



Field Performance Evaluation of the Cooper Environmental Services Ambient Metals Monitor (Xact 620) for Near-Real Time PM₁₀ Metals Monitoring

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High Time Resolution Multi-Metals Measurements

Field sampling, laboratory analysis

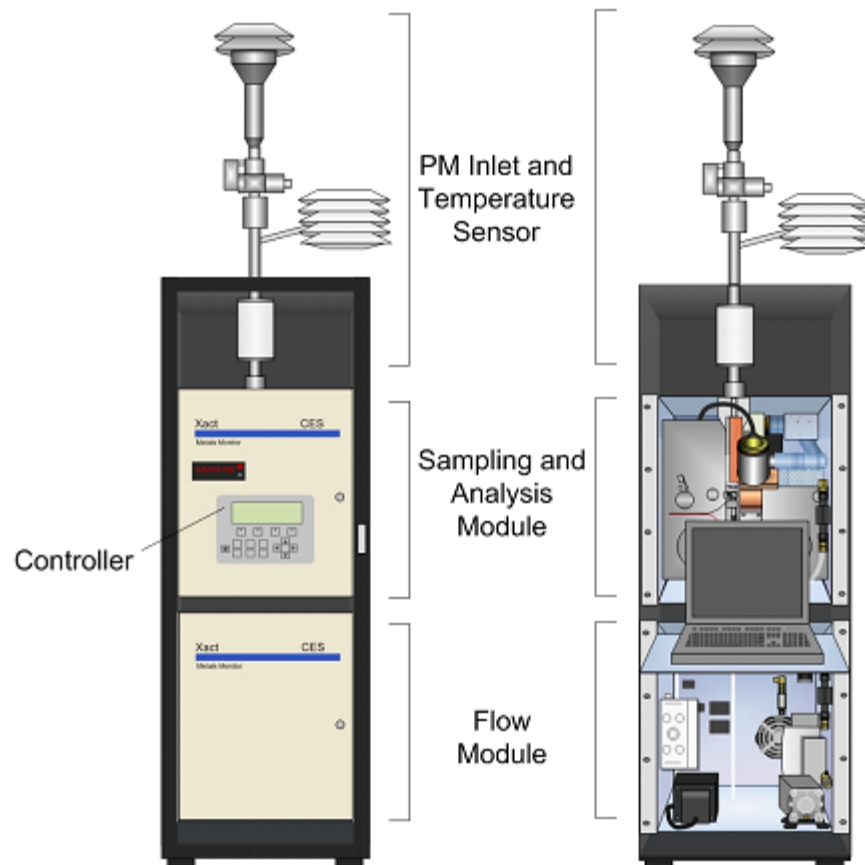
- Serial collection of filter samples
- Davis Rotating-drum Unit for Monitoring (DRUM)
- Semicontinuous Elements in Aerosol Sampler (SEAS)

Online, semi-continuous measurements

- Single particle mass spectrometry (e.g. TSI ATOFMS)
- Aerosol mass spectrometer (Aerodyne AMS)
 - no refractory elements
- Cooper Environmental Services field XRF analyzer



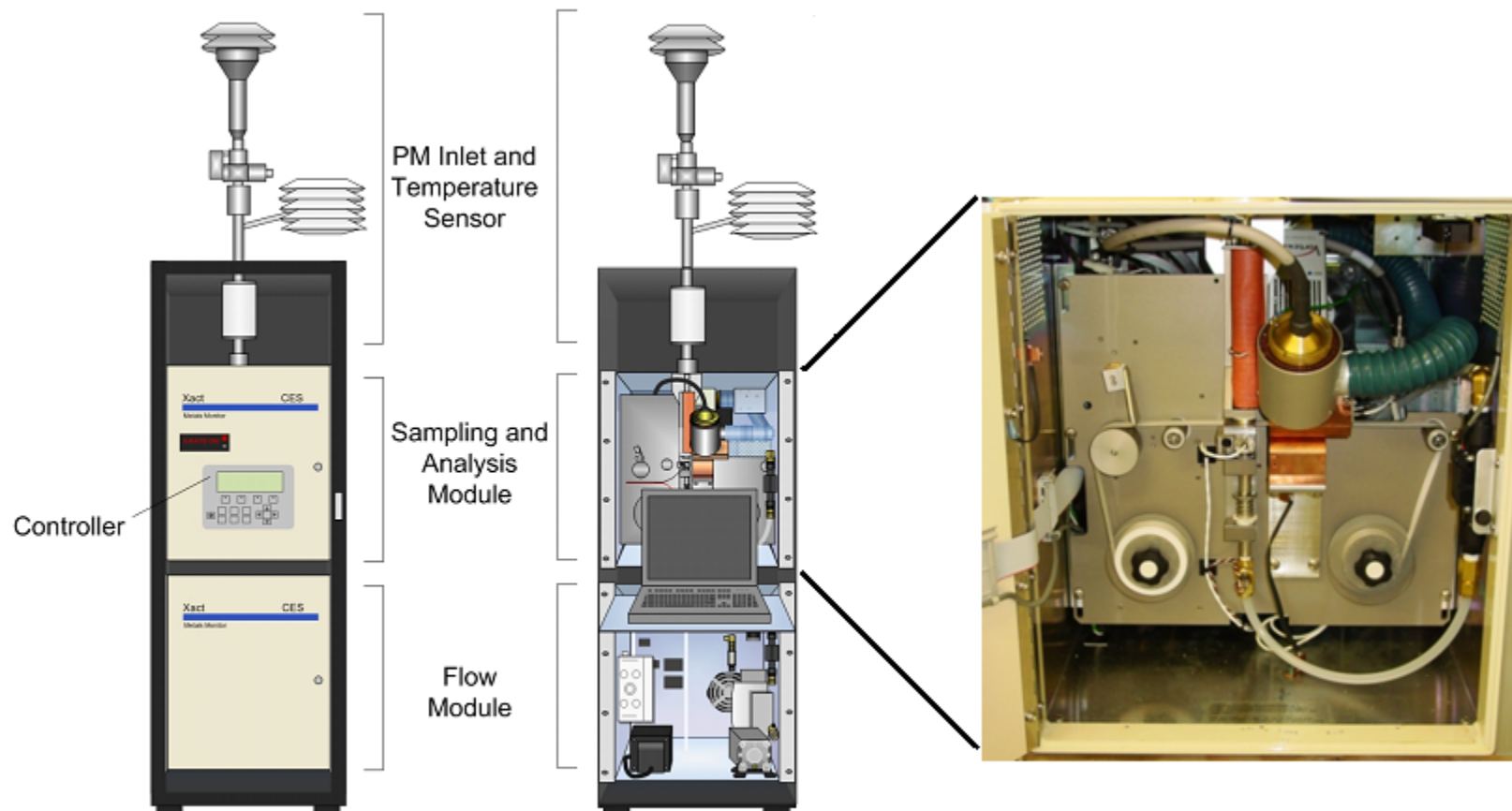
Cooper Environmental Services (CES) Xact 620



