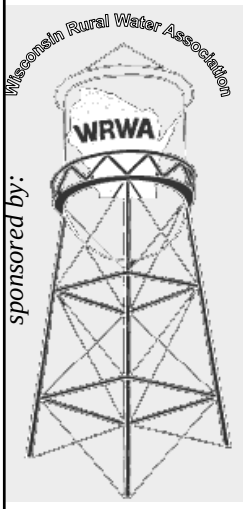
Advanced QA/QC for Wastewater Laboratory Testing



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Overview

- QA Manual Kit
- Dealing With Unacceptable LODs
- Spike Calculation Secrets
- Control Limit Tips
- Taking the Correct Corrective Action
- “There’s Something You Should Know About This Data”
- Documenting Your Documentation

Quality Control is all around us

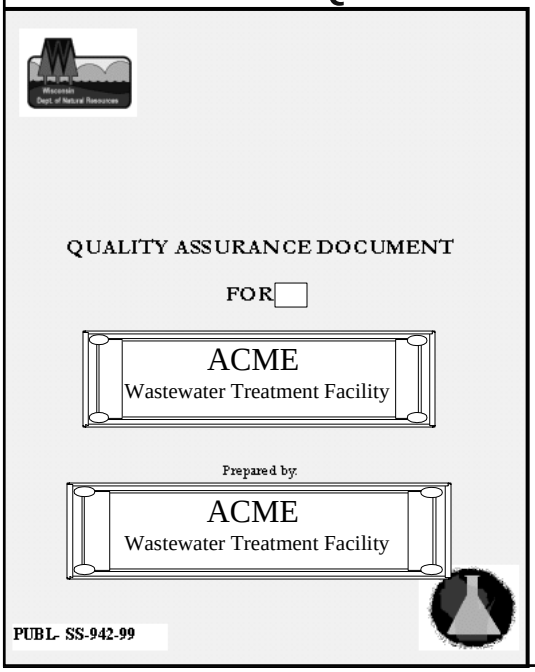
You often don’t notice it…
but it’s constantly at the root of daily news stories….
…we can see it in the movies or…
…subtley make reference to it in coversation

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

Essential Elements of QA Plan

- Schematic Diagram
- Sampling Plan (Permit & Process Control)
- Sample Handling, Preservation
- Analytical Methods
- ✓General Lab Quality Control Checks
- ✓ Quality Control Sample Frequency & Criteria
- ✓ Corrective Action Plan
- Preventive Maintenance Plan
- Data Reporting Requirements
- List of SOPs

The #1 QA Manual "DON'T"

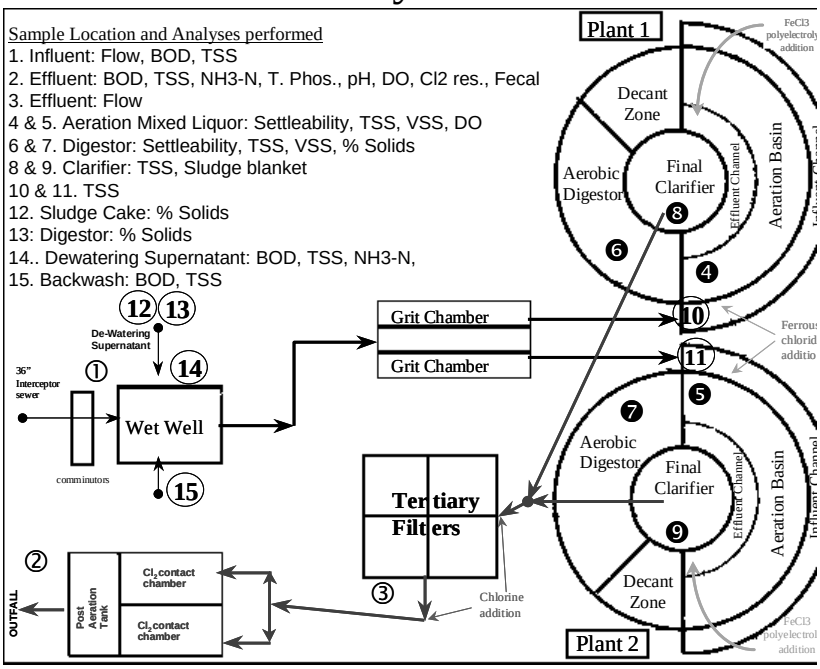


- This is NOT **your** QA plan
- It's a **tool** to help you develop your own QA Plan

