Collaboration on Calibration

Richard Burrows

Collaboration so far…

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- RSE added to Method 8000 and 600 series
- RSE added to TNI standards
- Relative error added to 8000 series
- Relative Error added to TNI standards

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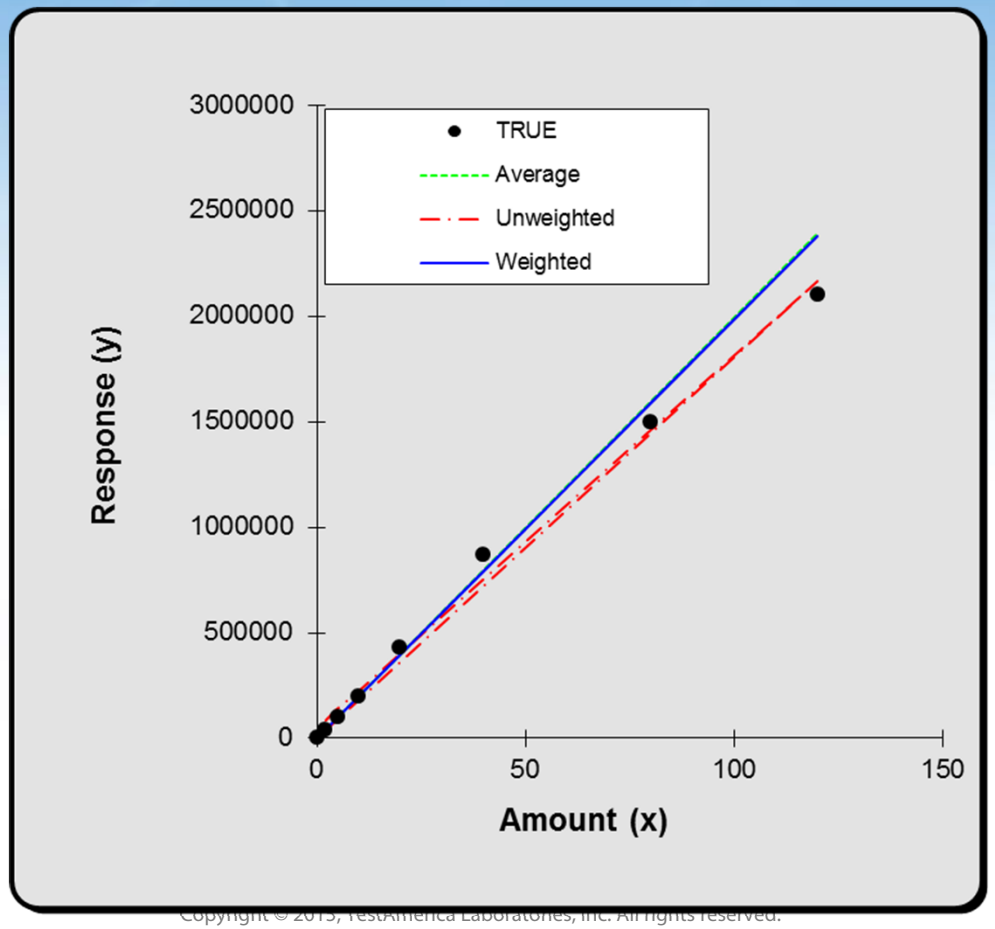
Are we done?

Lets analyze a curve

Criteria: RSD = RSE ≤ 20% r2 ≥ 0.990



Amount	Response
2.00	40000
5.00	100000
10.00	200000
20.00	430000
40.00	870000
80.00	1500000
120.00	2100000

Average

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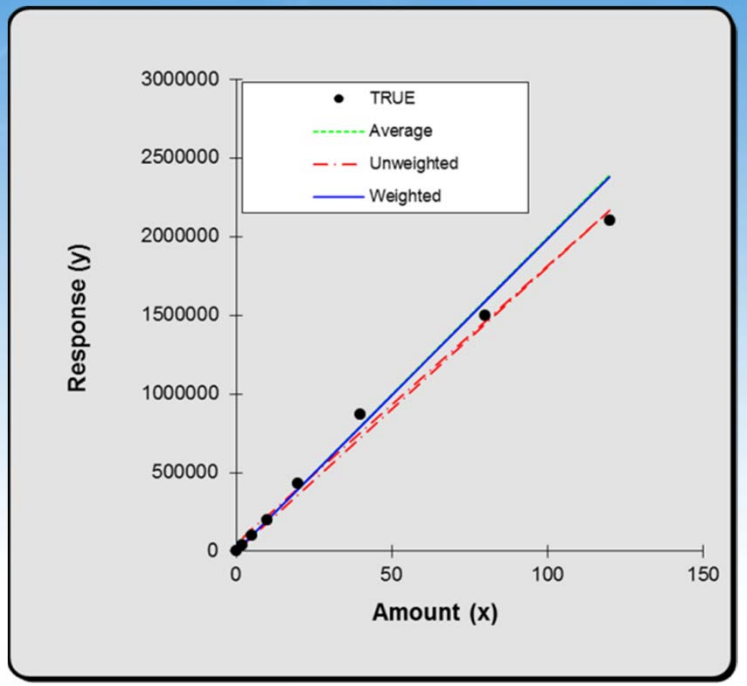
RSD = RSE = 7.4%

