The Coefficient of Determination (R^2) vs Relative Standard Error (RSE)

AUSTIN HABICH

FIALAB INSTRUMENTS INC

SEATTLE, WA

PRESENTED AT 2017 NEMC CONFERENCE

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www.flowinjection.com

Introduction – Purpose

- To explain why trusting R^2 could result in inaccurate data
- To introduce a new calibration metric that avoids overlooking inaccurate data
- To illustrate the points above with an example
- Provide recommendations on each technique

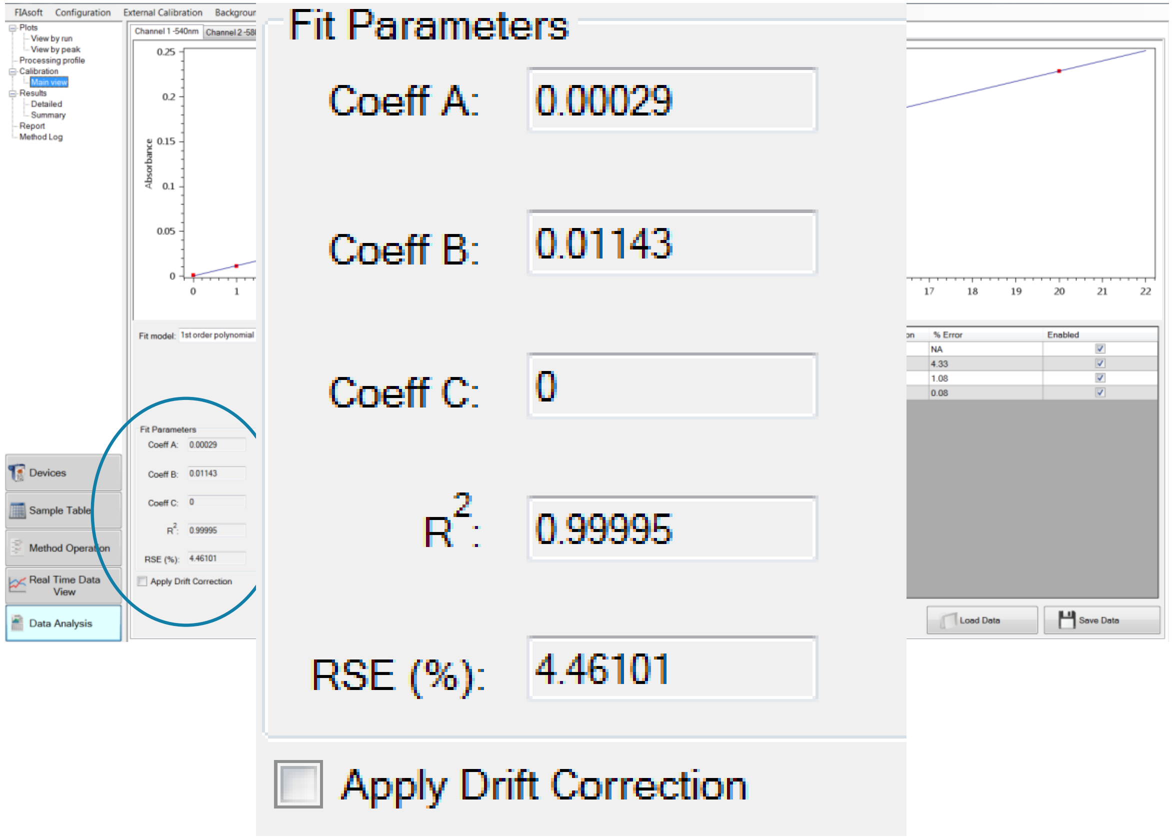
Current Methodology – R^2

- Coefficient of Determination:

$$R^2 = 1 - \frac{\sum e_i^2}{\sum (y_i - \bar{y})^2}$$

  - *where* y_i = known concentration at point i, $\bar{y}$ = average concentration, e_i = error at point i