- Xact series
 - I: Stack Sampling
 - II: Fenceline Monitoring
 - III: **Ambient Monitoring**

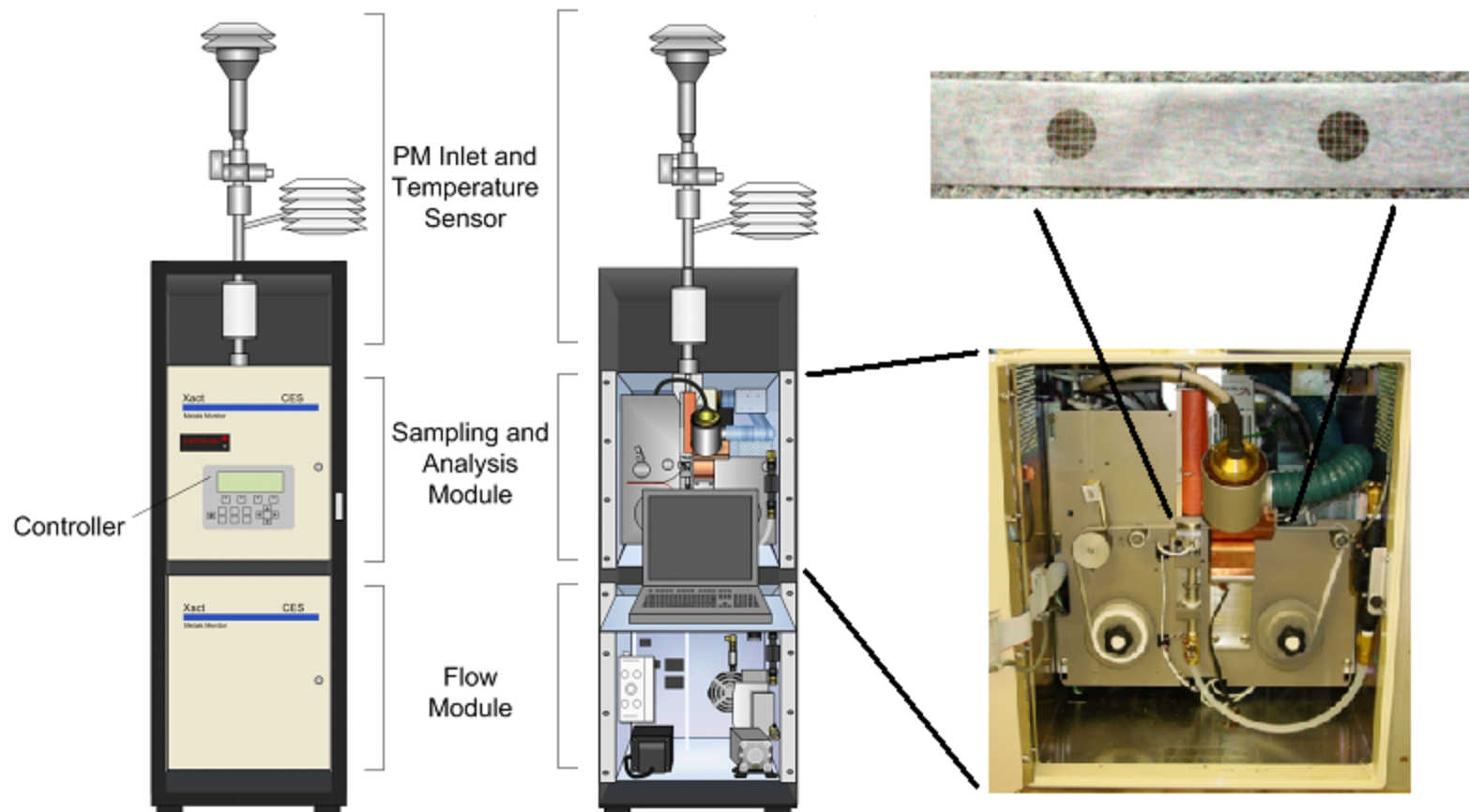


Cooper Environmental Services (CES) Xact 620





Cooper Environmental Services (CES) Xact 620



ELEMENTS THE XACT CAN MEASURE (IN BLUE)

1	1	2											13	14	15	16	17	18														
1	H 1.0079																		He 4.0026													
2	3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.18														
3	11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948														
4	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8														
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.9	54 Xe 131.29														
6	55 Cs 132.91	56 Ba 137.33	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.9)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	90 Th (261.1)	91 Pa (262.1)	92 U (263.1)	93 Np (262.1)	94 Pu (265.1)	95 Am (266.1)	96 Cm (268)	97 Bk (269)																					

Lanthanide Series	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.9)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide Series	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244.1)	95 Am (243.1)	96 Cm (247.1)	97 Bk (247.1)	98 Cf (251.1)	99 Es (252.1)	100 Fm (257.1)	101 Md (258.1)	102 No (259.1)	103 Lr (262.1)