Page 1

Flow Schematic of Beverly Hills 90210 WWTP

Sample Location and Analyses performed
1. Influent: Flow, BOD, TSS
2. Effluent: BOD, TSS, NH3-N, T. Phos., pH, DO, Cl2 res., Fecal
3. Effluent: Flow
4 & 5. Aeration Mixed Liquor: Settleability, TSS, VSS, DO
6 & 7. Digestor: Settleability, TSS, VSS, % Solids
8 & 9. Clarifier: TSS, Sludge blanket
10 & 11. TSS
12. Sludge Cake: % Solids
13: Digestor: % Solids
14.. Dewatering Supernatant: BOD, TSS, NH3-N,
15. Backwash: BOD, TSS



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Sampling Plan: Permit Monitoring

SAMPLE LOCATION	SAMPLE TYPE	SAMPLE POINT (Schematic Reference)	PARAMETERS TESTED	MONITORING FREQUENCY	PERMIT LIMITS Daily Minimum	Daily Maximum	Weekly Average (mg/L)	Monthly Average (mg/L)
Influent	Continuous	1	Flow	Totalized Daily				
Influent	24-hr composite XX flow proportional time proportional	1	BOD	3X weekly	there should be no limits here			
			TSS	3X weekly				
Influent	Grab							
Effluent Outfall 001	Continuous	2	Flow	Totalized Daily				
Effluent Outfall 001	24-hr composite XX flow proportional time proportional (May-October)	2	BOD	3X weekly	---	---	45	30
			TSS	3X weekly	---	---	45	30
			Ammonia	3X weekly	---	---	3.0	---
			Total Phosphorus	3X weekly	---	---	---	1.0
			Acute Toxicity	3X year				
			Chronic Toxicity	3X year				
Effluent Outfall 001	Grab May-September	2	pH	Daily	6.0 su	9.0su	---	---
			Chlorine Residual	Daily	38 ug/L	---	---	---
	May-September		Fecal Coliforms	weekly	---	---	---	400/100ml

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Sampling Plan: Process Control Monitoring

SAMPLE LOCATION	SAMPLE TYPE	SAMPLE POINT (Schematic Reference)	PARAMETERS TESTED	MONITORING FREQUENCY
Aeration Tank	Outlet grab	4 & 5	Settleability	Daily
			TSS	Daily
			VS	Daily
Aeration Tank	Contents in-place	4 & 5	Dissolved Oxygen	Continuous
Solids Concentrator	Product-grab	12 & 13	Percent solids	As needed
Solids Concentrator	Decant-grab	14	BOD	As needed
			TSS	As needed
			Ammonia	As needed
Digester Contents	Grab	6 & 7	Settleability (30 min.)	Daily
			%solids	Daily
			TSS	Daily
			VSS	Daily

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Sample Handling

SAMPLE HANDLING TABLE

PARAMETER	SAMPLE TYPE	PRESERVATION	CONTAINER	MAXIMUM@ HOLDING TIME	ANALYTICAL METHOD#
BOD	24-hr composite [flow proportional]	Cool, 4°C	Poly	48 hours	5210 B
TSS	24-hr composite [flow proportional]	Cool, 4°C	Poly	7 days	2540 D
Ammonia	24-hr composite [flow proportional]	Cool, 4°C; H_2SO_4 to pH <2	Poly	28 days	4500-NH3 F
Total Phos	24-hr composite [flow proportional]	Cool, 4°C; H_2SO_4 to pH <2	Poly	28 days	4500-P B(5) & 4500-P E
pH	Grab	None	Poly	Analyze immediately	4500-H+ B
Chlorine Res.	Grab	None	Poly	Analyze immediately	4500-CL G
Fecal Coliform	Grab	Cool, 4°C; 0.008% $Na_2S_2O_3$	Poly	6 hours	9222 D
Effluent Toxicity	24-hr composite [flow proportional]	Cool, 4°C;	Poly	28 days	subcontract

NOTES: Sample Type: (Grab, 24-hour composite [flow or time proportional])

@ From time of completed sampling

(Reference method source) # Standard Methods for the Examination of Water and Wastewater, 19th Ed., 1995

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General Lab Equipment QC

What am I checking?	How often should I check it?	What am I checking it against?	What if it doesn't meet specifications?
(Parameter)	(Frequency)	(Criteria)	(Corrective Action)
Sample Refrigerators	**Daily**	**> 0° C, < 4° C**	**Adjust temp.↑ or ↓**
Autosamplers	**Daily**	**> 0° C, < 4° C**	**Adjust temp.↑ or ↓**
Balance - 10 mg	**Weekly**	**9.7 to 10.3 mg**	**Re-certify weight or**
			Service balance
Balance - 1.0 g	**Weekly**	**0.995 to 1.005 g**	**Re-certify weight or**
			Service balance
TSS oven	**Daily**	**103-105 ° C**	**Adjust temp.↑ or ↓**
BOD Incubator	**Daily**	**19.0 to 21.0 ° C**	**Adjust temp.↑ or ↓**
Desiccators (bowl)	**Daily**	**Lid lifts easily?**	**Apply silicone grease to rim**
TSS Filter screens	**Daily**	**Pore blockage**	**Clean or replace**

