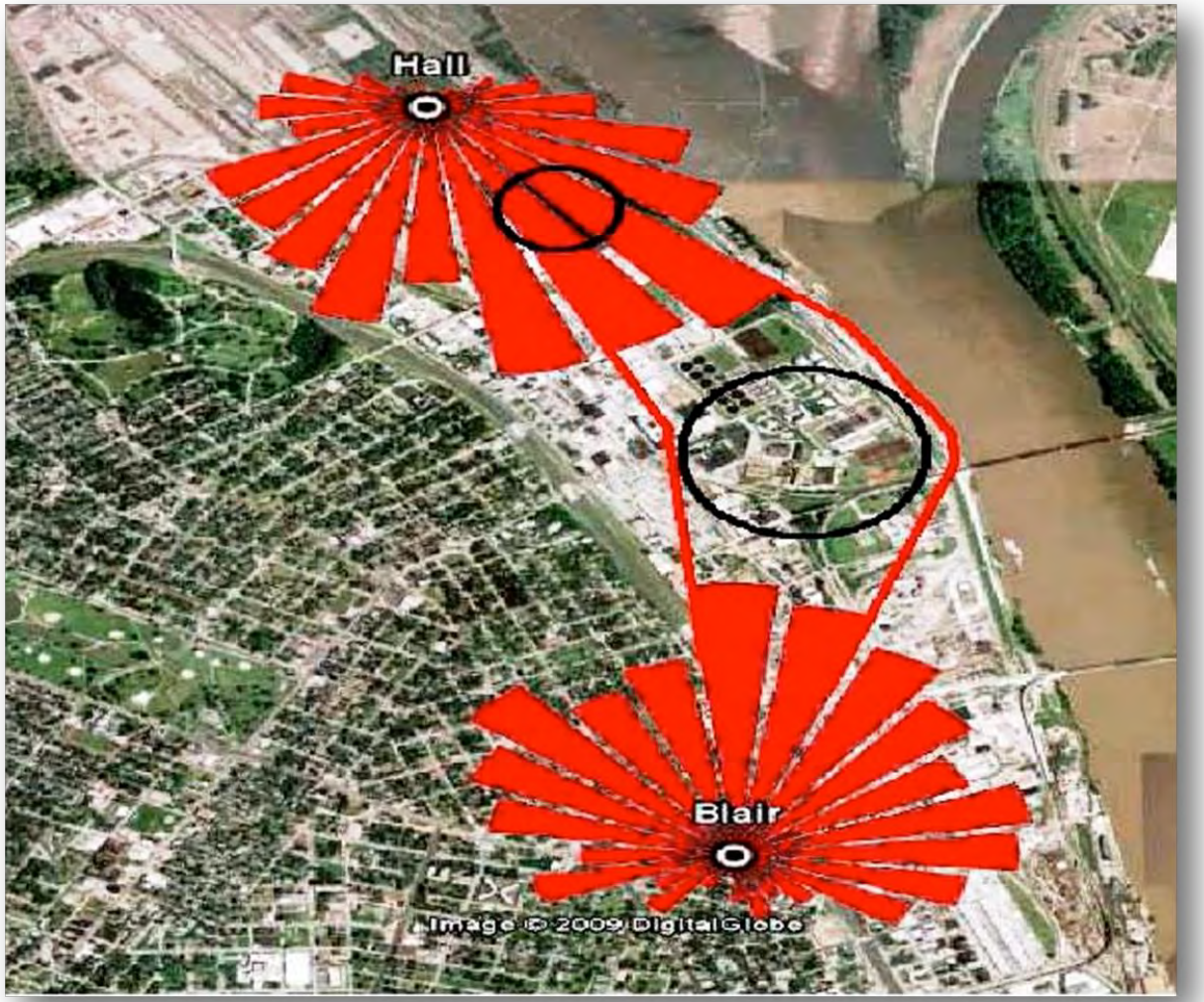
Emission Source Triangulation



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Automated Source Characterization Software