- Well defined acceptable limits; For example: $R^2 \geq 0.999$

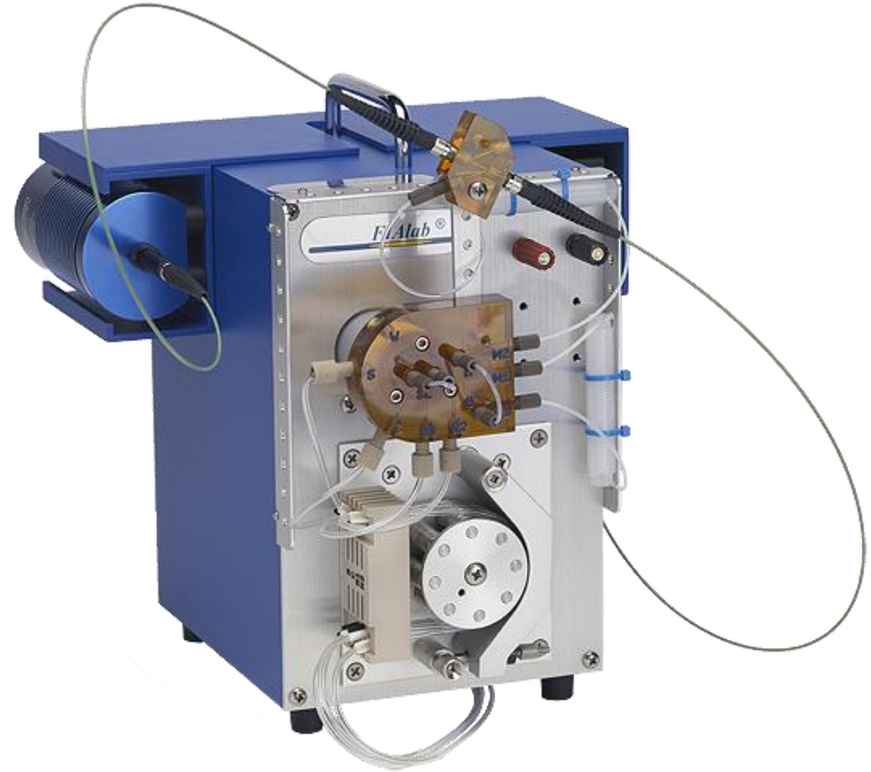


Disadvantage of R^2

- The *magnitude* of error e_i at point i matters

$$R^2 = 1 - \frac{\sum e_i^2}{\sum (y_i - \bar{y})^2}$$

- More concentrated standards have a larger affect R^2

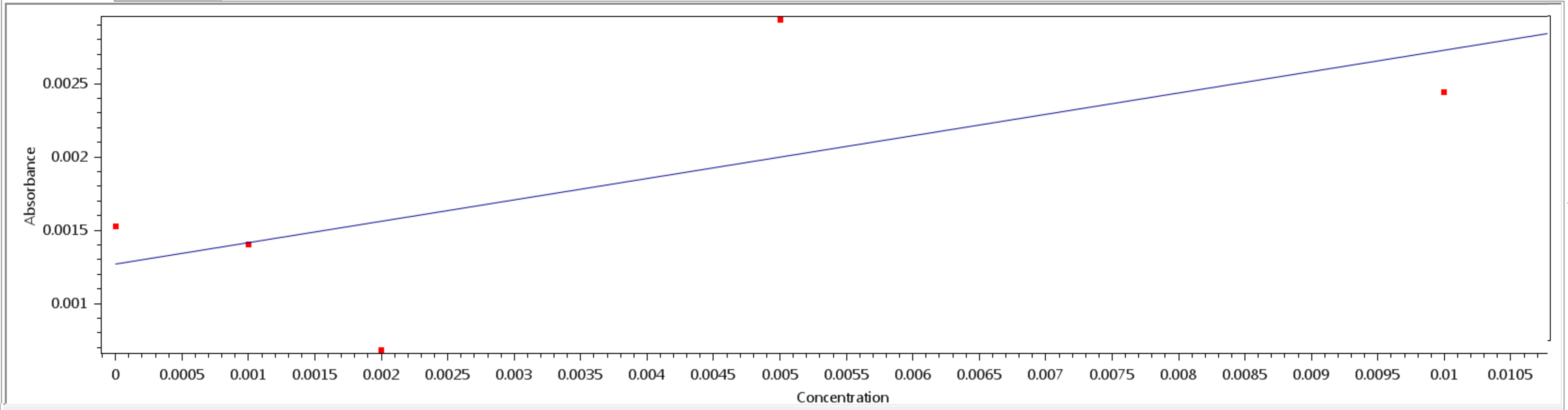


Disadvantage of R^2

Table 1: 20% Absolute Error Comparison

Standard [=] ppm	Error: e_i	Error² e_i^2
1	0.2	0.04
5	1	1
20	4	16

Channel 2 -650nm | Channel 1 -878nm



Fit model: 1st order polynomial

Fit Parameters

Coeff A: -0.00011

Coeff B: 0.21906

Coeff C: 0

R^2: 0.99987

RSE (%): 219.58848

Apply Drift Correction

Name	Peak Response	Known Concentration	Calculated Concentration	% Error	Enabled
0 ppm	0.0015	0	0.01	NA	☑
1 ppb	0.0014	0.001	0.01	589.07	☑
2 ppb	0.0007	0.002	0	80.09	☑
5 ppb	0.0029	0.005	0.01	178.09	☑
10 ppb	0.0024	0.01	0.01	16.39	☑
50 ppb	0.0097	0.05	0.04	10.44	☑
100 ppb	0.0251	0.1	0.12	15.05	☑
500 ppb	0.1097	0.5	0.5	0.28	☑
1 ppm	0.2132	1	0.97	2.63	☑
3 ppm	0.6487	3	2.96	1.27	☑
5 ppm	1.1013	5	5.03	0.56	☑

Load Data | Save Data

Example

	Name	Peak Response	Known Concentration	Calculated Concentration	% Error
▸	0ppm N-NO3	0.0012	0	0.08	NA
	1ppm N-NO3	0.0112	1	0.96	4.33
	5ppm N-NO3	0.0568	5	4.95	1.08
	20ppm n-NO3	0.2291	20	20.02	0.08

- Vary the calculated concentration of the 1 ppm standard, observe R^2
- Vary the calculated concentration of the 20 ppm standard, observe R^2
- Compare the results

