

Utilizing Data Trend Evaluations in Method Audits and Regulations Development

National Environmental Monitoring
and
The NELAC Institute (TNI) Conference
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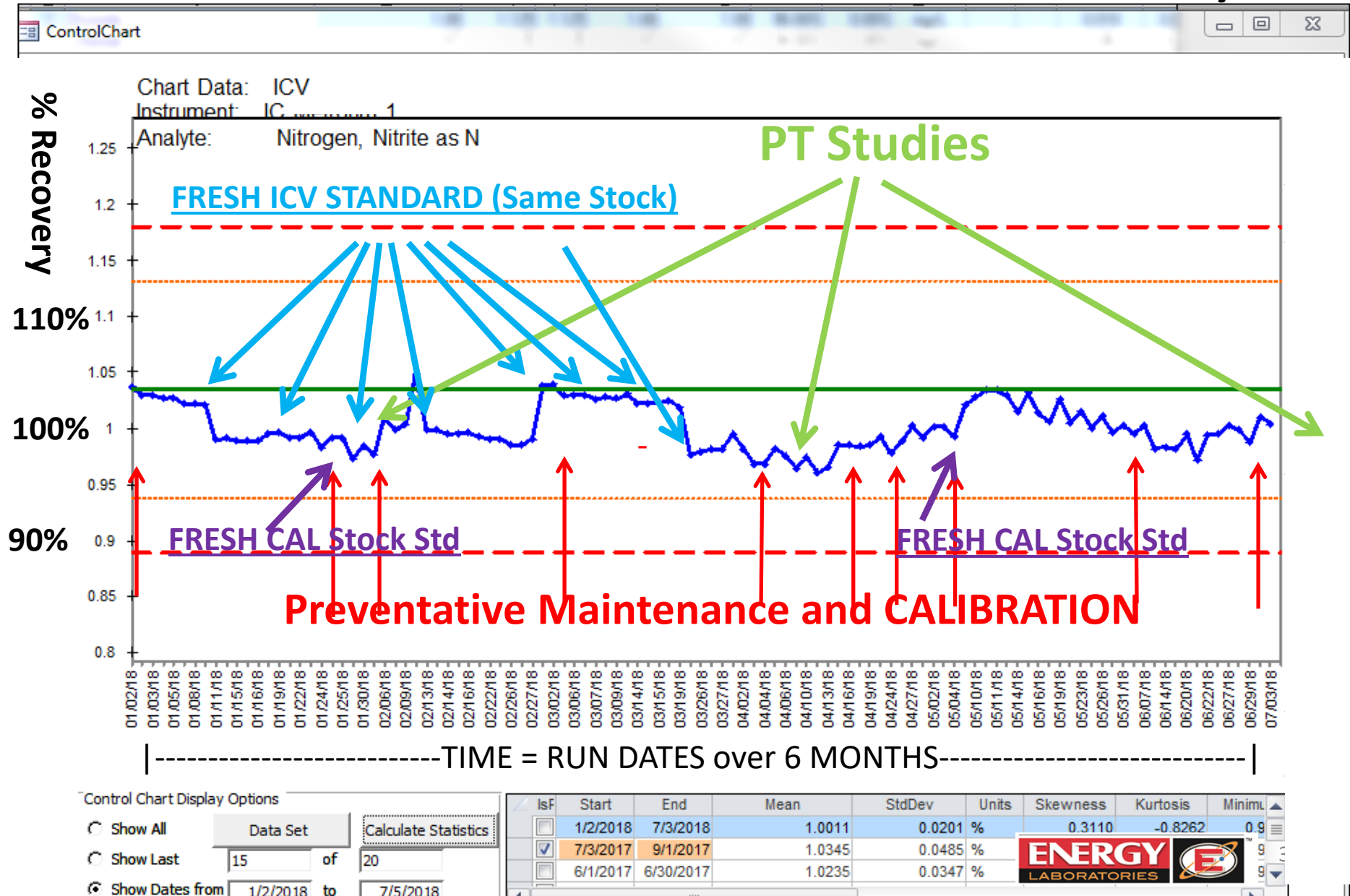


DISCLAIMER

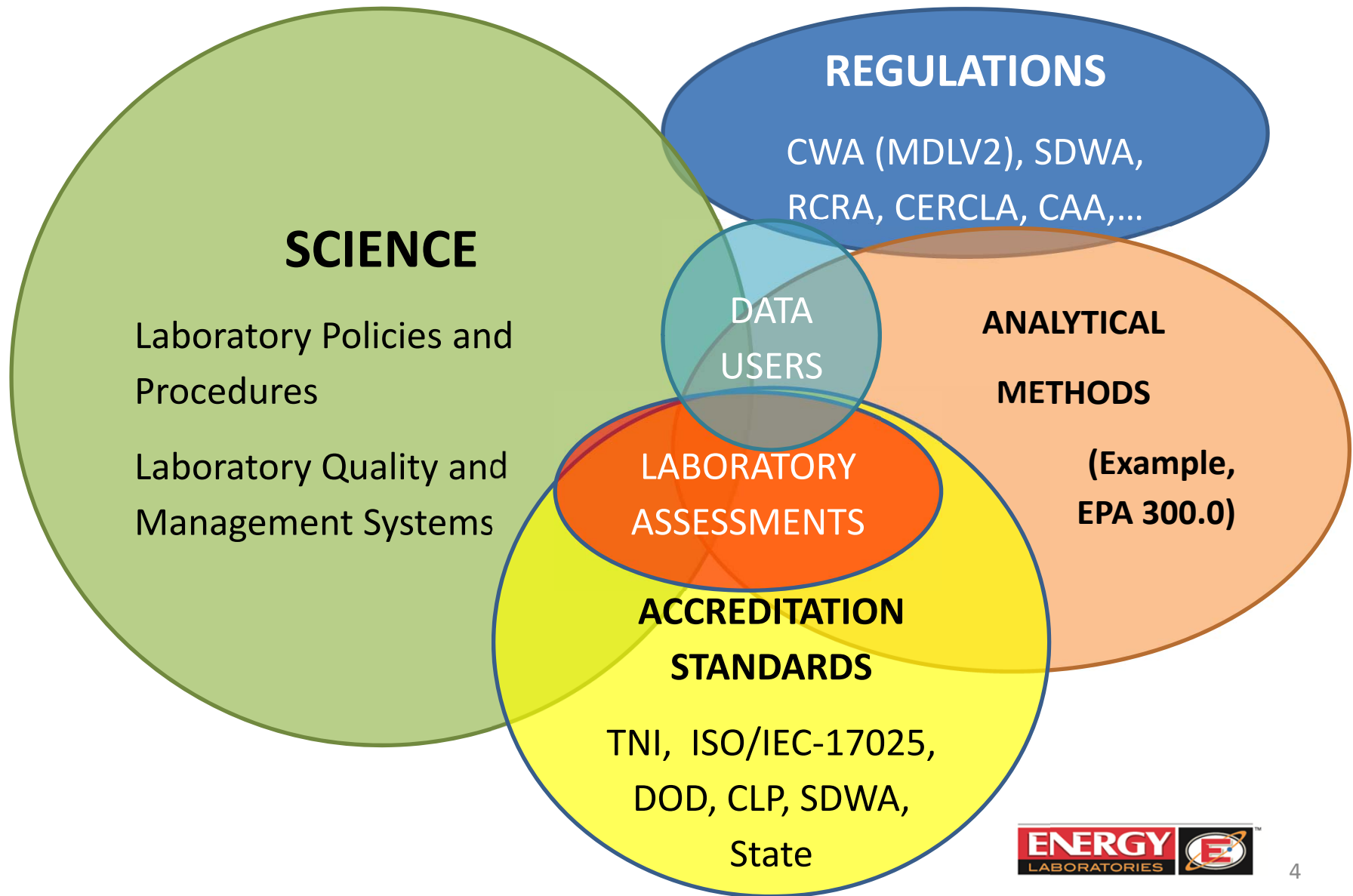
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EPA 300.0 – NITRITE-ICV % Recovery



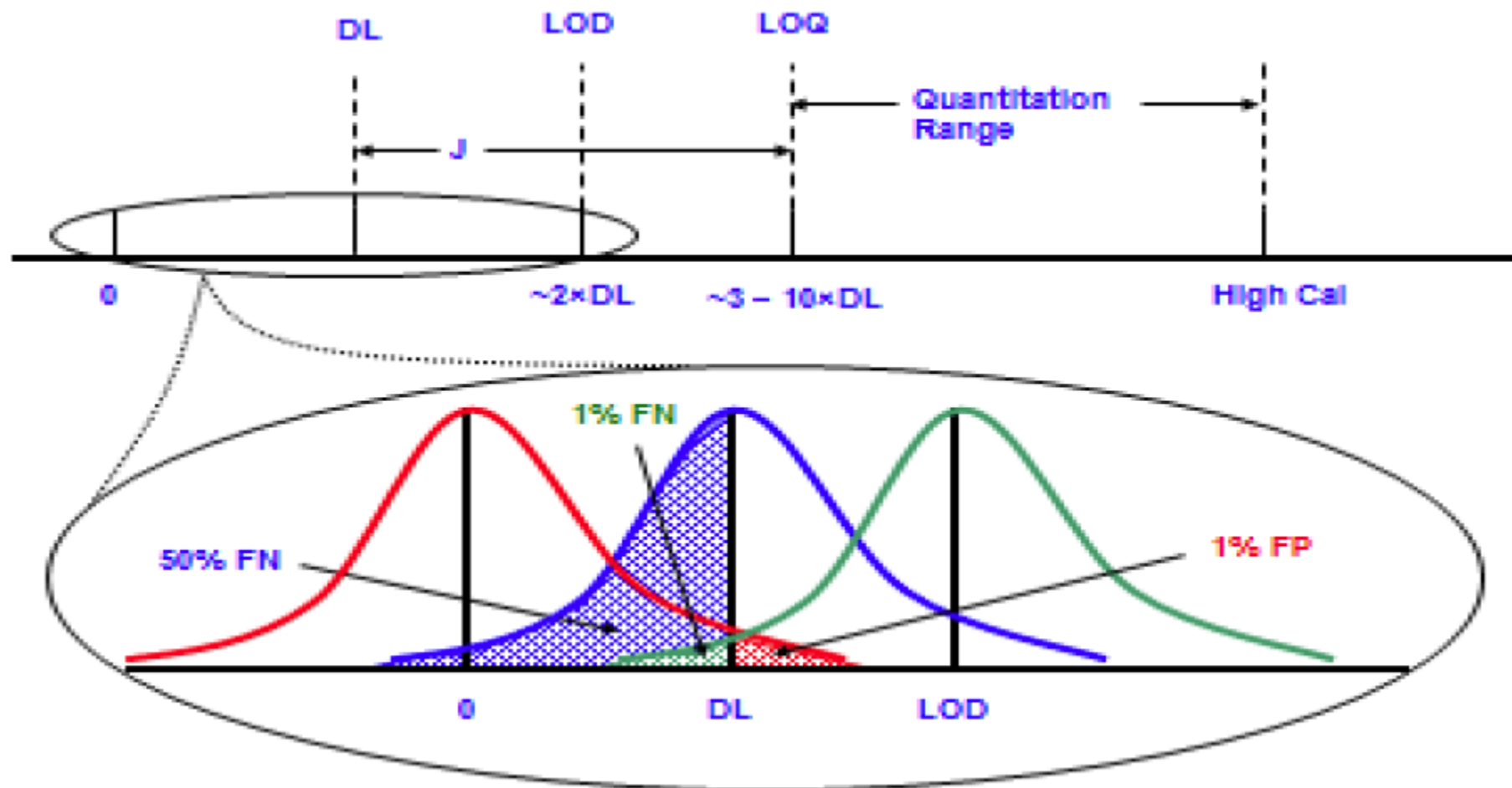
DATA TREND VENN Diagram from a LAB Perspective



