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Multi-Metals Continuous Water Analyzer Based on ED-XRF: Applications to Power Plant ELG Rule Compliance

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Cooper Environmental

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Presentation Outline

- Summary of Current State of Effluent Limitation Guidelines for Steam EGU
- Advantages of Real Time Monitoring
- Operation and Capabilities of Xact 920
- Laboratory Testing on Xact
- Field Testing monitoring Se in Bioreactor Effluent

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Effluent Limit Guideline (ELG) Rule Summary

- In November of 2019, EPA proposed changes to 2015 Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Sources
- These proposed changes affected the rules for two types of power plant waste streams
  - Flue Gas Desulfurization (FGD) Wastewater
  - Bottom Ash (BA) Transport Water
- For FGD wastewater the rule creates essentially five subcategories of sources – each with its own limits
  - Normal or typical FGD treatment
  - High flow FGD facilities
  - Low utilization boilers
  - Boilers retiring by 2028
  - Voluntary incentives program (VIP)

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ELG Rule Summary – Limits for Each Category

Subcategory	Pollutant	Long-Term Ave	Daily Max	Monthly Ave
Typical Facilities	Arsenic (µg/L) (ppb)	5.1	18	9
	Mercury (ng/L) (ppt)	13.5	85	31
	Nitrate/Nitrite as N (mg/L) (ppm)	2.6	4.6	3.2
	Selenium (µg/L) (ppb)	16.6	76	31
Voluntary Incentives Program for FGD Wastewater	Arsenic (µg/L) (ppb)	5.0	5	-
	Mercury (ng/L) (ppt)	5.1	21	9
	Nitrate/Nitrite as N (mg/L) (ppm)	0.4	1.1	0.6
	Selenium (µg/L) (ppb)	5.0	21	11
	Bromide (mg/L) (ppm)	0.16	0.6	0.3
	TDS (mg/L) (ppm)	88	351	156
Low Utilization and High Flow	Arsenic (µg/L) (ppb)	5.98	11	8
	Mercury (ng/L) (ppt)	159	788	356

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ELG Rule Summary

- Currently compliance would be required as “as soon as possible” once the rule is promulgated
- Most plants will need to use bioreactor technology to achieve Se limits
- Daily measurements of Se, As and Hg are required
- Plants not removed from service or in the Voluntary Incentives Program (VIP) must meet the limits by December 2025
- VIP plants must meet by December 2028

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Why Measure Pollutants in Real Time

- Disadvantages of Manual Measurements
  - Slow – results from commercial labs take days or even weeks
  - Expensive – on per sample basis results are expensive especially for quick turns
  - Can't get immediate feedback to know if adjustments to control strategies are working
  - Don't know until you may have exceeded a daily or monthly limit until its too late to do anything about it

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Why Measure Pollutants in Real Time

- Advantages of Real Time Analysis results
  - Can determine if an ELG limit exceedance will take place before it does
  - Allows plant operators to adjust controls to prevent an ELG limit exceedance
  - Allows for immediate feedback so that operators can fine tune controls to make them operate more efficiently – saving the power plant money
  - Minimize human error in the analysis process
  - Could do inlet and outlet measurements from bioreactor to determine treatment efficiency

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Xact 920 Continuous Metals In Water Analyzer

- Xact 920 can measure up to 65 elements simultaneously including **Se**, **As**, and **Br**
- Water is spray dried and sampled onto filter tape
- The resulting filter tape deposit is analyzed by X-ray Fluorescence (XRF)
- Builds on two technologies developed and commercialized by Cooper Environmental
  - Ambient Air XRF Analyzer (over 150 in field)
  - Quantitative Aerosol Generator (developed for calibration of PM CEMS for the power industry with EPRI Support)

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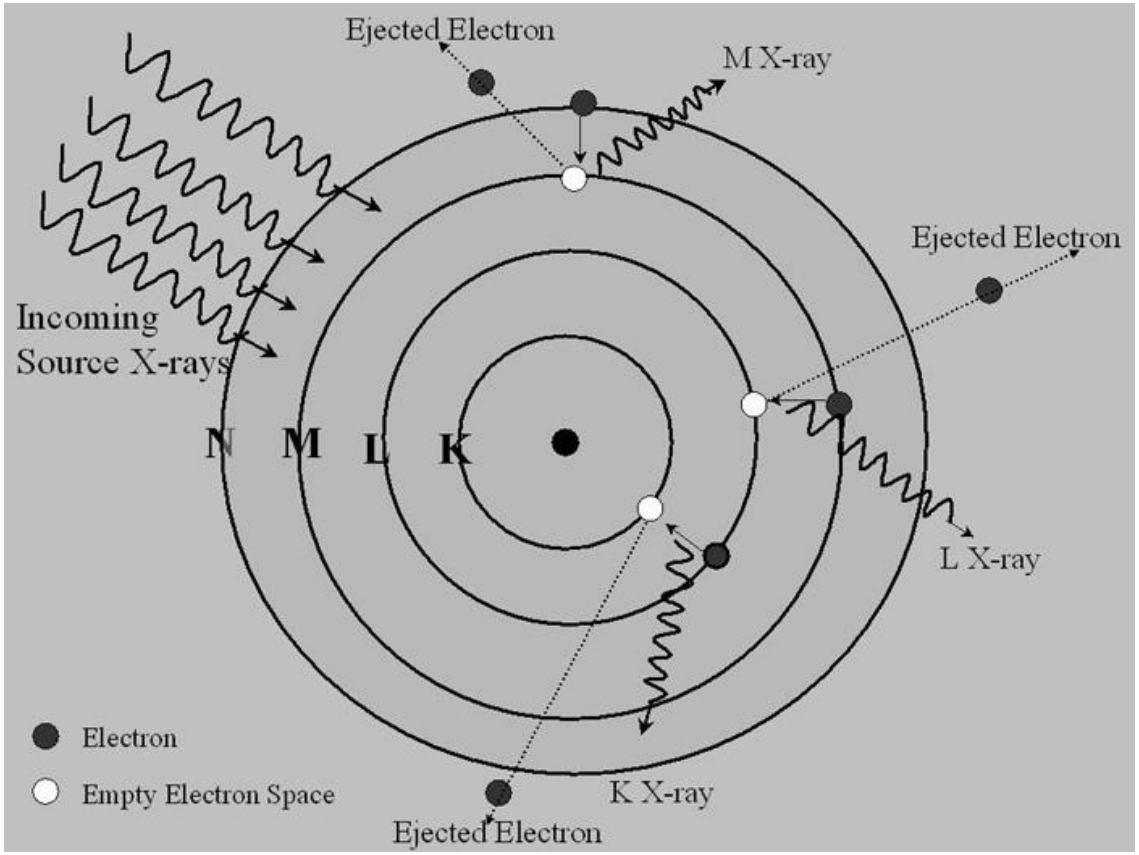
XRF Theory



- Incoming X-rays eject an inner shell electron
- Electrons from higher shells fill the vacancy
- This process releases energy in the form of fluorescing X-rays
- Energy is characteristic of each element
- Intensity or brightness is related to the mass of each element

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Strengths of XRF

- XRF utilizes inner shell electron transitions so the response is not dependent on what is chemically bound to the element
- Can measure a wide range of elements simultaneously
- XRF is non-destructive – so samples can be reanalyzed later
- XRF is very stable – calibrations can last for years
- XRF response is linear over a wide concentration range (over 5 orders of magnitude) – this means no additional standards required depending on concentration range