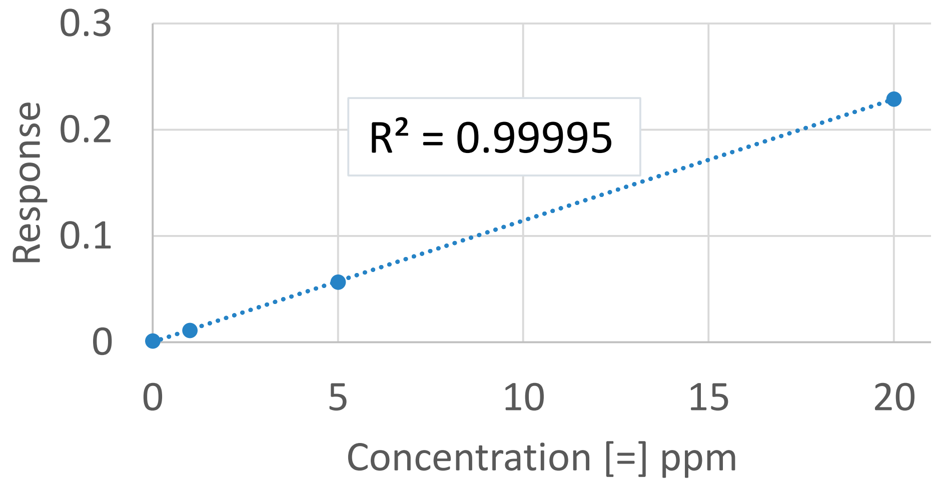


Figure 1: Standard Curve

At 15% error

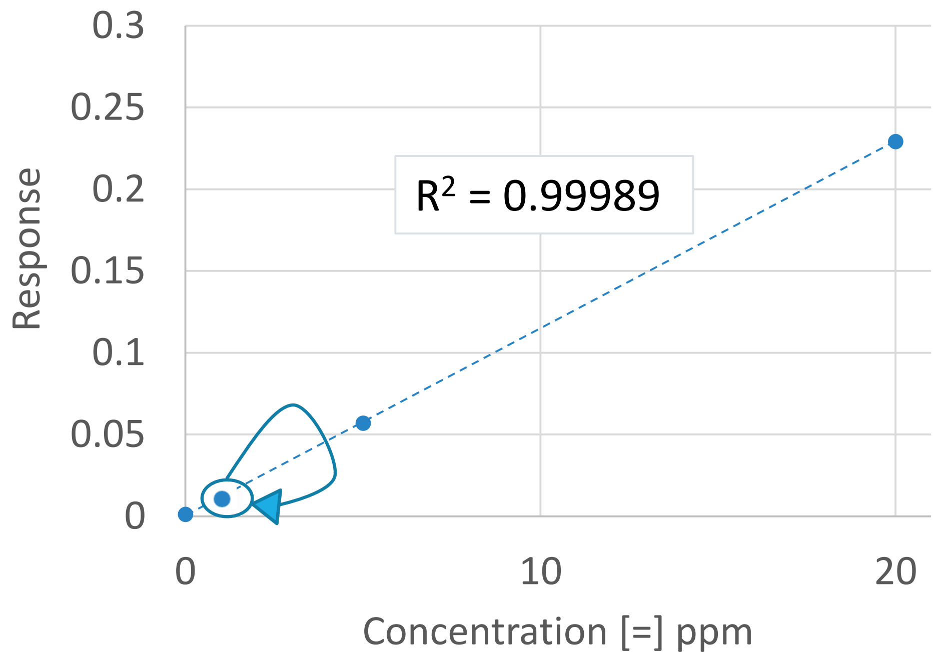


Figure 2: 1 ppm error

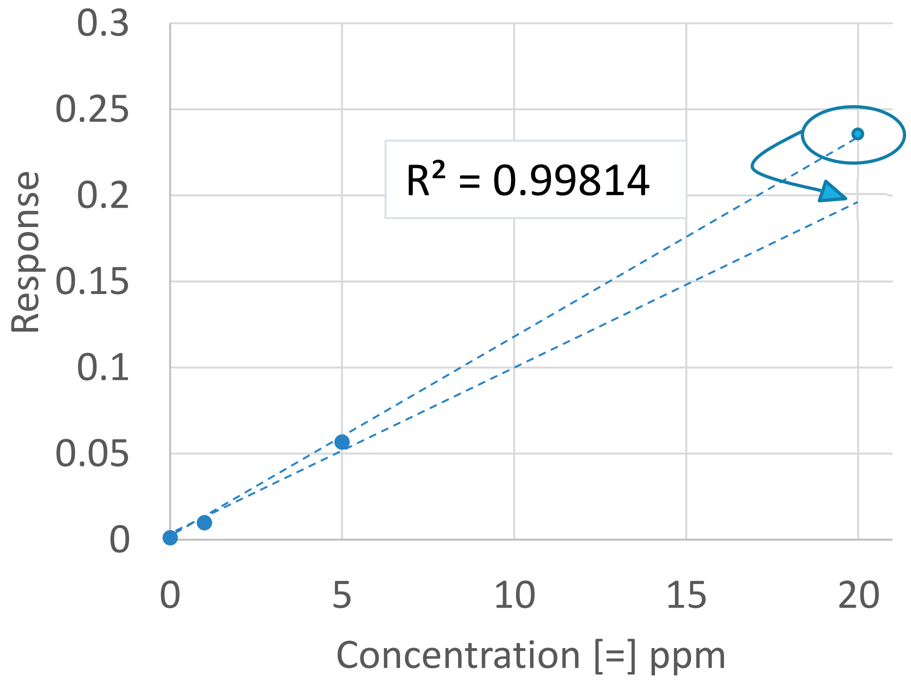


Figure 3: 20 ppm error

At 25% error

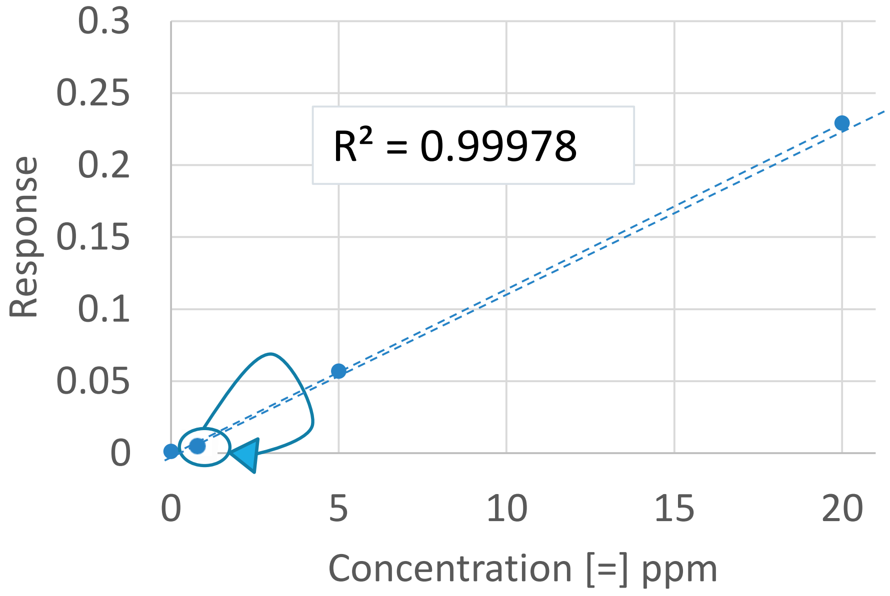


Figure 4: 1 ppm error

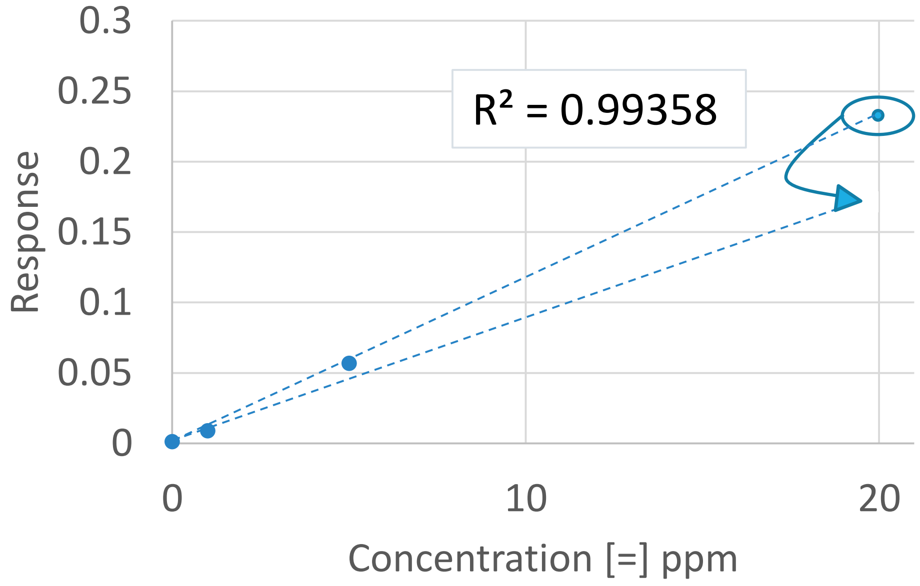


Figure 5: 20 ppm error

