TCEQ 2016

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Generating Data of Known and Documented Quality
What Does that Really Mean?

Is the Foundation Sound?

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TestAmerica Inc.

Chemistry Committee Members

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Francoise Chavan, NYC DEP
Eric Davis, Austin WU
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Gary Ward, ORELAP
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TNI proposal to EPA

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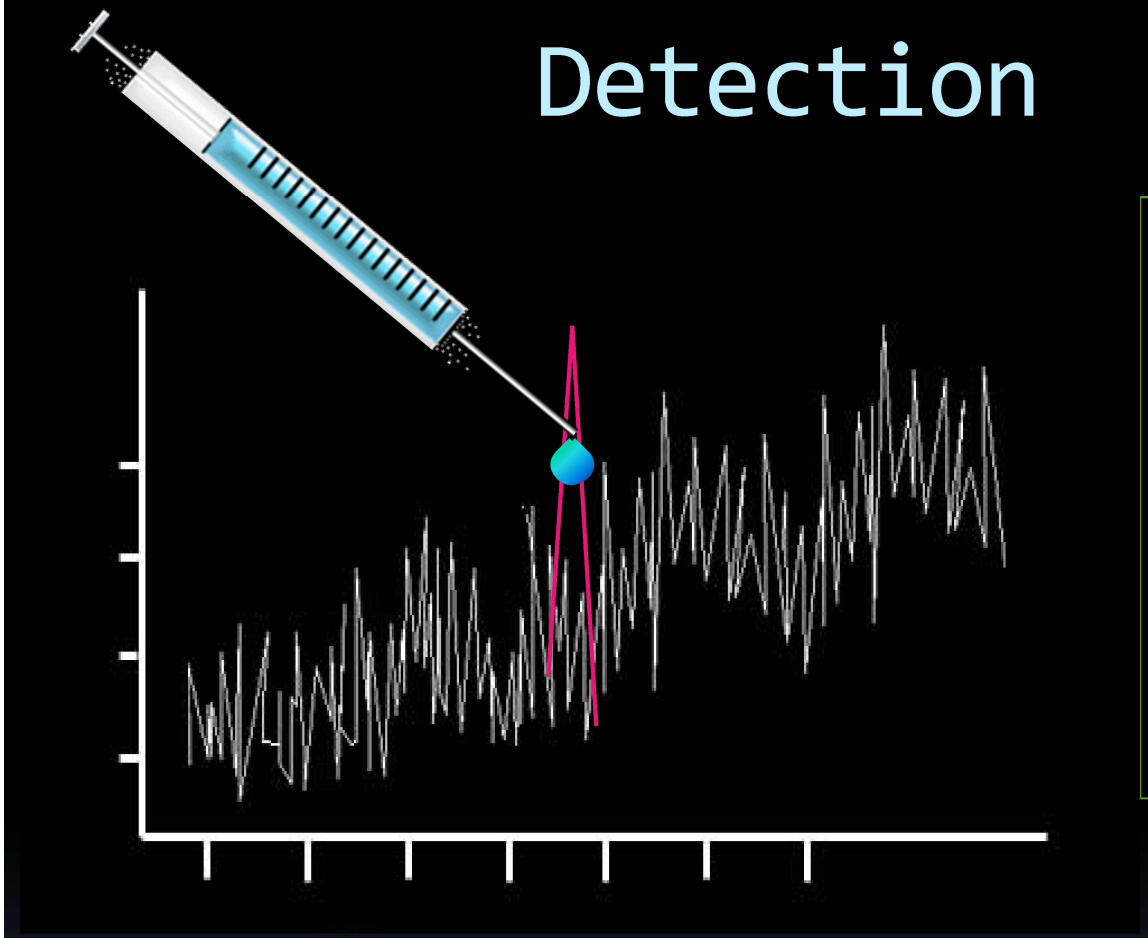
Form an Environmental Measurement Methods Expert Committee chartered to develop consensus standards that will establish requirements for fundamental measurement practices such as **Limit of Detection (LOD), Limit of Quantitation (LOQ), and instrument calibration** to reduce quality system vulnerabilities.

