QA/QC
for
Wastewater Laboratory Testing

WISCONSIN STATE LABORATORY OF HYGIENE

George Bowman
Inorganics Supervisor
State Laboratory of Hygiene

Wisconsin Dept. of Natural Resources

Rick Mealy
Regional Certification Coordinator
DNR-Laboratory Certification

Disclaimer

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Overview

- Why QC?
- What's in it for me?
- QC vs. QA ...what's the difference?
- General Components of a QA/QC Program
- Examples of QC
- Setting up an Effective QA Plan

Quality Contorl

Quality Control is all around us

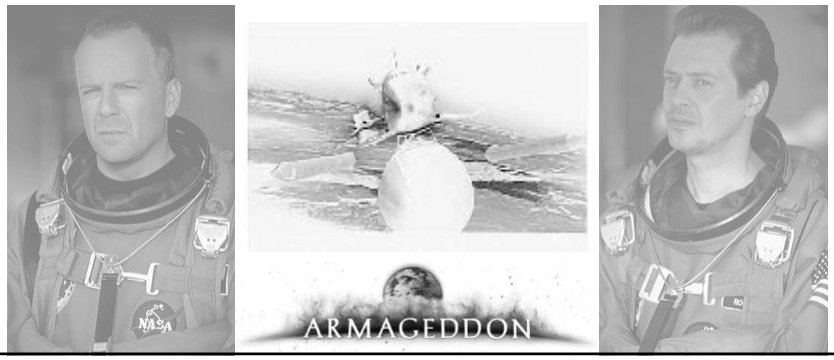
You often don't notice it…

but it's constantly at the root of daily news stories….

…we can see it in the movies or…

…subtley make reference to it in coversation

From the movie Armageddon, listen as Steve Buscemi's character makes a witty reference to QC (or lack thereof):



Why QA/QC?

Fundamental concept applies far beyond laboratory

Would you .... buy a Ford Explorer with Firestone tires?

….take the family to a Milwaukee area Sizzler restaurant?

Our apologies to Firestone and Sizzler…just trying to make a point here!

Common sense

"Checks and balances" is a universal concept. (aircraft)

"To err" is human (double key entry)

Prove data valid mostly through documentation

"He who has the best documentation wins."

Important to data user **and** the laboratory

User wants to make correct decisions....and sleep at night!

Laboratory wants to produce a good product....and pass audits!

What's in it for me?

⇒ Millions spent on plant upgrades based on lab data
(Consider the plight of plant designed and built using inaccurate flow measurement data that is later determined to be undersized)

⇒ Needed to maintain lab certification/registration

⇒ Quality data required to show plant functioning properly

⇒ Policy and guidelines promote uniformity

⇒ Decreased learning curve for new employees

⇒ Fewer repeated analyses

⇒ And.....?

⇩ **Better data can result in reduced NR 101 fees**

QA vs.QC

QC

Specific
technical, operational
measures or activities
to ensure lab data quality.

QA

General
management function
to ensure data quality
relies on:

- documentation and establishment of QC protocols,
- **evaluation** and summarization of their outcomes

QA? QC? What's the Difference?

	QC	QA
100 mg weight = 83 mg	✓	✗
spike control limits 90-110%	✓	✓
barometer reads 28.4 inches	✓	✗
no spikes for ammonia, TP	✗	✗
TP spike limits -275 to 3047%	✓	✗
TSS oven temp. kept 180 ± 1°C	--	✗
Filling out benchsheets in advance *dates and names in advance of collection*	✓	✗

Components of a good QA Program

The foundation

- Good facilities and equipment
- Training of personnel
- Operation plan (assigned responsibilities)
- Methods documented and followed

The structure

- Rigorous QC procedures
- Precision
- Accuracy
- Documentation to ensure traceability

A strong structure requires the use of the right materials.....

Types & Uses of QC Samples

Blanks

- Laboratory reagent water.
- Used to verify the absence of contamination in the lab.
- Particularly important in phosphorus and ammonia testing.

Known Standards

- Used to verify calibration curve accuracy, or
- absence of bias in laboratory procedure (vs. matrix-effects)
- best if these are prepared from a different standard than is used for calibration standards.

Replicates

Used to measure precision - the ability to reproduce your results.
You got it right once, but can you do it again?

Types & Uses of QC Samples

Spikes

Used to evaluate bias (*or accuracy*)
(i.e.., the recovery of the analyte from the specific sample matrix).

If you only get 25% spike recovery,
.....and your sample concentration is close to a permit limit
....isn't it likely the permit limit has actually been exceeded?

Reference Samples

- Annual requirement
- "Show me you can do this test right"

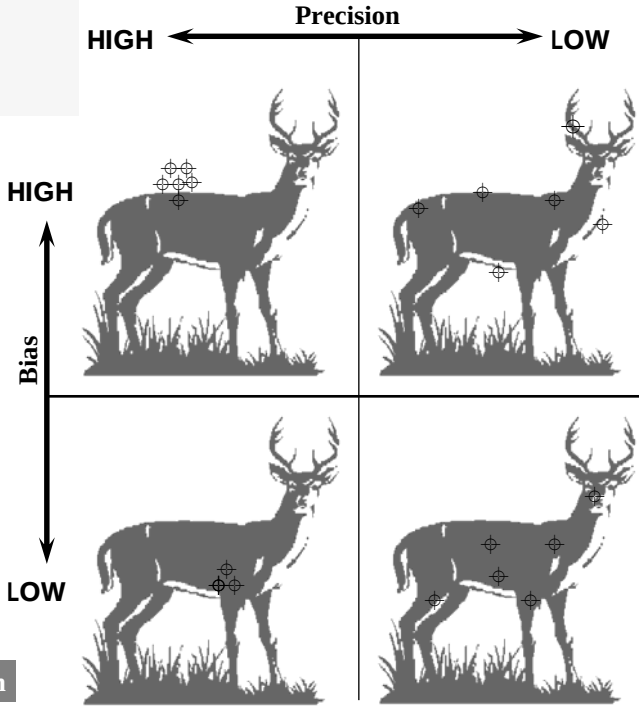
x

Blind Standards

Same as reference samples, but more timely.

But the materials must be used correctly to serve their purpose: precision and accuracy

& Precision Accuracy



Accuracy (Bias)
How close you can get to the true value.

You want LOW bias or HIGH accuracy
(*bias is not a good thing*)

Precision
Reproducibility of the method. The ability to get the right answer - again

You want HIGH Precision

Precision & Accuracy

Pitfalls of Poor P&A

☹ Report results that violate discharge limit... (when they actually didn't!).

$ Increased NR 101 fee$.

Periodic, unexplainable limit violations.

Bring overall ability to operate plant into question.

Setting Up an Effective QA Plan

- ✓ **Standard Operating Procedures (SOPs) should be available for anything not self-explanatory**

  Ex. How do you clean the phosphorus glassware?
  Essentially, if someone unconnected to the lab were to perform this task, what guidance would they need to do it?

- ✓ **You can simply reference SOPs, rather than including them in your QA Plan**

- ✓ If you don't do it, DON'T include it in the QAP.

Many QA Manuals are merely loaded with marketing "fluff" that doesn't say much

QA Plan "Don'ts"

DON'T allow your QA Manual to read like ....

The "baffle them with really serious, business-type words" approach

> Quality Assurance is a systematic design plan incorporating a number of related laboratory aspects.

We know what QA is, but it's too complicated to explain here.

.....

The "We do some really high-tech stuff here" approach

> Accurate and precise analytical data can only be realized by systems that are capable of comparing the response of a real world sample to the response of a known standard.

First you have to calibrate.

Setting Up an Effective QA Plan

- Tables are better than lots of text!
  - ✓the old "a picture is worth 1000 words" concept
  - ✓Tables FORCE you to be brief

3 rules for building a QA Plan by tables

What am I looking at? (parameter)

What am I looking at it for (criteria)

What if it doesn't meet specifications? (Corrective Action)

Sound easy enough? Let's see some real-life examples.....

Setting Up an Effective QA Plan

Evaluating?	Criteria	Corrective Action
Method Blank	Below LOD	1) Identify source 2) Correct & Reanalyze 3) or Qualify data
Known Standard	Within 90-110%	1) Check prep. data 2) Re-make & re-analyze 3) Make new curve
Matrix Spike	Within Control Limits (80-120%)	1) Re-make & re-analyze 2) Analyze known std. 3) Qualify data

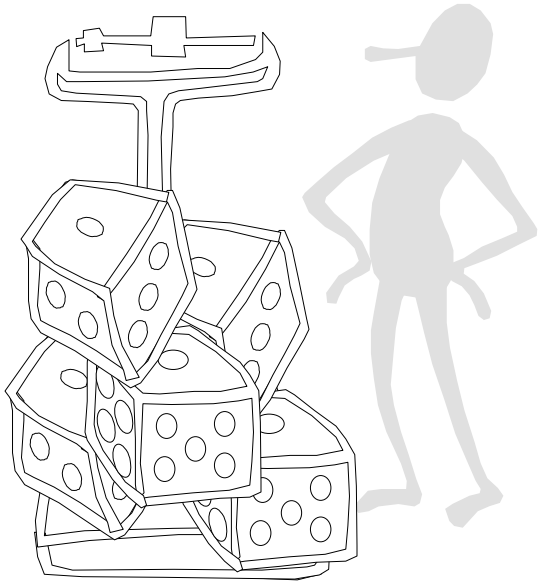
QA Plans - The Bottom Line

Brief	**- NOT -**	volumes
Realistic	**- NOT -**	marketing "fluff"
Guidance	**- NOT -**	Philosophy
Decision trees	**- NOT -**	generic options
Reference	**- NOT -**	paperweight
Tables	**- NOT -**	text

Quality

~~Contorl~~ *GTB 9/19/2000*

Cont**ro**l



Calibration

Calibration Issues

- Initial vs. continuing calibration
- How many standards to use?
- To include...or not to include (a blank)?
- Processing the data
  - » internal calibrations
  - » graph paper
  - » linear regressions
  - » software
- Evaluating a calibration
  - » visual
  - » statistical
  - » analytical

Calibration - Initial Considerations

Calibration Curve Frequency-Best Run Daily

- For best results, should be run daily.
- Alternatively, a "full" calibration can be analyzed initially and verified (with one or more standards) each day of analysis.

Use a minimum of 3 standards

MUST be constructed using at least 3 standards and a blank.

> *NR 149.13 (3) (b) … A calibration shall consist of at least 3 standards and a blank except as allowed in approved methods using ion selective electrodes or inductively coupled plasma.*

To include...or not to include (a blank)?

Rule of thumb:

if you can adjust your instrument to read zero with a blank, then include the blank in your calibration curve.

- Including a blank is generally appropriate for colorimetric procedures

Calibration - Other Considerations

Define your calibration range properly

- Range should be appropriate for the samples being analyzed
  (i.e. don't calibrate from 1- 5 mg/L if your samples fall between 0.05 - 0.5 mg/L).
- Better results are obtained when sample response is close to response of standards used to establish the calibration curve.
- Optimal results ==> when sample results fall near the mid-point.
- Standards should also be evenly spaced.

  1, 2, and 500 are NOT good levels for a calibration

- Whenever possible….bracket samples with calibration standards.
- Low standard not more than 2 to 5 times the LOD (best is = LOQ).