Measurable Elements

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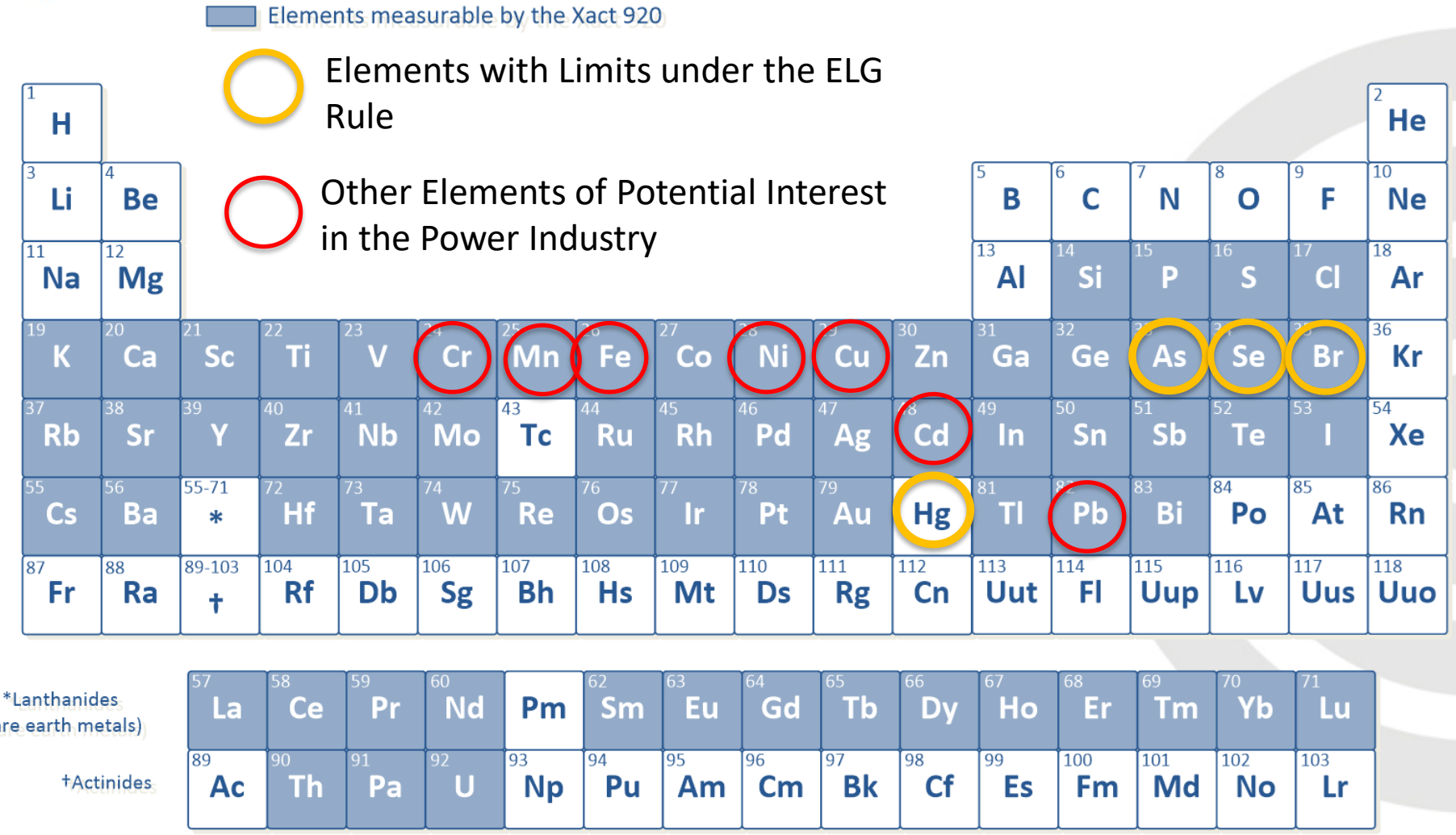

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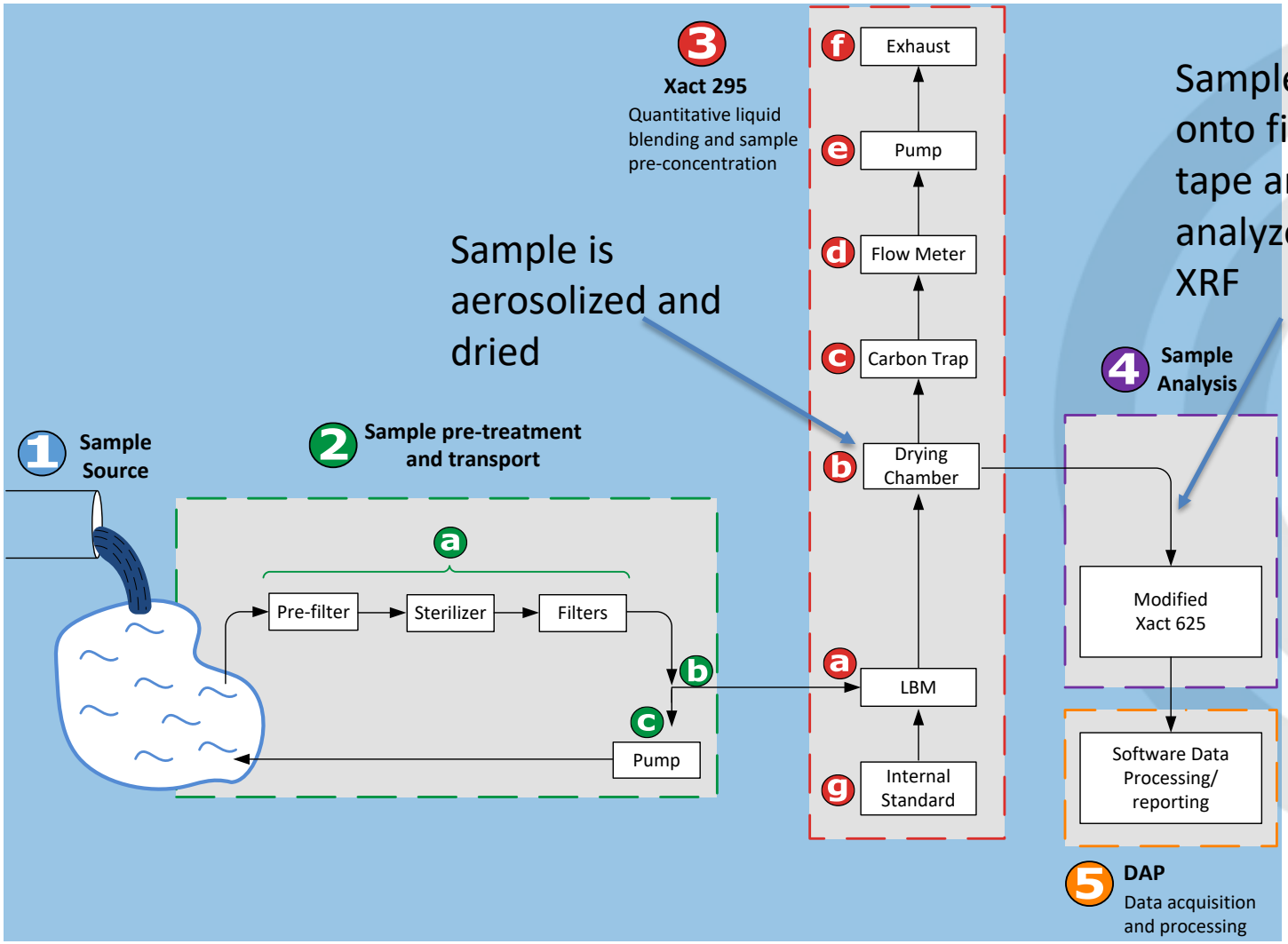
General Operation Schematic - Xact 920