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BOD-Specific Requirements

Page 1 of 2

Parameter: **BOD**

	Minimum Requirements	Facility Requirements
CALIBRATION		
Frequency	**Daily (DO meter)**	**Daily (DO meter)**
Calibration levels:	**1**	**1**
Evaluation criteria:	**N/A**	**Set to saturation point**
correlation "r"		**of oxygen in water**
Residuals		**based on temp and pressure**
KNOWN STANDARDS	**Exactly 6 mLs (2%) of a 150**	**Exactly 6 mLs (2%) of a 150**
Composition/True Value	**mg/L ea. glucose/glutamic acid**	**mg/L ea. glucose/glutamic**
Frequency	**acid 1/20; minimum 1/week**	**Weekly**
Evaluation criteria:	**198 ± 30.5 mg/L**	**198 ± 30.5 mg/L**
BLANKS		
Frequency	Each analysis day (except TSS)	**Daily**
Evaluation criteria:	**≤ 0.2 mg/L O_2 depletion**	**≤ 0.2 mg/L O_2 depletion**

BOD Requirements

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Page 6B

REPLICATES		
Frequency	1 per 20 samples per matrix	
Influent	1 per 20 samples	**Every other week (26/yr)**
Effluent	1 per 20 samples	**Every other week (26/yr)**
Evaluation criteria:		
Influent	Range or RPD?	**14.5%** Range or RPD?
Effluent	Range or RPD?	**0.75 mg/L** Range or RPD?
SPIKES		**Not Required**
Prepared by:	Preparation of spikes should not dilute the sample matrix by more than 10%. Generally, use the same volume of sample in both the spiked and unspiked samples.	
Adding		mLs
of a		ug/mL standard
to		mLs of sample
Final volume=		mLs
Frequency	1 per 20 samples per matrix	
Influent	1 per 20 samples	
Effluent	1 per 20 samples	
Evaluation criteria:		
Influent		
Effluent		
OTHER SPECIFICS		
Sample depletion	**> 2 mg/L residual DO ≥ 1**	**> 2 mg/L residual DO ≥ 1**
Sample pH	**6.5 to 7.5**	**6.5 - 7.5**
Residual chlorine	**Quench if detected**	**Quench if detected**
# of dilutions	**At least 2**	**At least 3 per sample**
Supersaturation		**Sample DO ≤ saturation**
Seed Controls		**Must treat exactly as samples**

Page 7B

Corrective Action

Parameter: **BOD**

	Minimum Requirements	Facility Requirements
CALIBRATION	**(DO meter)**	**Set to saturation point of oxygen in water**
Evaluation criteria:	**N/A**	
correlation "r"	**N/A**	
Residuals	**N/A**	
Corrective Action	**Re-calibrate if blank DO_I > saturation point** **If sample DO_I > sat. point, bring to room temp & shake**	
KNOWN STANDARDS		
Evaluation criteria:	**198 ± 30.5 mg/L**	**198 ± 30.5 mg/L**
Corrective Action	**GGA < 167.5: Weak seed (add more)or bad GGA (replace)** **GGA > 228.5: Contamination. Identify source and correct** **Clean all tubing & glassware**	
BLANKS		
Evaluation criteria:	**≤ 0.2 mg/L O_2 depletion**	**≤ 0.2 mg/L O_2 depletion**
Corrective Action	**If blanks gain oxygen: Suspect calibration problem** **If depletion > 0.2 mg/L Check for contamination. Clean tubing and still. Obtain new water source.**	

BOD Corrective Action-2

REPLICATES		
Evaluation criteria:		
Influent	Range or RPD?	**14.5%** Range or RPD?
Effluent	Range or RPD?	**1.3 mg/L** Range or RPD?
Corrective Action	**Presence of "chunks" in one but not both?….document. Qualify data on DMR. Re-evaluate control limits.**	
SPIKES		
Evaluation criteria:		
Influent		
Effluent		
Corrective Action	**Not Required**	
OTHER SPECIFICS		
Sample depletion	**> 2 mg/L; residual DO ≥ 1**	**Do not use result.**
Sample pH	**6.5 to 7.5**	**Adjust pH, document, seed.**
Residual chlorine	**Quench if detected**	**Quench, document, seed**