Calibration Data Processing Options

Pre-programmed calibrations	Linear regressions
Graph paper	Software

- Use of pre-programmed calibrations is <u>unacceptable</u>
  - Laboratory must generate its own standard curve.

NOTE: *A manufacturer's claims that their method is "EPA-approved" <u>does not</u> mean that the approval extends to pre-programmed calibrations.*

- Hand drawn curves make traceability virtually impossible
  - Significant variability in how the <u>size</u> of the graph constructed
  - Significant variability in how the <u>scales</u> of the graph are constructed
  - Significant variability in <u>how any individual draws the "best fit"</u> line
- A standard procedure can eliminate sources of variability.

Regardless of technique used, it is critical to <u>evaluate</u> the calibration to ensure that is is valid

Calibration - Hand Drawn Graphs

Calibration exercises

1. Graph paper

Make a calibration graph from:

Calibration Data	
mg/L P	Abs.
0	0
0.1	0.051
0.5	0.25
2	0.72
5	1.24

....then

Find Concentrations for these <u>Absorbances</u>

0.118
0.531
0.770
0.853
1.092

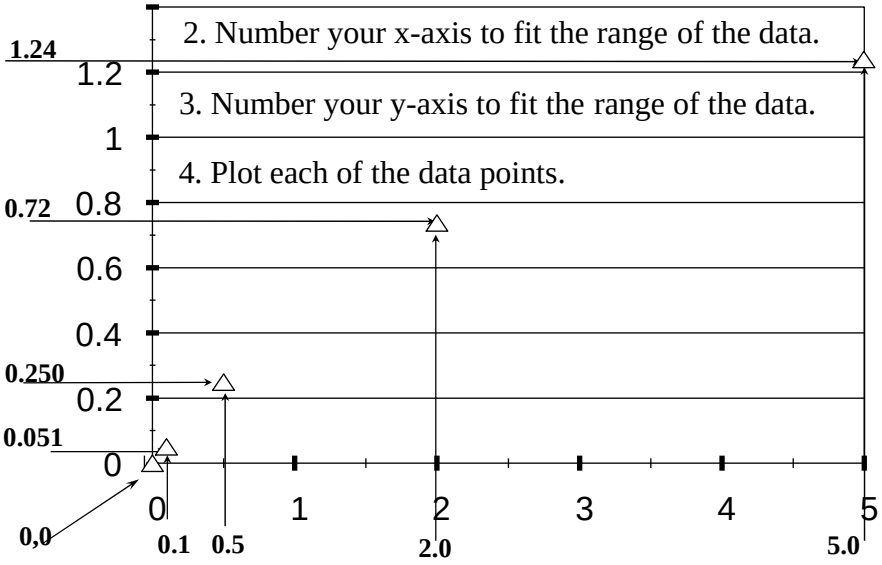
Calibration - Hand Drawn Graphs-2

1. Draw the X and Y axis (graph frame)

2. Number your x-axis to fit the range of the data.

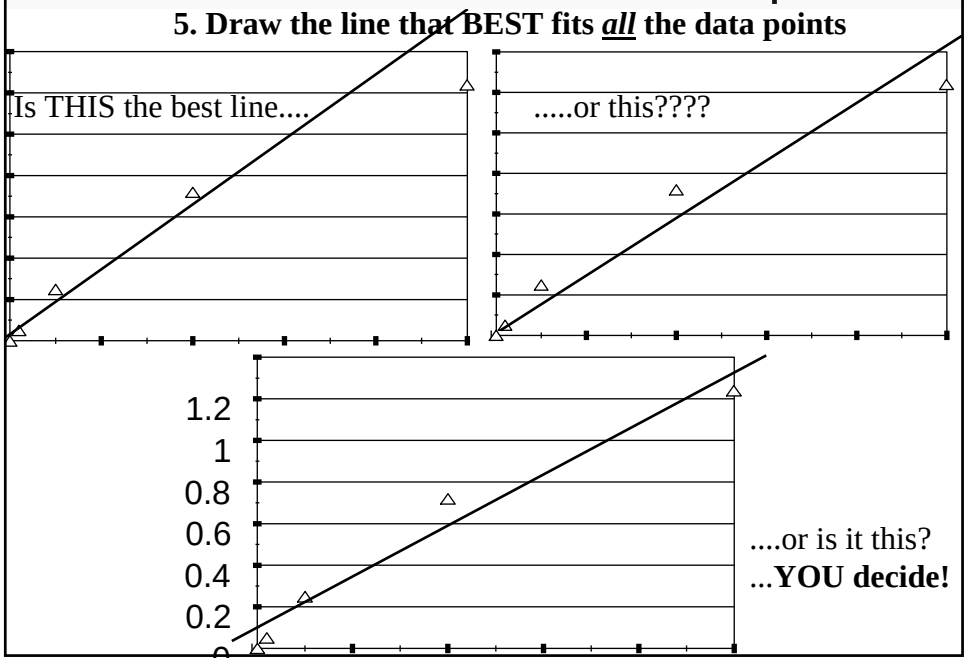
3. Number your y-axis to fit the range of the data.

4. Plot each of the data points.

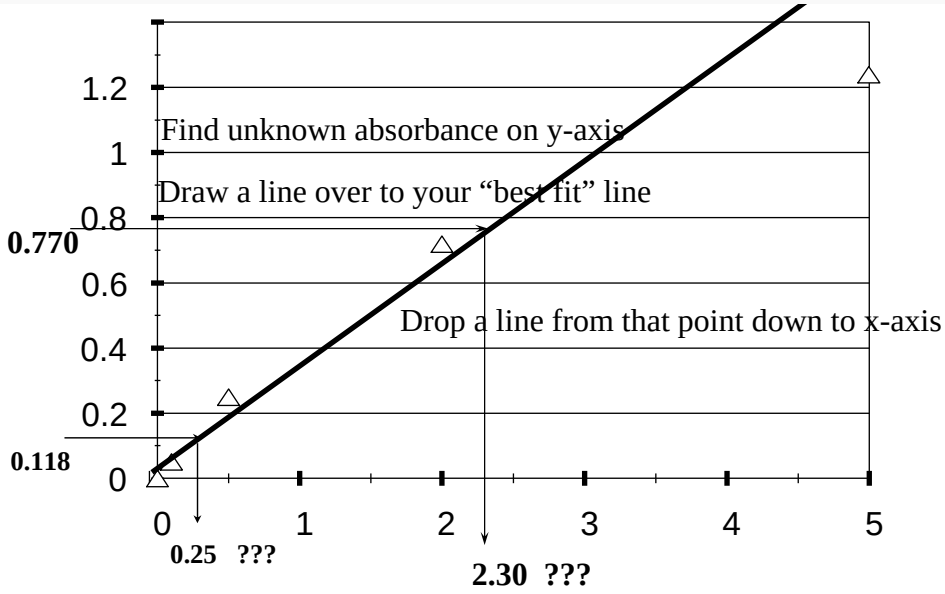


Calibration - Hand Drawn Graphs-3

5. Draw the line that BEST fits *all* the data points



Calibration - Hand Drawn Graphs-4



Calibration - Hand Drawn Graphs-summary

Observations

Some prepared graph landscape vs. portrait

Some used the whole page, others just part of the page

Quite a bit of spread in the data....range of 1 ppm or more

Some read to nearest 0.01 ppm; others to nearest 0.1

Food for thought....

What if your permit limit is right about 1 ppm?
Should the line pass through the origin (0,0)?
How different would a linear regression be?

Calibration - Linear Regression

Calibration exercises
2. Linear Regression

Calculate a regression line from:

Calibration Data	
mg/L P	Abs.
0	0
0.1	0.051
0.5	0.25
2	0.72
5	1.24

....then

Find Concentrations for these Absorbances

0.118
0.531
0.770
0.853
1.092

Sharp EL-520L basics

Basics

- MODE button: **0** = basic calculator, **1** = mean & SD, **2**= regression
- 2nd F button (yellow, upper left of calculator).
- **2nd F** and **DEL** button clears memory...do this several times to be sure!
- STO button: adds the "X" component of an XY data pair
- M+ button: adds single datum or 2nd of a data pair to memory.
- RCL button: think "Re-call"; retrieves information.
- ****You may want to use a pen or pencil to push buttons!****

- Calculator instruction sheets include instructions on how to turn the calculator off.
- Don't need to do this now...but you should be know how to do it if you need to.
- Will automatically shut-off after about 10 minutes if not being used.

Sharp EL-520L - Entering Regressions

Calibration Data

mg/L P	Abs.
0	0
0.1	0.051
0.5	0.25
2	0.72
5	1.24

Calculator steps

Set Mode to "2": MODE 2

Clear the registers: 2nd F DEL

Enter 1st data pair: 0 STO 0 M+

Enter 2nd data pair: 0 • 1 STO 0 • 0 5 1 M+

Enter 3rd data pair: 0 • 5 STO 0 • 2 5 M+

Enter 4th data pair: 2 STO 0 • 7 2 M+

Enter 5th data pair: 5 STO 1 • 2 4 M+

Sharp EL-520L - Regression Info and Sample Calculations

Obtain the calibration evaluation information

✓ Get the Correlation coefficient..: RCL ÷ r = 0.982442272

✓ Get the Slope.....: RCL) b= 0.244713124

✓ Get the Intercept: .....: RCL (a = 0.080236051

Converting a sample absorbance to concentration

Absorbance = 0.118: 0 • 1 1 8 2nd F (**0.154**

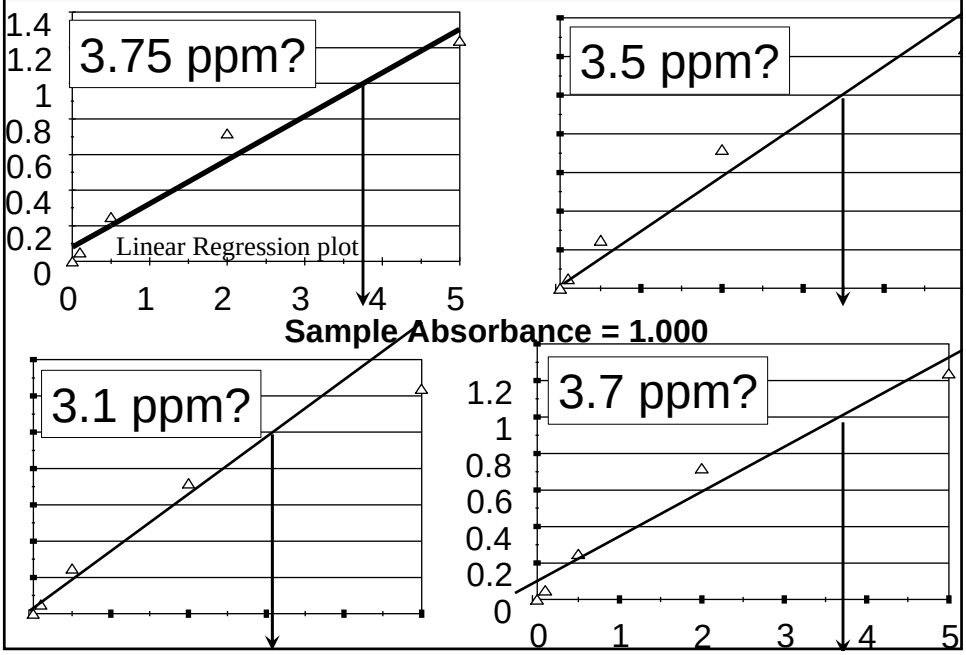
Absorbance = 0.531: 0 • 5 3 1 2nd F (**1.842**