PT Studies

- WS Studies Anions: Fluoride +/- 10% Accuracy
 - CFR Part 141 Specified
- WP Studies - Fluoride
 - PT Study is statistically based - approx. +/- 15% Accuracy, and with concentration dependent criteria
- For Direct Analysis Methods - A PT sample is Equivalent to a Third Source Calibration Standard
 - Can be utilized to evaluate the stability and accuracy of Primary and Secondary standards - Calculate % recovery

DL(MDL Version 2), LOD, LOQ – DOD Guidance



- “Detection and Quantitation – What Project Managers and Data Users Need to Know”, DOD Environmental Data Quality Workgroup, October 2017.

- DOD QSM 5.1.1

CWA Method Update Rule 2017 MDL Version 2

Laboratory Implementation Plan

- PHASE ONE - Initial MDL Determination
 - Perform 7 MDL-Spikes done over 3 days/3 batches (Implemented in 2015)
 - Perform 7- MDL-Blanks done over 3 days/3 batches
 - (Individual analyst training on calibration and data processing procedures for proper blank data evaluation required)
 - Calculate MDL-Spike and MDL-Blank data and set MDL to whichever is higher
 - Perform LOD analysis to confirm validity of MDL-FINAL
 - Schedule Next Quarterly MDL spike analysis
 - Qualify Blanks above MDL-FINAL when justified
- PHASE TWO (Due 2019)
 - Calculate Quarterly MDL-Spike Results
 - Evaluate Method Blank Data for MDL-Blank Value
 - Set Method MDL-FINAL values to whatever is higher
 - Implement suitable corrective action processes



MDL Version 2, Phase One - Issues

- **Data Collection and MDL module changes required.**
 - Most methods and LIMS data reporting is not setup to address negative values
 - MDL module not setup to process MDL blank values
 - Most methods do not have method blank results being processed down to MDL levels. Generally, Method Criteria is < PQL, or ½ of PQL, or 1/10 of sample amount
- **Accurate data processing and quantitation at MDL levels is needed for Blanks.**
 - Calibration curve modeling training and blank data processing review required.
 - Calibration Curve Y intercepts above/below the calculated MDL value not acceptable.
 - Proper blank integrations down to MDL level important

MDL V2, PHASE I, Results

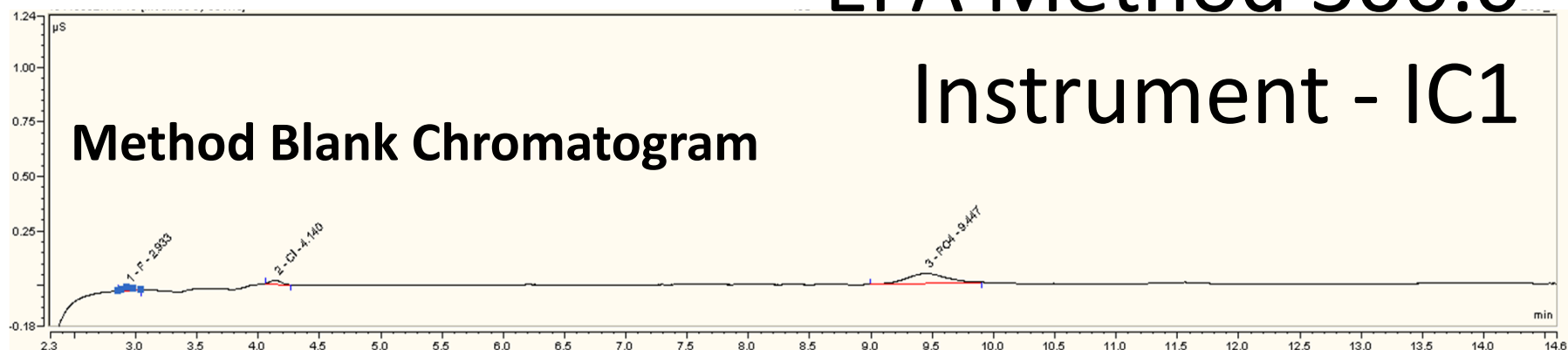
EPA 300.0 - Chloride

Date: 6/4/2018		Test Code(s): IC-300.0-SEL-W	
Instrument: xxx-IC1		Test Code Info: LLOQ 0.1 LOQ 1	
		Units mg/L	
MDL Initial Spike Calculations		MDL Initial Blank Calculations	
MDL _s Spike Concentration	0.20	MDL _b Number of Results (n)	7
MDL _s Number of Results (n)	7	MDL _b Mean	0.0073
MDL _s Mean	0.1813	MDL _b Std Dev	0.0030
MDL _s Average Recovery	90.7	MDL _b Calculated Result	0.0167
MDL _s Std Dev	0.0037	MDL _b Largest Value or 99th Percentile	0.0107
MDL_s Calculated	0.0115	MDL_b Final Result	0.0167
Blank Zero Type		LOD Date	LOD SpkVal
Non-numeric		6/27/2018	0.05
			0.0555
			0.0104
*Numeric = MDL _s Calculated Result			
*Non-numeric = MDL _s Largest Value or 99th Percentile			
Initial MDL	2x MDL		
0.0167	0.0333		