Corrective Action

General Concerns

Page 7A

What am I checking? (Parameter)	What am I checking it against? (Criteria)	What if it doesn't meet specifications? (Corrective Action)
Desiccator seal	**Adequate?**	**Apply silicon grease to rim**
Indicating Drierite	**Mostly blue**	**Replace/regenerate**
TSS Oven	**Maintains 103-105°C**	**Adjust...repair...replace**
		(*forced air ovens are better***)**
Balance	**✓ w/ mg & gm wts**	**Have re-calibrated/ repaired**
Class "1" weights	**Statistical criteria**	**Have re-certified**
Thermometers	**Compare to NIST**	**Apply correction factors**
Thermometers	**✓ for column breaks**	**Replace**
Barometer	**✓ vs. WWW/airport**	**Re-calibrate…replace**

If problem continues despite all efforts, call DNR auditor_____ at (___)

Preventive Maintenance Plan

Each instrument must have a maintenance "history" (record)

pre·ven·tive Pronunciation Key (prĭ-vĕn'tĭv) also **pre·ven·ta·tive** *adj.*
Intended or used to prevent or hinder; acting as an obstacle.
Preventing or slowing the course of an illness or disease; prophylactic.

- Clean or replace sample tubing at regular intervals
- Change DO membranes at a specific frequency
- Clean/replace all tubing used in BOD testing regularly
- Regularly scheduled balance maintenance
- Routine verification of thermometer accuracy
- Replace NH3 probe membranes at a specific frequency
- Spectrophotometer: Regularly check λ accuracy

a dilute $KMnO_4$ solution should have peaks at 526 and 546 nm

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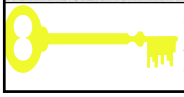
Preventive Maintenance Chart

Preventive Maintenance Procedures

What am I checking? (Equipment/Part)	What action am I taking? (Action)	How often should I do it? (Frequency)
Sampler tubing	**Clean with dilute bleach**	**Every 2 weeks**
Sampler tubing	**Replace**	**Every 6 months**
DO membrane	**Change**	**Every 3 weeks**
Electrode filling solution	**Replace**	**Every week**



Corrective Action: Taken to fix a problem
Preventive Maintenance: Taken to prevent Corrective Action

Lab Equipment Maintenance Log

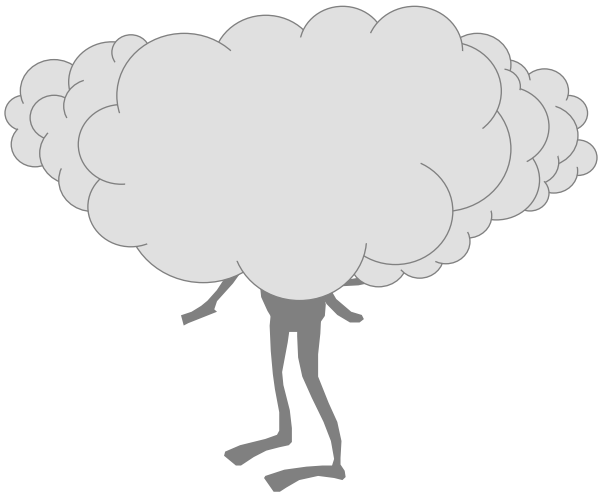
Lab Equipment Maintenance and Calibration Log

Month October Year 2002

Date	Analyst Intials	Sampler Temp. (°C)	Refrig. Temp. (°C)	TSS Oven Temp °C	BOD Incubator Temp °C	Fecal Incubator Temp °C	pH Meter buffers	BOD Barometer reading	BOD Room Temp °C	Comments
1	GTB	2.7	5.1	104	20.2	44.6	4,10	735mm	20.8	Refrig adjusted ↓
2	RGM	1.5	3.8	103	19.8	44.5	4,10	745mm	20.4	Sampler adjusted ↑
3	GTB	2.3	4.0	67	20.4	44.3	4,10	739mm	19.7	Replaced oven thermometer
4	RGM	1.5	3.8	103	19.8	44.5	4,10	745mm	20.4	
5	WG	2.2	3.4	108	20.5	44.5	4,10	748mm	21.3	TSS Oven adjusted ↓
6	WG	2.6	3.7	100	20.3	44.5	4,10	741mm	21.1	TSS Oven adjusted ↑
7			4					755 mm		
8			4					762 mm		
9			4					770 mm		
10			4					765 mm		
11			4					752 mm		
12			4							
13			4							
14			4							
15			4							
16			4							
17			4							