- Automated Data Analysis Plotting Toolset (ADAPT)
  - Integrated software for easy assessment of data collected on system
  - Meteorological sensor included for immediate source direction detection
  - User-friendly interface with touch screen
  - Option to connect remotely to Xact (Wi-Fi required)
  - Automatically creates graphical displays to help identify sources based on time resolution, chemistry, and meteorology

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ADAPT Features
Time of Day Trends

- Identifies time periods when metal concentrations peak due to typical daily emission pattern of sources
- Each bar-and-whisker details the metal's distribution during that specific sampling interval over the user-selected time period
- Includes sampling interval completeness chart

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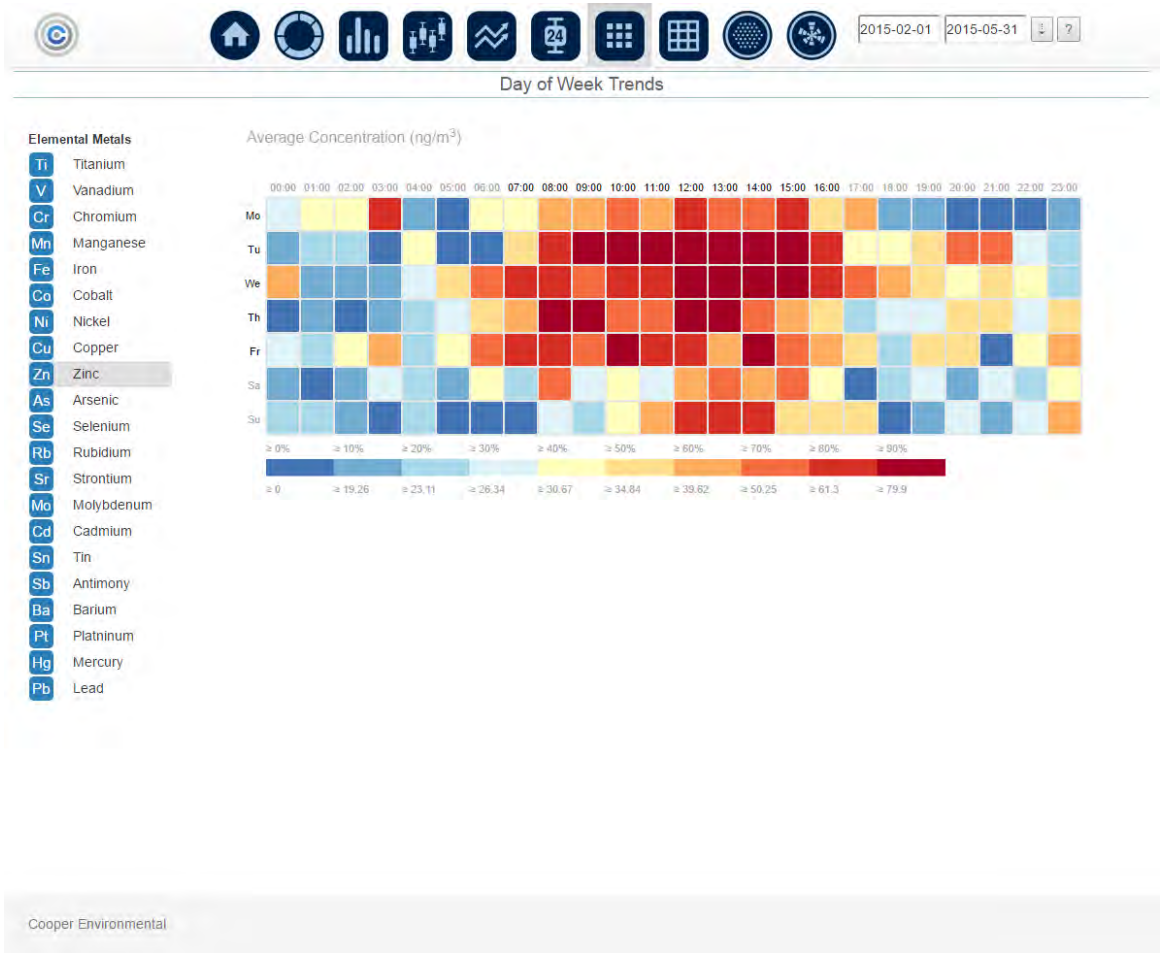
ADAPT Features
Day of Week Trends