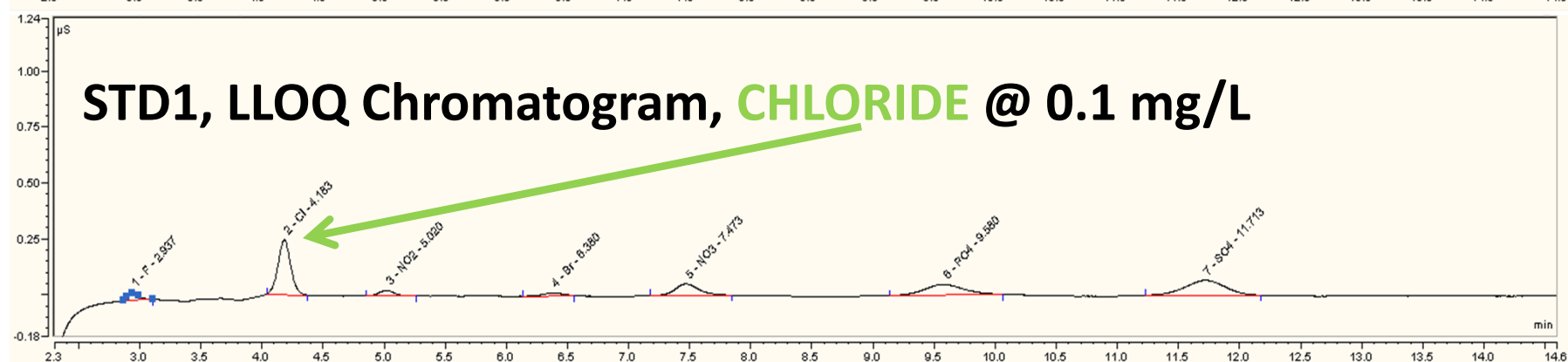
EPA Method 300.0

Instrument - IC1

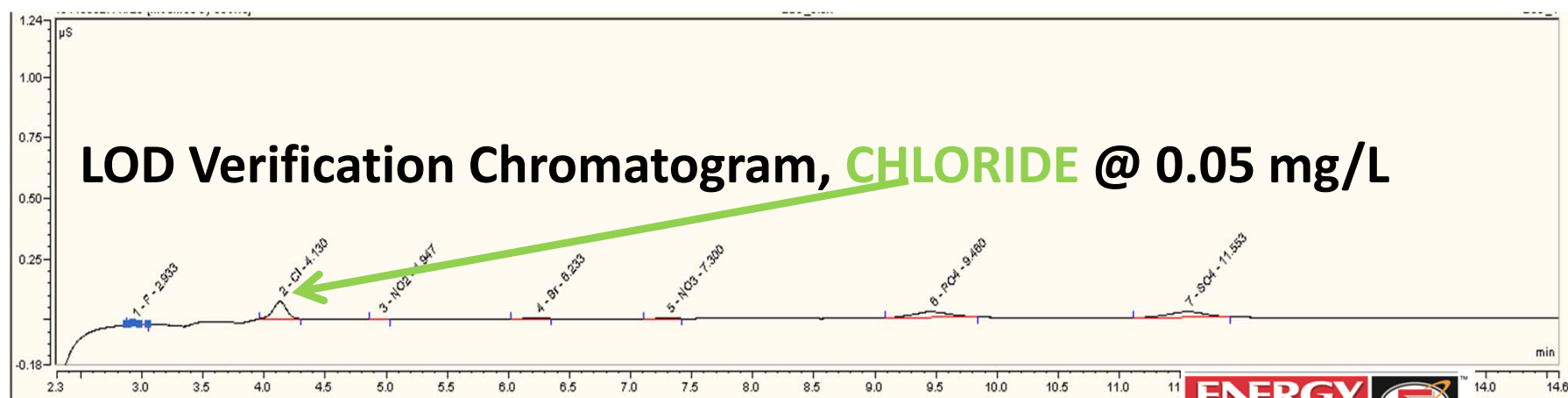
Method Blank Chromatogram



STD1, LLOQ Chromatogram, CHLORIDE @ 0.1 mg/L

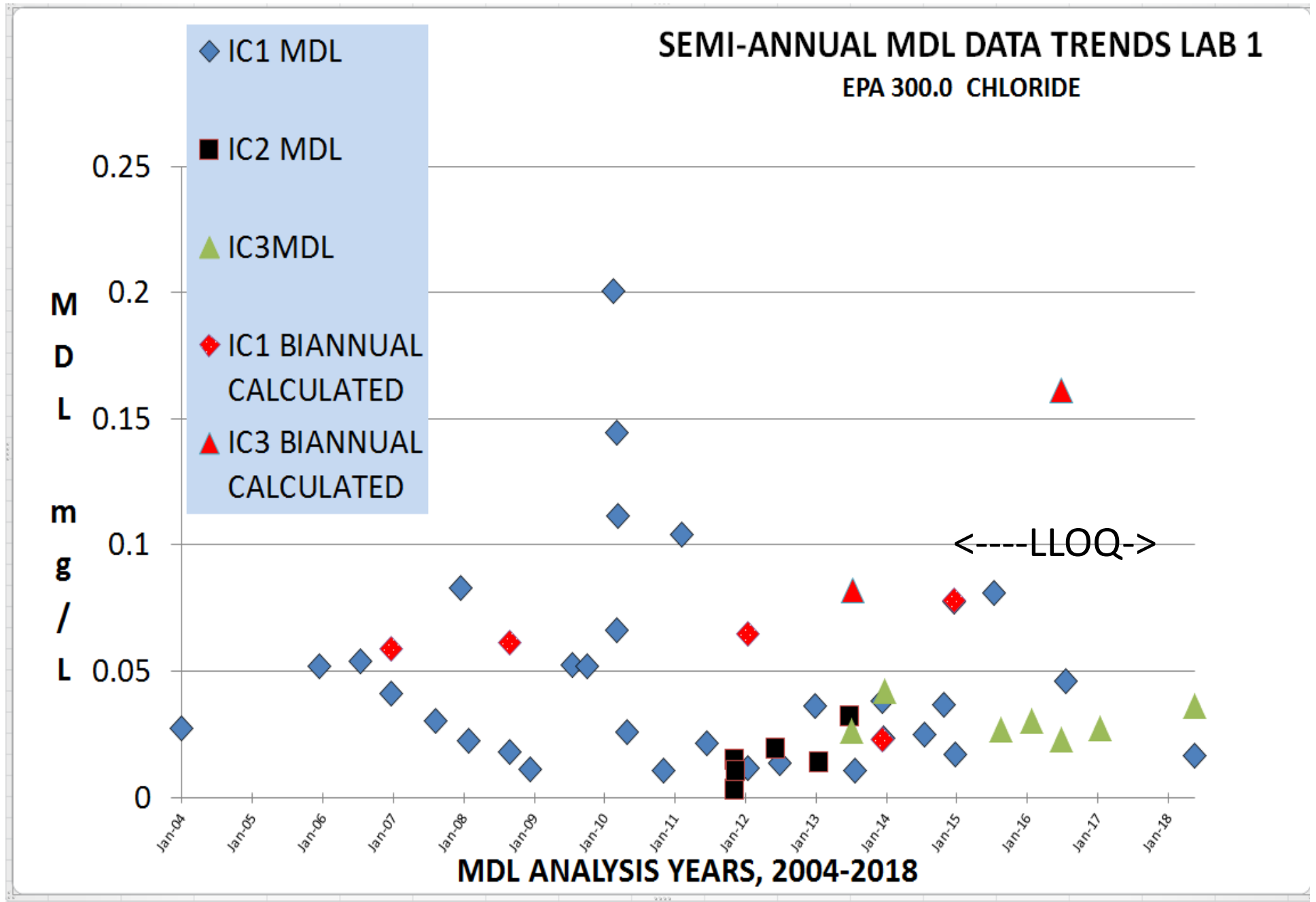


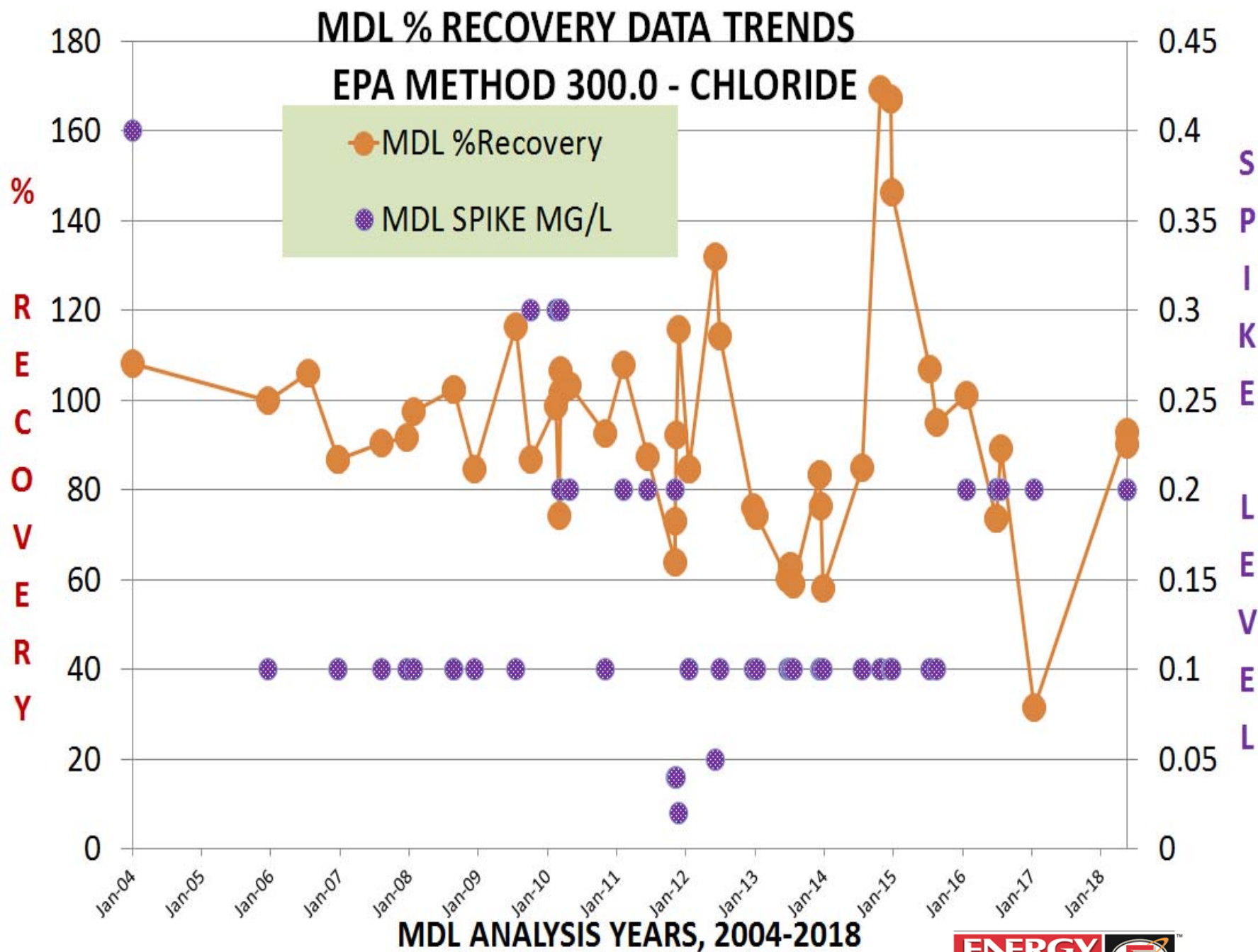
LOD Verification Chromatogram, CHLORIDE @ 0.05 mg/L



