Why we need a standard on calibration

Richard Burrows

- **OVERVIEW INFORMATION**
- **U.S. Environmental Protection Agency Office of the Science Advisor**
- ***Forum on Environmental Measurement***
- **SUPPORT TO DEVELOP MEASUREMENT TOOLS, ACCREDITATION STANDARDS, AND TECHNICAL SUPPORT**

- **2.1 Develop Measurement Tools to Improve the Quality of Method Information, Understanding, and Flexibility**
-
- TNI proposes to:
- 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.
- Develop a Methods Interpretation Request process, comparable to the process already used by TNI for responding to interpretation requests on the TNI Standard.
- Build a Methods Compendium that would contain, or link to, all test methods used for environmental analyses.
- Work with EPA's Environmental Laboratory Advisory Board.

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EMMEC

- Environmental Measurement Methods Expert Committee
  - ~ A TNI subcommittee
  - ~ Specific request in EPA RFP to develop tools for detection, quantitation and calibration

EMMEC Charter

- The objectives are to:
  - ~ create and adopt standards to support a strong technical approach to quantitation, detection and calibration;
  - ~ develop standards that are useable across various EPA and state programs.

EMMEC Members

Richard Burrows, Chair
TestAmerica

Ken Jackson, Program Administrator
The NELAC Institute

Brooke Connor
US Geological Survey

Dan Dickinson
New York State DOH

Tim Fitzpatrick
Florida DEP

Nancy Grams
Advanced Earth Technologies, Inc.

Anand Mudambi
US EPA

John Phillips
Ford Motor Co

Lee Wolf
Columbia Analytical Services

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EMMEC Charter

- Considerations are:
  - developed tools should address: data comparability; flexible methods assessment; statistical assessment; uncertainty;
  - any standard developed should incorporate data quality objectives;
  - effective communication of standards and tools

Issues with Calibration

- Analyze at least 5 points
- RSD, linear regression, quadratic regression
- r, $r^2 > 0.990$ (0.995)
- Periodic mid point verification

Weaknesses of calibration practices in EPA methods

- Some older methods have very little guidance
  - Inject three standards, prepare a calibration curve
- Some methods allow the use of a number of standards that would generally be considered inadequate
- Evaluation of a calibration curve is almost always done with the correlation coefficient or coefficient of determination
- There is little if any guidance on which type of calibration curve to use

Weaknesses of calibration practices in EPA methods

- There is often little verification that results at the high or low ends of the calibration curve are accurate
- Unweighted linear regression is allowed and even preferred
- Methods often do not have controls over deletion of points from a curve
- There is no distinction made between calibration requirements for detected and not-detected analytes
- Only single replicates are required for each level

The curve that cannot fail

Conc	Resp
1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
10	0.00
100	117
slope	0.81564
corr	0.99679
int	4.16667

GC ECD Hexahlorobenzene

	Ave	Lin	Lin1/X	quad
10	26%	14%	3%	4%
20	3%	10%	5%	4%
40	5%	7%	9%	8%
100	12%	3%	3%	5%
200	9%	3%	3%	2%
400	13%	1%	1%	0%
RSE	15%	10%	6%	6%
r^2	0.960	0.999	0.999	1.000

GC ECD TCMX

	Ave	Lin	Lin1/X	quad
5	6%	72%	17%	6%
10	3%	26%	0%	2%
25	8%	2%	10%	2%
50	3%	4%	6%	4%
100	2%	8%	6%	1%
200	11%	2%	6%	0%
RSE	7%	39%	11%	4%
r^2	0.99	0.996	0.995	1.00

GC/MS 2-nitropropane

	Ave	Lin	Lin1/X	quad
2	20%	105%	26%	26%
4	11%	40%	3%	11%
10	12%	5%	17%	5%
20	4%	14%	17%	6%
40	16%	6%	3%	2%
80	31%	2%	7%	0%
RSE	19%	57%	18%	17%
r^2	0.96	0.995	0.988	1.00

GC/MS Indenopyrene

	Ave	Lin	Lin1/X	Lin 1/X2
0.05	26%	39%	10%	1%
0.1	3%	18%	6%	3%
0.2	10%	7%	12%	11%
0.5	0%	10%	10%	8%
0.8	18%	2%	3%	7%
1	20%	2%	4%	8%
RSE	17%	22%	10%	9%
r^2	0.96	0.995	0.993	0.99

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GC PCB

	Ave	Lin	Lin1/X	Lin 1/X2	Quad 1/X2
50	61%	243%	45%	4%	1%
250	11%	9%	21%	17%	4%
500	1%	12%	22%	13%	1%
1000	15%	10%	10%	0%	6%
2000	25%	4%	0%	10%	4%
3000	32%	3%	8%	17%	9%
RSE	34%	122%	28%	15%	7%
r^2	0.79	0.994	0.987	0.98	0.998