Detection



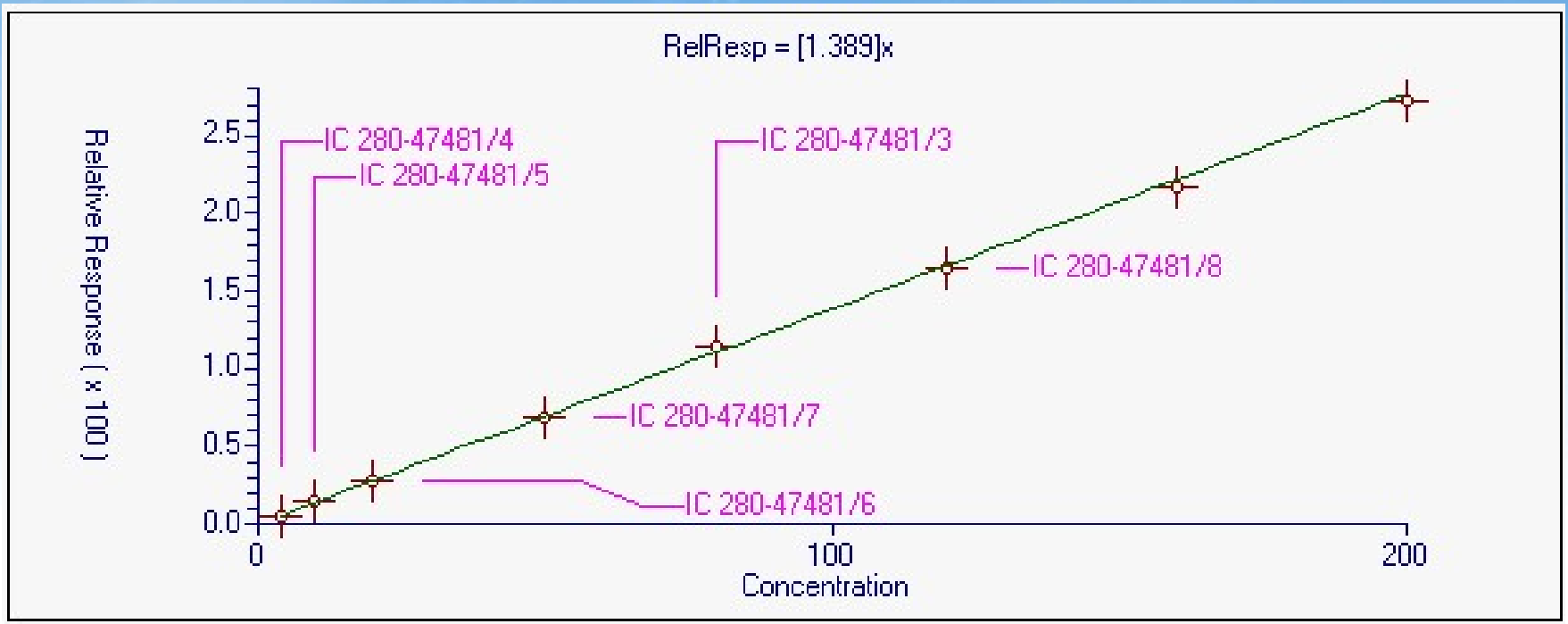
"Detected"

≠

"Any Measurable Signal"

When the signal can be distinguished from noise, then we have detection

Calibration and Quantitation



What does TNI do?

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The mission of TNI is to foster the generation of environmental data of known and documented quality…"

Prepare standards that help ensure that the methods are being performed properly, by people who both know what they are doing and document what they are doing

If the methods are not adequate, develop additional requirements to help ensure the quality of the data

2009 standard on Detection, Quantitation and Calibration

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A quick look at Detection

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EPA had just competed the DQFAC

- Created a bunch or reports and a procedure for determining detection and quantitation limits, but…..ultimately a failure

2012 NEMC

- Who thinks the MDL is OK?
- No one

Conclusion:

We need to do something about detection

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Calibration

Calibration 2009 status

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- TNI standard – essentially, follow the method
- Methods
  - Average response factor or linear regression
  - Preference for unweighted linear regression
- Measures
  - Average response factor – RSD
  - Linear regression – Correlation coefficient (coeff. of determination)

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WTQA '98 - 14th Annual Waste Testing & Quality Assurance Symposium

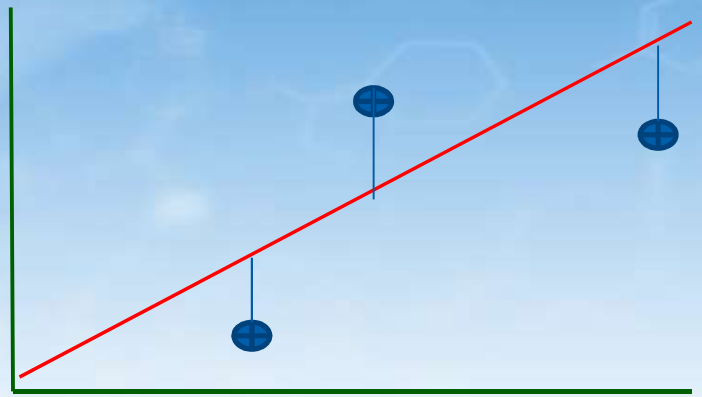
TECHNIQUES FOR IMPROVING THE ACCURACY OF CALIBRATION IN THE ENVIRONMENTAL LABORATORY

Dennis A Edgerley
Quanterra Environmental Services, 880 Riverside Parkway, West Sacramento, California 95605

Average RF minimizes relative error in the calibration

Unweighted regression minimizes absolute error in the calibration

Minimize absolute or relative?