○ measured by Xact in this study

○ EPA Air Toxics PM metals



Xact Performance Evaluation



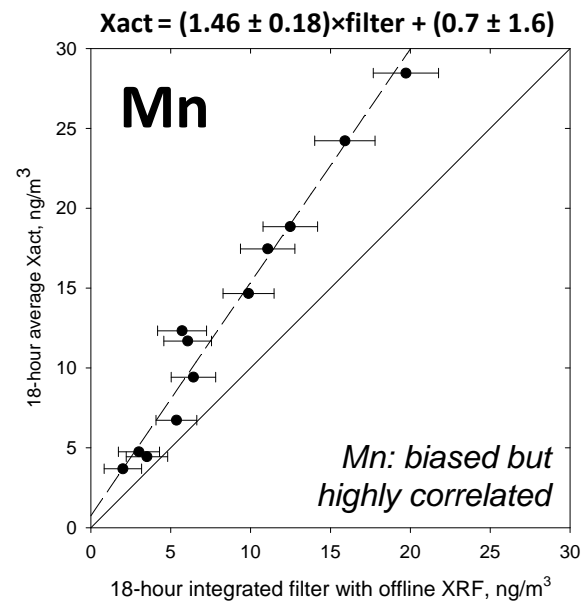
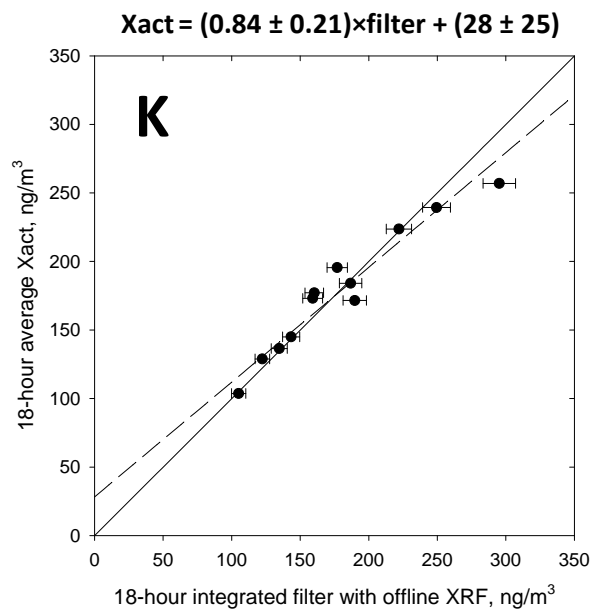
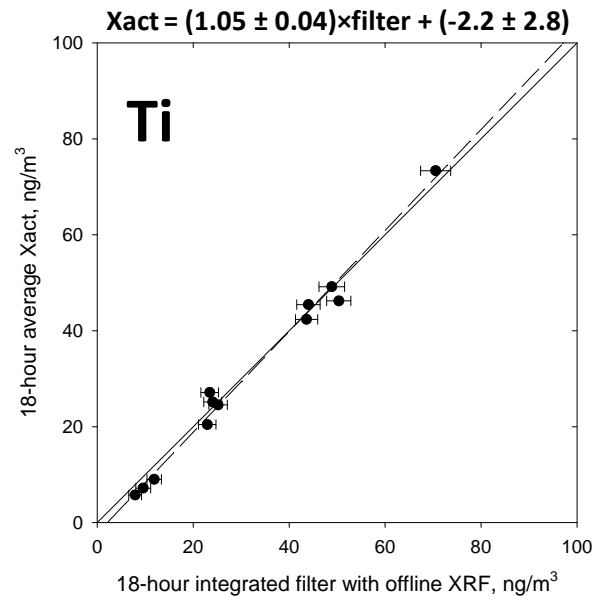
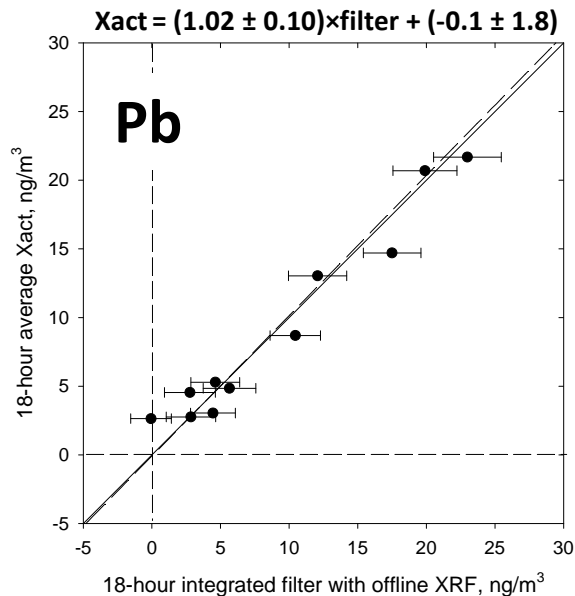
LowVol PM₁₀ (FRM) / Teflon filter
XRF: Ca, Fe, K, Mn, Pb, Ti...



HiVol PM₁₀ / quartz filter
NATTS digestion protocol
ICP-MS: As, Pb, Se...