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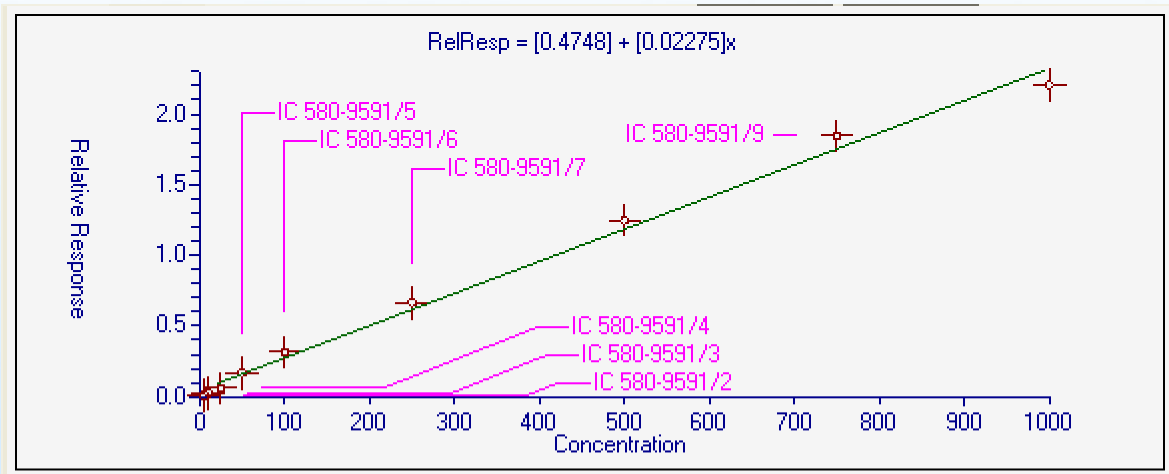
Calibration issues



r= 0.997, r^2 = 0.994 RSE = 179%

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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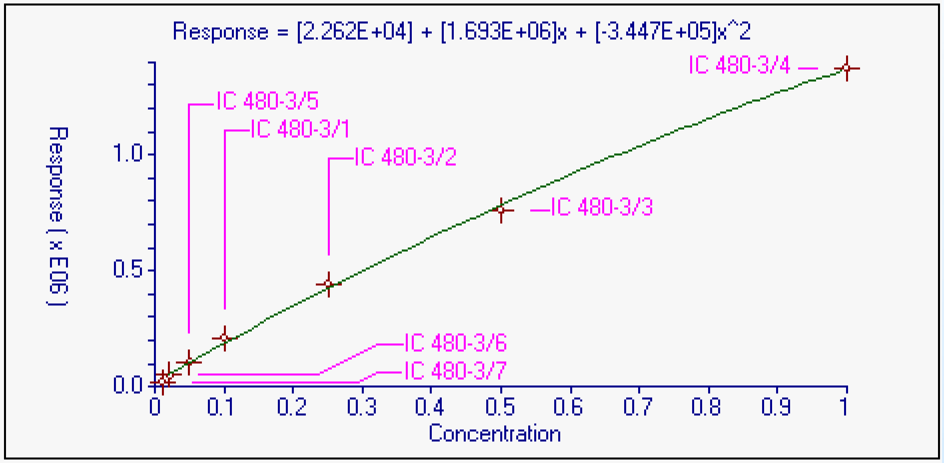

$r^2 = 0.999$

RSE = 63%

Level	Used	Amoun	Area	%Error
IC 480-3/7	☑	0.01	22047	103.37
IC 480-3/6	☑	0.02	49262	21.07
IC 480-3/5	☑	0.05	106980	0.68
IC 480-3/1	☑	0.1	211249	14.05
IC 480-3/2	☑	0.25	442363	4.74
IC 480-3/3	☑	0.5	762496	3.04
IC 480-3/4	☑	1	1374873	0.38

%Error
103.37
21.07

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Solutions to Calibration

- Calculate “readback” for each level
  - Recent drinking water methods
  - Recent SW-846 methods
- Pros
  - Provides an indication of the error introduced at each level
  - Conceptually straightforward
- Cons
  - Lots of numbers!
  - Difficult to compare different curve types
  - Need to be careful with criteria

Solutions to calibration

- RSE
  - ~ Extends applicability of RSD (used for average curve) to all other curve types
- Pros
  - ~ Allows easy comparison of curve types
  - ~ Will indicate failing calibration if any point (high or low concentration) has a high deviation from the curve
  - ~ Can use same criteria as RSD
- Cons
  - ~ Not currently available in most chromatographic data systems

Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures

When a regression curve is calculated as an alternative to using the average response factor, the quality of the calibration may be evaluated using the Relative Standard Error (RSE). The acceptance criterion for the RSE is the same as the acceptance criterion for Relative Standard Deviation (RSD), in the method. RSE is calculated as:

$$RSE = 100 \times \sqrt{\frac{\sum_{i=1}^{n} \left(\frac{x_i - x'_i}{x_i} \right)^2}{n - p}}$$