SEMI-ANNUAL MDL DATA TRENDS LAB 1

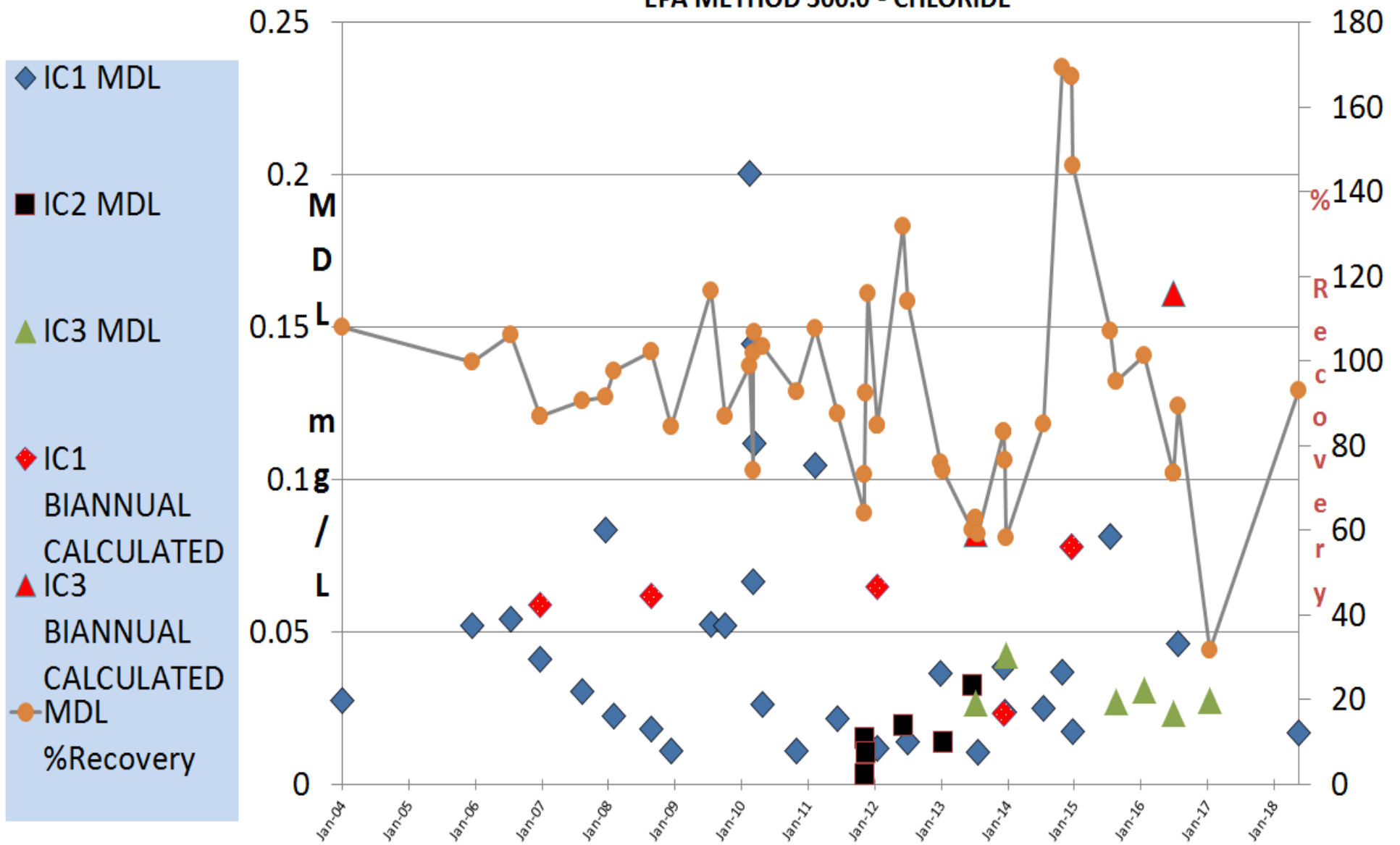
EPA 300.0 CHLORIDE





SEMI-ANNUAL MDL DATA TRENDS

EPA METHOD 300.0 - CHLORIDE



MDL ANALYSIS YEARS, 2004-2018

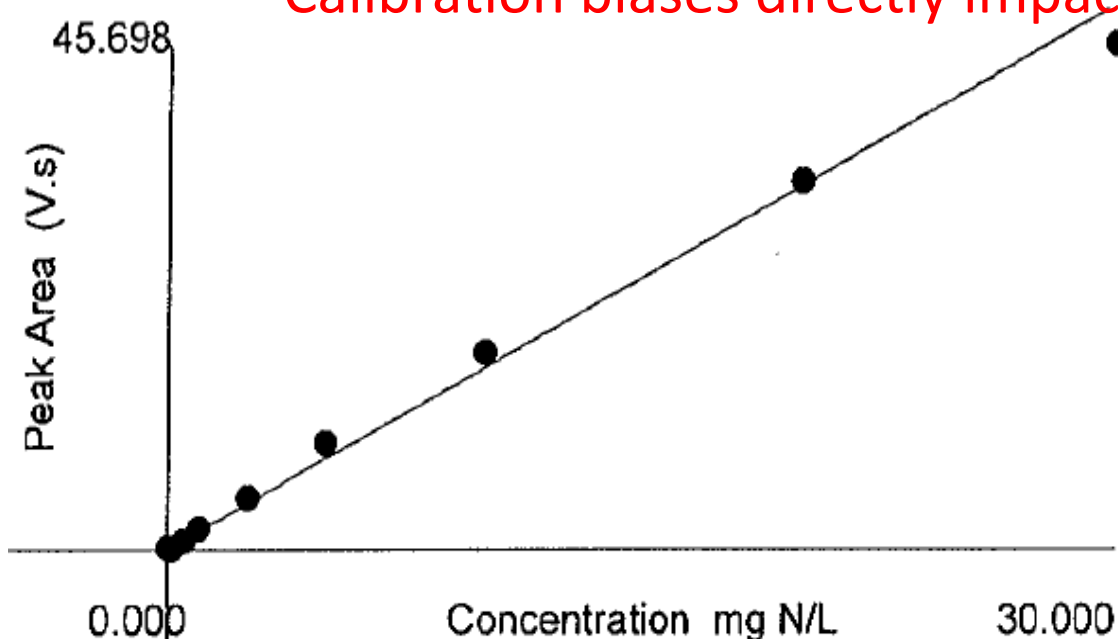
UPCOMING TNI REQUIREMENTS

Per EL-V1MG-2017-Rev2.2: *Chemical Testing. 1.7 Technical Requirements, Section 1.7.1.1 Initial Calibration*

- (k) the laboratory shall use and document a measure of relative error in the calibration;
 - ...ii. for calibrations evaluated using correlation coefficient or coefficient of determination, the laboratory shall evaluate relative error by either:
 - A. Measurement of Relative Error (%RE)...
 - B. Measurement of Relative Standard Error %RSE...

	Known Conc. (mg N/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Residual	Det. Conc (mg N/L)	Detection Date
1	30.000	1	45.698	3.403	0.0	7.3	27.566	11/29/2012
2	20.000	1	33.274	2.691	0.0	-1.2	20.066	11/29/2012
3	10.000	1	17.809	1.489	0.0	-8.2	10.729	11/29/2012
4	5.000	1	9.638	0.821	0.0	-16.8	5.796	11/29/2012
5	2.500	1	4.665	0.399	0.0	-12.5	2.794	11/29/2012
6	1.000	1	1.893	0.162	0.0	-12.4	1.121	11/29/2012
7	0.500	1	0.787	0.065	0.0	8.9	0.452	11/29/2012
8	0.100	1	0.040	5.361e-3	0.0	80.4	1.884e-3	11/29/2012
9	0.000	1	0.150	0.012			0.068	11/29/2012

Figure : 1 (TKN)



Calibration biases directly impact the MS %Recovery calculation

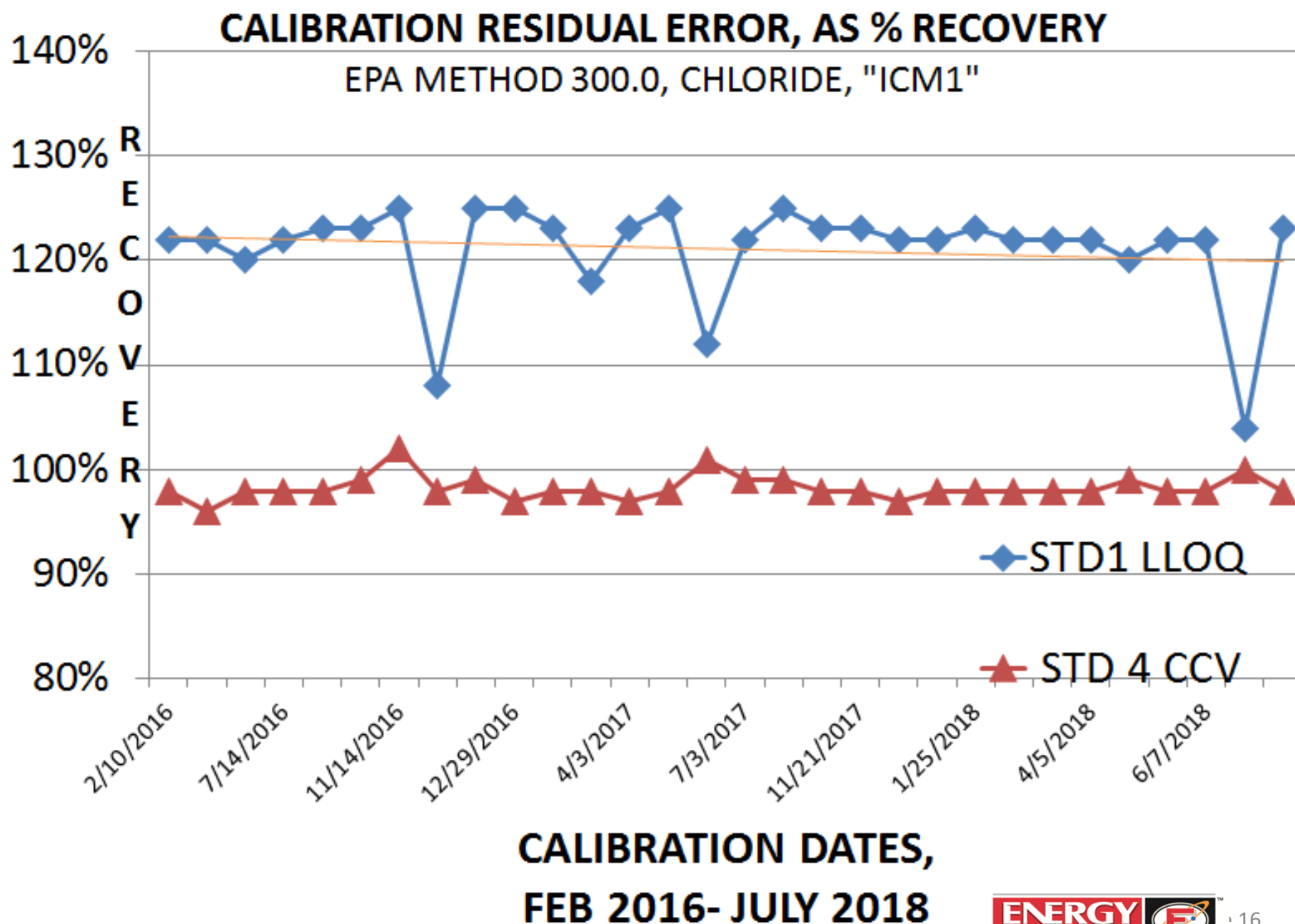
$$\begin{aligned} \text{Area} &= 1.642 * \text{Conc} + 0.042 \\ \text{Conc} &= 0.604 * \text{Area} - 0.022 \\ \text{Correlation Coefficient (r)} &= 0.99979 \end{aligned}$$