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Instrument Systems

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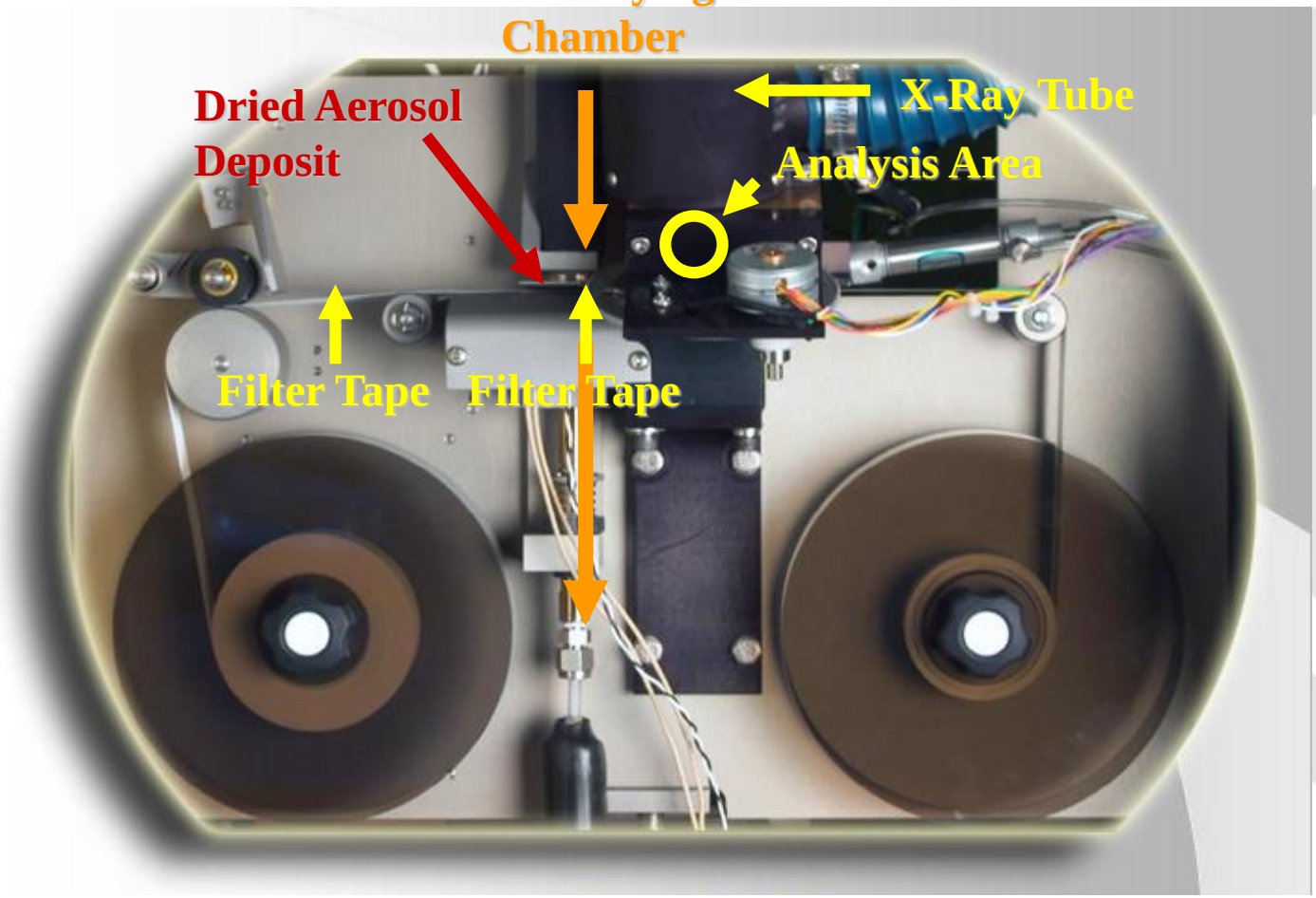
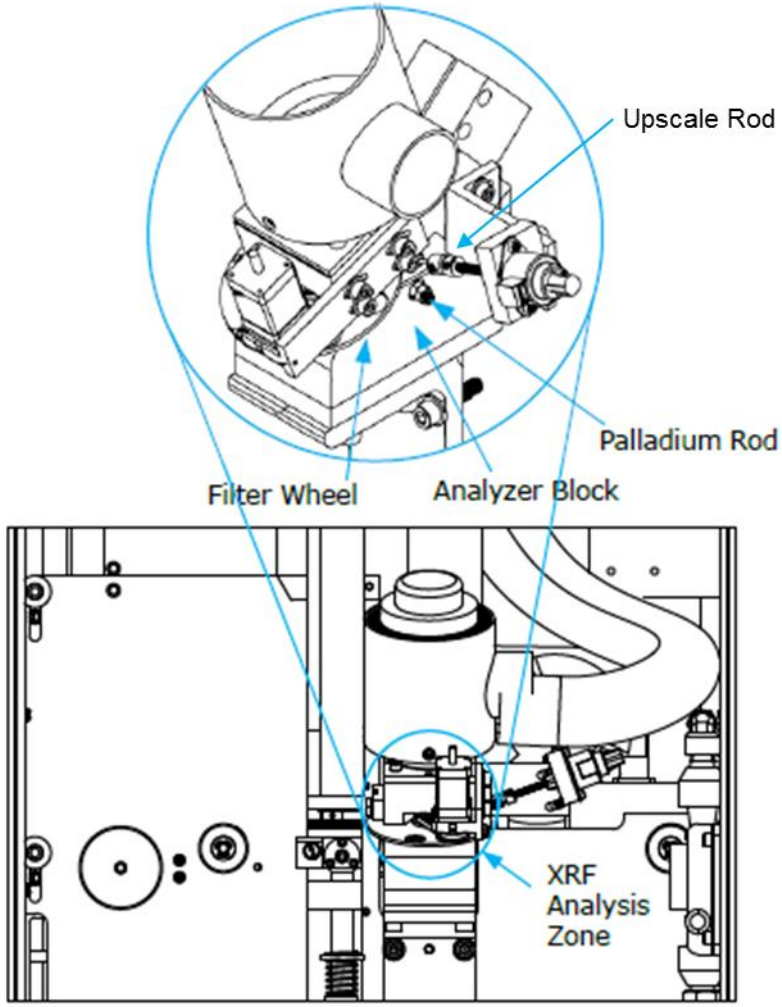
XRF Sampling and Analysis



Xact 920 – Quality Assurance

- XRF Portion Calibrated with Traceable to NIST Thin Film Standards
- Automatic XRF spectrometer stability check with every sample
- Daily upscale check of XRF
- Stability – XRF calibration frequency about once/year – sometimes years between calibrations



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Laboratory Testing

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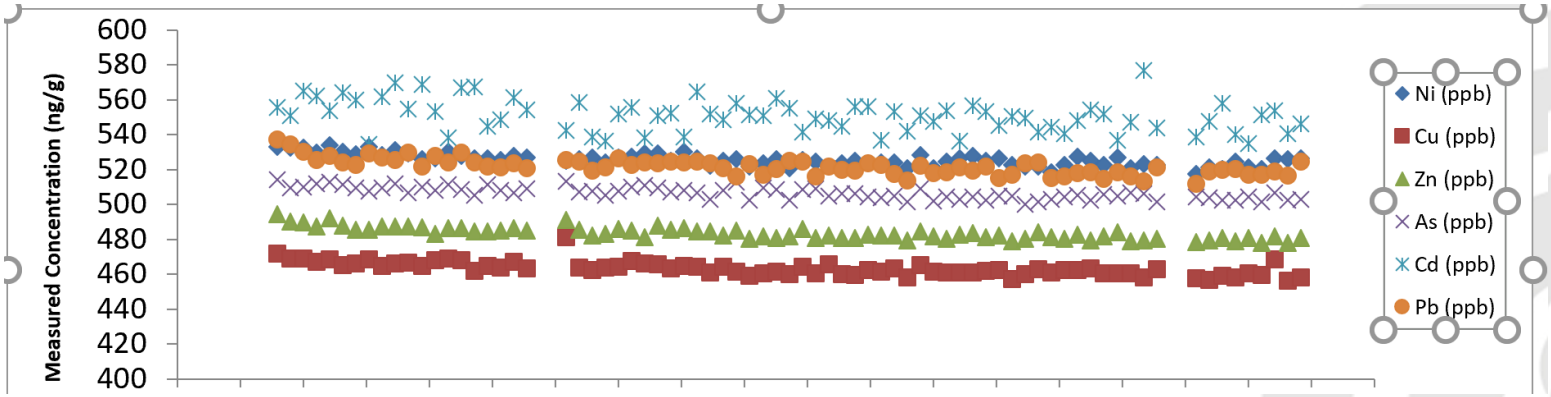
Laboratory Results – Low Concentration Drift



Metal	Zero Drift	Average Measured Value (ng/g)	Standard Deviation (ng/g)	N	% RSD	Actual Value (ng/g)	RPE
Ni	0.3%	525.6	3.6	75	0.7%	501.8	-5%
Cu	-0.5%	463.3	4.0		0.9%	508.1	9%
Zn	-0.2%	483.4	3.5		0.7%	501.8	4%
As	0.1%	506.5	3.4		0.7%	505.7	0%
Cd	0.8%	550.7	9.3		1.7%	497.7	-11%
Pb	0.3%	521.7	4.7		0.9%	509.4	-2%