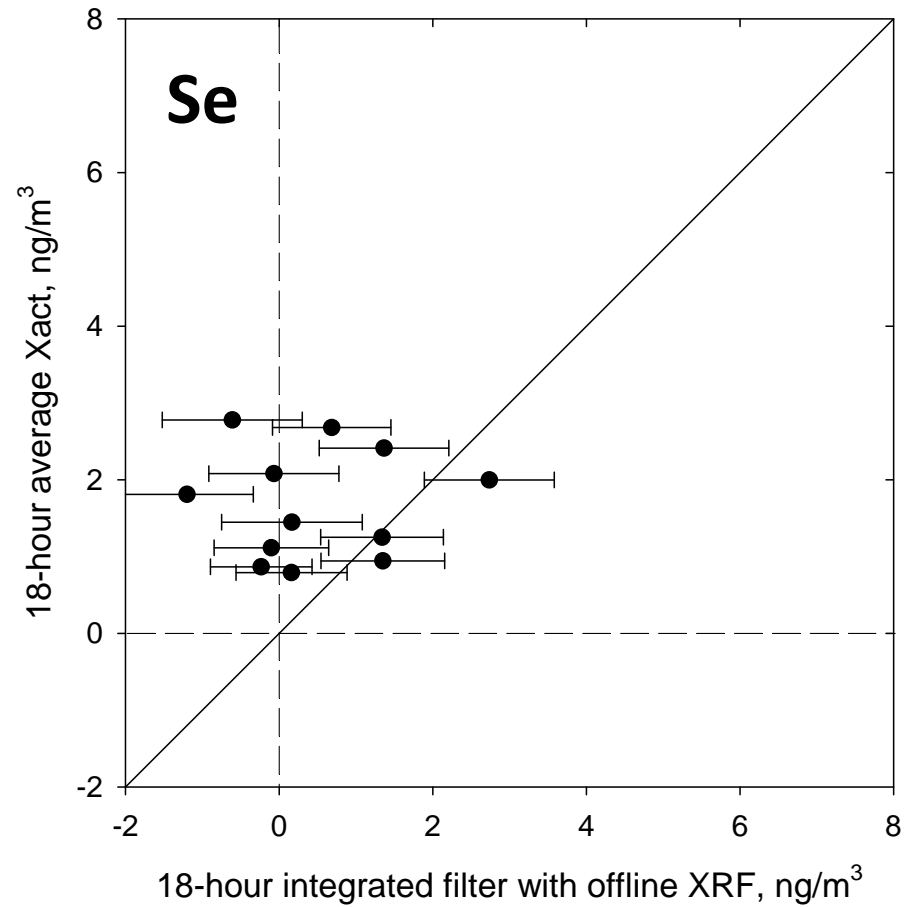
Xact vs. LowVol PM10 FRM / XRF





Xact vs. LowVol PM10 FRM / XRF

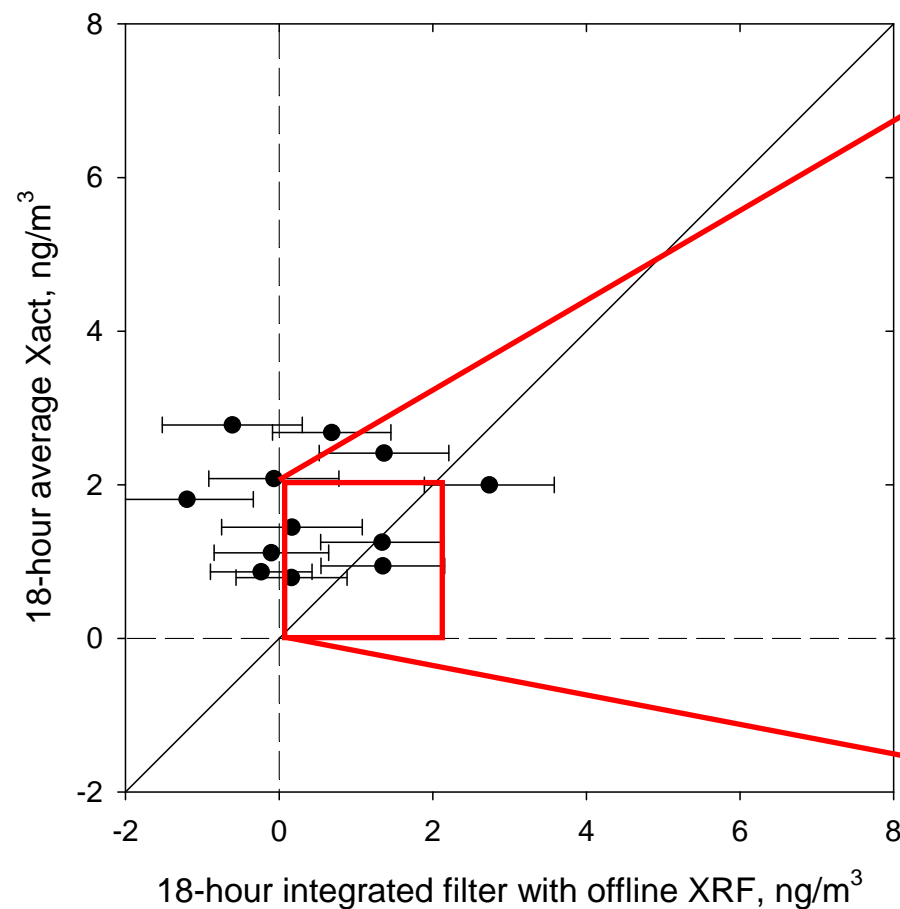
Xact vs. LowVol filter / lab XRF



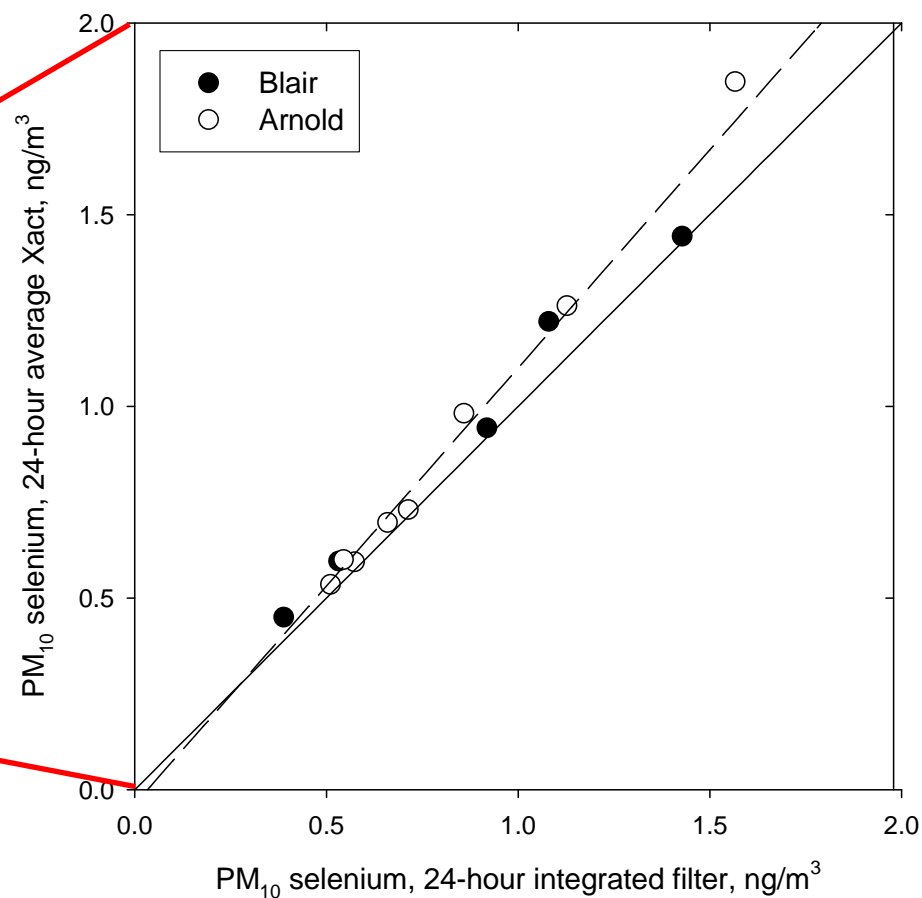


Selenium: Xact vs. Filter-Based Measurements

Xact vs. LowVol filter / lab XRF



Xact vs. HiVol filter / lab ICP-MS



Se: favorable comparison between Xact and PM₁₀ HiVol samples with analysis by ICP-MS