Weighting : 1/x

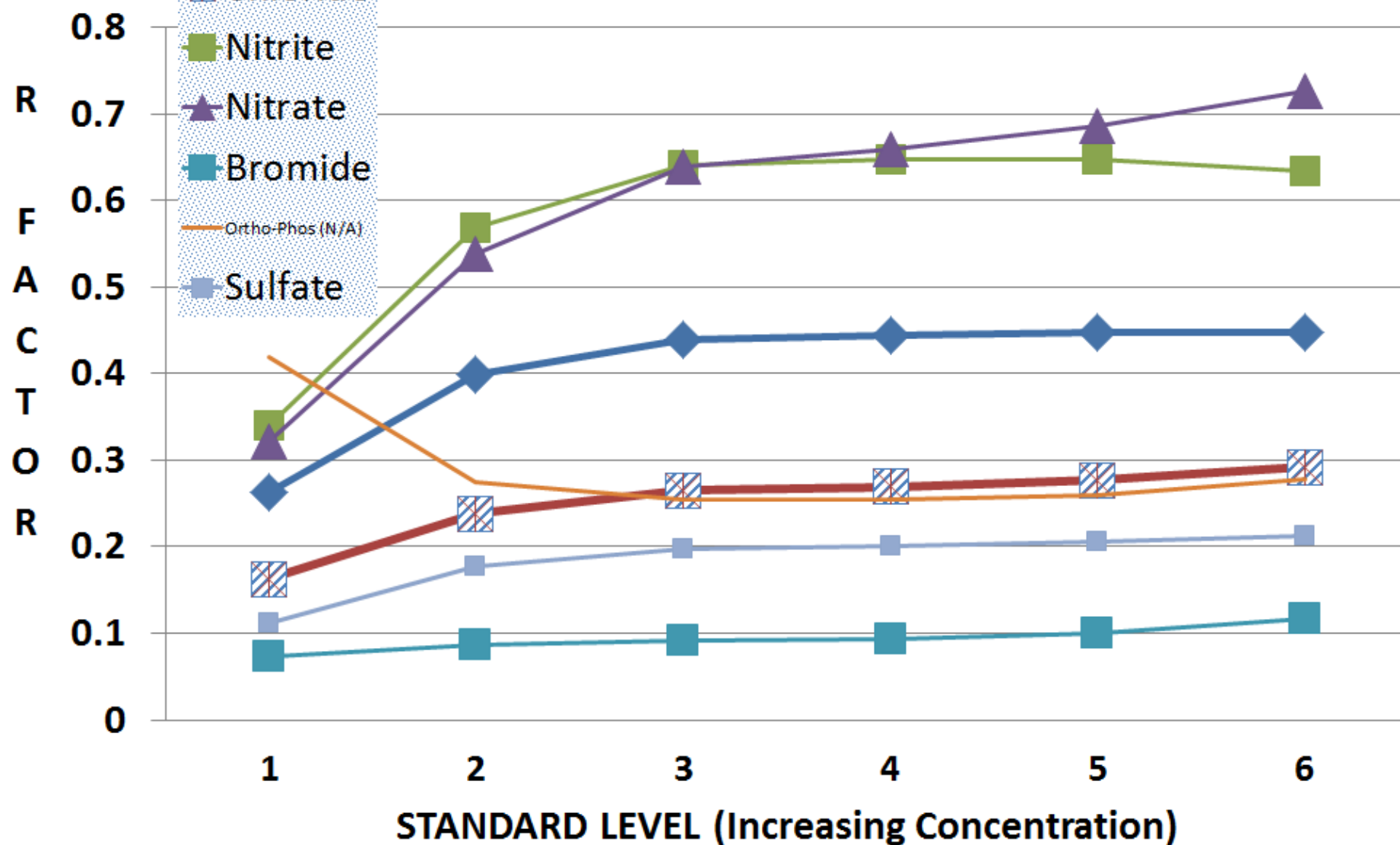
andy

7/19/2016 1:57:05 PM

Residuals measure fit of line to calibration points. Linear model has substantial error especially for mid and highest points when calibrating above 10. This 1st order PLOT shows the true "Linearity of the system"

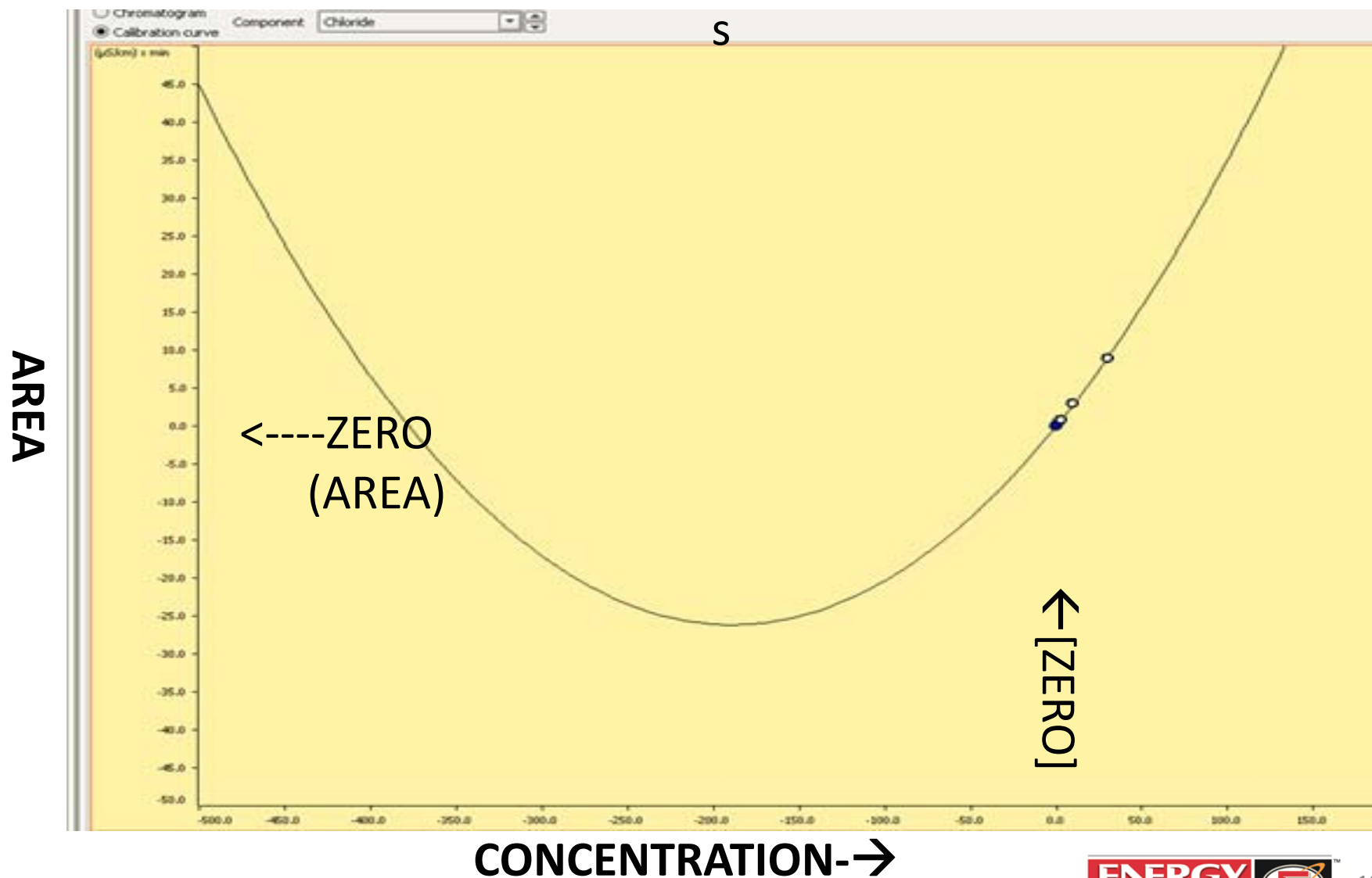


EPA 300.0, CALIBRATION STANDARDS RESPONSE FACTORS **Area/Concentration - Average of 10 Calibrations ICM1**