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True	Result	Absolute Error
100	105	5
1	-4	5

True	Result	Relative Error
100	110	10%
1	0.9	10%

We want to minimize relative error

Calibration options

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Unweighted regression
Minimizes the sum of the squares of the **absolute** errors

1/(Conc)^2 weighted regression
Minimizes the sum of the squares of the **relative** errors

Conclusion:

1/(Conc)^2 weighted regression should always be our first choice, assuming we want to minimize relative error

Note: Average RF is the same as linear 1/(Conc)^2 forced through zero

EPA 1631 guidance (2001)

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"An unweighted regression is incorrect for nearly all instruments and analytical systems."
"The calibration included a data point at the Method 1631 MDL (0.2 ng/L). The RSD for the CF/WR approach was 7.8 percent. The coefficient of determination (r2) for the unweighted approach was 1.000, indicating no error in calibration. The reason for the indication of zero error is that the low calibration points are, essentially, unweighted. **Therefore, the unweighted regression is equivalent to a single-point calibration at the highest calibration point. We do not believe that this form of calibration is consistent with the best science."**

OK, unweighted regression is bad

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But:

We have our measuring stick

If we have a bad calibration the correlation coefficient (or Coeff. Of Determination) will tell us that

Right??

IUPAC, 1998

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Guidelines for Calibration in Analytical Chemistry

The correlation coefficient, which is a measure of two random variables, has no meaning in calibration because the values x are not random quantities

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Taylor, Statistical Techniques for Data Analysis, 1990

"The author has seen cases where a correlation coefficient of 0.997 was believed to be a better fit than 0.996 of a 5 point calibration curve. One can even find requirements in quality assurance plans to recalibrate if the correlation coefficient is less than 0.995!"

Charlie's curve that cannot fail

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Conc	Resp
1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
10	0.00
100	10000

Nitrate by 300.0

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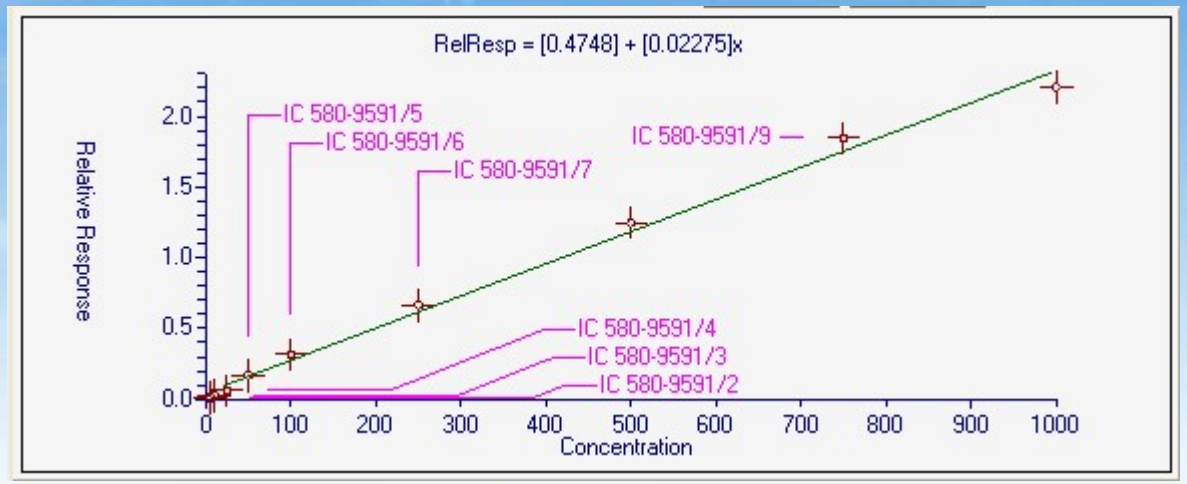
		Linear unweighted	Linear 1/x	Linear $1/X^2$
0.05	2247869			
0.5	20450323			
2.5	1.06E+08			
5	2.23E+08			
10	4.84E+08			
	r	0.999	0.998	0.997

Calibration issues 2007



$r = 0.997$, $r^2 = 0.994$

Calibration Standard Levels

Level	Used	Amount	Area	ISArea	%Error
IC 580-9591/2	☑	5	1348	618332	421.63
IC 580-9591/3	☑	10	3250	647316	198.43
IC 580-9591/4	☑	25	7697	646400	78.87
IC 580-9591/5	☑	50	23729	700099	7.13
IC 580-9591/6	☑	100	47131	748204	17.47
IC 580-9591/7	☑	250	111297	833662	8.93
IC 580-9591/8	☑	500	229185	917698	5.52
IC 580-9591/9	☑	750	371628	1005615	5.43
IC 580-9591/10	☑	1000	499631	1131444	5.11

421.63

198.43

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Correlation coefficient / COD is not an effective measuring stick

Calibration

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We are using a measure for our calibrations that:

1. Should not be used based on statistical principles
2. Does not work in practice

We are commonly using a regression type that

1. Causes huge relative errors at the low end of the curve

Conclusion: We need to do something about calibration

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Questions?