- PASS

R^2 = 0.976

- FAIL



Linear $1/X^2$ weighted

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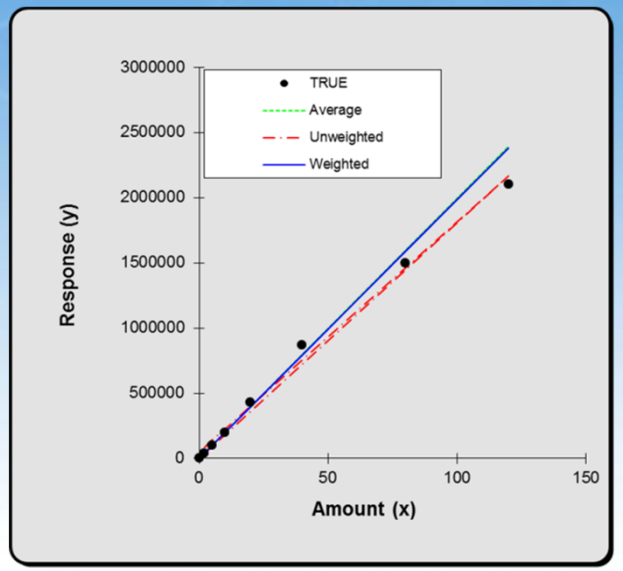
RSE = 8.1%

- PASS

R^2 = 0.975

- FAIL



Linear 1/X weighted

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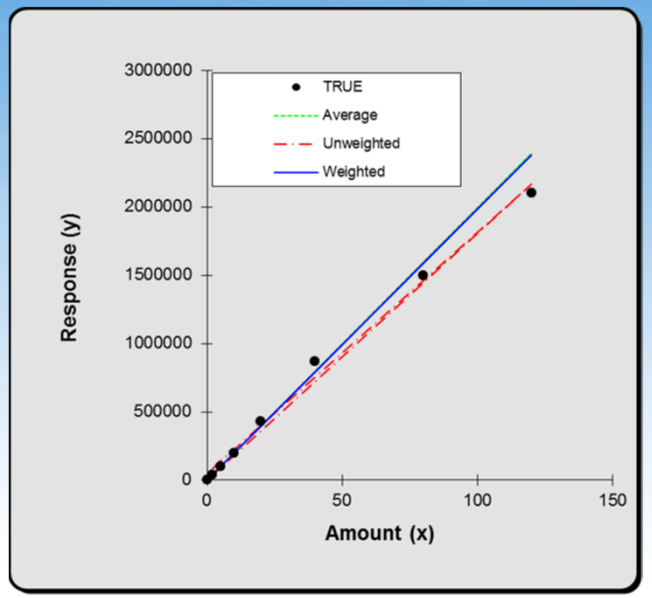
RSE = 12.8%

- PASS

R^2 = 0.989

- FAIL



Linear unweighted

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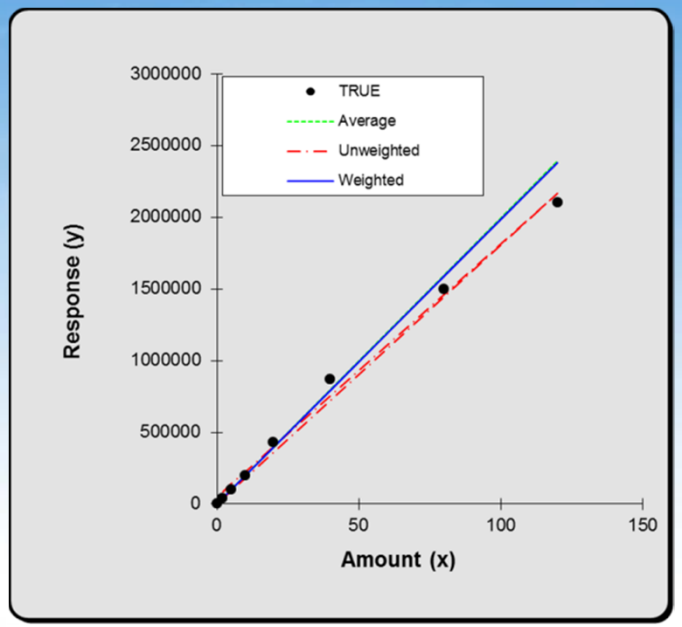
RSE = 64.4%