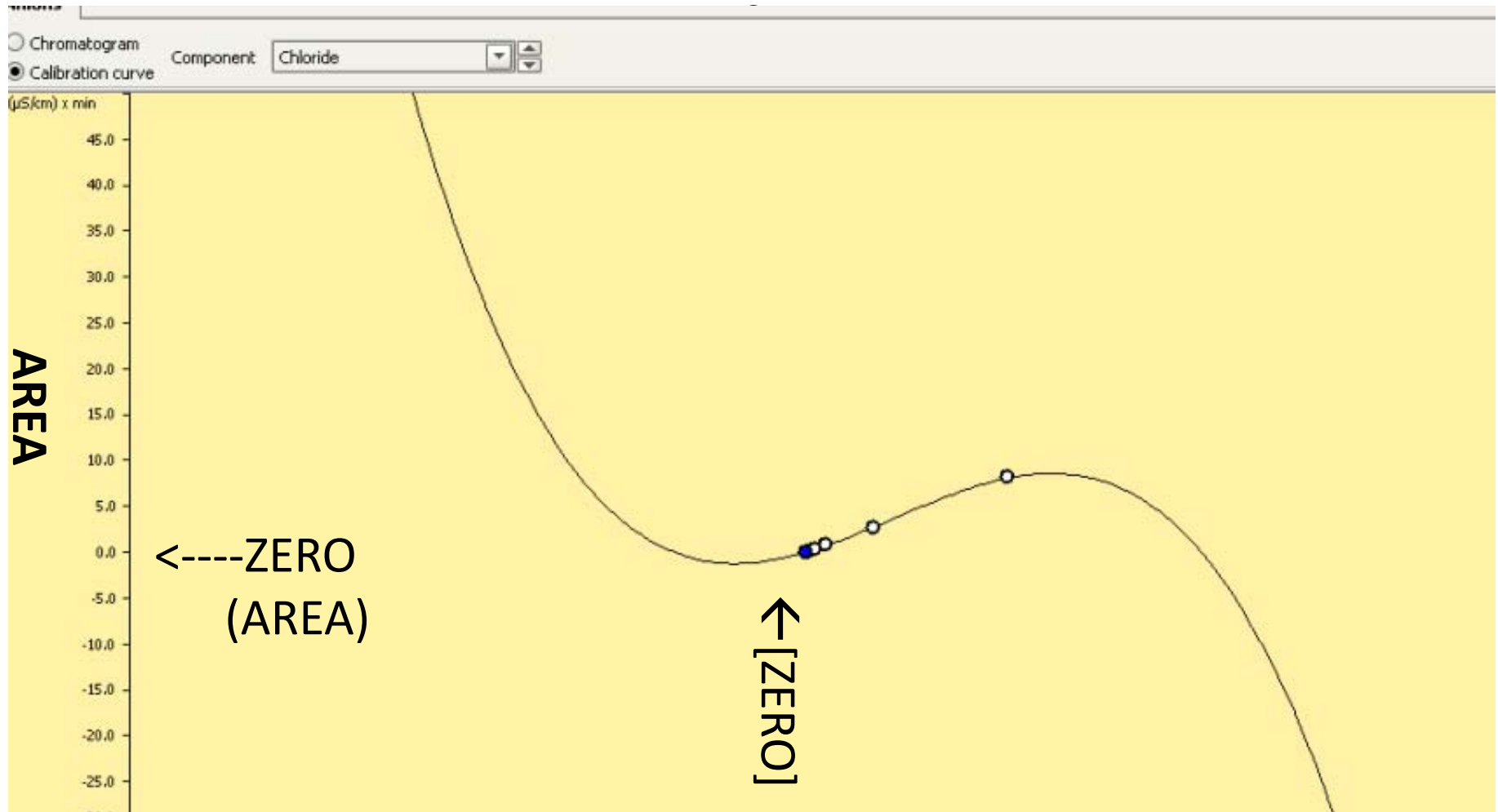
Non-Linear Calibration Models

Quadratic Calibration Model, EPA 300, Chloride, ICM1



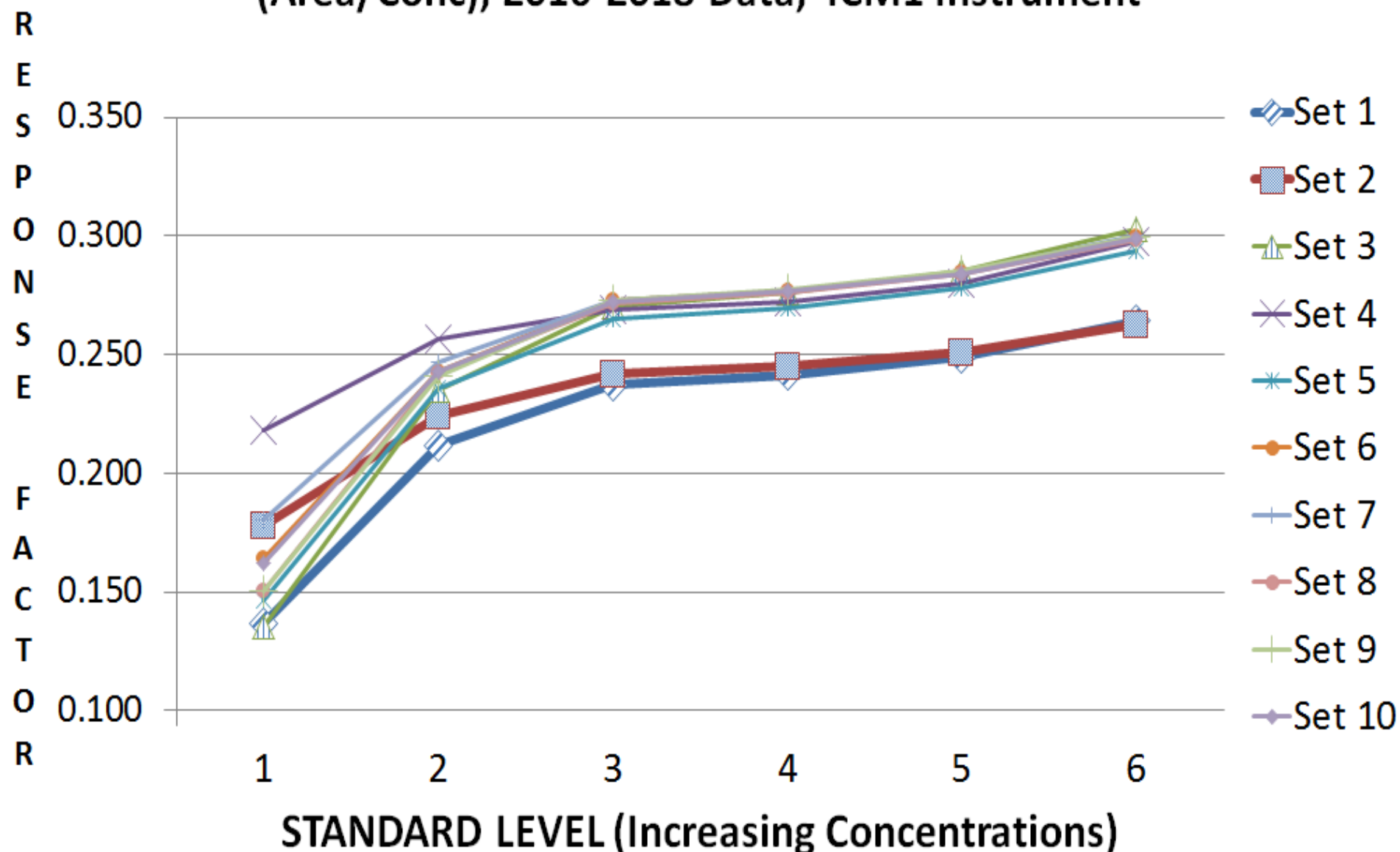
Non-Linear Calibration Models

Polynomial calibration Model, EPA 300, Chloride, ICM1

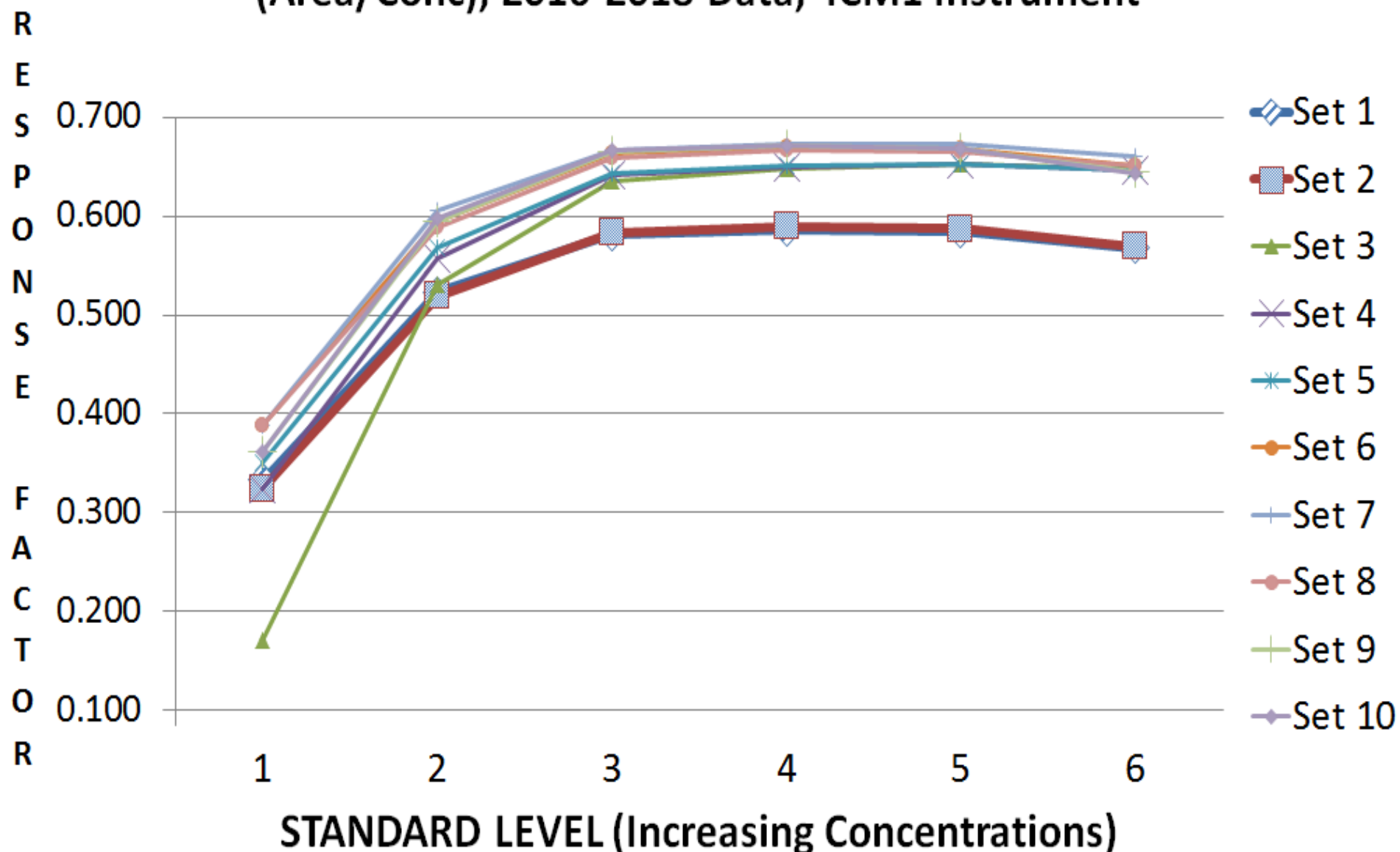


CONCENTRATION-→

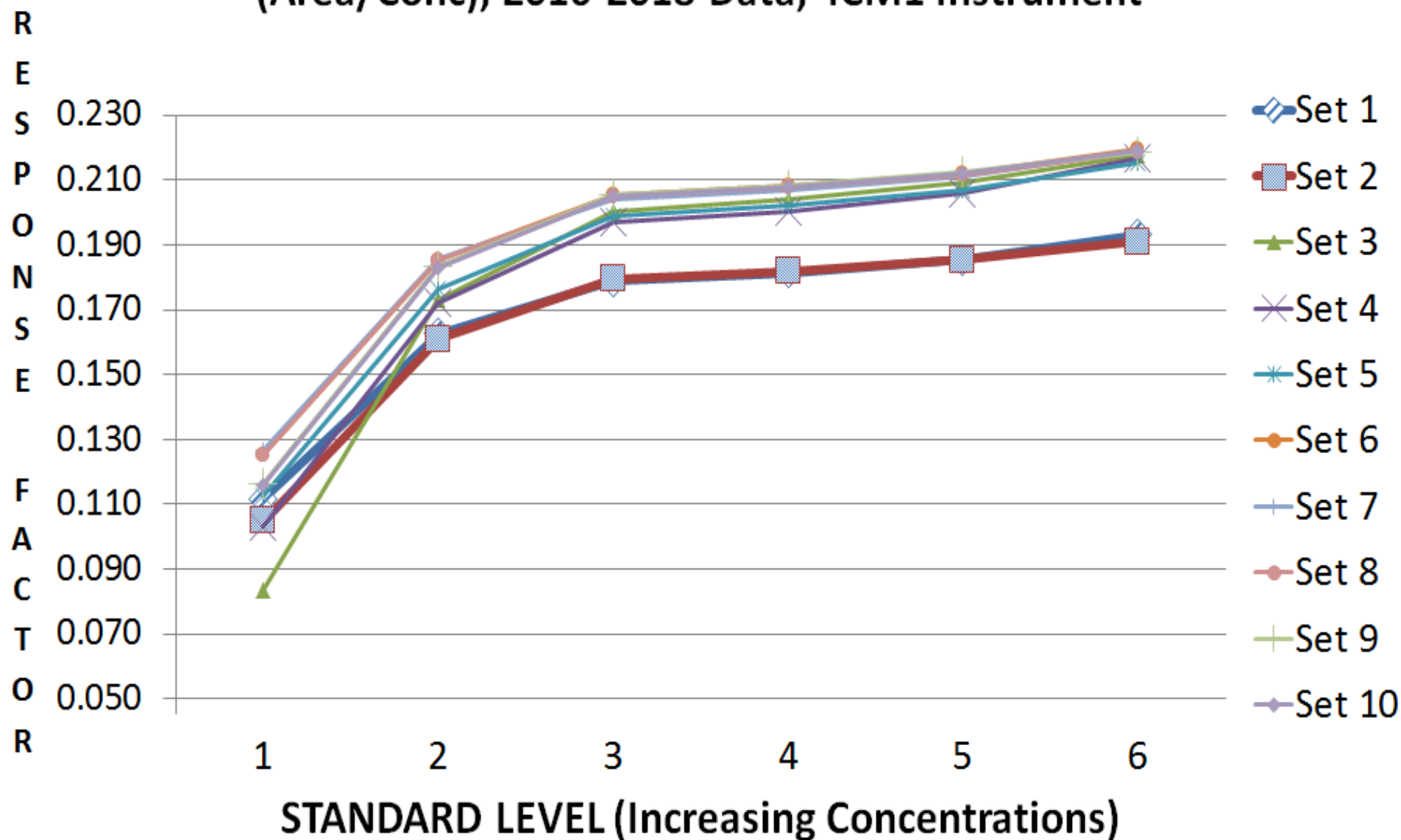
EPA Method 300.0, CHLORIDE RESPONSE FACTORS (Area/Conc), 2016-2018 Data, ICM1 Instrument