- Xact 920 shows excellent stability over the course of the two day test
- The relative standard deviation for most elements was less than 1%

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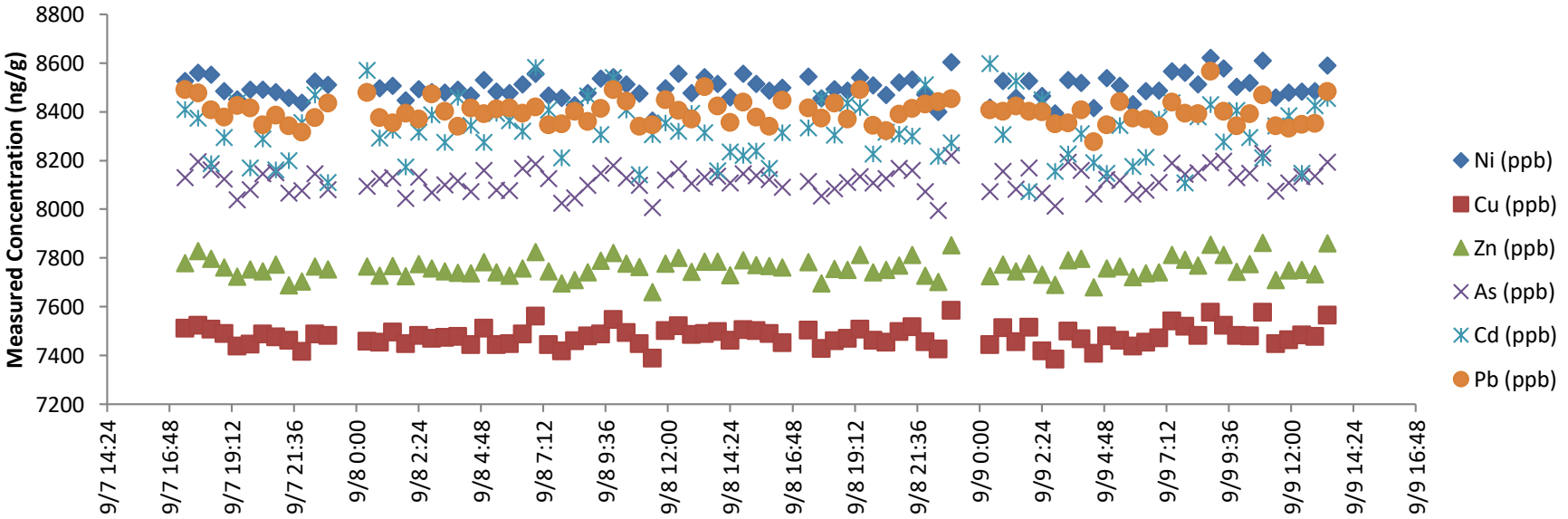
Laboratory Results – Span Drift



30 MINUTE MODE

Metal	Span Drift	Average Measured Value (ng/g)	Standard Deviation (ng/g)	N	% RSD	Actual Value (ng/g)	RPE
Ni	-1.7%	8498.5	47.6	84	0.6%	7930	-7.2%
Cu	-1.9%	7479.4	39.7		0.5%	7994	6.4%
Zn	1.4%	7760.4	40.7		0.5%	7894	1.7%
As	-1.5%	8117.8	48.8		0.6%	7957	-2.0%
Cd	-2.6%	8320.3	117.9		1.4%	7831	-6.3%
Pb	1.4%	8397.9	50.7		0.6%	8015	-4.8%

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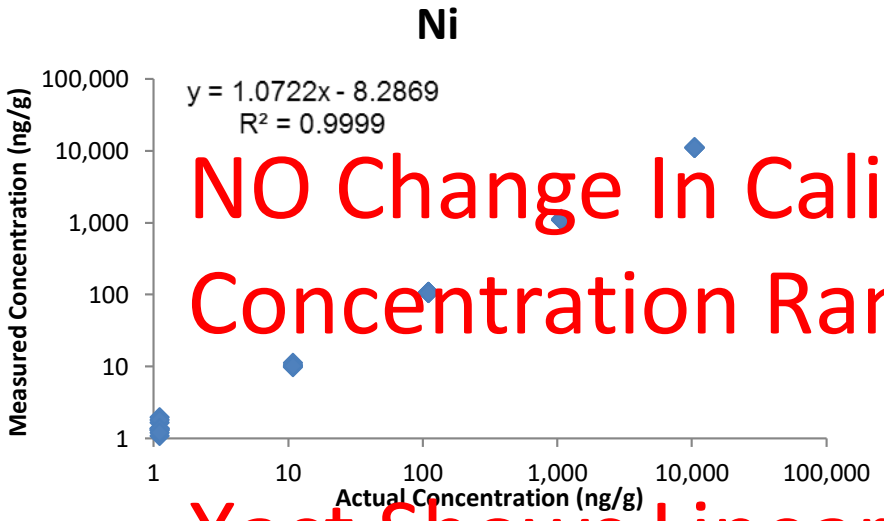
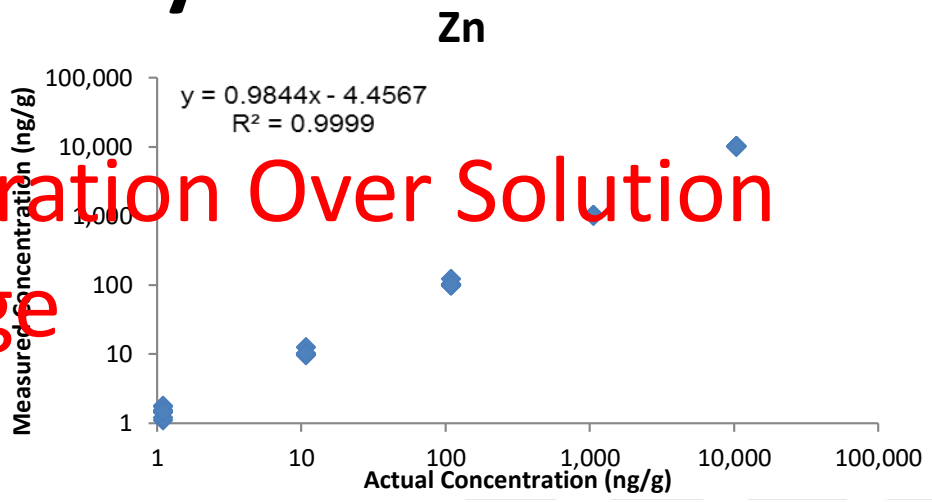
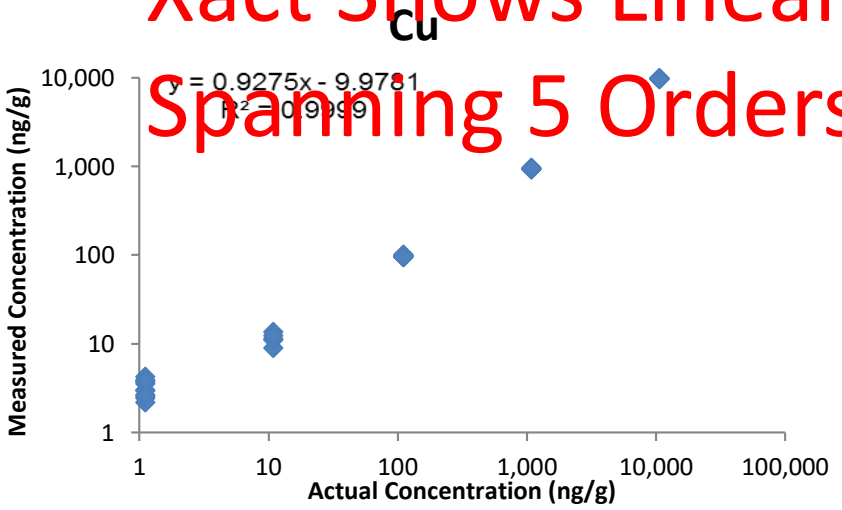
Laboratory Results – Linearity