Absorbance = 0.770: 0 • 7 7 2nd F (**2.819**

Absorbance = 0.853: 0 • 8 5 3 2nd F (**3.158**

Absorbance = 1.092: 1 • 0 9 2 2nd F (**4.134**

Linear Regression vs. Hand-Drawn



Calibration Evaluation Tools

Mandatory

Ongoing calibration checks

Optional

Visual

Slope, Intercept, Correlation coefficient (if using linear regression)

Linearity check (response factors)

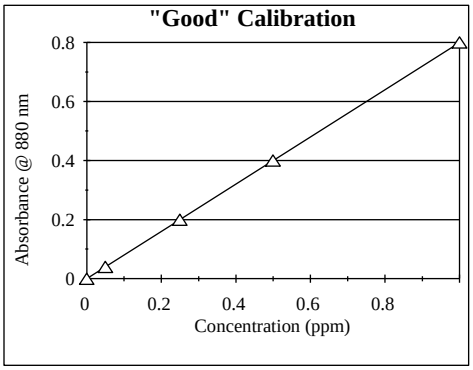
Residual analysis ("*back-calculation*")

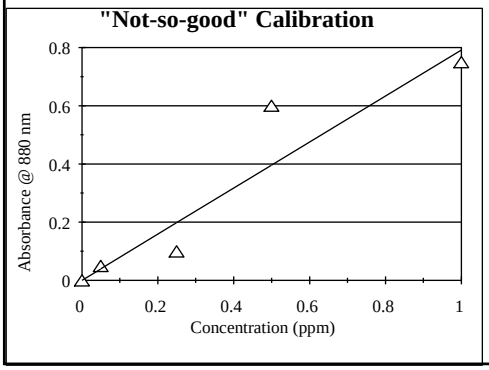
★★★ **While these tools are not strictly required…** ★★★

1) They are critical in obtaining a valid calibration
2) Often, calibration data will pass one or more, but not all of these checks

Calibration Evaluation - Visual Method

Simple Visual Evaluation
Data points should very closely fit the resultant calibration line.





The Value of Regression Coefficients

Value of the Slope (b)
- With electrodes, helps tell condition of the electrode (-54 to -60)
- Can keep records to show when the analysis is changing

Value of the Intercept (a)
- Represents the concentration associated with NO (0) response
- Thus gives an approximation of detection limit
  if your intercept exceeds your LOD, there may be contamination

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The ONLY downside to using a calculator vs. a spreadsheet program is that you do NOT get the visual evaluation power afforded by charting the data and regression line.

Calibration Evaluation - Correlation coefficient

If using a linear regression, the correlation coefficient "r" provides a measure of the acceptability of a particular calibration curve.

- " r " = complex mathematical equation
- Values between 0 (no correlation) and 1 (perfect correlation).
- Correlation coefficients can be obtained using:
  - any scientific calculator with 2-variable statistics capability
  - most spreadsheet programs, e.g., Excel, Lotus, QuattroPro

BOTTOM LINE: "r" *SHOULD* be 0.995 or greater

$r^2 \neq r$

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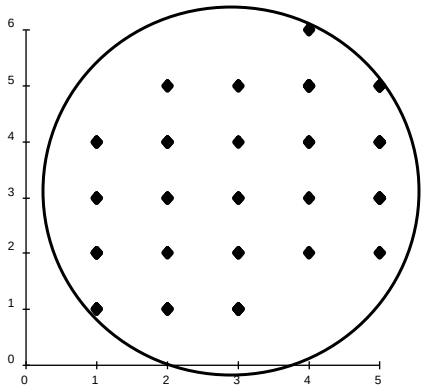
if your instrument/software provides r^2, then:

- take the square root of r^2 (which equals r) or
- an r^2 of 0.990 = r of 0.995

$$\sqrt{r^2} = r$$

How the correlation coefficient works

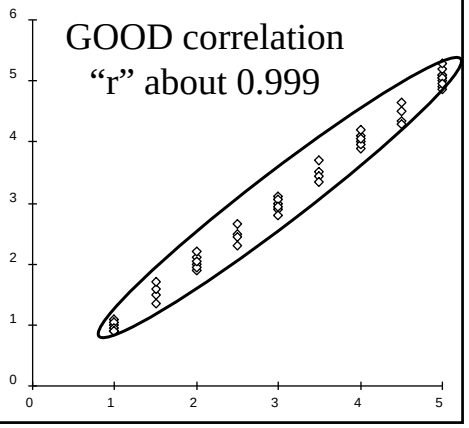


POOR correlation
"r" = 0

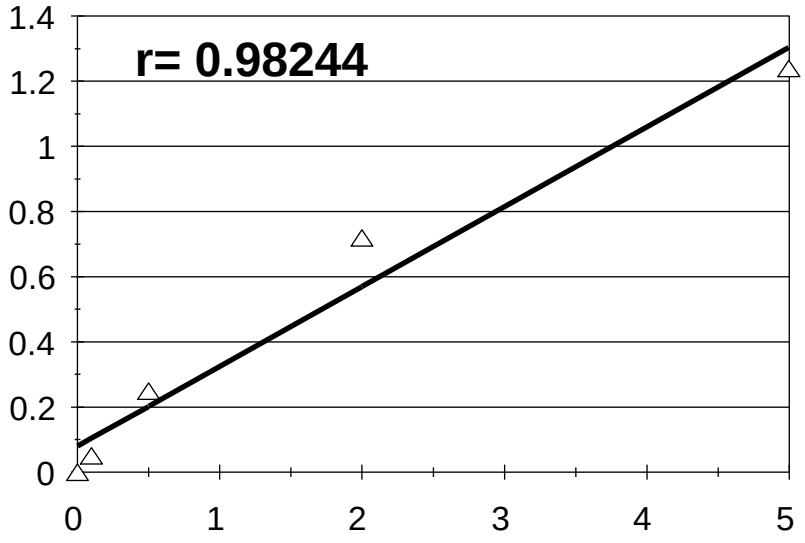
...the more it is stretched taut in a "cigar" shape, the higher the correlation.

The "Rubber Band" test

…simply visualize how a rubbe band would "fit" the data...



Correlation + Visual



Unacceptable correlation...will result in biased data

Calibration Evaluation - Linearity Check

- Most analyses have a limited linear range
- Deviation from linearity usually related to concentration
- Can occur at both the lower and the upper end
- Unsure? Review “response factors” for each calibration level
- Look for the point at which deviation occurs

Response Factor (RF) = $\frac{\text{Response } \textit{(= Absorbance)}}{\text{Concentration}}$

*** If you identify **non-**linearity, reduce the calibration range ***

Linearity Checks - Response Factors

mg/L	Abs.	RF = Abs / mg/L
0	0	
0.20	0.175	0.875
0.40	0.325	0.813
0.60	0.500	0.833
0.80	0.675	0.844
1.00	0.825	0.825
1.20	0.950	0.792
1.40	1.000	0.714
1.60	1.050	0.656
1.80	1.075	0.597
2.00	1.150	0.575

Low end variability

Midpoint: stability

Steady decline in RF characteristic of exceeding linear range

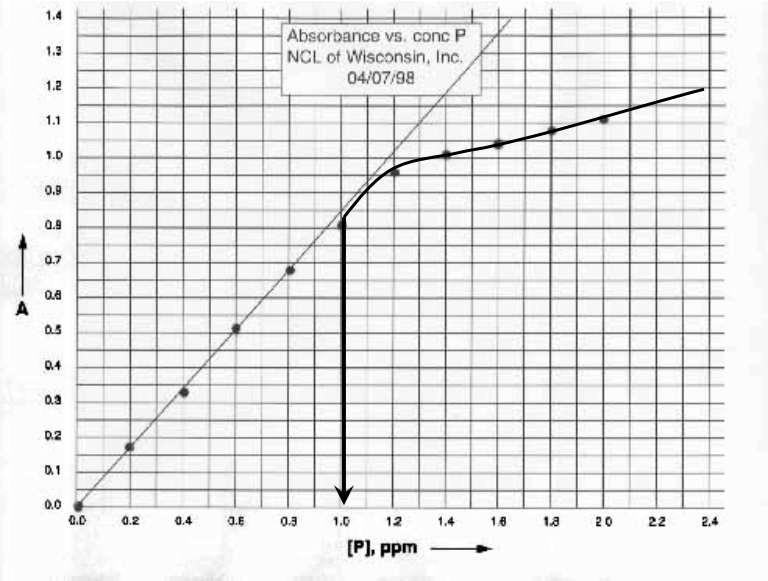
Rise in Abs. Per 0.2 mg/L

0.175
0.150
0.175
0.175
0.150
0.125
0.050
0.050
0.025
0.075

Data Source: North Central Labs at www.nclabs.com

Linearity - Phosphorus Calibration

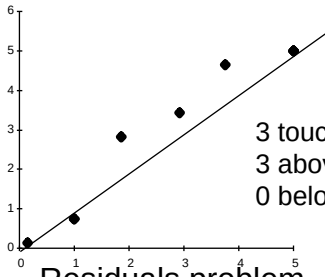
Phosphorus is non-linear above about 1.0 mg/L



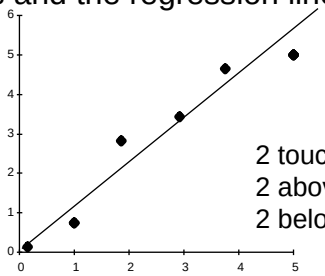
Source: North Central Labs at www.nclabs.com

Calibration Evaluation - Back-calculation

The purpose of a linear regression is to mathematically minimize the distance between all data points and the regression line



Residuals problem



Residuals minimized

"Residuals" represent the degree of agreement between True Value and back-calculated concentration

- ☆ "Plug" responses of standards into the regression equation
- ☆ Compare recovery: regression concentration vs. true value
- ☆ Recoveries should generally be within 90-110%
- ☆ It's more difficult to achieve ± 10% as you get close to the LOD
- ☆ The "apparent" concentration for the blank must not be > LOD

Back-calculation…Y = mx + what?

- Linear regression equations are in the form **Y = mX + b**
- m = slope; b = intercept
- Since X = concentration, and Y = absorbance…..
- This solves for absorbance…which we already KNOW
- Therefore we have to "re-arrange" the equation….