EPA Method 300.0, NITRITE RESPONSE FACTORS (Area/Conc), 2016-2018 Data, ICM1 Instrument



EPA Method 300.0, SULFATE RESPONSE FACTORS (Area/Conc), 2016-2018 Data, ICM1 Instrument



ISO/IEC 17025-2017

“RISK ANALYSIS”

- **QA Examples:**

- **Query MDL Database for MDLs determined by blanks**

- Calculate Ratio of MDL to LLOQ (PQL or Reporting Limit)
- Sort Data by Ratio of MDL/LLOQ and audit those methods with highest MDL/LLOQ ratio

- Query LIMS database for method blank performance

- Audit methods having method blanks above MDL value

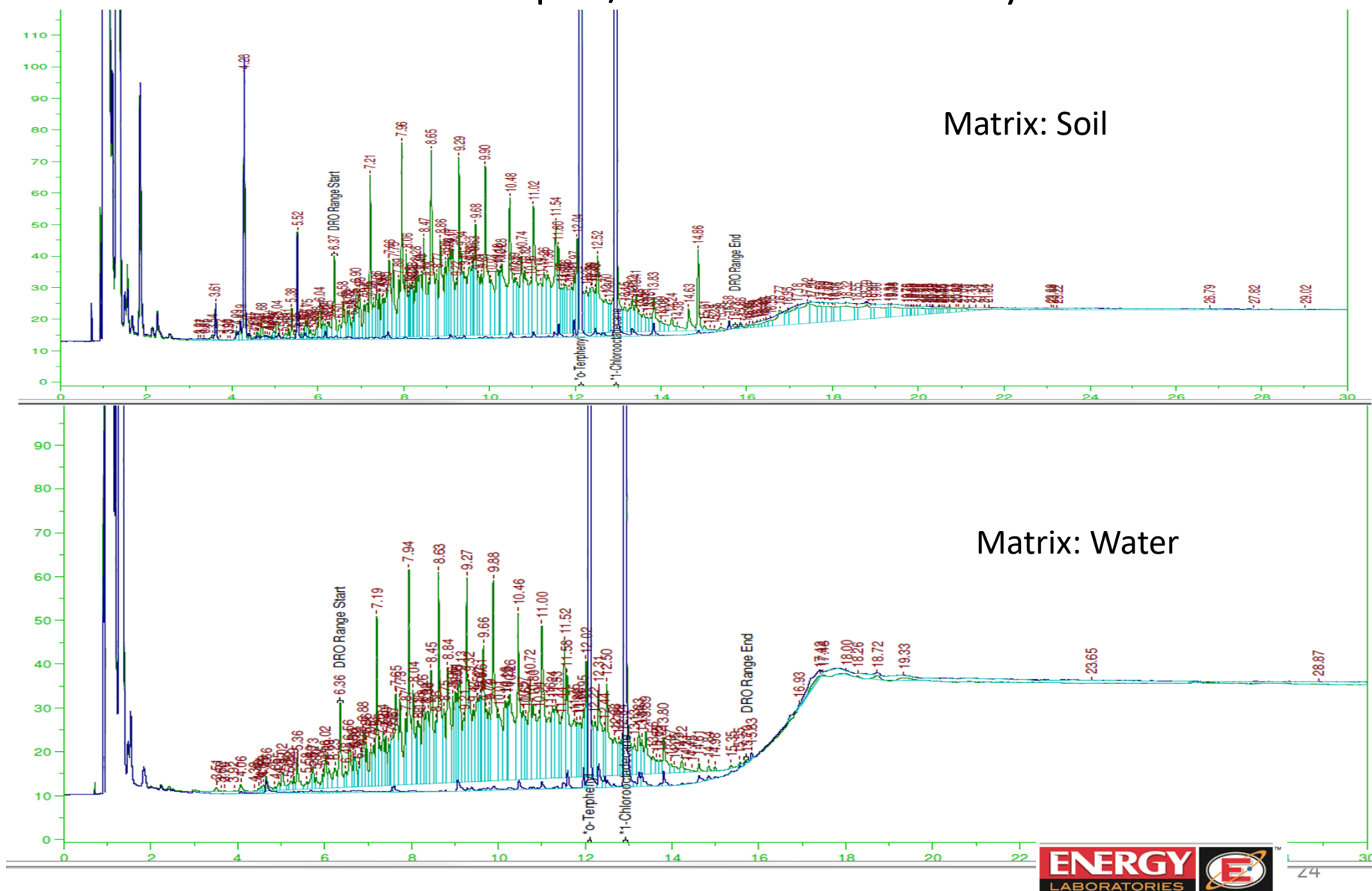
- Audit Methods having an analyst new to a procedure