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



Detection Limits

LOD vs. LOQ

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

LOD

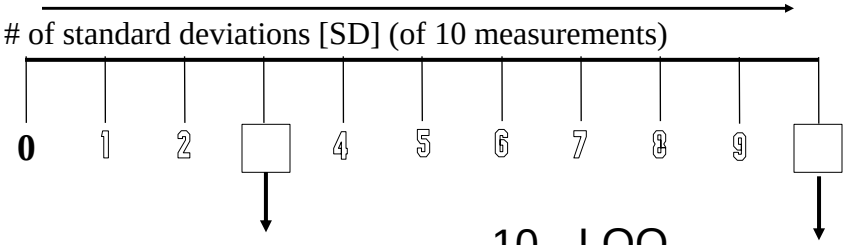
- ✓ Lowest concentration determined to be <u>significantly different</u> from a blank
- ✓ Formerly known as the MDL (Method Detection Limit)

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)

Where does the “10/3” come from?

Early MDL theory was based on replicate measurements (10) of a blank



3X the SD was deemed to be the MDL or LOD

$$\frac{10}{3} = \frac{LOQ}{LOD}$$

10X the SD deemed to be the LOQ

Close enough for gov’t work?

The t-value for 7 replicates = 3.143

The t-value for 8 replicates = 2.998 (or 3)

LOD Evaluation: The 5-point check

(these first 3 are mandatory checks)

Spiked at 0.1
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

S/N ratios above 10 suggest that you COULD spike lower

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%

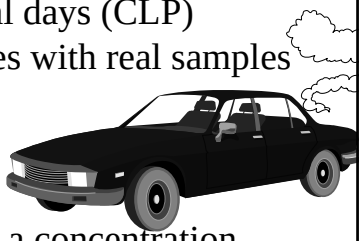
Mean recovery above 120 suggests high bias (contamination)
Mean recovery below 80 suggests low bias (less detectable)

What if I cannot meet the "5-point check"?

Some instruments are simply too precise.

- analyze the replicates over several days (CLP)
- alternatively, intersperse replicates with real samples

If all else fails… …back into it!



- Prepare and analyze a blank spike at a concentration equal to your calculated LOD/MDL
- Can you quantitate it within 20-30% of expected value?
- If not, repeat this process at a higher concentration until you achieve a quantitative result (within 20-30% of target value)

"Backing into" the LOD

LOD Evaluation: The 5-point check

Spiked at 0.5ppm
LOD= 0.009 ppm

1. Is LOD greater than 10% of the spike level? **NO!**

Spiked at **0.5**, so LOD should be > 0.05

If LOD < 10% of spike level, re-do at lower spike leve

DO NOT prepare LOD replicates: below 0.2 ppm for ammonia
below 0.1 ppm for phosphorus

"Backing into" the LOD

Ammonia **Spiked at 0.5ppm** **LOD= 0.009 ppm**

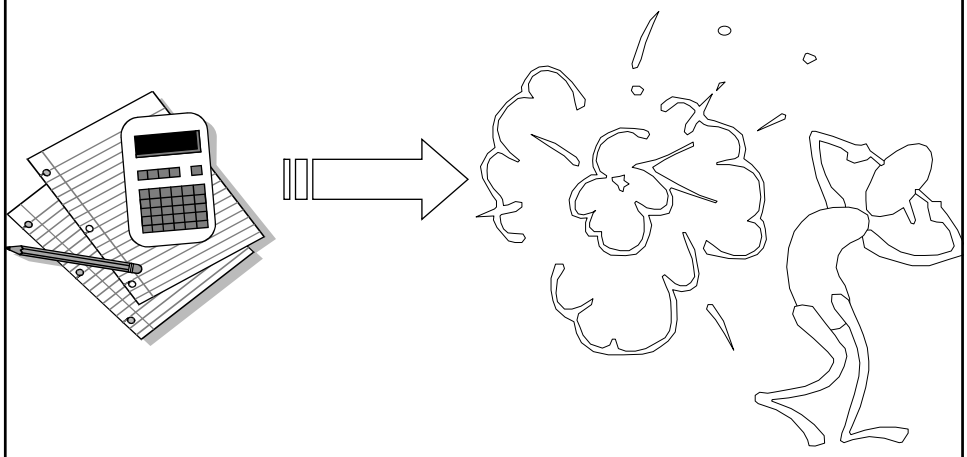
IF**...** you have repeated the "7 replicates" **more than twice**

OR**...** you have reached the lowest recommended spike levels

AND ...you still don't have a valid LOD...