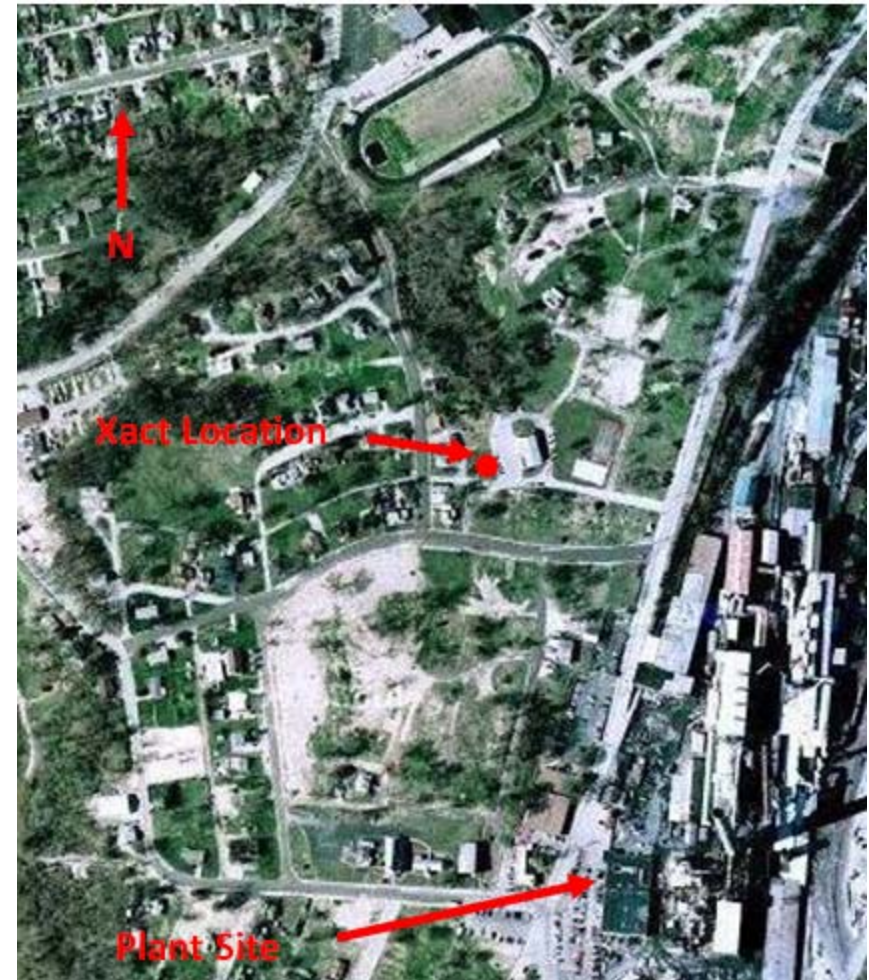
Collocated Study - Opportunities

- One month of collocated Xact data collected near the Doe Run primary lead smelter in Herculaneum, MO
- Examine collocated precision and practicable detection limits for various metals
- Uncertainties for source apportionment modeling (CMB, PMF)
- Missouri DNR instrument optimized for As, Hg, and Pb at remote areas



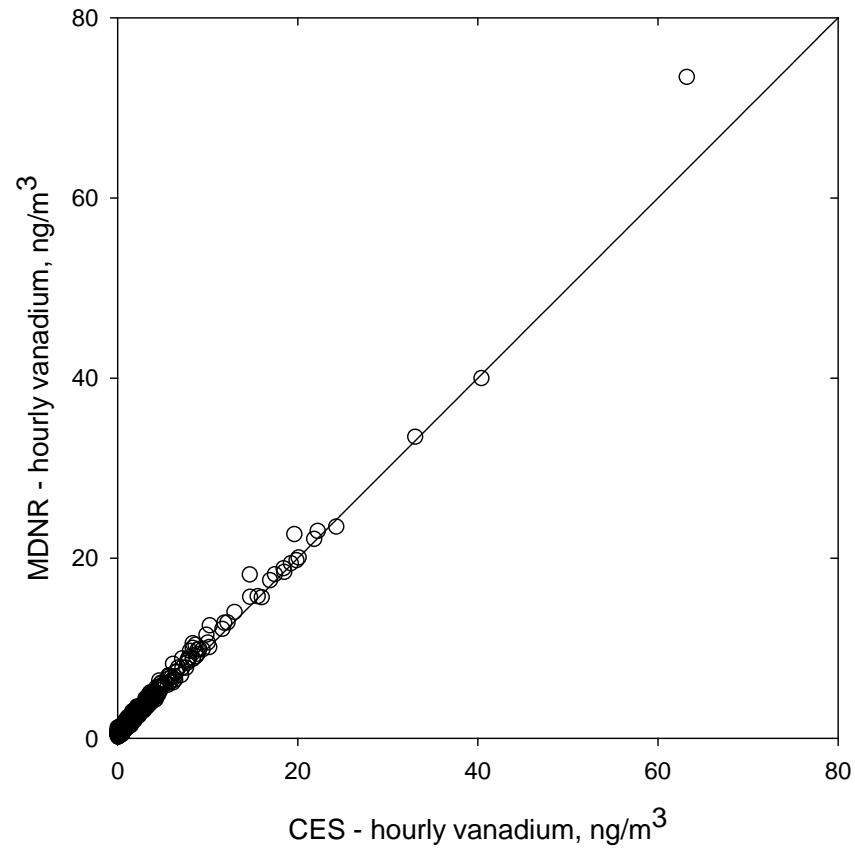
Collocated Study - Challenges

- High concentrations of lead and other elements observed
- Spectral interferences by lead and/or other elements in the plumes
- Removal of instrument-to-instrument bias for collocated precision



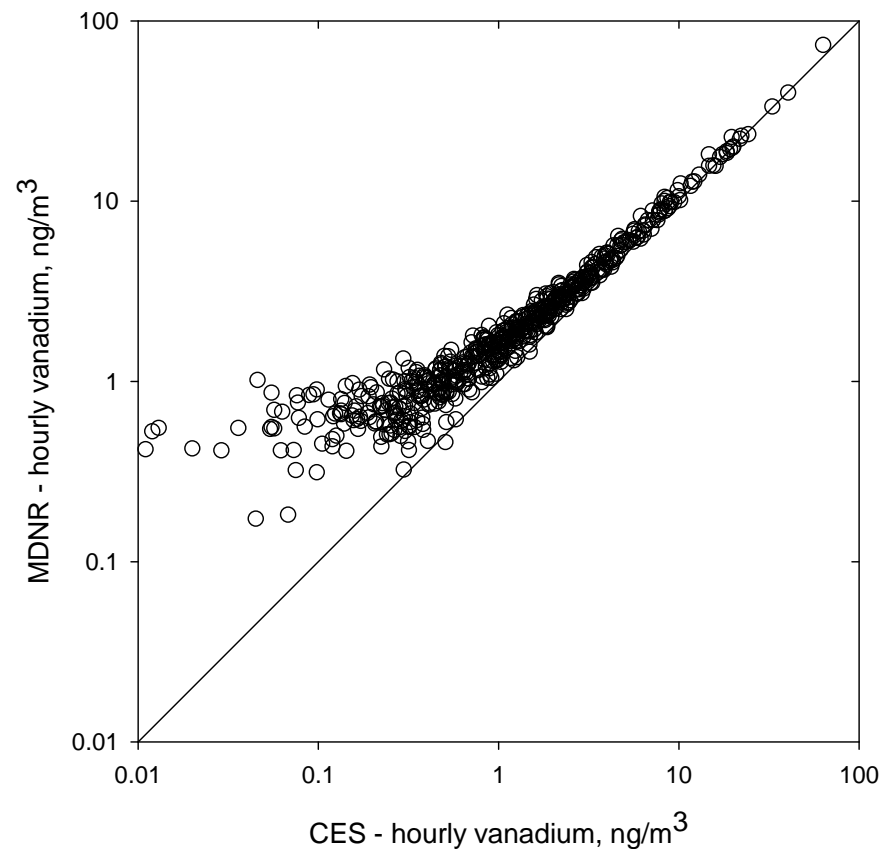
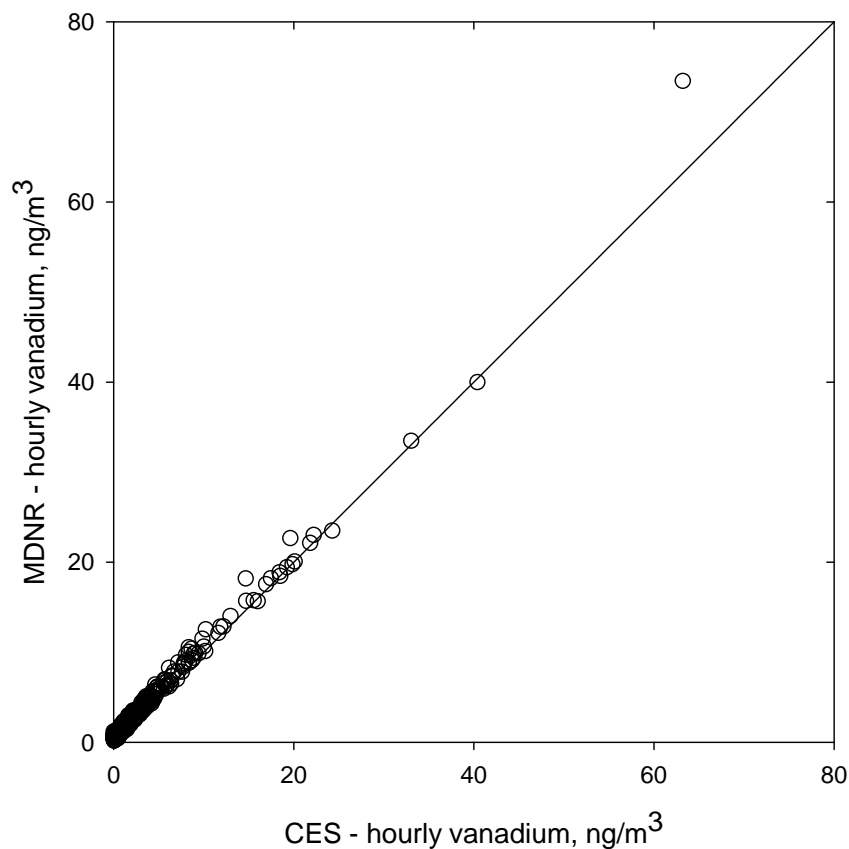