- FAIL

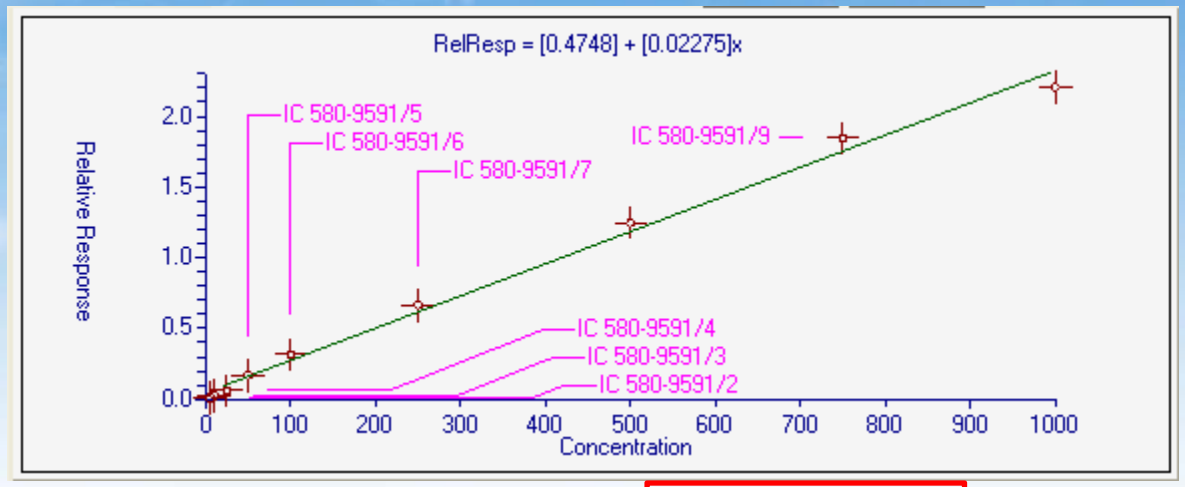
R^2 = 0.994

- PASS



	Average	1/X	$1/X^2$	Unweighted
2	0.36%	17.96%	1.08%	**118.33%**
5	0.36%	3.19%	0.08%	**40.13%**
10	0.36%	1.73%	0.47%	14.06%
20	7.31%	12.01%	7.59%	6.02%
40	8.37%	13.04%	8.74%	13.09%
80	6.29%	0.22%	5.81%	2.66%
120	13.88%	7.14%	13.35%	3.05%
RSE	**7.4%**	**12.8%**	**8.1%**	**64.4%**
R2	**0.976**	**0.989**	**0.975**	**0.994**

Calibration issues



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

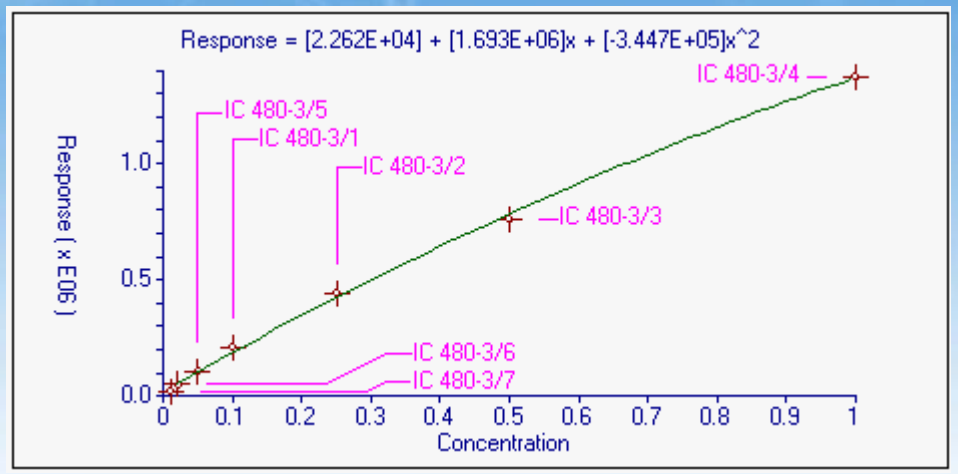
Calibration Standard Levels

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

Dalapon



$r^2 = 0.999$

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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"Very common mistakes in the analytical calibration process are the use of correlation and or determination coefficients…

Evaluation of analytical calibration based on least squares linear regression for instrumental Techniques, Francisco Raposo, TrAC 77, Match 2016, Pages 167-185

Correlation coefficient

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IUPAC, 1998
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

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!"