- = Training Opportunity
- Evaluates supervision and training processes

- Audit Methods/Processes associated with a Corrective Action

LOD DIESEL RANGE ORGANICS EPA METHOD 8015C

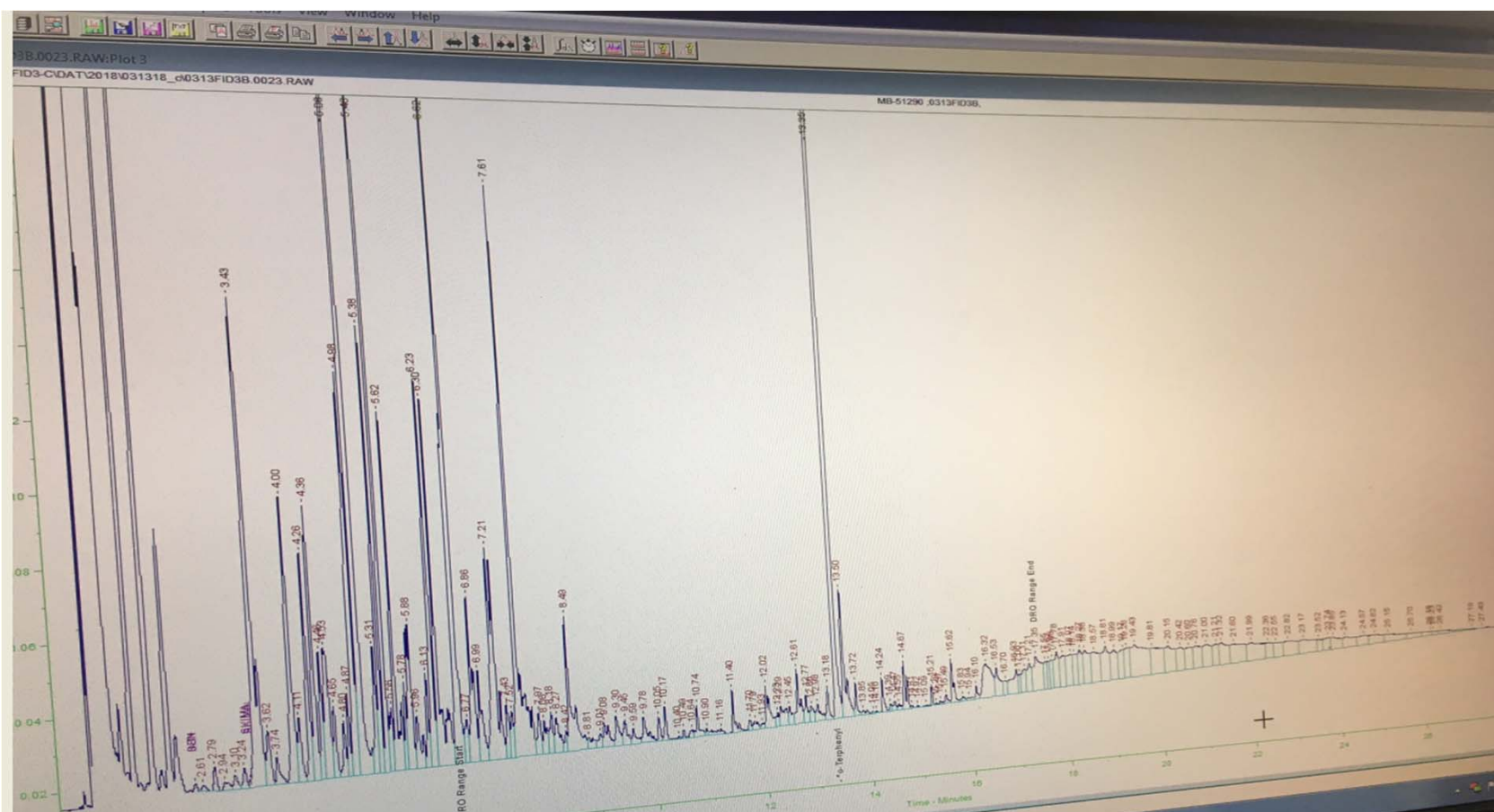
Diesel #2 Spike/Method Blank Overlay



LOD GASOLINE RANGE ORGANICS

EPA METHOD 8015C

GASOLINE Spike/ No Method Blank Overlay



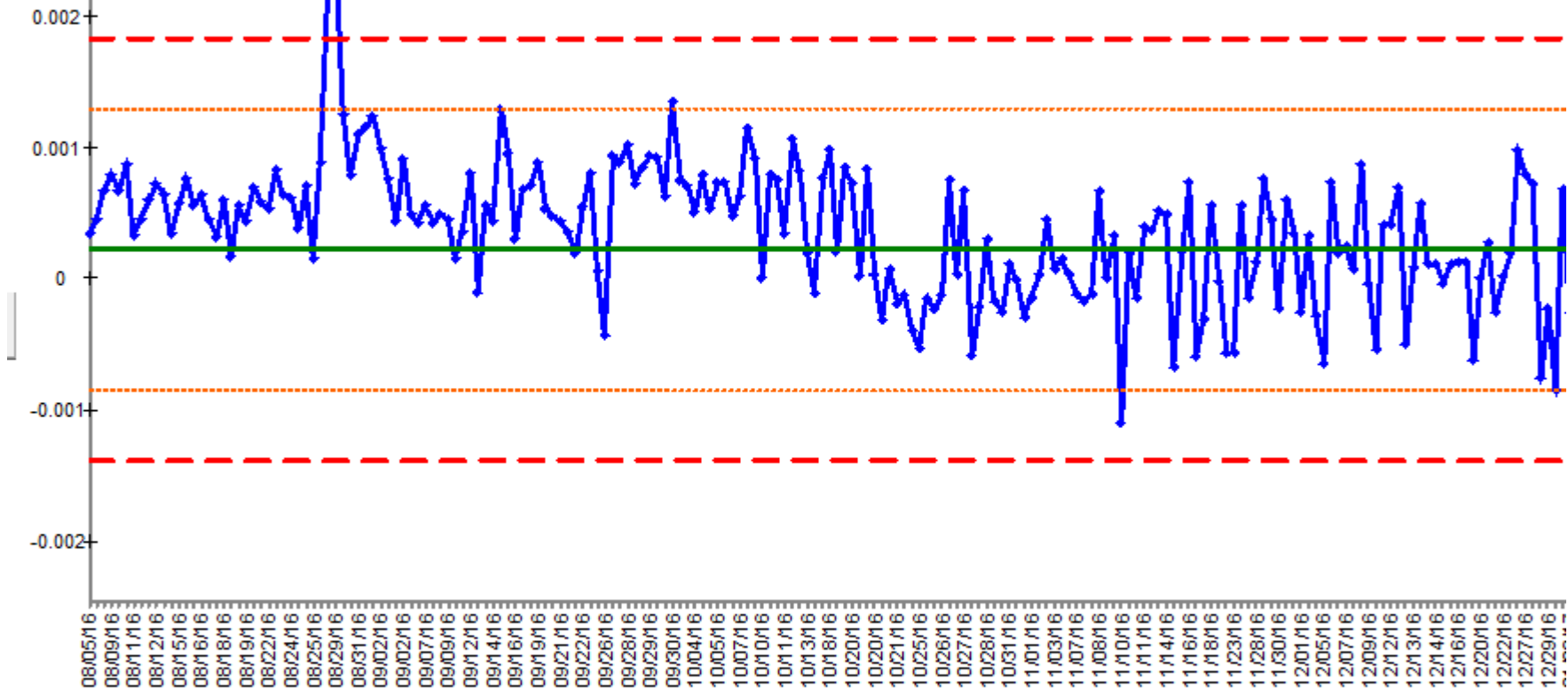
EPA 200.7/200.2 Method Blank Data Control Chart

Chart Data: MBLK— Raw Values

Instrument: ICP203-B

Analyte: Manganese

MDL - V2, 99% Rule Working Well Here

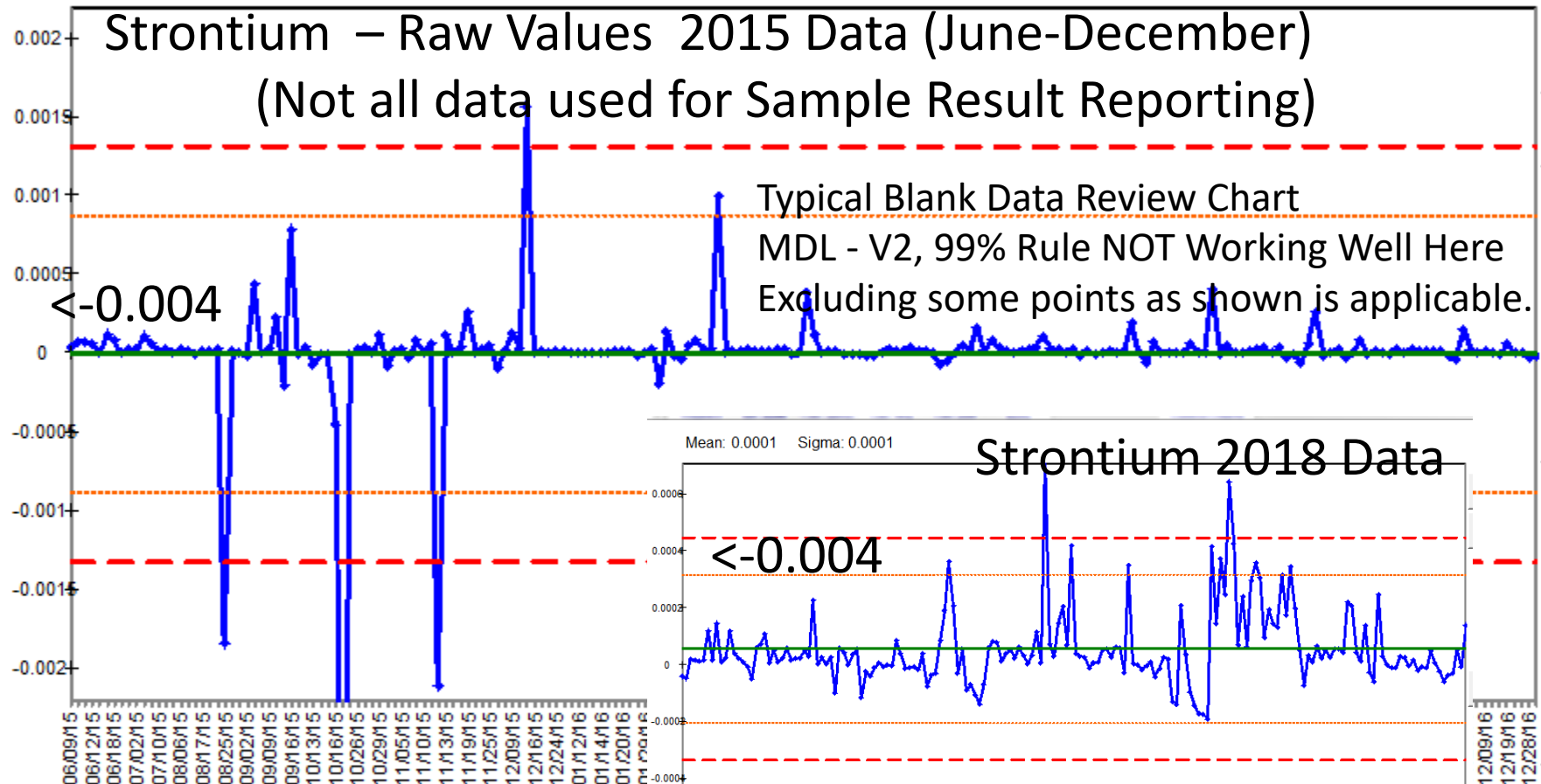


Control Chart Display Options		IsF	Start	End	Mean	StdDev	Units	Skewness	Kurtosis	Minimum	Maximum
☐ Show All	Data Set	☐	8/5/2016	1/4/2017	0.0004	0.0005	mg/L	0.1800	1.5728	-0.0011	0.0011
☒ Show Last	200 of 200	☒	2/1/2016	5/4/2016	0.0002	0.0005	mg/L	-0.7397	0.1562	-0.0013	0.0013

EPA 200.8/200.2

Method Blank Data Control Charts

Mean: 0.0000 Sigma: 0.0004



Control Chart Display Options

☐ Show All

Data Set

Calculate Statistics

☒ Show Last

200

of

200

Control Chart Display Options

☐ Show All

Data Set

Calculate Statistics

☒ Show Last

180

of

180

Start	End	Mean	StdDev	Units	Skewness	Kurtosis	Minim
6/9/2018	7/28/2018	0.0001	0.0001	mg/L	1.9528	5.9782	-0.0
6/6/2018	7/28/2018	0.0000	0.0003	mg/L	-3.3992	15.7188	-0.0

Other Data Trend Evaluations

...from Part 1, 2016 TNI Presentation

- Evaluate Instrument Stability
 - Plot area or area response factors
 - Internal Standard Areas
- Evaluate Calibration Curve Accuracy and Models
 - 2016 NELAC Standard Requirement
 - Plot Response Factors to determine applicable calibration models
- Evaluate each Method QC Type
 - Blanks (MUR 2015 Proposed), CCVs, low-level CCVs, MS/MSDs, Dups, Tune, MDLs, ICSA, etc.
 - Correlate CCVs to LCSs
 - Related to Calibration Frequency
- PT Study results against assigned nominals. PT precision data.
- ...Trends per Method Specifications

SUMMARY

In Support of:

- TNI NELAP Program, Changes in 2016 Pending Standard are complimented.
 - DOD –
 - MDL/LOD/LOQ Guidance
 - TNI Interpretations
- CWA MURs
 - 12 Essential Quality Control Steps
 - MUR MDL V2 – 3-Day/3Batches, Implementation of Blank data review in establishing method MDLs
- Environmental Regulations
- PT Studies
- External Assessor Guidance

AREAS TO BE ADDRESSED

- CWA MUR 2017
 - 600 Series Methods – Update methods to address reviewer comments
 - Allow higher order polynomial calibration models
 - Revise language regarding CCV monitoring with ICV standard
 - MDL V2
 - MDL-Blanks
 - Numeric negative values –Address Single versus Two tail Student T values
 - Quarterly MDL-Spike Calculation
 - Provide Corrective Action Steps Guidance
 - » Recommend performing initial MDL-Spikes and MDL-Blanks for MDL-Quarterly Calculated Results of Concern based on detailed review of method
 - Specify MDL-FINAL Confirmation by LOD Analysis

Thank You for your time!

OTHER AREAS TO BE ADDRESSED

EPA 300 and 400 Series Methods

- Update Methods, remove LDR requirement Language.
- Allow LCS Statistical Control Limits to be used for MS analysis

TNI Standards

- Implement Risk Based QA Process requirements
 - Provide training
- Require MDL/LOD analysis for all methods (if spike is applicable)
- Create General Standardized Application Form using TNI Method and Analyte Codes and suitable to generate Certificates for State Certifications
 - Useful for State reciprocity applications. Standardizes compound naming conventions and method referencing.