Collocated XACT – Vanadium (N=606)





Collocated XACT – Vanadium (N=606)

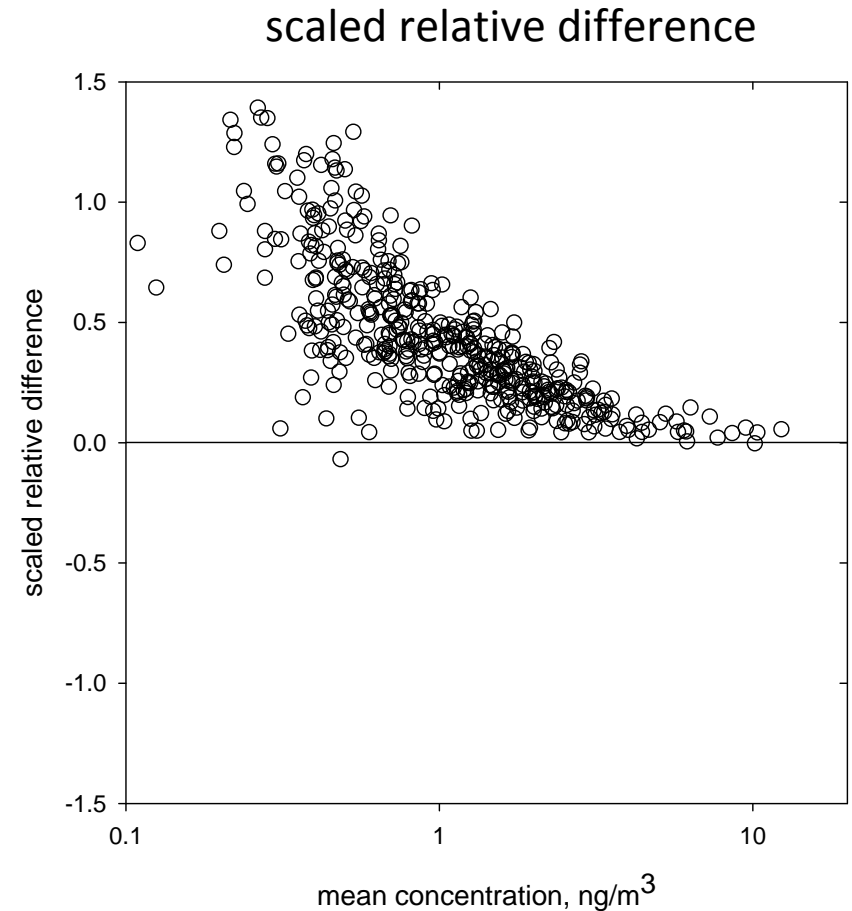
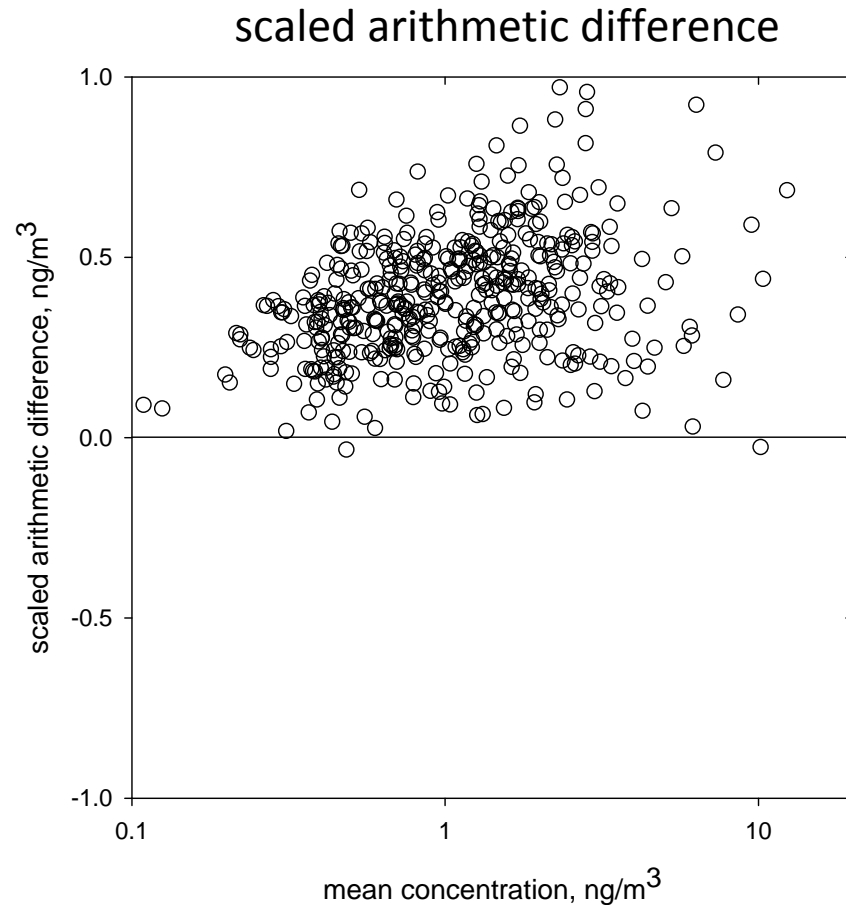