At 30% error

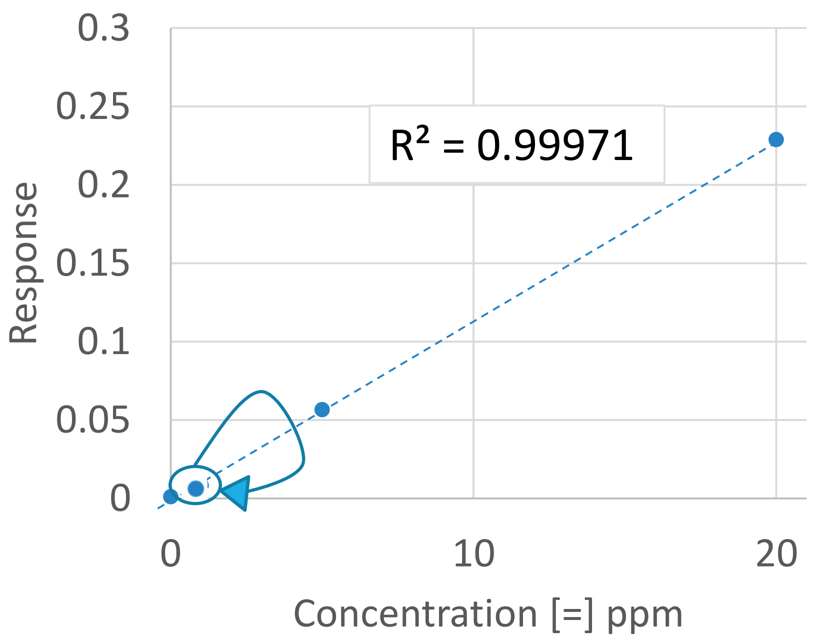


Figure 5: 1 ppm error

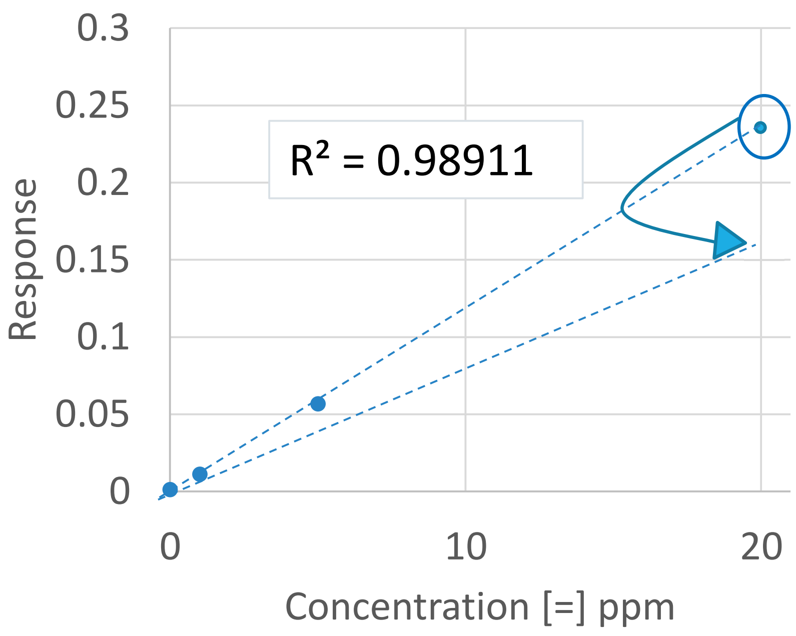


Figure 7: 20 ppm error

Summary of Example

Table 2: 20 ppm vs. 1 ppm R2 Comparison

Absolute error	1 ppm R^2	20 ppm R^2
0%	0.99995	0.99995
15%	0.99989	0.99814
25%	0.99978	0.99358
30%	0.99971	0.98911

Summary of Example