1. Prepare and analyze a single standard at (or close to) the calculated LOD — 0.01 ppm
2. If you obtain a result within 20-30% of the concentration you prepared, then you have validated your LOD — 0.007 - 0.013
3. If you DO NOT obtain a value within 20-30% of the prepared concentration then… — 0.000 ppm
4. Prepare another single standard at a concentration slightly higher — 0.02 - 0.05 ppm
5. Repeat 2-4 until you obtain a result within 20-30% — 0.014 - 0.026 ppm, 0.035 - 0.065 ppm

Spike Calculations



Forget What You Know

…it's just not as simple as

$$\frac{\text{SPIKE - SAMPLE}}{\text{SPIKE AMOUNT}} \times 100$$

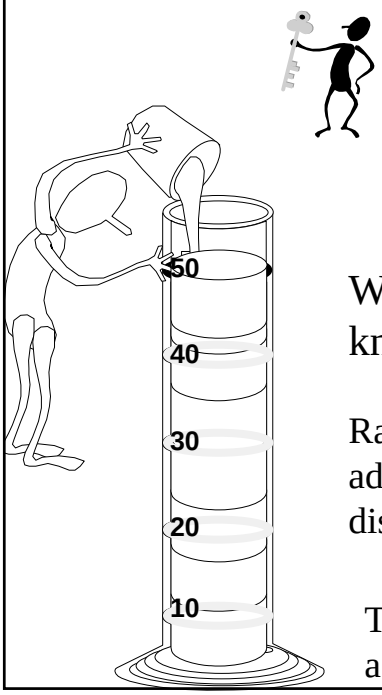
(although it *can* be…in some circumstances)

The correct equation...implied, but never said, is:

$$\frac{\text{SPIKE - SAMPLE}\left(\begin{smallmatrix}\text{Corrected}\\ \text{for dilution}\end{smallmatrix}\right)}{\text{SPIKE AMOUNT}\left(\begin{smallmatrix}\text{Corrected}\\ \text{for dilution}\end{smallmatrix}\right)} \times 100$$

Common Spike Calculation Errors

- Calculating by concentration and
  - not accounting for dilution of the sample,
  - not accounting for dilution of the spike solution,
  - or both.
- Calculating a ratio rather than a recovery.
- Using an incorrect formula.
  - The only acceptable formula is
  - $\frac{\text{Spiked Sample - Unspiked sample}}{\text{Spike Amount}}$



Mass vs. concentration

to understanding spike calculations is remembering that you are dealing with MASS (weight) rather than CONCENTRATION.

With spikes, you are adding a known MASS of analyte.

Rather than dealing with the problems of adding solid material directly, you dissolve a specific salt in reagent water.

The volume of reagent water is merely a vehicle for delivery of the analyte

Concentration Terms

ppm = parts per million = $\frac{1 \text{ part}}{1{,}000{,}000 \text{ parts}} = \frac{1 \text{ part}}{1000 \times 1000 \text{ parts}}$

ppm = mg/L = milligrams per Liter =

$$= \frac{1 \text{ mg}}{\text{L}} \boxtimes \frac{1 \text{ mL}}{1 \text{ g}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ L}}{1000 \text{ mL}}$$

ppm = ug/mL = micrograms per milliliter =

$$= \frac{1 \text{ ug}}{\text{mL}} \times \frac{1 \text{ mg}}{1000 \text{ ug}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mL}}{1 \text{ g}}$$

Concentration basics

Joe analyzes a sample for ammonia.
He takes 50 mLs of sample, adds his buffer solution
After stabilizing, the meter reads 5.0 mg/L.

The concentration value, 5.0 mg/L, means that in a liter of water, you would find 5.0 mg of ammonia dissolved in it.

But Joe only analyzed 50 mLs of sample; how many mgs of ammonia were in that 50 mLs?

5.0 $\frac{\text{mg}}{\text{L}}$ is the same as 5.0 $\frac{\text{ug}}{\text{mL}}$

5.0 $\frac{\text{ug}}{\text{mL}}$ ⊠ 50 mL = 250 ug ⊠ $\frac{1 \text{ mg}}{1000 \text{ ug}}$ = **0.25 mg**

Concentration ⊠ volume = **mass**

A concentration...

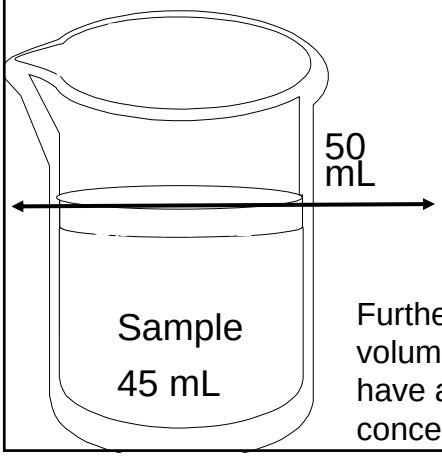
$$X\ \frac{ug}{mL} \times Y\ mLs$$

...times a volume

$$= XY\ ug$$ = a mass

Diluting to Known Volume

- If you dilute spike (with sample) to a known volume….
  (sample volume used in spike is LESS than that in the unspiked *sample concentration* must be adjusted.