Absorbance = *slope* x Concentration + *intercept*

- intercept ***- intercept***

$$\frac{\text{Absorbance} - \textit{intercept}}{\textit{slope}} = \frac{\textit{slope} \times \text{Concentration}}{\textit{slope}}$$

$$\frac{\text{Absorbance} - \textit{intercept}}{\textit{slope}} = \text{Concentration}$$

NOTE: Be aware that some calculators switch Concentration & Absorbance

Back-calculation Example

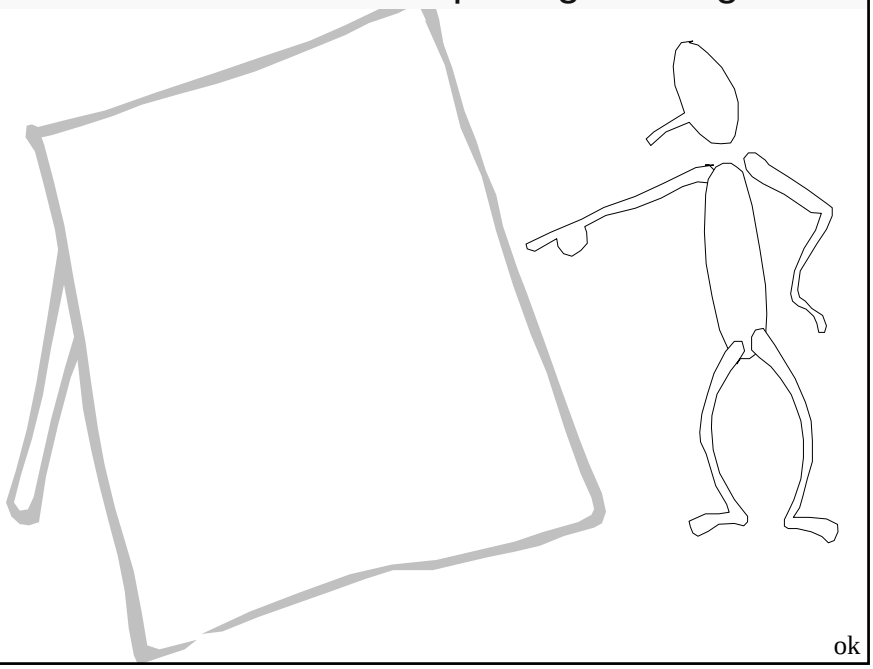
Calibration Data	
mg/L P	Abs.
0	0
0.1	0.051
0.5	**0.25**
2	0.72
5	1.24

Slope (m) = 0.244713124
Intercept (b) = 0.080236051

	True Concentration (mg/L)	Regression Concentration (mg/L)	Percent Recovery
Absorbance = 0.000:	0	-0.328	**???**
Absorbance = 0.051:	0.1	-0.119	**ND**
Absorbance = 0.250:	0.5	0.69	**138%**
Absorbance = 0.720:	2	2.61	**130.5%**
Absorbance = 1.24:	5	4.74	**94.8%**

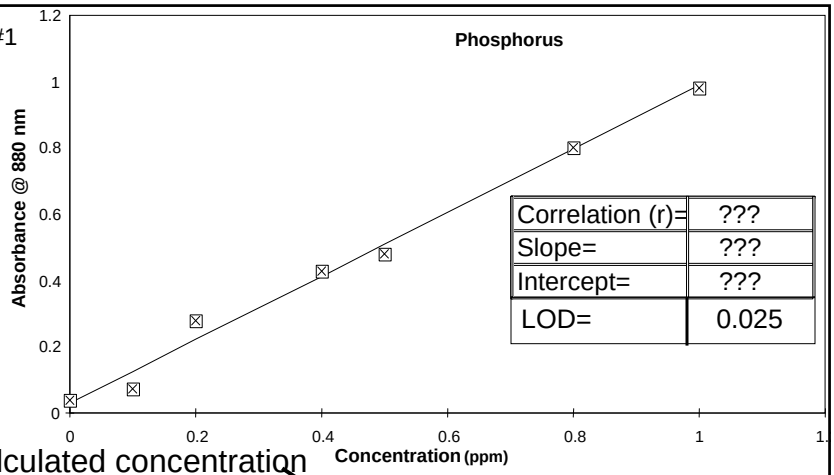
0.250 - 0.08024 = 0.16976 → 0.16976 / 0.2447 = 0.694

Calibration Evaluation - putting it all together



ok

Exercise #1



Correlation (r)=	???
Slope=	???
Intercept=	???
LOD=	0.025

Back-calculated concentration

Concentration (mg/L)	Abs. (Measured)	Residual mg/L
0	0.040	**??**
0.1	0.075	**??**
0.2	0.280	**??**
0.4	0.430	**??**
0.5	0.480	**??**
0.8	0.800	**??**
1	0.980	**??**

YOU be the auditor!

Acceptable calibration?

Step 1: Set up the regression

Calibration Data	
mg/L P	Abs.
0	0.040
0.1	0.075
0.2	0.280
0.4	0.430
0.5	0.480
0.8	0.800
1.0	0.980

Set Mode to “2”: MODE 2

Clear the registers: 2nd F DEL

Enter 1st data pair: 0 STO • 0 4 M+ n=1

Enter 2nd data pair: • 1 STO • 0 7 5 M+ n=2

Enter 3rd data pair: • 2 STO • 2 8 M+ n=3

Enter 4th data pair: • 4 STO • 4 3 M+ n=4

Enter 5th data pair: • 5 STO • 4 8 M+ n=5

Enter 6th data pair: • 8 STO • 8 0 M+ n=6

Enter 7th data pair: 1 STO • 9 8 M+ n=7

Steps 2-3: regression info and back-calculation

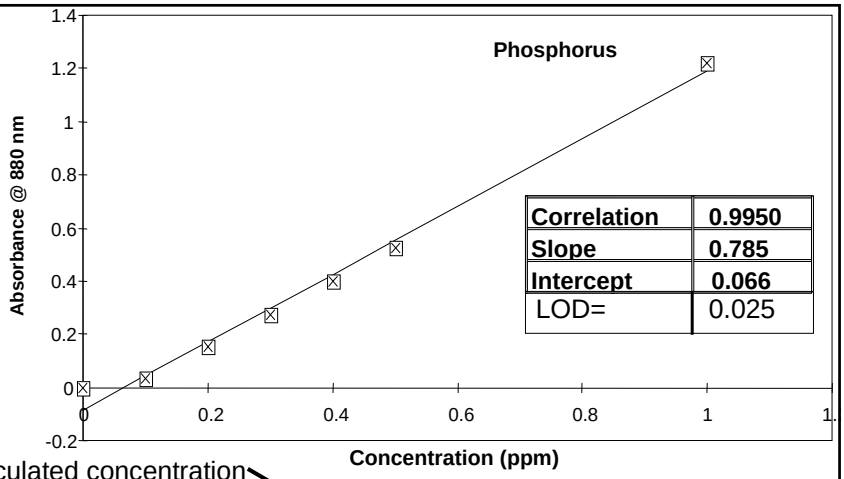
Obtain the calibration evaluation information

- ✓ Get the Correlation coefficient..: RCL ÷ r = 0.9951…..
- ✓ Get the Slope.....: RCL) b= 0.9497…..
- ✓ Get the Intercept: .....: RCL (a = 0.03368…..

Converting a sample absorbance to concentration

0.04:	• 0 4	2nd F (	**0.007**	**This value should be < LOD**
0.075:	• 0 7 5	2nd F (	**0.044** ÷ • 1 × 1 0 0 =	**44 %**
0.28:	• 2 8	2nd F (	**0.26** ÷ • 2 × 1 0 0 =	**130 %**
0.43:	• 4 3	2nd F (	**0.42** ÷ • 4 × 1 0 0 =	**105 %**
0.48:	• 4 8	2nd F (	**0.47** ÷ • 5 × 1 0 0 =	**94 %**
0.8:	• 8	2nd F (	**0.80** ÷ • 8 × 1 0 0 =	**100 %**
0.98:	• 9 8	2nd F (	**0.99** ÷ 1 × 1 0 0 =	**99 %**

Exercise #3



Back-calculated concentration

Concentration (mg/L)	Abs. (Measured)	Residual mg/L
0	0	0.07
0.1	0.031	0.09
0.2	0.151	0.18
0.3	0.273	0.28
0.4	0.399	0.38
0.5	0.525	0.48
1	1.22	1.02

YOU be the auditor!

Acceptable calibration?

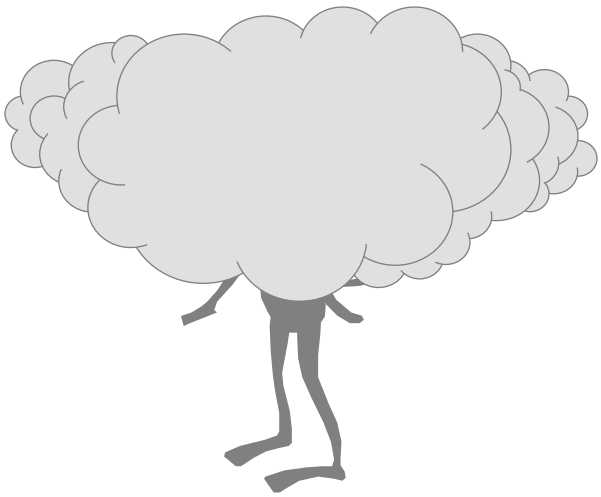
Calibration Evaluation - On-going checks

- Periodically confirm that response has not changed from initial.
- Use a midpoint standard (check standard) and blank.
- Calculate % recovery.
- Check at beginning, every 10 samples and end of each batch.

  For WWTPs doing 1-2 samples/day, only need one

  Recovery must be within 90-110% for phosphorus and ammonia.

$$\% \text{ Recovery} = \frac{\text{measured Value}}{\text{True value}} \times 100$$



Detection Limits

LOD vs. LOQ

Limit of Detection (LOD) & Limit of Quantification (LOQ)

LOD

- ✓ Lowest concentration determined to be significantly different from a blank
- ✓ Formerly known as the MDL (Method Detection Limit)

LOQ

- ✓ Analyte concentration at which one can state with a specified degree of confidence that an analyte is present at a specific level in the sample tested.
- ✓ Defined in code [NR 149.03 (16)] as 10/3 times the LOD (i.e. 3.33 x LOD)

Why is it important to know the LOD

⇒ Confidence in results reported

⇒ Alerts data-user to uncertainties or limitations of the data

⇒ Proper decisions can be made based on data

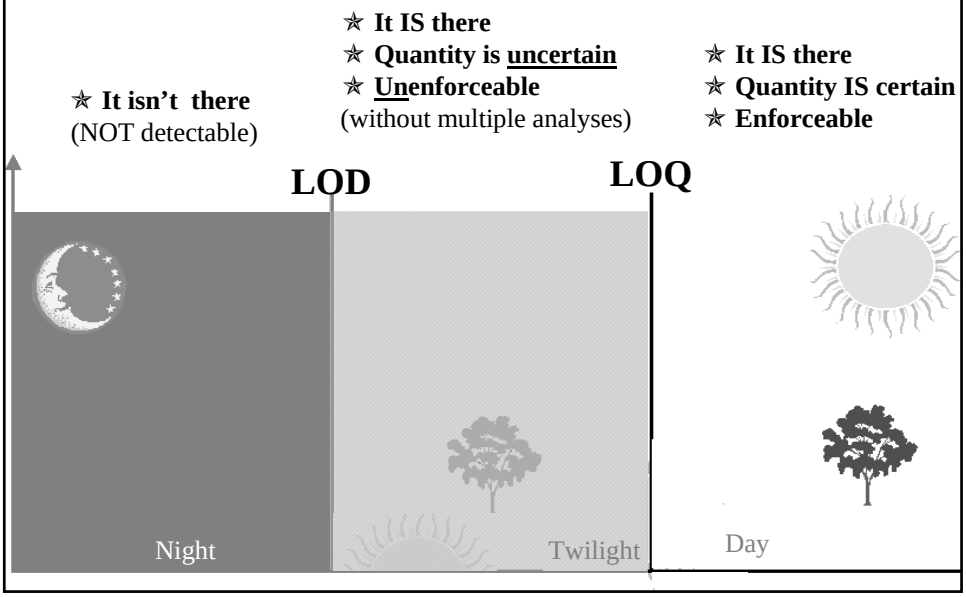
- Compliance decisions often made from pooled data
- What do you do with data of: **<25, 32, <40, 22.5, <50**

Why is it important to know the LOD

⇒ Censoring data biases data sets and restricts its usefulness
- Analyte X detected at 50 ppm.
- Decision is made to report < 100 ppm
  (which is certainly accurate)
- But what if the actual LOD is 10 ppm?