- With the same *relative* error, more concentrated samples have a greater negative effect on the R^2

- R^2 may be deceptive in that, a high percent error of a low standard can still yield a high coefficient of determination

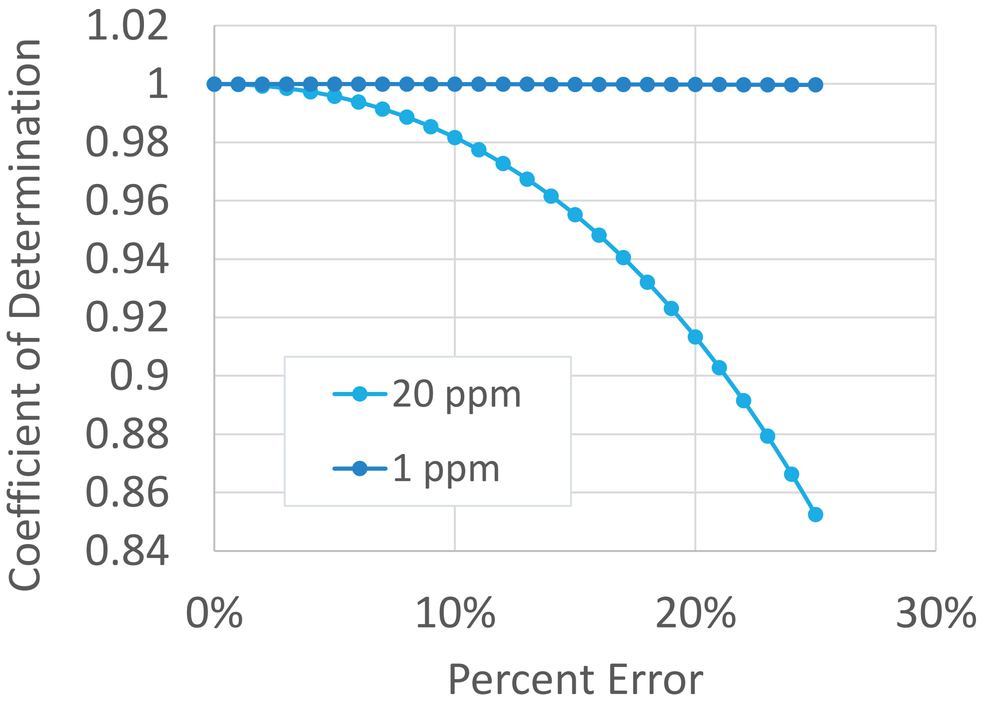


Figure 8: 20 ppm vs. 1 ppm R^2 Comparison

New Technique: Relative Standard Error

- Uses normalized error, so magnitude does not produce bias for concentrated standards

$$\%RSE = 100 * \sqrt{\frac{\sum_i^n \left(\frac{e_i}{y_i}\right)^2}{n-2}}$$

Where

$n = number\ of\ calibration\ points;$

$e_i = error\ at\ point\ i;$

$y_i = known\ concentration\ at\ point\ i$

New Technique: Relative Standard Error

Table 3: Absolute Error Comparison [15%]