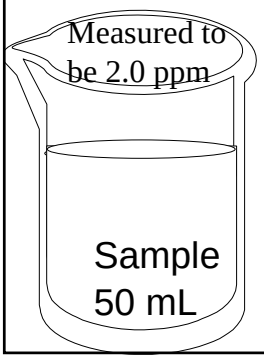


Since there is LESS sample-volume in the SPIKE than there is the SAMPLE, we cannot simply subtract the unspiked sample concentration

Furthermore, because we've added volume from the spike solution, we have actually DILUTED the sample concentration

Corrections: Dilution to Known Volume

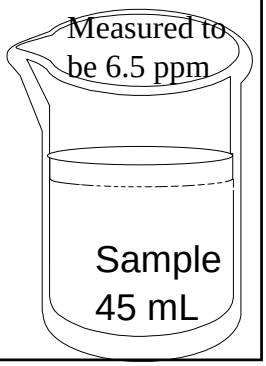
You cannot directly subtract background sample concentration when using the "Dilute to Known Volume" method.



In this case, rather than subtracting 2.0 ppm from the spiked sample,

you must subtract only 45/50 x 2.0 [*i.e.*,**1.8**]

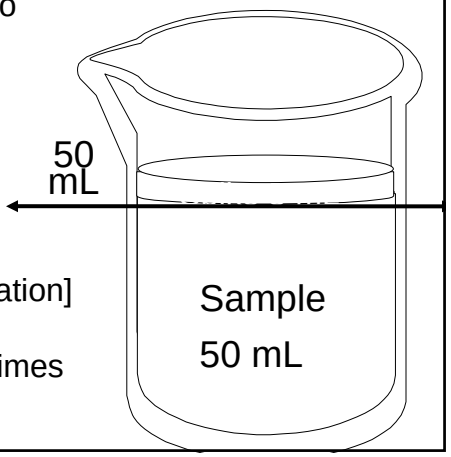
to account for the fact that less sample (and thus less concentration) was in the spike



"Adding on top"

- 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.

Analysts are often "tricked" into thinking that 10 mLs of spike solution added to 100 mLs of sample represents a 10-fold dilution of the spiking solution.



The TRUE spike amount [concentration] is determined as the ratio of spike volume to TOTAL sample volume times the spike solution concentration.

Adding on top - differential effects

If there is **no** pre-treatment or sample volume reduction involved (*e.g., digestion, distillation*):

TWO correction factors are required:

- one for the dilution of sample concentration, and
- another for dilution of spike concentration

If there **is** a pre-treatment step or sample volume reduction involved (*e.g., digestion, distillation*):

No correction factor is required.

Examples: Total phosphorus by hot plate, distilled ammonia

Spiked sample result – Unspiked sample result / Spike Amount

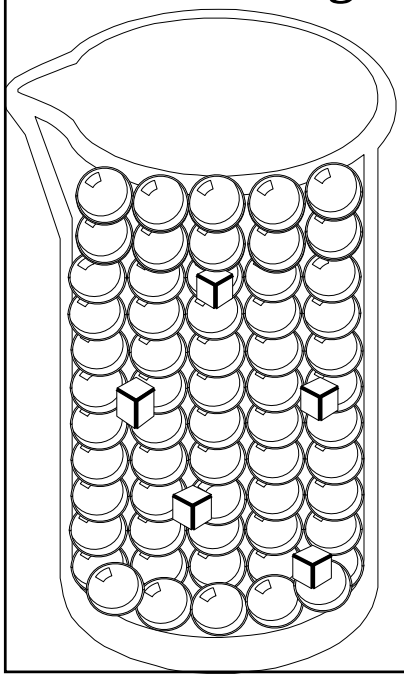
I analyze 50 mLs of sample. It measures 0.1 ppm [ug/mL] ammonia
I take another 50 mLs of sample and add 10 mLs of a 1.0 ppm [ug/mL] ammonia standard. I analyze this spike and I get 0.2 ppm [ug/mL]

$$\frac{0.2 \text{ ppm} - \overset{0.0833}{\cancel{0.1}} \text{ ppm}}{0.2 \text{ ppm}} \times 100 = \overset{58.3}{\cancel{50}}\% \quad \textbf{Right?}$$

Remember: we are dealing with concentrations here.
If the concentration of unspiked sample was 0.1 ug/mL,
and 50 mLs of sample were used,
then we know 5.0 ug (50 x 0.1) of ammonia came from the sample.