⇒ Potentially harmful levels of X may exist..…
...but <u>below</u> our ability to detect them
- To remediate this situation successfully, need to know.....
- <u>if</u> analyte is present
- <u>if</u> the concentration is *changing*

LOD / LOQ Interpretation



Determining the LOD for BOD

BOD detection limits are <u>theoretically based</u>.

- Assumption**:** the LEAST amount of depletion allowable is 2 mg/L.
- Based on the highest volume of sample used in a dilution series.
- This technique doesn't consider seed correction.

BOD bottle maximum volume!

$$\text{LOD mg/L} = 2\ \text{mg/L} \times \frac{300\ \text{mL}}{\text{mL sample}}$$

If the highest sample volume used is:	The LOD for **that** sample is:	The LOQ for **that** sample is:
300 mL	**2**	**6.7**
200	**3**	**10**
100	**6**	**20**
75	**8**	**26.7**
50	**12**	**40**

BOD: Another LOD example

<u>Example:</u>

Dilution 1 50 mL Depletion: < 2 mg/L
Dilution 2 25 mL Depletion: < 2 mg/L

What value should be reported?

What can be done in the future?

Report a BOD of " < 12"
Insufficient depletion; highest volume used is 50 mLs
Should be using more sample

Determining the LOD for TSS

Like BOD, detection limits are <u>theoretically based</u>.

•Assumption**:** Minimum capture weight of 1 mg (of residue).

•Based on: Volume of sample filtered.

Thus, if 1 liter of sample is filtered, then you can "detect" 1 mg per liter.

$$\textbf{LOD mg/L} = 1000 \times \frac{\textbf{1 mg}}{\textbf{mL sample filtered}}$$

Volume filtered	LOD	LOQ
25 mL	40 mg/L	133 mg/L
50	20	67
100	10	33
250	4	13
500	2	6.7
1000	1	3.3

Since most permit limits are about 30 mg/L, you will need to filter at least 50 mL of sample.

The EPA procedure for determining LOD

1. Determine a spike concentration (close to the expected LOD)
2. Prepare at least 7 spiked replicates of reagent water at this spike level

NOTE: Be aware that some older permits may specifically require the LOD to be determined in effluent.
This is particularly true for chlorine determinations.
Realistically, it may be best to determine your LOD in effluent.
Practically, however, by doing so, may not be able to achieve a valid LOD.
If there is a question, bring it up with your area engineer

3. Calculate the mean (**X**) and standard deviation (**SD**)
4. Obtain the "**t**"-value associated with the number of replicates
5. Calculate the LOD: **SD** times **t**
6. Perform the "5-point check" of the LOD

EPA's LOD Procedure Example

Ammonia Example

Spike level = 0.1 mg/L

Rep. 1	0.104
Rep. 2	0.082
Rep. 3	0.096
Rep. 4	0.1
Rep. 5	0.087
Rep. 6	0.114
Rep. 7	0.108
mean	**0.099**
st dev.	**0.01135**
t-value	**3.143** =

# replicates	t-value
7	3.143
8	2.998
9	2.896
10	2.821

from table based on # replicates

LOD= 0.035684 = t-value x std deviation

LOQ= 0.118948 = 3.333 x LOD

Discussion: If LOQ is theoretically equal to 10xSD, why doesn't that work here?

Using the Sharp EL520L to calculate LOD

Going through the Ammonia LOD data

Set Mode to "1": MODE 1

Clear the registers: 2nd F DEL

Enter 1st value (0.104): • 1 0 4 M+

Enter 2nd value (0.082): • 0 8 2 M+

Enter 3rd value (0.096): • 0 9 6 M+

Enter 4th value (0.100): • 1 M+

Enter 5th value (0.087): • 0 8 7 M+

Enter 6th value (0.114): • 1 1 4 M+

Enter 7th value (0.108): • 1 0 8 M+

Using the Sharp EL520L to calculate LOD

Obtain the LOD

✓ Get the Mean ($\bar{x}$)..... : RCL 4 $\bar{x}$ = 0.098714285

✓ Get the standard deviation (SD): RCL 5 Sx= 0.011353623

✓ Calculate the MDL (SD x t)..: × 3 • 1 4 3 = **0.0356844**

Calculator window will say ***ANS * 3.143=***

Now that you have the LOD, perform a 5-step procedure to determine whether or not the LOD is valid.

# replicates	t-value
7	3.143
8	2.998
9	2.896
10	2.821

LOD Evaluation: The 5-point check

(these first 3 are mandatory checks) **LOD= 0.036**

1. Is LOD greater than 10% of the spike level? **yes**

Spiked at **0.1**, so LOD should be > 0.01
If LOD < 10% of spike level, re-do at lower spike level

2. Is the spike level greater than the LOD? **yes**

Common sense: if LOD > spike level, couldn't detect it

3. Is the LOD below any relevant permit limit? **N/A**

(if there is one) Permit limit =_____

LOD Evaluation: The 5-point check

(additional checks)

Though not specifically required by the EPA method....
these checks help you obtain the best estimate of the LOD.

4. Is the signal-to-noise ratio (S/N) between 2.5 and 10? **yes**

S/N = Mean/std dev. S/N= 8.69

RCL 4 divided by **RCL 5 =** on Sharp EL-520L calculator

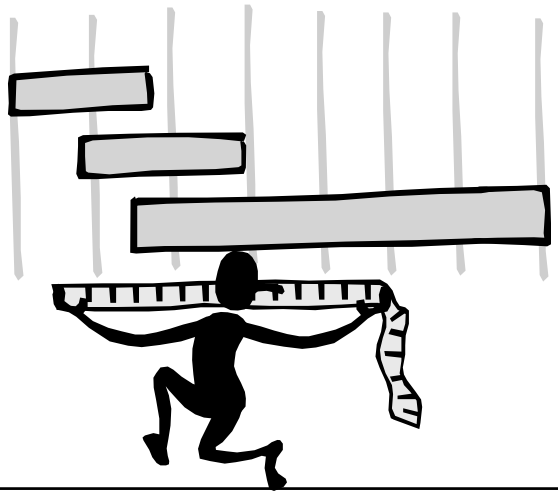
5. Is mean recovery within reasonably expected limits? **yes**

Mean recovery= mean/spike level x 100 = 98.71%

Expected range is approximately 80 to 120%

Accuracy

(spikes)



Spikes: Discussion Items

⇒ Why do we do matrix spikes?

⇒ How much should I spike? (spike to background ratio)

⇒ How much can I dilute my sample?

⇒ Calculating recovery

⇒ What does my recovery mean?

⇒ Exercise : review calculation examples

DO NOT need matrix spikes for:
- BOD
- Suspended Solids

Spike Basics

Why: To evaluate the accuracy of method as influenced by specific matrices (sample types).

How: Add known amount of analyte to randomly selected routine samples

When: 5% of samples (1 per 20 samples) PER MATRIX

NOTE: Raw + effluent = 2 DIFFERENT MATRICES

What:
1. Calculate % recovery
2. Evaluate performance against control limits

Matrix Spikes: How much should you spike?

1. Consider the upper calibration range!

If you calibrate to 1 ppm...
your effluent is about 0.25 ppm....
and you spike at 1.0 ppm.....will exceed the calibration range.

2. Spike at 1 to 5 times the level in the sample

If effluent averages 1 ppm, spike between 1 and 5 ppm

- If you spike at less than 1x, risk the ability to recover it.
- As spike increases beyond 5X, TOO easy to recover.

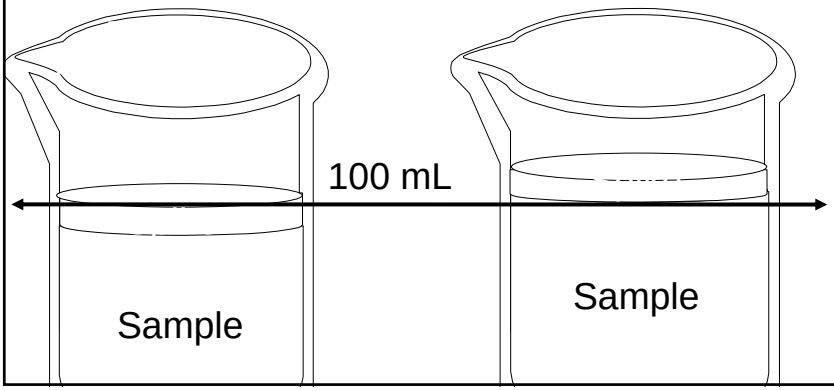
3. Limit additional volume to <10% of sample

(i.e., 0.5 mL standard to 5 mL with sample)

- The spike faces less matrix than in the unspiked sample

Matrix Spikes: Dilution Scenarios

- If you dilute spike (with sample) to a known volume….
  (amount of sample used in spike is LESS than that in the unspiked)
  sample concentration must be adjusted.
- If the spike is added "on top of" the sample
  (amount of sample used in spike is SAME as in the unspiked)
  the *spike concentration* must be adjusted.



Spike Dilution Issues

The goal of a matrix spike is to provide us with information regarding how accurate our sample analysis results are.

If spike recovery is only 50%, then the potential exists that the true concentration of the target parameter is as much as twice the measured concentration.

Dilution - How much is too much?

- The bottom line is that you want to use as much sample for the matrix spike as you did for the sample itself.
- References vary on how much dilution is TOO much.
- Our guidance has been to limit dilution to 10% or LESS.

We frequently see laboratories that prepare spikes by diluting a sample 50:50 with the spike solution. The next slide provides a more graphic explanation for why this is inappropriate.

Packers analogy for spike dilution---too busy to provide on handouts

Spikes - Calculating Recovery

Calculation of % Recovery

$$\% \text{ Recovery} = \frac{\text{Spiked Sample} - \text{Unspiked sample}}{\text{Amount of spike added}} \times 100$$

seems simple enough.....BUT.....

Results will vary depending on whether you

- simply add the spike on top of the sample, or you
- add the spike first, then dilute to a fixed volume with sample, and
- is further compounded by whether or not you are digesting

Remember: Do NOT perform any rounding until the last step!

Spike Recovery Exercise

Calculation of % Recovery

$$\% \text{ Recovery} = \frac{\text{Spiked Sample} - \text{Unspiked sample}}{\text{Amount of spike added}} \times 100$$

Wastewater Lab operator/analyst "Joe" measures out 50 mLs of sample, and places the beaker on a stir plate. He then adds 1 mL of buffer solution. After stabilizing, the meter reads 2.0 mg/L ammonia.

Unspiked sample 2.0 ug/mL
Unspiked Sample Volume 50 mL

Joe" then measures out another 50 mLs of sample to prepare a mnatrix spike. To the 50 mLs of sample he adds 5 mL of a 25 mg/L ammonia standard. This beaker is then placed on the stir plate. He then adds 1 mL of buffer solution. After stabilizing, the meter reads 4.25 mg/L ammonia.