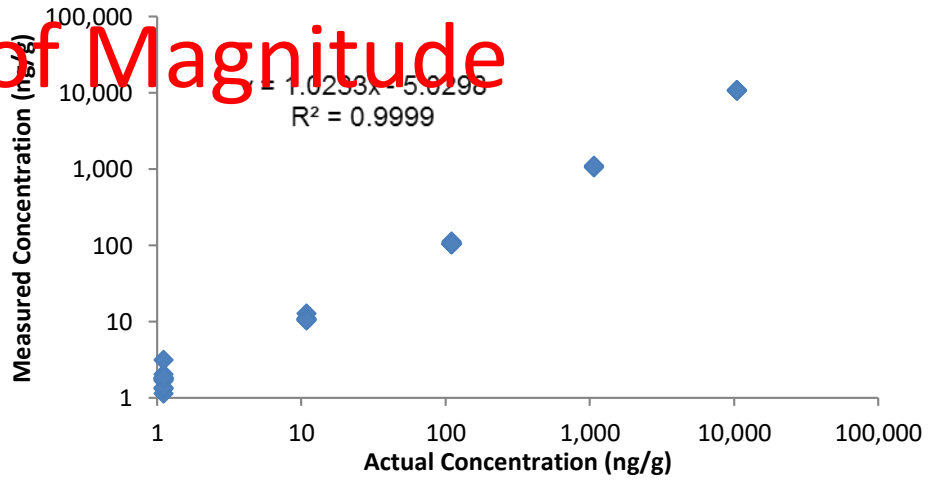




NO Change In Calibration Over Solution Concentration Range

Xact Shows Linearity Over a Range Spanning 5 Orders of Magnitude





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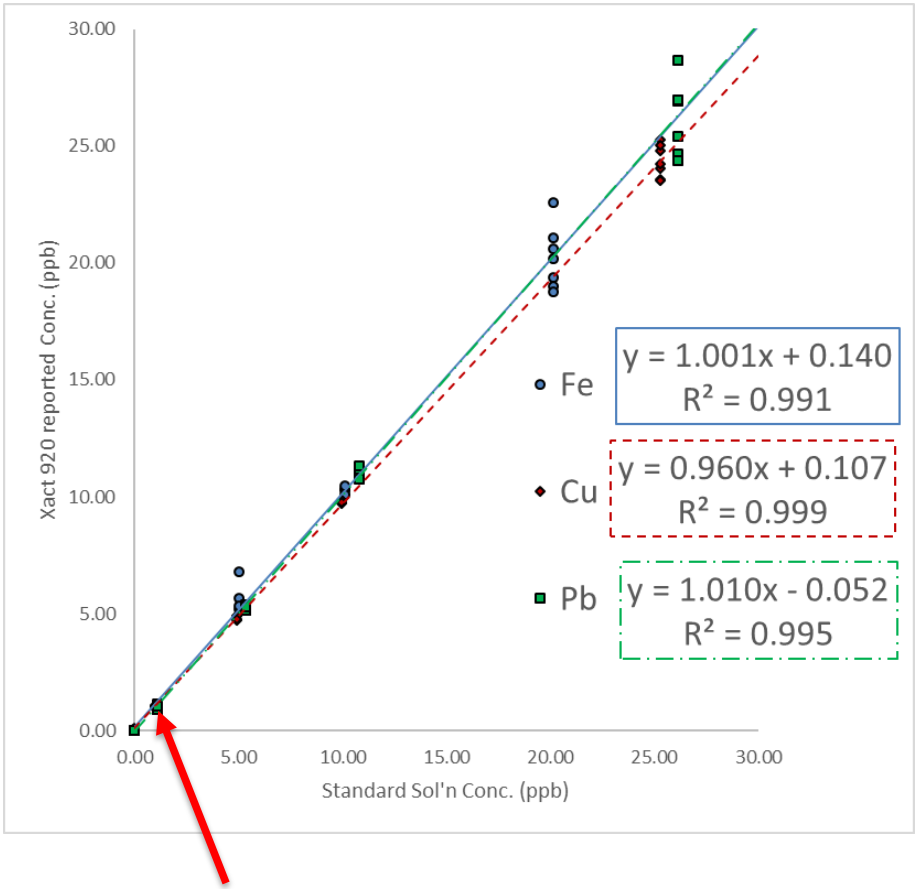
Low Concentration Level Accuracy Testing



- Testing done as a factory acceptance test for Nuclear Power Plant Application
- Compared the Xact 920 response to a known solution concentration at very low concentration levels
- The slope of the best fit line is very nearly 1.0 indicating good agreement between the Xact reported concentration and the known solution concentration

Demonstrated Measurement Accuracy down to 1 ppb

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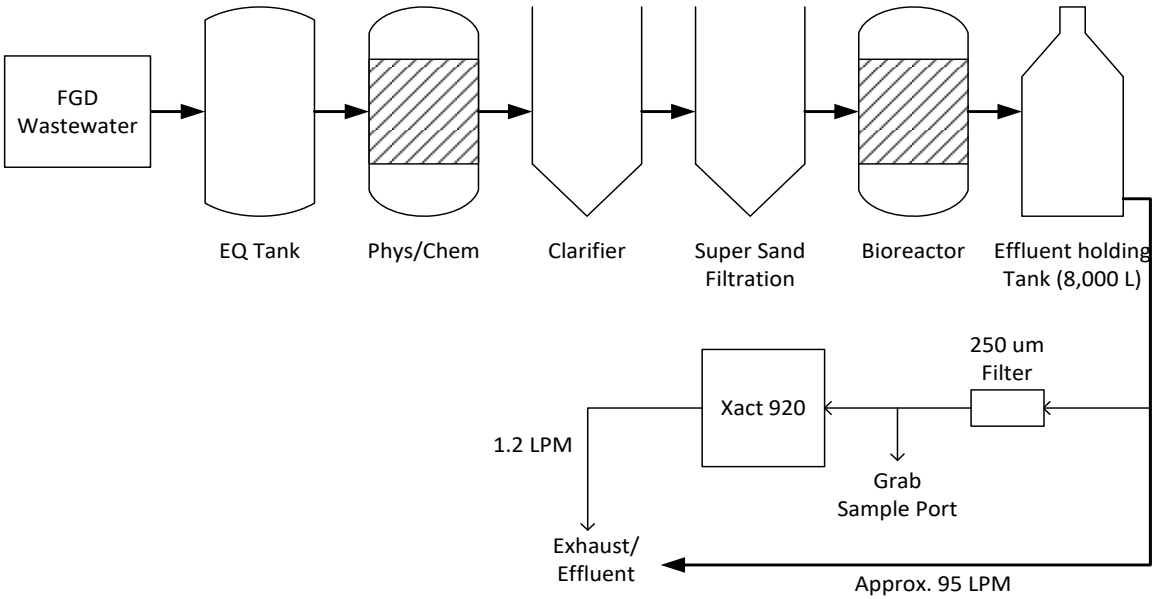
Field Testing

Xact 920 Field Evaluation

- Xact 920 sampling bioreactor effluent at a large (multi boiler) power plant
- Instrument installed January 6, 2020 – operational within 4 hours
- Sampling from bioreactor effluent holding tank



Plant FGD Wastewater Control Process Schematic

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Xact 920 Field Evaluation Study

- Xact operated continuously from January 9th to March 13th
- This presentation includes data from January 9 to March 13th
- Uptime of 97.5% in the data time frame
- Bioreactor operation started approximately 2/19/2020
- Xact results compared to laboratory (Brooks Lab, Bothell Washington)
- Two different types of samples
  - Analysis of the same grab sample – Xact analyzes the same sample as shipped to lab
  - A grab sample acquired while the Xact was operating continuously
- Three grab sample campaigns
  - 1/7/2020 to 1/9/2020
  - 1/24/2020 to 1/25/2020
  - 2/20/2020 to 2/24/2020