Correlation Coefficient

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For most applications, and calibration curves in particular, the correlation coefficient must be regarded as a relic of the past

- Meier and Zund, Statistical Methods in Analytical Chemistry, 2000

Correlation Coefficient

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"One practice that should be discouraged is the use of the correlation coefficient as a means of evaluating goodness of fit of linear models"

- Van Arendonk and Skogerboe, Anal. Chem. 53, 1981, 2349-2350

RSE Status

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- RSE adoption should be relatively straightforward because:
  - For the average RF calibration RSE = RSD
  - RSE essentially just allows RSD to be applied to all types of curves, instead of just Average RF
- However:
- Virtually unused
  - May increase after 2016 standards are adopted
  - Needs to be incorporated into major manufacturer instrument software
  - Needs removal of correlation coefficient option??
  - Needs champions

So what is important?

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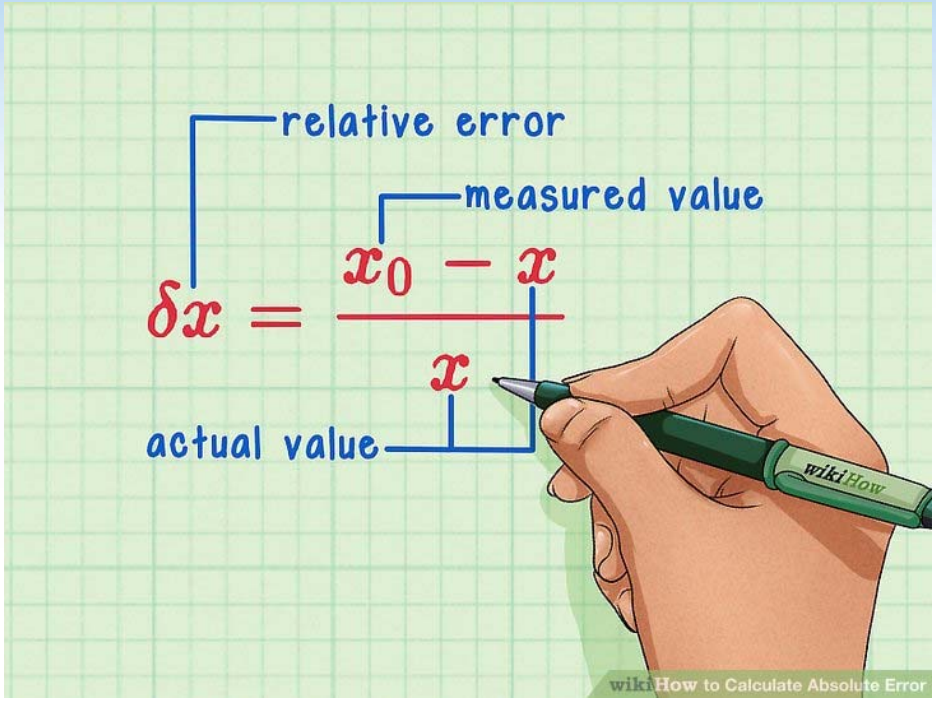
- Measuring relative error
- Do we already have measures of relative error in EPA methods?



Method 524.4

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- Linear or quadratic regression may be used
- Calibration points ≤ MRL must calculate within 50% of true value (Relative Error)
- Calibration points above the MRL must calculate within 30% of true value (Relative Error)
- **No correlation coefficient or coefficient of determination!**

Relative error (Method 524)

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Using relative error of each point is less desirable than RSE, but it is good:

- Measures what is important, relative error
- Consistent with TNI standards
- Consistent for different curve fits

8270E Relative Error

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Average curve fit – RSD (Relative Error)

Linear or quadratic regression

- Has RSE option (Relative Error)
- Recalc at low point 50%, other points 30% (Should) (Relative Error)
- Consistent with method 524
- Unfortunately includes correlation coefficient and coefficient of determination

Just drop them!!

624.1 Relative Error

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Average curve fit – RSD

Linear or quadratic regression

- Has RSE option (Relative Error)
- No recalc
- Unfortunately includes coefficient of determination

Just drop COD and add Recalc!

What Next?

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- Raise your hand if you think calibration is an important part of an analytical chemical method
- Keep it raised if you think that a good measure of whether a calibration is acceptable is important
- Keep it raised if you think a bad measure of calibration acceptability is a problem

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Keep it raised if you will be part of the irresistible force of collaboration that gets rid of the correlation coefficient and coefficient of determination.