Nominal Concentration [=]ppm	*Absolute Error*	*Calculated Concentration* [=]*ppm*	$\left(\frac{e_i}{y_i}\right)^2$
0.1	0.015	0.085	0.0225
5	.75	4.25	0.0225
20	3	17	0.0225

New Technique: Relative Standard Error

- Normalized error reduces bias for RSE
- Concentrated standard's error is normalized by it's concentration value

→ Its error has as much weight as less concentrated standards

- Rule of Thumb for good calibration
  - $Good\ Calibration: RSE < 10\%$

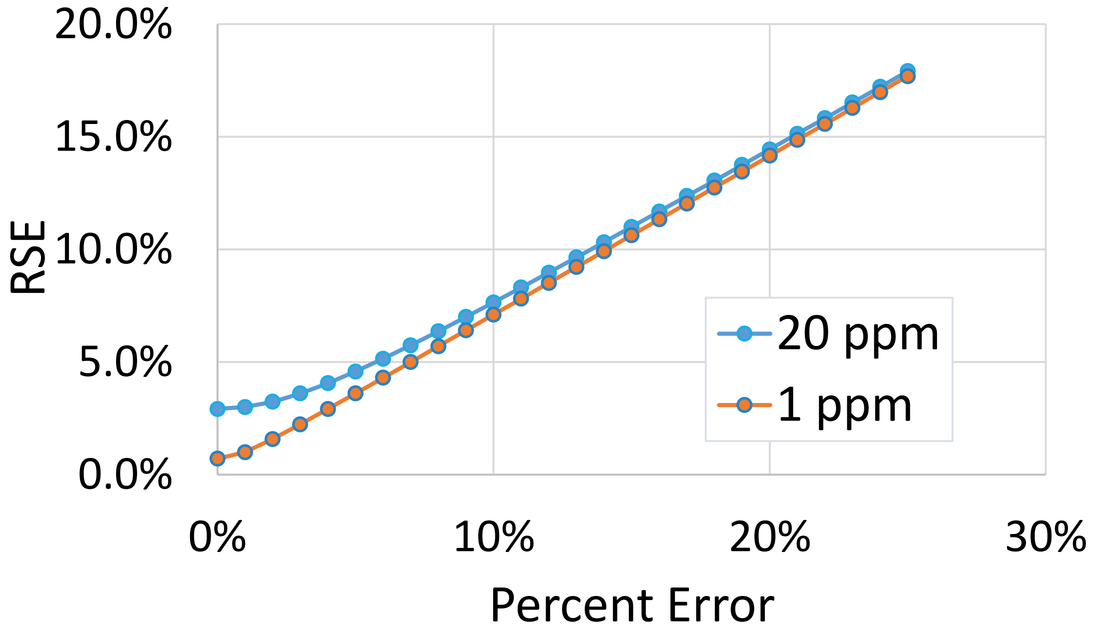


Figure 9: RSE for 20 ppm and 1 ppm variation

RSE / R^2 Comparison

	Absolute error	R^2	RSE
20 ppm Error	0%	0.99995	2.92%
	15%	0.99814	11.00%
	25%	0.99358	17.92%
	30%	0.98911	21.41%
1 ppm Error	0%	0.99995	0.71%
	15%	0.99989	10.63%
	25%	0.99978	17.69%
	30%	0.99971	21.23%

Recommendations

- R^2 heavily weights concentrated standards relative to less concentrated standards of the same percent error

  → A good R^2 may not mean all standards are acceptable

- To avoid this, one of the following actions can be taken:
  - ✓Reduce dynamic range
  - ✓Implement two channels for low and high concentrated standards
  - ✓Observe error of each standard compared to known value

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Conclusion

- RSE *does* normalize error terms to yield a less biased result
- RSE can catch errors in low standards since all error terms are relative to their standards
- Rule of Thumb for good calibration
  - ✓ $Good\ Calibration\colon\ RSE < 10\%$
  - ✓ Observe error of each standard compared to known value

Thank You!

For More Information:

FIAlab Instruments Inc

2151 N Northlake Way

Seattle, WA 98103   USA

sales@flowinjection.com

(206) 258-2290

http://www.flowinjection.com