Spike volume	**5 mL**	**Spiked sample**	**4.25 ug/mL**
Spike Conc.	**25 ug/mL**	**Total volume**	**55 mL**

What's the % recovery?

Is the Recovery….

A) 90%
B) 98%
C) 99%
D) 107%, or
E) None of the above

?

Conventional Calculation: “spike “on top”

Matrix Spikes: Ammonia example- adding “on top”

Unspiked sample	**2.0 ug/mL**	**Spiked sample**	**4.25 ug/mL**
Unspiked Sample Volume	**50 mL**	**Total volume**	**55 mL**

Spike volume 5 mL
Spike Conc. 25 ug/mL

A. Correct the concentration in the unspiked sample = 1.82
2.0 ug/mL X (50/55) mL = 2.0 x 0.91

B. Correct the spike concentration = 2.27
25 ug/mL X (5/55) mL = .091

C. Calculate recovered concentration = 2.43
=(4.25 ug/mL - 1.82 ug/mL

% Recovery = 107.0%
= (C / B) x 100 *=(2.43 / 2.27) X 100*

Calculating Recovery: A New Way

A. Determine the contribution (ug) from the sample in the spike
1. Subtract the mLs of the spike from the total mLs of sample + spike
2. Multiply the answer from A.1 (above) by the sample concentration

B. Determine the # of ug (of analyte) **spiked**
Multiply the concentration of the solution used to spike by the # mLs spiked

C. Determine the # of ug (of analyte) **in the spiked sample**
Multiply the spiked sample concentration by the # mLs of this sample

D. Determine the # of ug (of analyte) **recovered**
Subtract "A" from "C"

% Recovery = *Divide "D" by "B" and multiply by 100*

key relationship: mg/L = ppm =ug/mL

NEW Calculation: "spike "on top"

Unspiked sample 2.0 ug/mL **Spiked sample 4.25 ug/mL**
Unspiked Sample Volume 50 mL **Total volume 55 mL**

Spike volume 5 mL
Spike Conc. 25 ug/mL

A. Contribution (ug) from the sample in the spike = 100
2.0 ug/mL X (55 mL - 5 mL) = 2.0 X 50

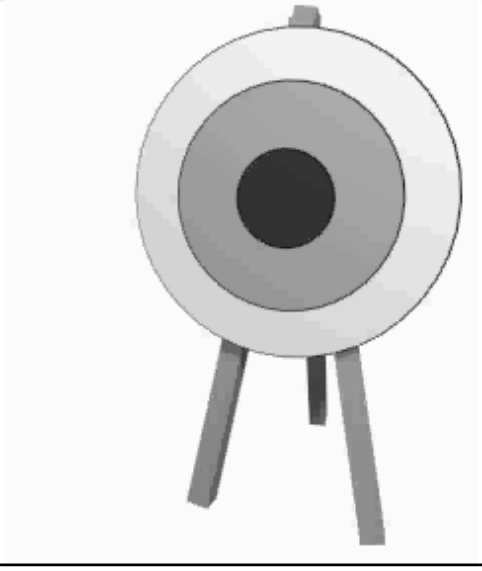
B. The # of ug (of analyte) **spiked = 125**
25 ug/mL X 5 mL

C. The # of ug (of analyte) **in the spiked sample = 233.75**
4.25 ug/mL X 55 mL

D. The # of ug (of analyte) **recovered = 133.75**
= C - A = *233.75 - 100*

% Recovery = 107.0%
= D / B =*(133.75 / 125) X 100*

Precision



Replicate Basics

Why: Used to evaluate repeatability (reproducibility)

How: Analyze randomly selected routine samples in duplicate (including digestion steps)

When: 5% of samples (1 per 20 samples)

NOTE: Raw + effluent = 2 samples

What: 1. Calculate Range (or RPD)
2. Evaluate performance against control limits

NOTES:
1. Replicates are frequently termed “Duplicates”. The terms are interchangeable.
2. Precision is concentration dependent

Measuring Precision

Example
Sample = 22
Replicate =18

Evaluating Replicates
Based on absolute difference (Range) or Relative percent difference (RPD) between duplicates

Range
expressed in same units as values
= Absolute Difference
= Larger value – smaller value

Range = 22 - 18 = 4

RPD
expressed as %

$$RPD = \frac{\text{Range}}{\text{Mean of the replicates}} \times 100$$

RPD = Range / Mean
Range = 4
Mean = (22 + 18)/2
= 20
RPD = (4/20) x 100
= 20%

Concentration Dependency

"Precision is concentration dependent"

Which is a brief way of saying that precision is difficult to evaluate without knowing the concentration levels involved.

Consider the analysis of TSS

- The range of replicates is 200 mg/L
- First thought: "Gee...that's terrible!"
- But.....what if the two values were 12,400 and 12,600?
- Now 200 doesn't look so bad.
- But....your opinion changes if the two values are 250 and 50

Dealing with Concentration Dependency

- Consider using RPD
- Separate control limits based on concentration

  Ex. effluent TSS about 4 to 10 ppm; influent 100 to 150 ppm

- Start at 10 x the LOD or LOQ…or even the permit limit?
- MAY need more than two levels

  But you don't want so many different levels that you will never generate enough data to create your own limits either

RPD? Or Range?

Sample	Replicate	Range	RPD
152	161	9	5.8%
161	168	7	4.3%
143	151	8	5.4%
136	142	6	4.3%
155	160	5	3.2%
172	177	5	2.9%
164	155	9	5.6%
150	158	8	5.2%
145	137	8	5.7%
140	147	7	4.9%
125	119	6	4.9%
170	162	8	4.8%
143	149	6	4.1%
132	136	4	3.0%
152	146	6	4.0%
144	138	6	4.3%
189	180	9	4.9%
167	175	8	4.7%
130	140	10	7.4%
153	146	7	4.7%
Mean	**151.75**	**7.1**	**4.7%**
Stdev			1.1%
UWL		17.8	6.8%
UCL		**25.3**	**7.9%**

Sample	Replicate	Range	RPD
200	230	30	14.0%
300	330	30	9.5%
400	**430**	**30**	**7.2%**

As concentration increases, a point is reached where range fails but RPD passes.

Sample	Replicate	Range	RPD
100	107	7	6.8%
50	57	7	13.1%
25	32	7	24.6%
10	17	7	51.9%
5	12	7	82.4%

As concentration decreases, a point is reached where range passes but RPD fails.

Will RPD work for you?

Sample	Replicate	Range	RPD
200	216	16	7.7%
250	270	20	7.7%
300	324	24	7.7%
350	378	28	7.7%
400	**432**	**32**	**7.7%**

As concentration increases, the absolute range can increase accordingly with NO CHANGE in RPD

For a given range, as concentration increases, RPD decreases

For a given range, as concentration decreases, RPD increases

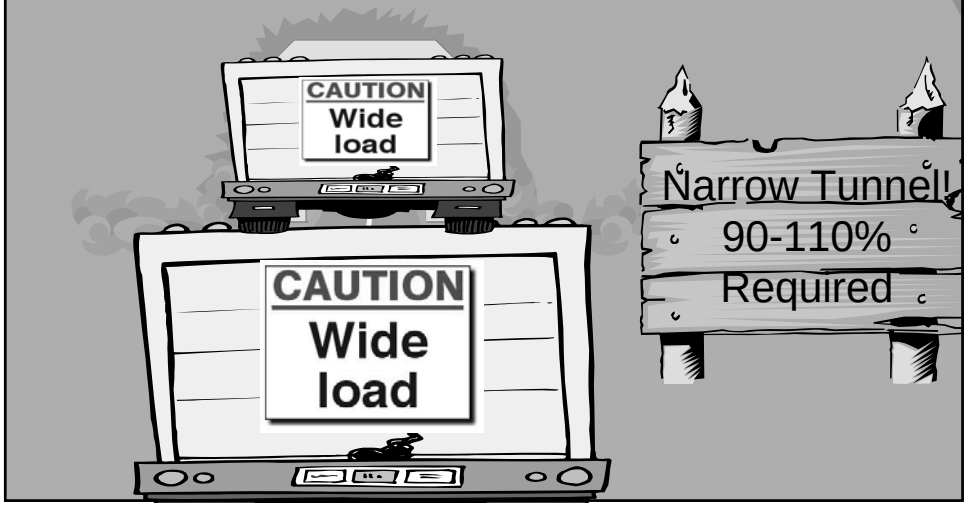
When might this be of use?

If your system is susceptible to high I & I

If your system exhibits high variability in influent loading

It might be a good idea to use RPD for raw; range for final

Control Limits



Do I need Control Charts?

NO..... but.....

☺ Control chart use is "strongly encouraged"

☺ Control charts are useful in heading off problems

☺ Control charts provide a visual tool

What exactly do I need?

NR 149.14 (3) (g)

Quality control limits

for replicate sample and spiked sample analysis

shall be calculated for each matrix type

using a method from an authoritative source

[NR 149.03 (5) (a - w)].

.....

When quality control data

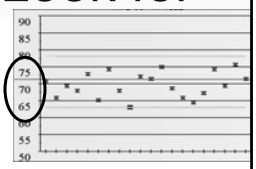
shows a dependency on concentration,

the laboratory **shall** calculate separate control limits

to address the concentration dependency.

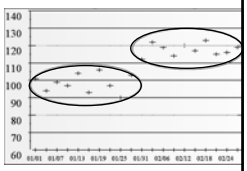
.....

Control Charts…Things to Look for



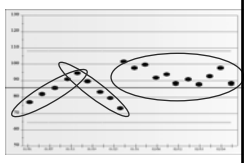
Signs of analytical bias

- a recovery mean much lower than 100%
- a recovery mean much greater than 100%



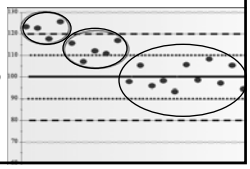
Signs of trends

- sudden or gradual changes in where data fall on the charts



Other trends

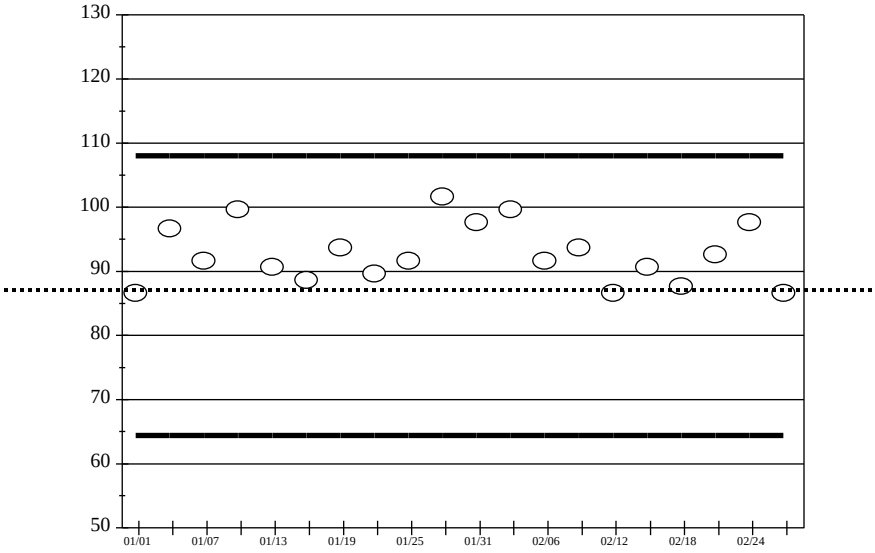
- 7 successive points on same side of the mean
- 5 or more points moving in the same direction



From Standard Methods

- 3 of 4 successive data points outside warning limits
- 4 of 5 successive data points exceeding the mean ± 1 standard deviation

Is this analysis "in control"?