- Instrument-to-instrument Bias highlighted
- Similar trends seen for Cr, Mn, Ni and Ba



Collocated XACT – Vanadium

- Removed records with zero V concentration
- Removed records for top 25th percentile Pb

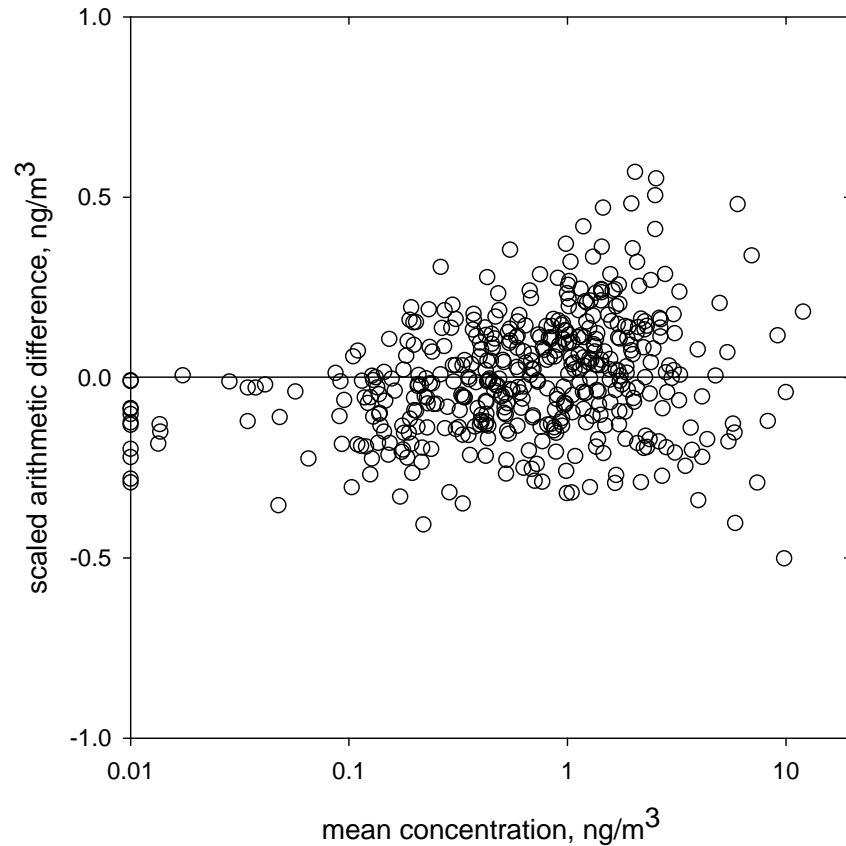


- Collocated precision = 0.42ng/m^3 (29%)