- Identifies days and times when metal concentrations peak due to typical weekly emission pattern of sources
- Enables examination of weekday vs weekend patterns of metal concentrations at monitoring site

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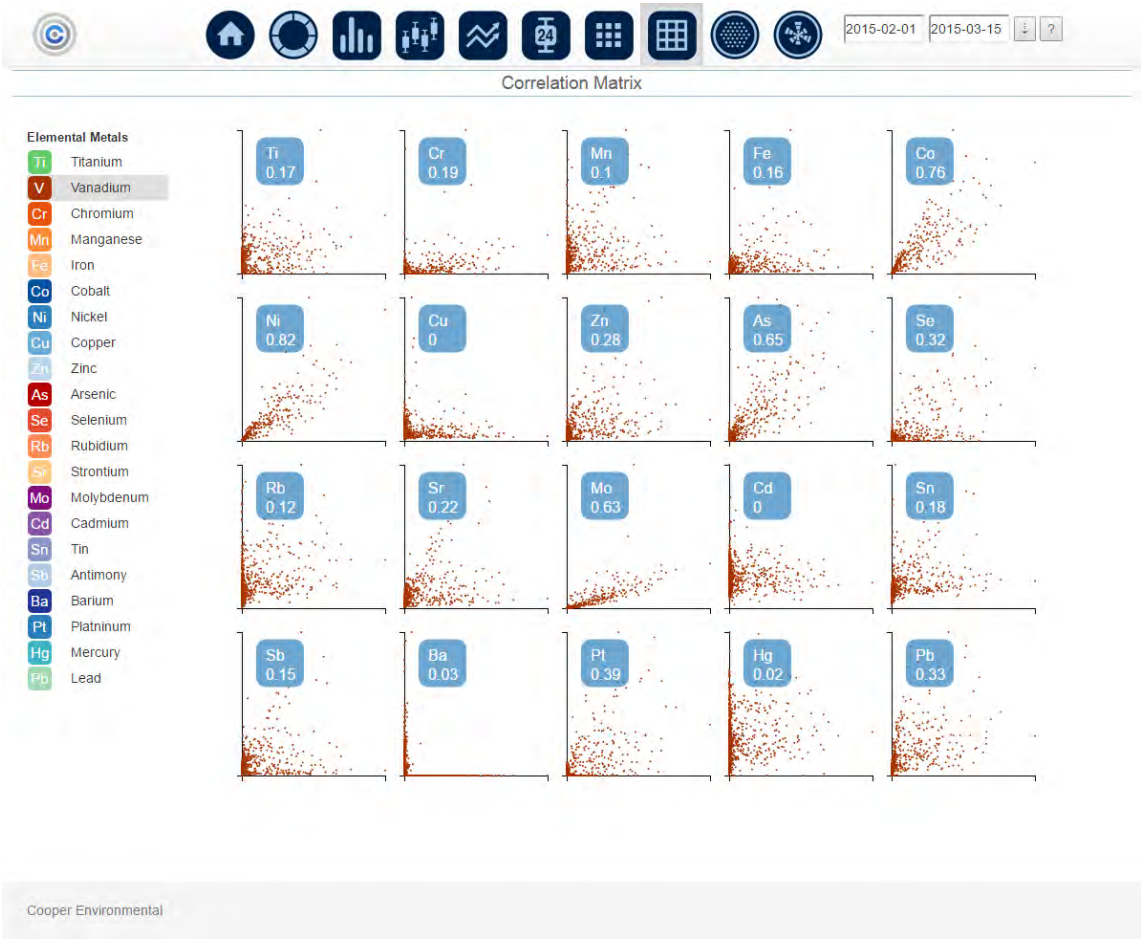
ADAPT Features Correlation Matrix



- Examine correlation across all metals simultaneously with displayed RMA regression correlation coefficient
- Identify metals potentially originating from similar emission sources/patterns (high R^2) and those originating from independent sources (low R^2)
- Option to separately view individual correlation plots for additional details