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Lab Comparison Results

Xact 920 - Percent Error Comparison between Xact and ICP-MS								
Identification		Grab ID and Sample Prep			Xact 920		Lab Data	Comparison
Lab Analysis Group	Lab ID	Date	Time	Location	N	Avg Se Conc. (ppb)	Se Conc. (ppb)	Xact % Error
A	010720a	1/7/20	13:00	Clarifier Overflow	6	26.99	31.18	-13.4%
	010920b	1/9/20	9:30	Clarifier Overflow	66	21.60	22.5	-4.0%
	010920c	1/9/20	9:30	Clarifier Overflow	8	126.0	119	5.9%
	010920d	1/9/20	9:30	Clarifier Overflow	5	106.0	127	-16.5%
	010920e	1/9/20	14:00	SeHAWK BioEff 2A	5	61.53	59.3	3.8%
	011020a	1/9/20	14:00	SeHAWK BioEff 2A	6	79.28	80.3	-1.3%
	010920f	1/9/20	14:00	SeHAWK BioEff 2B	5	65.32	73.4	-11.0%
B	012720c	1/24/20	10:38	SeHAWK BioEff Tank	1	46.04	51.2	-10.1%
	012620a	1/24/20	12:25	SeHAWK BioEff Tank	7	52.94	48.9	8.3%
	012620b	1/24/20	12:25	SeHAWK BioEff Tank	7	152.2	153	-0.5%
	012520a	1/24/20	16:25	SeHAWK BioEff Tank	7	51.84	46.5	11.5%
	012520b	1/24/20	16:25	SeHAWK BioEff Tank	6	141.9	127	11.8%
	012720b	1/24/20	17:25	SeHAWK BioEff Tank	1	48.74	51.1	-4.6%
	012720a	1/25/20	15:05	SeHAWK BioEff Tank	18	99.47	101	-1.5%
C	200124.1600	1/24/20	16:00	Clarifier Overflow	22	95.29	97.7	-2.5%
	200220.1235	2/20/20	12:35	SeHAWK BioEff Tank	1	128.2	129	-0.6%
	200220.1505	2/20/20	15:05	SeHAWK BioEff Tank	1	129.2	129	0.2%
	200221.0805	2/21/20	8:05	SeHAWK BioEff Tank	1	107.8	107	0.8%
	200221.1240	2/21/20	12:40	SeHAWK BioEff Tank	1	107.0	107	0.0%
	200221.1605	2/21/20	16:05	SeHAWK BioEff Tank	1	79.25	78.4	1.1%
	200222.1905	2/22/20	19:05	SeHAWK BioEff Tank	1	76.07	80.7	-5.7%
	200223.1230	2/23/20	12:30	SeHAWK BioEff Tank	1	52.01	53.2	-2.2%
	200224.1005	2/24/20	10:05	SeHAWK BioEff Tank	1	44.25	44.3	-0.1%
Total Number of Lab Comparison Samples								**23**
Total Average Percent Difference with the Lab								**-1.3%**
Standard Deviation of Percent Difference								**7.1%**

- Tested concentrations range from about 20 ppb to about 150 ppb (includes spike samples)
- Average Percent Error is -1.3%

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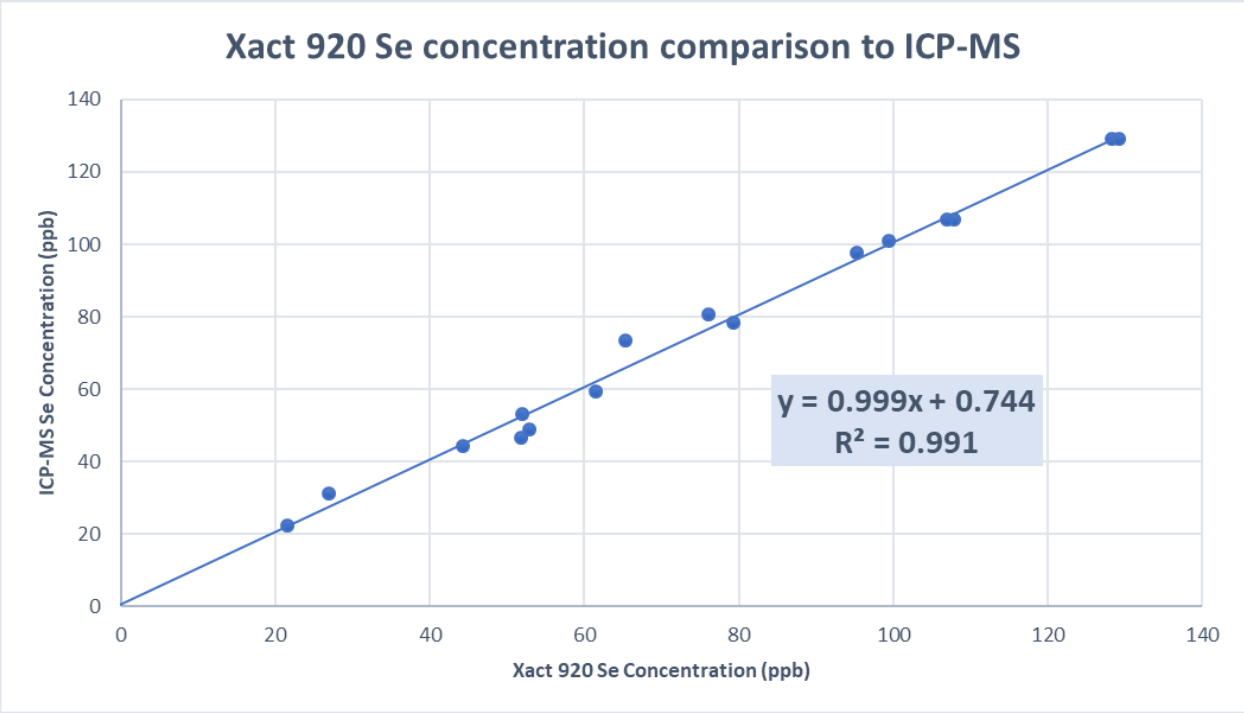
Bioreactor Effluent Parity Plot with Laboratory



NO data has been excluded

- The slope shows excellent agreement with laboratory ICP-MS
- The R^2 for this also shows excellent precision between the Xact and laboratory analysis

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Spike Recovery

Spike Recovery Summary Xact 920 and ICP-MS										
Identification		Grab ID and Sample Prep				Spike		Xact 920		ICP-MS
Series	Lab	Date	Time	Location	Filter (um)	Se Spike (ppb)	Spike Type	N	**Spike Recovery (%)**	**Spike Recovery (%)**
A	010920c	1/9/20	9:30	Clarifier Overflow	250	100.4	SeVI	8	**105.8%**	**97.8%**
	010920d	1/9/20	9:30	Clarifier Overflow	250	102.7	SeIV	5	**83.9%**	**103.8%**
	011020a	1/9/20	14:00	SeHAWK BioEff 2A		21.40	SeVI	6	**83.3%**	**98.5%**
B	012620b	1/24/20	12:25	SeHAWK BioEff Tank	250	109.7	SeIV	7	**92.5%**	**97.0%**
	012520b	1/24/20	16:25	SeHAWK BioEff Tank	250	85.53	SeVI	6	**106.9%**	**95.5%**

Notes:
1. EPA Method 200.8 matrix spike recovery range is 70 to 130%
3. Spike Recovery = (SpikeResult - BaselineResult) / (SpikeConc * DilutionFactor)

- US EPA recommended range for spike recovery is between 70% and 130%
- Both the Xact and ICP-MS percent recoveries fall within this range
- Xact and ICP-MS spike recovery is within range for both Se (VI) and Se (IV)

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Detection Limit Determination

Xact 920 - Minimum Detection Limit Calculations for Clarifier Overflow Sample Matrix											
Meta		Measured Concentration (ppb Se)							DL Calculation (ppb Se)		
ID	Date	Rep 1	2	3	4	5	6	7	StDev	99% DL	Avg. 99% DL
1	1/15/20	22.89	21.44	22.18	21.51	22.66	21.06	21.62	0.68	**2.14**	**3.12**
2	1/16/20	22.71	22.66	21.60	21.24	20.33	22.97	21.63	0.95	**3.00**	
3	1/17/20	21.10	20.91	22.16	19.89	19.97	22.49	22.12	1.06	**3.34**	
4	1/20/20	23.54	23.02	21.17	23.19	21.68	22.01	22.19	0.87	**2.73**	
5	1/21/20	20.37	22.41	20.18	20.38	21.42	19.89	17.88	1.40	**4.39**	