N = 20 SD = 7.28 Mean = 88.85 Limits = 67 to 110.7%

What if I don't have enough data?

If you do QC any less frequently than once every 2 weeks, you will not have enough data. NR 149.14 (3) (g)

For labs with

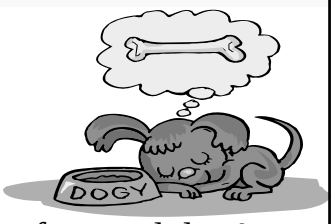
- less than 20 quality control results
- within 12 months,

the laboratory may set quality control limits based on

- information given in the authoritative sources,
  - Standard Methods 18th ed., Table 1020I
    - Spikes: 80-120%
    - RPD (high concentration): ± 10%
    - RPD (low concentration): ± 25%
- laboratory experience,
  - Be prepared to defend what you've come up with!
- or the experience of other laboratories.
  - Could use limits from an adjacent facility. Only do this if the facility has similar processes to your own and they are using the same procedure as you are.

What if I think my control limits are TOO tight?

This is every lab auditor's dream!



1. Be sure that you are not excluding out-of-control data!
   Outliers should be excluded, but
   all out-of-control points are **not** outliers.

2. Include enough significant figures.
   - If values are whole numbers (e.g., 10, 89%), you can use one or even two decimal points to include some variability (10.**2**, 89.**3**%).
   - This same problem has been observed when a laboratory only reported recoveries to the nearest 5%.

1	110
2	90
3	78
4	91
5	83
6	91
7	81
8	92
9	102
10	80
11	94
12	83
13	79
14	140
15	82
16	92
17	80
18	94
19	98
20	80
Mean	**91**
stdev	**14.3966**

Test the furthest value from the mean value

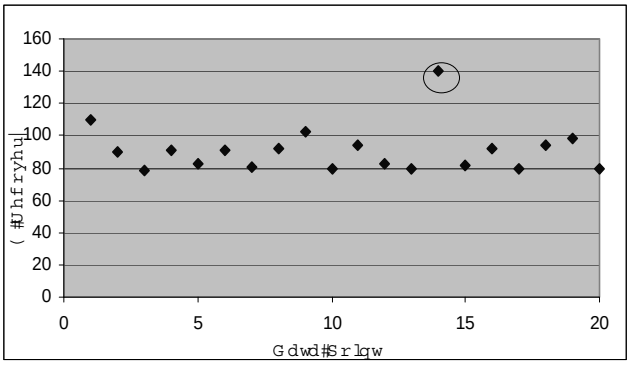
Highest: **(140)** − mean = 49 * *CHECK* *

Mean − Lowest: **(78) =** 13

$$Z = \frac{(140 - 91)}{14.39664}$$

Z= **3.4035726** >>> *criterion= 2.709*

REMOVE



Control limits WITHOUT outlier: 61.9 to 115.0

Control limits WITH outlier: 47.8 to 134.2

	Sample	Replicate	Range
1	7	7	**0**
2	8	8	**0**
3	5	5	**0**
4	6	5	**1**
5	8	9	**1**
6	8	8	**0**
7	4	5	**1**
8	7	7	**0**
9	11	11	**0**
10	10	10	**0**

	Sample	Replicate	Range
11	6	6	**0**
12	7	7	**0**
13	8	7	**1**
14	9	9	**0**
15	15	15	**0**
16	19	19	**0**
17	8	8	**0**
18	7	6	**1**
19	10	10	**0**
20	5	6	**1**

p hdq@ 316

vw1#ghy1@ 317:349

Z duqlqj#Olp lw= 5184#[#P hdq@ 31:8

Frqwurd#Olp lw= 615:#[#P hdq@ 4187

	Sample	Replicate	Range
1	7.4	6.8	**0.6**
2	8.5	7.6	**0.9**
3	5	5.1	**0.1**
4	6.2	4.9	**1.3**
5	7.7	9.4	**1.7**
6	8.2	7.8	**0.4**
7	3.6	5.4	**1.8**
8	6.7	7.3	**0.6**
9	11.3	10.8	**0.5**
10	9.5	10.5	**1**

	Sample	Replicate	Range
11	6.3	6.1	**0.2**
12	7.3	6.8	**0.5**
13	8.5	6.6	**1.9**
14	9.2	9.1	**0.1**
15	15.4	14.8	**0.6**
16	18.8	19.4	**0.6**
17	7.9	8.4	**0.5**
18	7.4	5.9	**1.5**
19	9.5	10.2	**0.7**
20	4.9	6.2	**1.3**

p hdq@ 31;7

vw1#ghy#VG,1@ 3189378

Z duqlqj#Olp lw= 5184#[#P hdq@ 5144

Frqwurd#Olp lw= 615:#[#P hdq@ 51:8

Calculating Control Limits

Matrix spike & RPD Control limits

1. Test the data for and eliminate outliers before proceeding.
2. Calculate the mean and standard deviation of the data.
3. Warning limits = Mean ± 2 standard deviations
4. Control limits = Mean ± 3 standard deviations

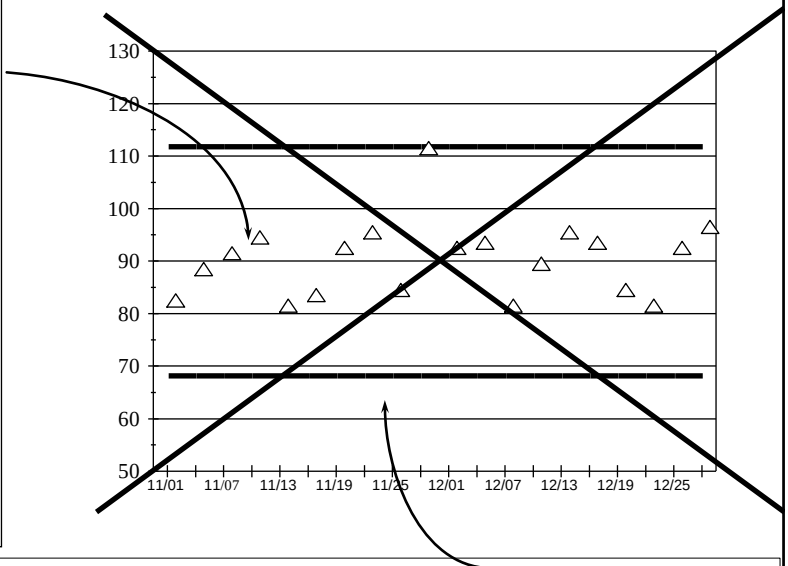
NOTE: RPD is a 1-tailed test, so only Mean +

Range Control limits

1. Test the data for and eliminate outliers before proceeding.
2. Calculate the mean of the data.
3. Warning limits = 2.51 x Mean
4. Control limits = 3.27 x Mean

DO NOT plot the data used to create limits against those same limits!

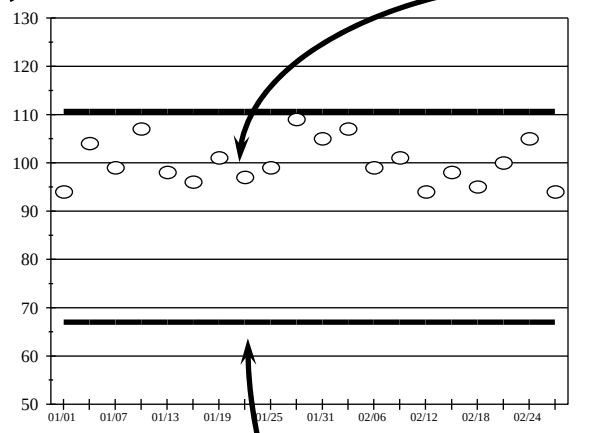
DATE	%R
11/01	81
11/04	87
11/07	90
11/10	93
11/13	80
11/16	82
11/19	91
11/22	94
11/25	83
11/28	110
12/01	91
12/04	92
12/07	80
12/10	88
12/13	94
12/16	92
12/19	83
12/22	80
12/25	91
12/28	95



N = 20 SD = 7.28 Mean = 88.85 Limits = 67 to 110.7%

DO plot data from period B-C against the limits created from data set A-B!

DATE	%R
11/01	81
11/04	87
11/07	90
11/10	93
11/13	80
11/16	82
11/19	91
11/22	94
11/25	83
11/28	110
12/01	91
12/04	92
12/07	80
12/10	88
12/13	94
12/16	92
12/19	83
12/22	80
12/25	91
12/28	95



DATE	% R
01/01	94
01/04	104
01/07	99
01/10	107
01/13	98
01/16	96
01/19	101
01/22	97
01/25	99
01/28	109
01/31	105
02/03	107
02/06	99
02/09	101
02/12	94
02/15	98
02/18	95
02/21	100
02/24	105
02/27	94

N = 20 **SD = 7.28** **Mean = 88.85** **Limits = 67 to 110.7%**

Dealing With Outlier Data

There are many statistical tests available for identifying outliers. One that is relatively easy to use is the Grubbs test.

$$Z = \frac{|\text{mean - questionable data point}|}{SD}$$

- Ignore the sign of the "Z" value….is always " **+** "
- For replicates, test only the highest value
- For spikes, test both the lowest & highest values
- Include suspect outlier when calculating mean, SD
- If the calculated Z-value **>** Critical Z value
  ...for that number of data points,
  ...then the value is an outlier

N	Critical Z
18	2.65
19	2.68
20	2.71
21	2.73
22	2.76
23	2.78
24	2.80
25	2.82
26	2.84
27	2.86
28	2.88
29	2.89
30	2.91
35	2.98
40	3.04
50	3.13
60	3.20

Outlier Test Example?

DATE	%R
11/01	81
11/04	87
11/07	90
11/10	93
11/13	80
11/16	82
11/19	91
11/22	94
11/25	83
11/28	110
12/01	91
12/04	92
12/07	80
12/10	88
12/13	94
12/16	92
12/19	83
12/22	80
12/25	91
12/28	95

1. Calculate the mean and SD

Mean = 88.85 SD = 7.278 Limits =67 - 110.7

2. Test the high value (110)

$$Z = \frac{110 - 88.85}{7.278} = 2.9058$$

N	Critical Z
18	2.65
19	2.68
20	2.71

3. Test the low value (80)

$$Z = \frac{88.85 - 80}{7.278} = 1.2159$$

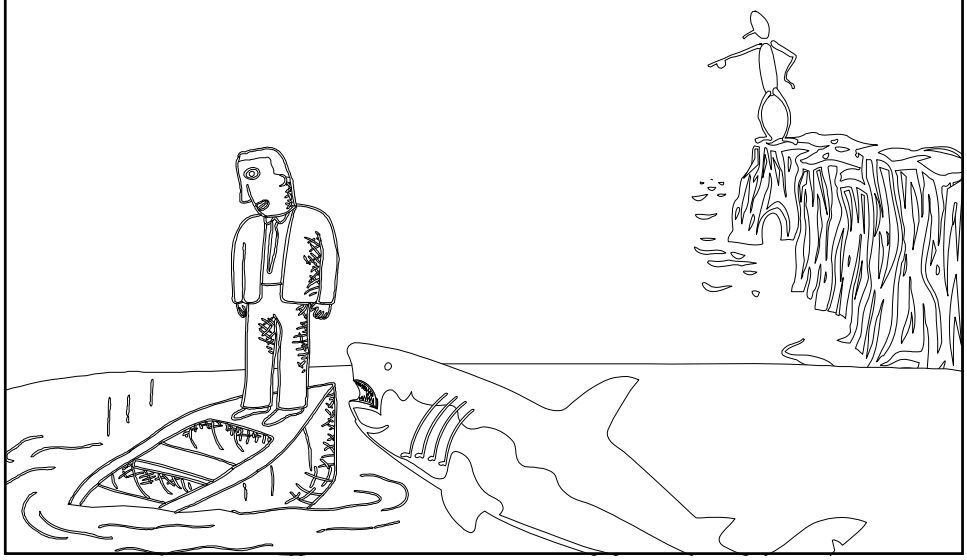
4. Discard outliers; re-calculate mean and SD

Since Z_{110} > criterion, 110 is an outlier

Mean =87.737 SD= 5.4553 Limits = 71 - 104

NOTE: Step 4 may also require a re-check for additional outliers!