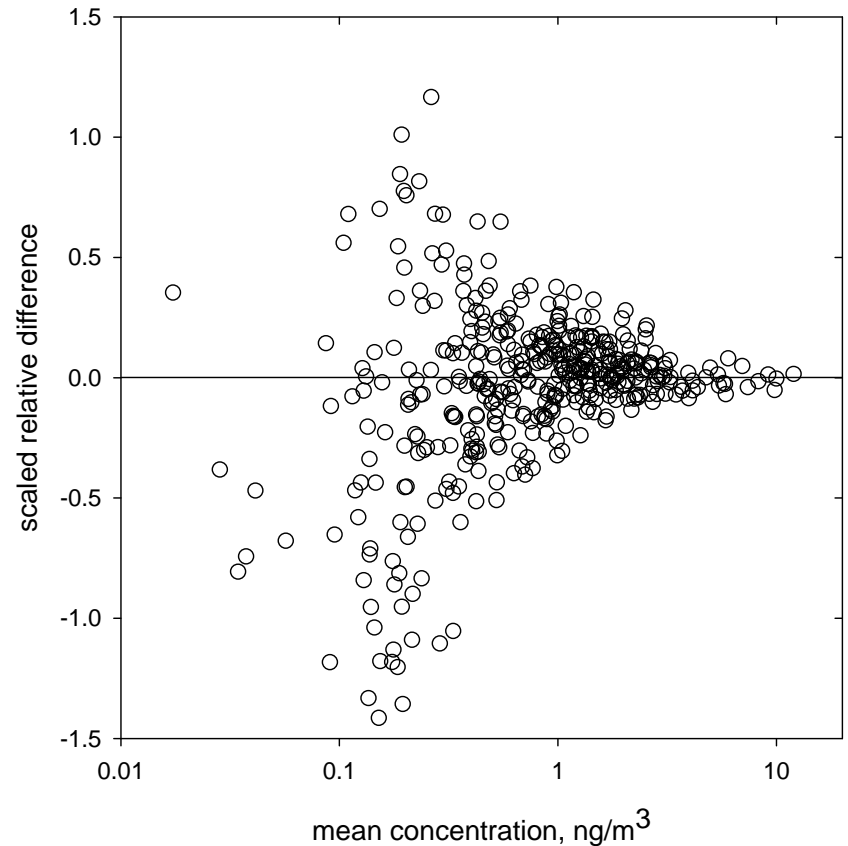


Collocated XACT – Vanadium

scaled arithmetic difference



scaled relative difference

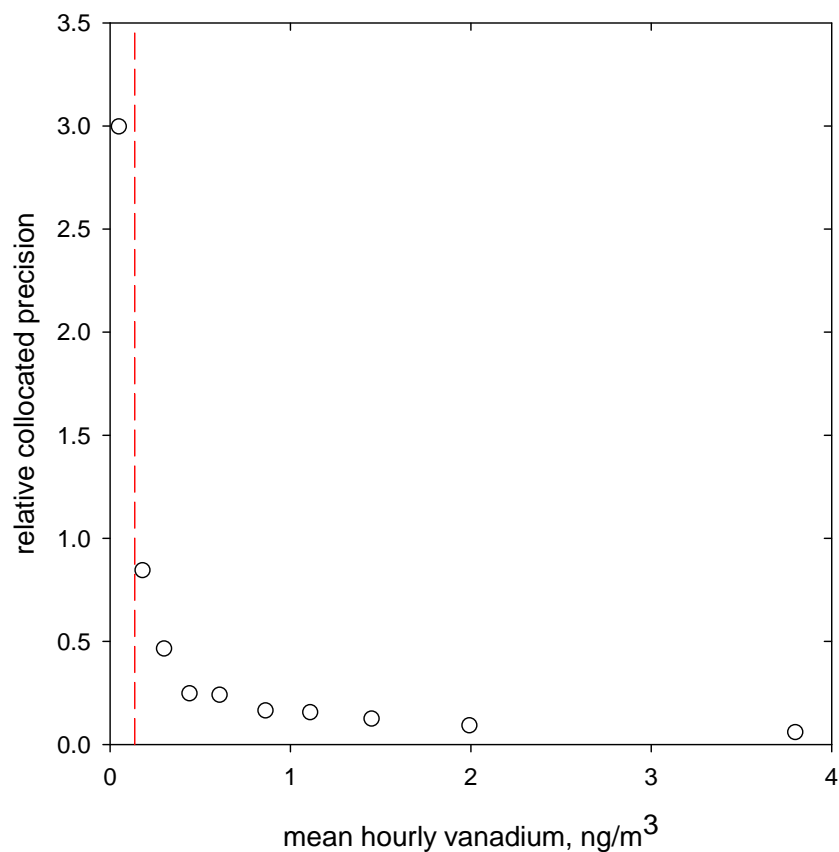


- Regression-adjusted MDNR data
- Collocated precision = 0.17 ng/m^3 (14%)

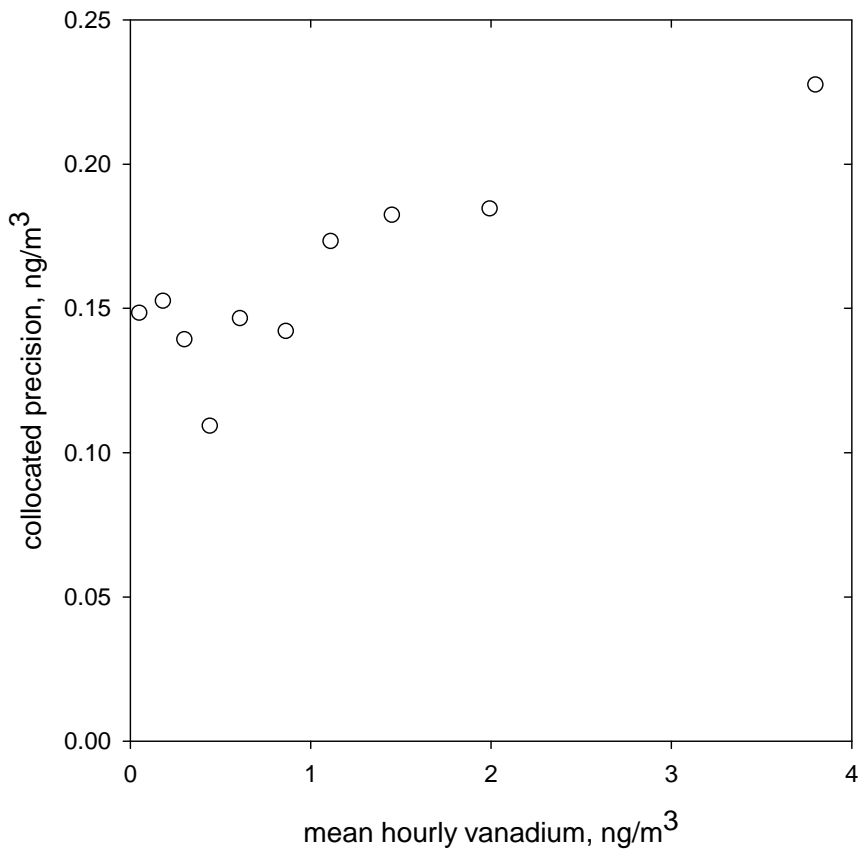


Collocated XACT – Vanadium

relative collo precision



absolute collo precision



- Binned collocated precision (33 records/bin)



Summary

- V, As, Ba, Cd, Cr, Mn, Ni, Se, Ti, Zn
 - Relative precision better than 10% at higher concentrations (exception Cd)
 - Practicable MDL greater than reported MDL
 - No data near MDL for As, Se, Ti, Zn
- Ca, Fe, K
 - Data range well over MDL
(e.g. 5th percentile $\text{Ca} > 300 \times \text{MDL}$)
 - Relative precision better than 10% over entire data range
- Co, Hg, Sn, Sb
 - Removal of high Pb, leaves no trend in lower concentration data

Next steps ...

- XRF analysis of additional lowvol filters
- ICP analysis of lowvol filters
- Examine spectral interference due to lead on other elements
- Analysis of covariance of error

Acknowledgements

- Missouri Department of Natural Resources
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 - Mike Jones
- U.S. EPA / Region VII
 - Gwen Yoshimura
- Washington University
 - Stephen Feinberg, Victoria Martin

Xact 620 Minimum Detection Limits (ng/m3)

Element	Atomic No.	4 hour	3 hour	2 hour	1 hour	30 min.	15 min.
Si	14	0.018	0.028	0.051	0.144	0.41	1.15
K	19	0.101	0.156	0.287	0.811	2.29	6.49
Ca	20	0.040	0.062	0.113	0.321	0.91	2.56
Ti	22	0.022	0.034	0.063	0.177	0.50	1.42
V	23	0.017	0.026	0.048	0.137	0.39	1.10
Cr	24	0.014	0.021	0.039	0.109	0.31	0.87
Mn	25	0.008	0.013	0.024	0.067	0.19	0.54
Fe	26	0.010	0.015	0.028	0.080	0.23	0.64
Co	27	0.006	0.009	0.017	0.047	0.13	0.37
Ni	28	0.004	0.007	0.013	0.035	0.10	0.28
Cu	29	0.008	0.012	0.023	0.064	0.18	0.51
Zn	30	0.005	0.008	0.015	0.043	0.12	0.35
Ga	31	0.003	0.005	0.008	0.024	0.07	0.19
As	33	0.003	0.005	0.010	0.027	0.08	0.22
Se	34	0.004	0.006	0.011	0.032	0.09	0.26
Pd	46	0.070	0.108	0.198	0.560	1.58	4.48
Ag	47	0.103	0.158	0.290	0.821	2.32	6.57
Cd	48	0.169	0.260	0.479	1.353	3.83	10.83
Sn	50	0.318	0.489	0.899	2.543	7.19	20.35
Sb	51	0.083	0.128	0.235	0.665	1.88	5.32
Ba	56	0.050	0.076	0.140	0.397	1.12	3.18
Pt	78	0.006	0.009	0.017	0.048	0.14	0.39
Au	79	0.006	0.009	0.017	0.048	0.14	0.38
Hg	80	0.005	0.008	0.015	0.043	0.12	0.35
Tl	81	0.006	0.009	0.016	0.046	0.13	0.37
Pb	82	0.007	0.010	0.019	0.053	0.15	0.43
Bi	83	0.007	0.011	0.019	0.055	0.16	0.44

^aBased on US EPA IO Method 3.3 one sigma interference free.

Optimizing Sampling Time Interval