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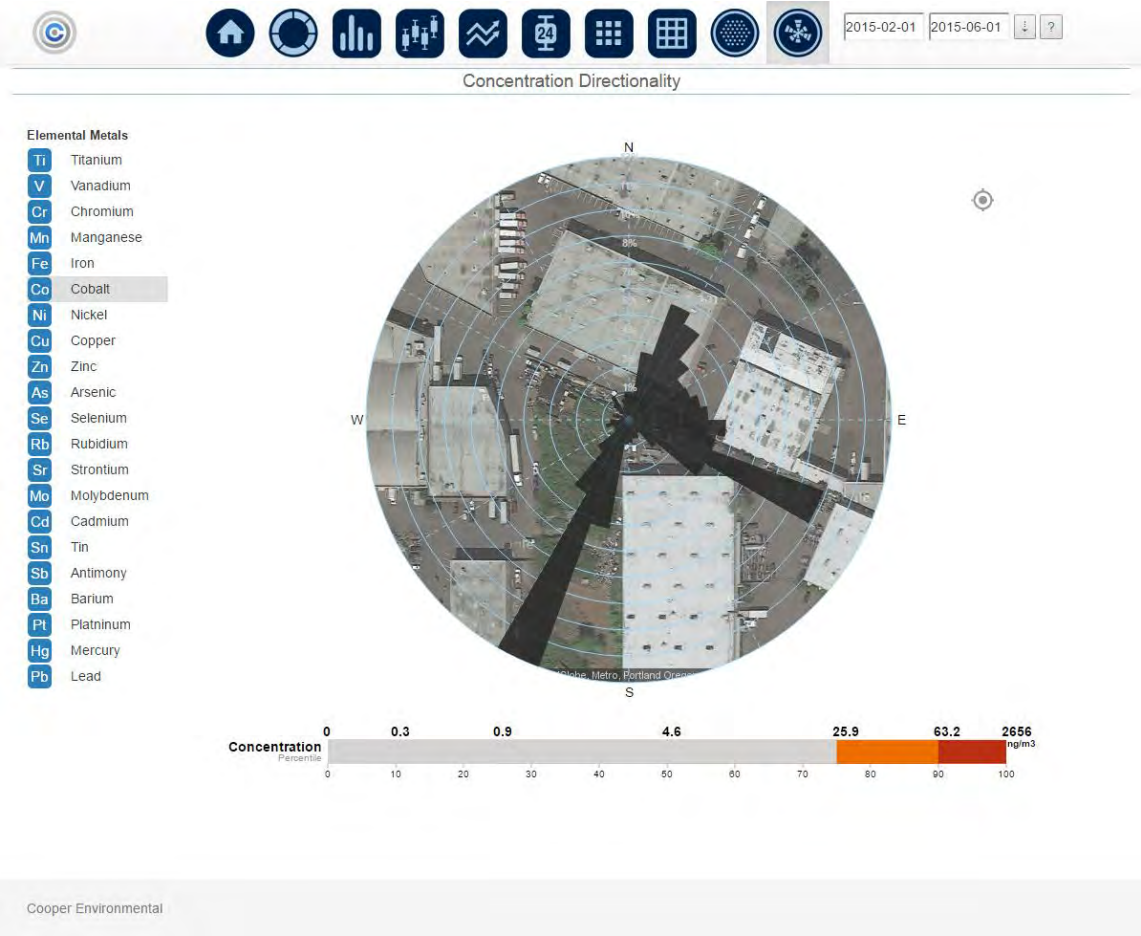
ADAPT Features
Concentration Directionality



- Identifies statistically most probable direction of emission source(s) for user-selected high concentration percentile ranges
- Enables differentiating local emission source directionality from direction of regional background
- Option to overlay graph on satellite map view

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Conclusions

- Xact 625 Provides highly accurate, highly time resolved metals concentration data
- Xact is comparable to reference methods of measuring metals
- Automated Quality Assurance procedures assure the user that the data is accurate and reliable during field use
- Data can be useful in source apportionment and identification

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Questions?

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