Corrective Action



What **is** Corrective Action?

- In a nutshell, Corrective Action is anything done in response to an out-of-control situation.
- It MUST, however, be designed to identify the reason for the failure, and then correct it.
- There should also be a plan to quickly verify that the action taken has the desired effect.

What is NOT considered adequate Corrective Action

- Writing "I don't know why it failed"
- Simply labeling all matrix spike failures as "matrix effects"
- Checking calculations only
- Simply re-running the samples

What do I do with affected data?

NR 149.14(3) (h, i) requires the laboratory to:

- **Repeat all samples**
  - back to the last valid QC sample **of the same type**
  - unless you can show that ONLY that one sample is affected
- **If samples cannot be re-analyzed....**
  - results must be qualified back to the acceptable check.

DMRs require you to...

- mark the "QC Exceedance" box, and also
- identify (*) all sample results that are affected.

What does “qualify” mean?

- ***NR 149.03 (21m)*** "Qualify" means to place a written statement accompanying the test results which identifies anomalies encountered in generating the data.
- ***NR 149.14 (3)(h)*** If the results of known standards, spiked samples, method blanks, or replicates exceed the quality control limits…

  ...results are qualified by reporting that the laboratory analysis was not within the acceptance limits for this test.

* Matrix spike recovery (61%) exceeded QC limits (80-120%) on this day. Results must be qualified from this date back to xx/xx/xx, the date of the last acceptable matrix spike recovery.
* The GGA (232 mg/L) exceeded QC limits (167-228 mg/L) on this day. GGA is run daily, so only these results are affected.
* Method blank (0.07ppm) was higher than the LOD (0.05 ppm)

Are there preventive measures I can take?

- **You may wish to ...**

  ...increase the frequency of QC sample analysis

  ...above the minimum

  ...to minimize the amount of data which must be qualified

  ...in the event of an exceedance.

- **It’s a good idea to create some sort of logbook or form to document these situations.**

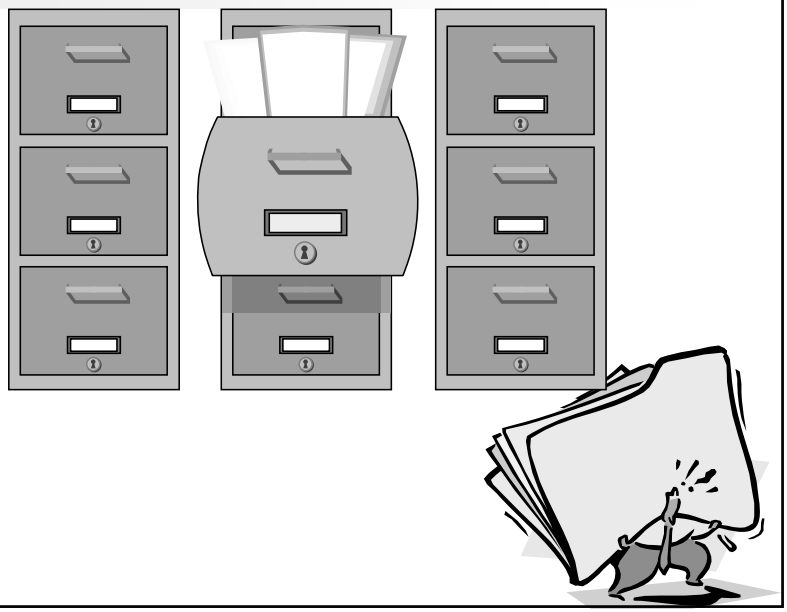
  - HOW did you become aware of the problem?
  - WHAT action did you take to fix the problem?
  - HOW do you know the problem has been resolved?

  …*essentially leave a “trail of breadcrumbs” that others can follow in similar circumstances*

Creating a Corrective Action Plan

Situation	**Corrective Action**
BOD: GGA failing high	1) Was initial calibration done properly? 2) Change in seed source? 3) Possibility of nitrification? 4) Qualify data on DMR back to last good GGA.
NH_3 electrode slope < -54 mV	1) Check that membrane is intact; no bubbles. 2) Make sure fresh filling solution is used. 3) Is the electrode stablizing normally? too slow? 4) Is the intercept climbing above the LOD?
Phosphorus calibration.... "r" is <<<0.995	1) View plot...does a single standard look funny? 2) Beyond linear range? (about 1 ppm for most) 3) Contamination..especially at low level?

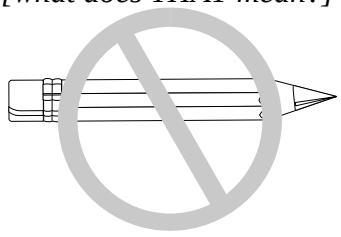
Documentation



Requirements At A Glance

A laboratory is required to:
maintain records: **NR 149.06 [esp. (5)]**

- which are un-alterable, *[what does THAT mean?]*



- which enable complete traceability *[whose definition?]*
- for a given three-year compliance period

Operating Principles

☑ If you didn't document it, you didn't do it

☑ You did the work.....take credit for it!

But.... no one ever looks at this stuff....

- Consider it insurance: pay it and hope you won't need it
- If your data comes under scrutiny, you lose without it
- It can actually help identify problems
- Your auditor WILL look at this
- Provides credibility for test results
- Shows you are doing the test properly
- *Keeps those DNR auditors off your back!*

Basic Items to document

- Refrigerator & autosampler temperatures
- Oven temperatures during solids analyses
- pH calibration
- Reagent preparation
- Balance calibration verification
- Annual balance maintenance
- Raw data from sample analysis
- When the membrane is changed on the DO probe

Not-so-obvious items to document

Corrective actions taken

if an auditor asks what you did in response to a GGA failure… can you ***show*** them? (ability to *tell* doesn't count!)

Historical QC limits

can you find control limits in use 3 years ago?

Blind Sample Performance History

Can you show an auditor your performance over the past 3 years?

Instrument maintenance

Matrix Spike Preparation details

- often overlooked!

What the code says: [NR 149.06 (1)(intro.)]

Records to be retained include but are not limited to ... the following:

(b) Quality control data for spikes, replicates, method blanks, blind standards reference samples, calibration standards and known standards.
Quality control results shall be traceable to all of the associated sample results.

What it means (as it relates to spikes):

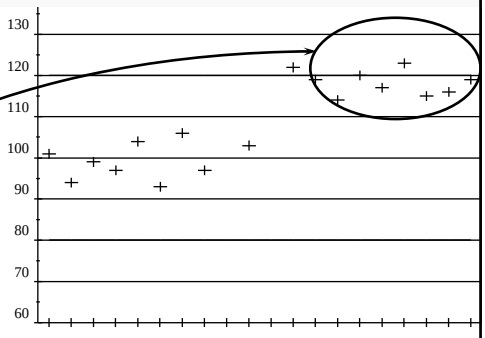
An auditor must be able to verify spike concentration, which means

- Concentration of the solution used to prepare spikes
- Information necessary to show that spike solution had not expired.
- The volume of spike solution used
- The volume of sample used
- The final volume of sample + spike
- The sample that was used to prepare the spike

What happened? How would you document it?

Documentation Exercise

What happened here?



Possible Causes

How would you know (Documentation)

_____

_____

_____

_____

_____

_____

Summary

- ☑ Formulate a gameplan [*your QA manual*]
- ☑ Calibrate (and evaluate it)
- ☑ Determine your detection capability
- ☑ Measure your accuracy
- ☑ Measure your precision
- ☑ Evaluate your precision and accuracy
- ☑ Implement a corrective action plan
- ☑ Provide documentation

Questions?

George Bowman
(608) 224-6278

State Laboratory of Hygiene
2601 Agriculture Drive
Madison, WI 53718

Rick Mealy
(608) 264-6006

Wisconsin DNR
PO Box 7921
Madison, WI 53707

State Lab web address:
http://www.slh.wisc.edu/outreach/

DNR's LabCert homepage:
http://www.dnr.state.wi.us/org/es/science/lc/

LabCert "toolbox":
http://www.dnr.state.wi.us/org/es/science/lc/toolbox/

Spike Recovery Exercise

Wastewater Lab operator/analyst "Joe" measures out 50 mLs of sample, and places the beaker on a stir plate. He then adds 1 mL of buffer solution. After stabilizing, the meter reads 2.0 mg/L ammonia.

Unspiked sample 2.0 ug/mL
Unspiked Sample Volume 50 mL

Joe" then measures out another 50 mLs of sample to prepare a mnatrix spike. To the 50 mLs of sample he adds 5 mL of a 25 mg/L ammonia standard. This beaker is then placed on the stir plate. He then adds 1 mL of buffer solution. After stabilizing, the meter reads 4.25 mg/L ammonia.

Spike volume 5 mL
Spike Conc. 25 ug/mL

Spiked sample 4.25 ug/mL
Total volume 55 mL

What's the % recovery?

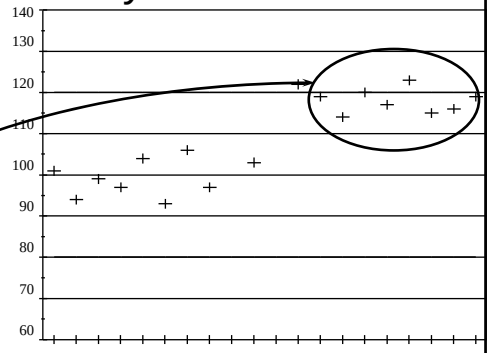
~~A) 90%~~
~~B) 98%~~
~~C) 99%~~
D) 107%
~~E) None of the above~~

If you got 90%, you didn't account for dilution of EITHER the sample or the spike
If you got 98% you accounted for dilution of the sample but not for the spike
If you got 99%, you accounted for dilution of the spike, but not for the sample

What happened? How would you document it?

Documentation Exercise

What happened here?



Possible Causes	**How would you know (Documentation)**
New analyst	Write start date on chart
New reagents	Reagent log should show date of 1st use
New calibration curve	Compare responses of old vs. new curve
Wrong calculation	Probably traced to new analyst
Contamination	Check blank results