Notes:
1. Single-tailed student t-value for 99% confidence level, for 7 replicates equals 3.143
2. The replicate measurements are the first seven replicates of each day

Clarifier Overflow Detection Limit (ppb)

Xact 920 - Minimum Detection Limit Calculations for Bioreactor Effluent Sample Matrix											
Meta		Measured Concentration (ppb Se)							DL Calculation (ppb Se)		
ID	Date	Rep 1	2	3	4	5	6	7	StDev	99% DL	Avg. 99% DL
1	3/14/20	4.20	4.98	3.42	5.90	4.32	3.71	5.15	0.87	**2.73**	**2.55**
2	3/15/20	5.86	6.05	7.82	6.22	6.77	6.71	5.40	0.79	**2.47**	
3	3/16/20	7.89	8.64	7.71	8.75	7.96	8.83	8.61	0.47	**1.47**	
4	3/17/20	6.61	7.54	9.44	8.73	8.67	9.91	8.74	1.12	**3.52**	

Notes:
1. Single-tailed student t-value for 99% confidence level, for 7 replicates equals 3.143
2. The replicate measurements are the first seven replicates of each day

Bioreactor Effluent Detection Limit (ppb)

- Detection limit determined based on your sample matrix –

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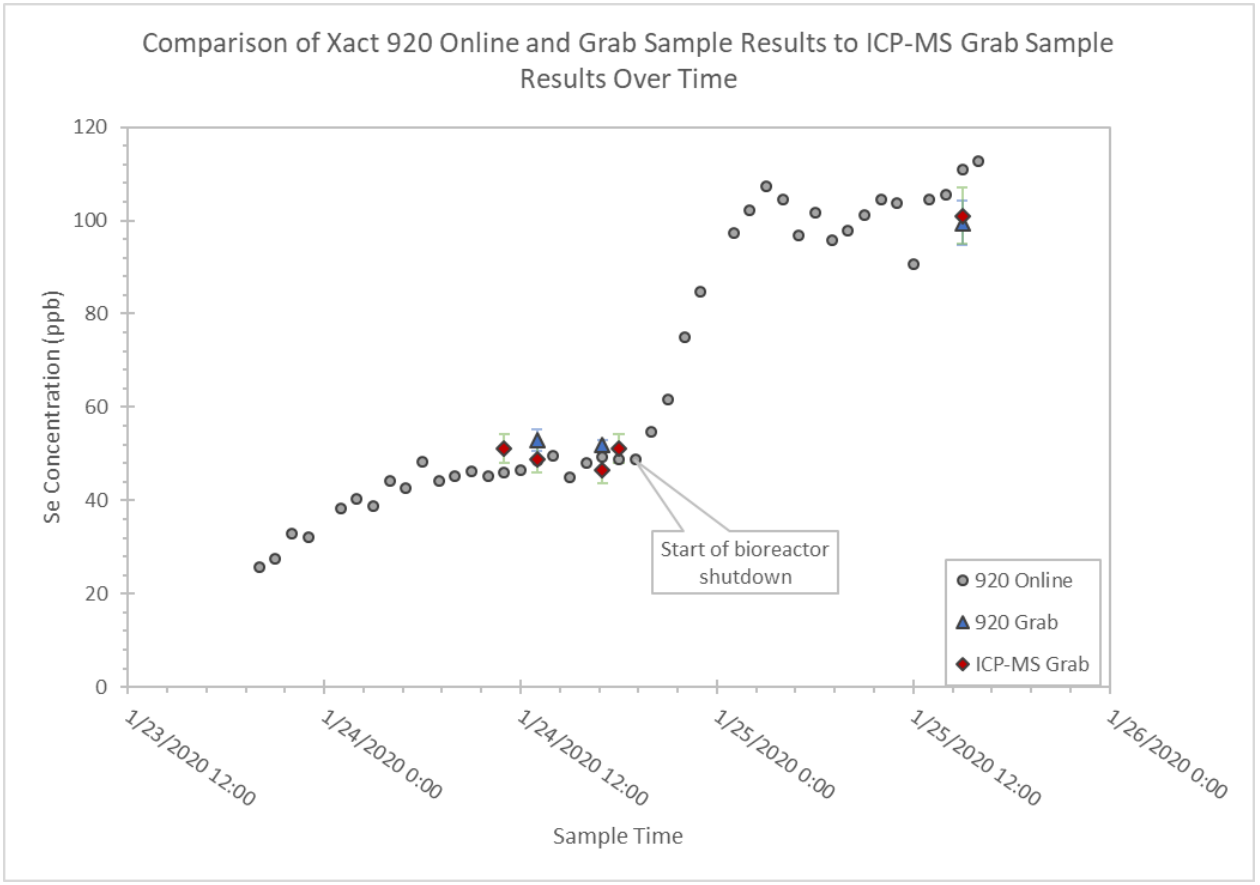
Xact Operational Data Versus Laboratory



- Data is from short term operation of Bioreactor from 1/23 to 1/25
- During normal instrument operation the Xact data matches the lab data very well
- Xact data matches laboratory data during bioreactor Shutdown

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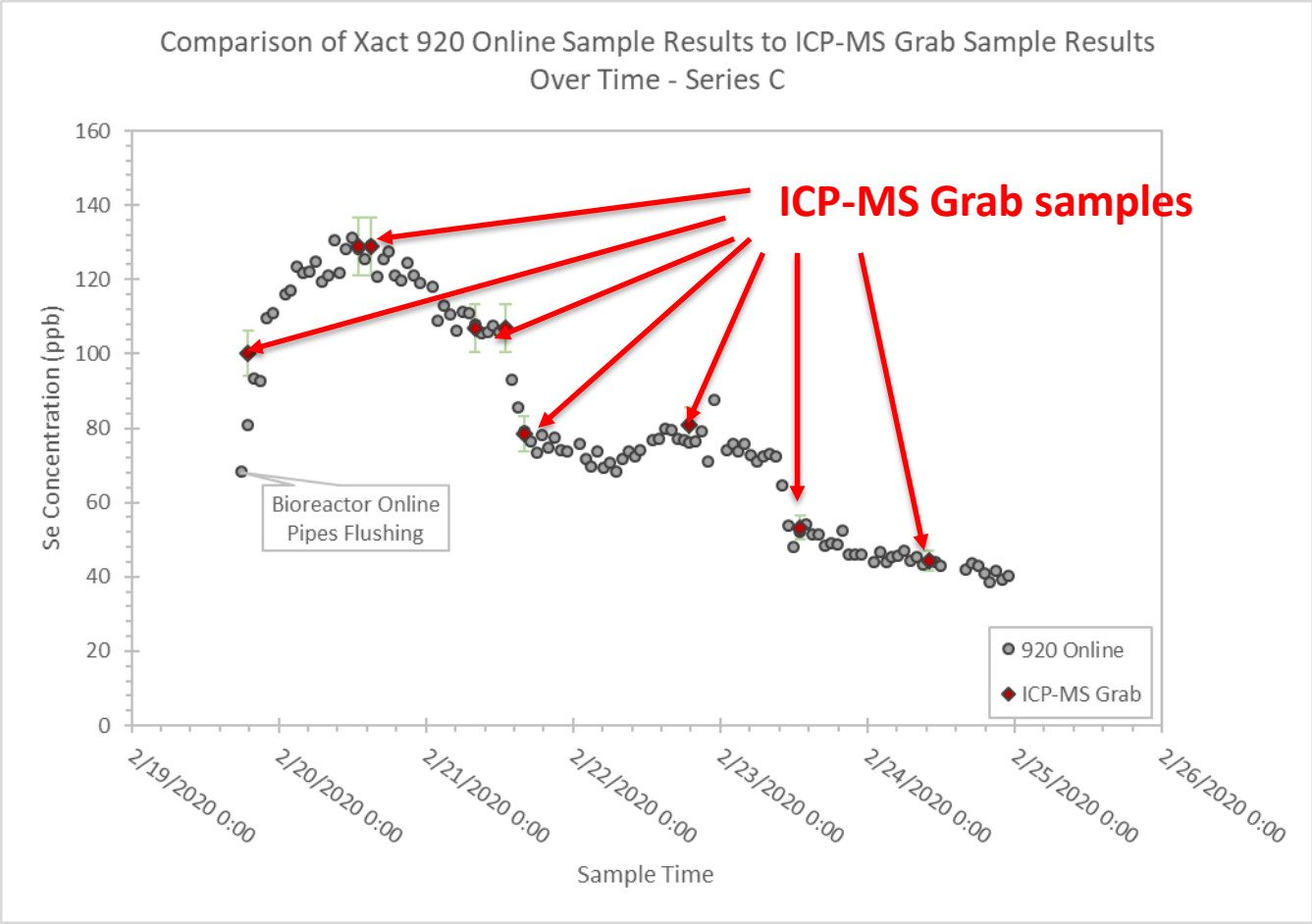
Xact Operational Data Versus Laboratory



- Data is from operation of bioreactor from 2/20 to 2/25
- During normal instrument operation the Xact data matches the lab data very well
- Xact data matches laboratory data during bioreactor startup

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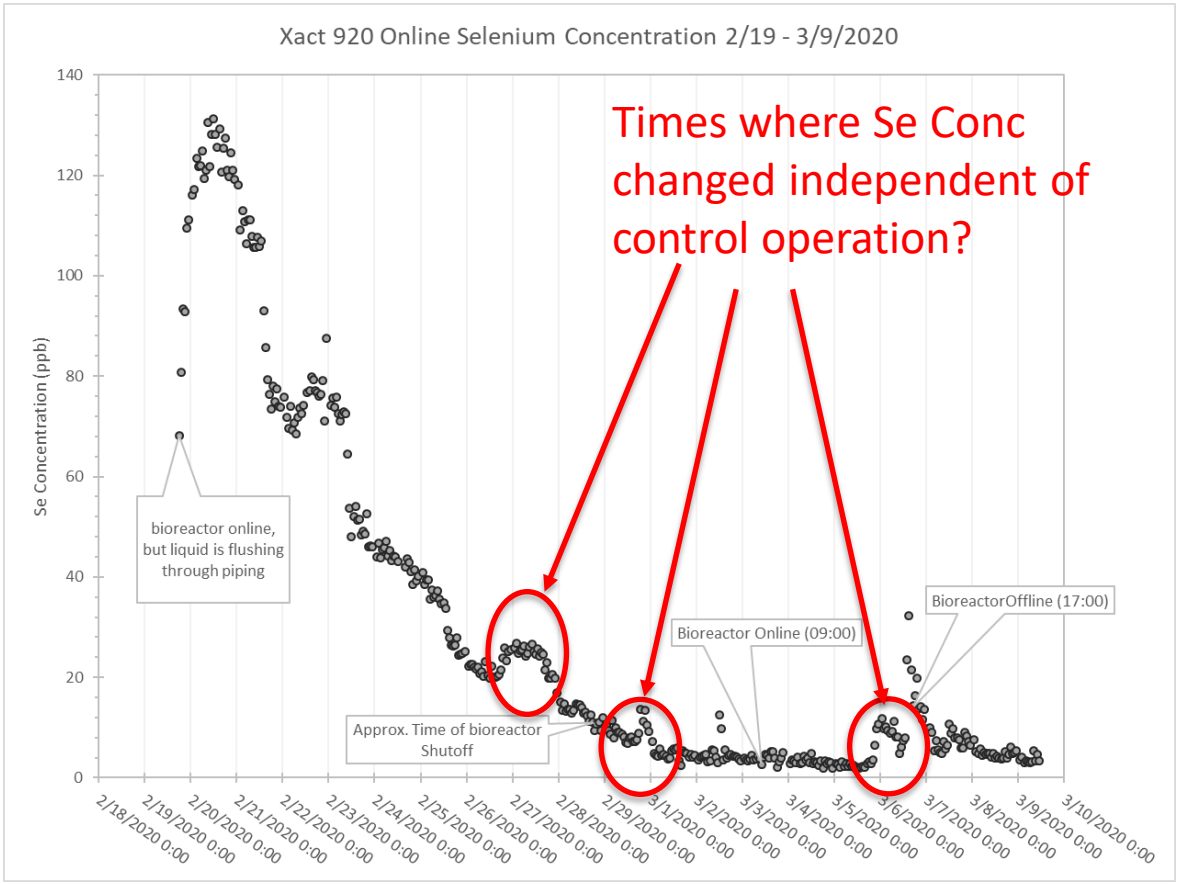
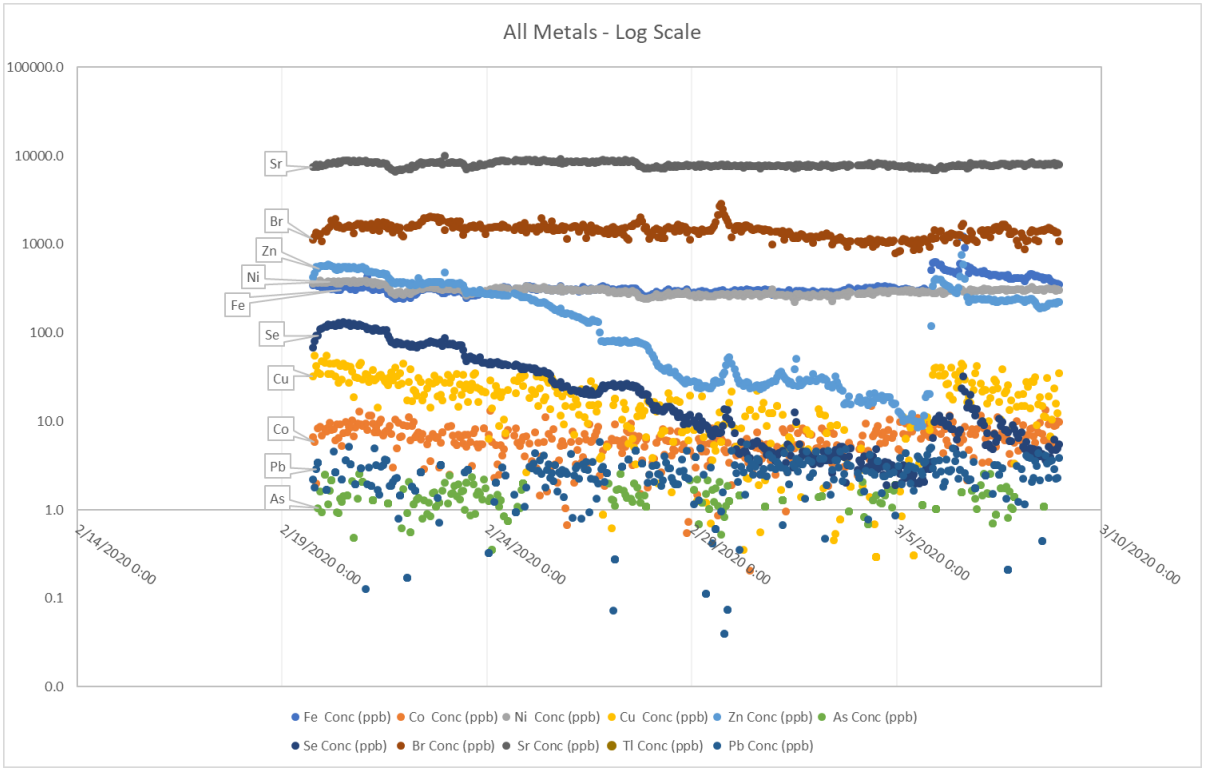
Concentration During all Bioreactor Operation



- There are times when Se concentration data does not correlate with changes in bioreactor effluent operation
- Understanding these changes could lead to more efficient bioreactor operations

Other Elements measured by the Xact



- Note log scale
- Xact able to measure other elements besides Se

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Conclusions

- Real time data can provide useful feedback for plants trying to comply with ELG limits
- Xact 920 provides data that is accurate, reliable and compares well with independent lab analysis
- Xact 920 is easy to install and operates very reliably

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Questions?

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