We also know that the total volume of the sample + spike was 60 mLs.
Thus the concentration of the unspiked sample is now $\frac{5 \text{ ug}}{60 \text{ mLs}} = 0.0833$ ppm

Understanding sample dilution



Here is 50 mLs of sample with 5 ug of analyte dissolved.

The concentration is 5 ug/50mL equaling 0.1 ug/mL or 0.1 ppm

If we add 10 more mLs of reagent water, (*the water volume from a spike*)

The concentration of analyte is now 5 ug per 60 mLs
or 5/60 = 0.08333 ug/ml
= 0.08333 ppm

 = 1 mL of sample

 = 1 ug of analyte

Spiked sample result – Unspiked sample result
Spike Amount

I analyze 50 mLs of sample. It measures 0.1 ppm [ug/mL] ammonia
I take another 50 mLs of sample and add 10 mLs of a 1.0 ppm [ug/mL] ammonia standard. I analyze this spike and get 0.2 ppm [ug/mL]

$$\frac{0.2 \text{ ppm} - 0.0833 \text{ ppm}}{0.2 \text{ ppm}} \times 100 = 58.3\%$$

(0.1667)

70.0

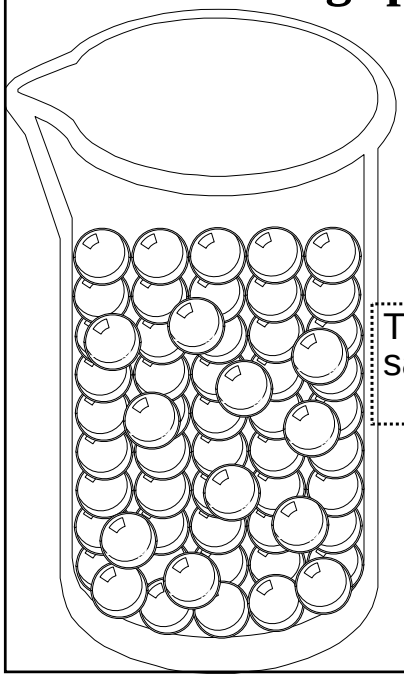
Right?

Yes …70%

Nope! We ALSO have to correct for the dilution of the spike solution.
If 10 mLs of a 1.0 ug/mL spike solution were spiked,
then we know 10 ug of ammonia were added from the spike.

We also know that the total volume of the sample + spike is 60 mLs.
Therefore the concentration of the unspiked sample is $\frac{10 \text{ ug}}{60 \text{ mLs}}$ = 0.1667 ppm

Understanding spike dilution



Take 50 mLs of sample with ZERO analyte in it (*or reagent water*)

Add 10 mLs of a spike solution with a concentration of 1.0 ppm (*1.0 ug/mL*)

The concentration of the spiked sample is NOT 0.2 ppm ($\frac{10}{50}$ x 1.0 ppm)

There are 10 ug, but the total volume is 60 mLs.

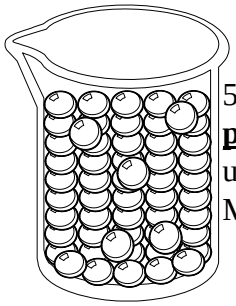
10 ug/60 mLs = 0.1667 ug/mL

= 0.1667 ppm

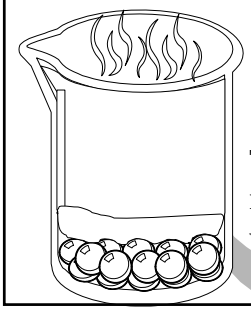
= 1 mL of sample

= 1 mL of spike solution

Why phosphorus is different



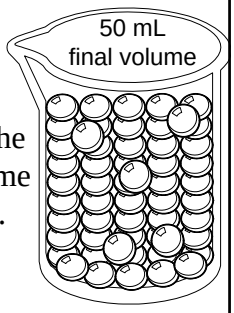
50 mLs of sample **plus** 5 mLs of 1 ug/mL spike solution. Mixed well.



The sample is heated and volume reduced to 10-15 mLs.

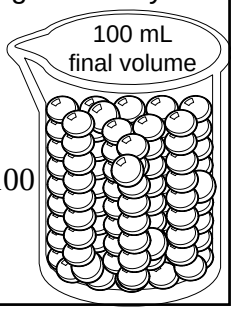
The 5 ug of analyte remain; just in less volume of water.

Then you dilute to final volume



Whether the final volume is 50 mL...

There's still only 5 ug of analyte



…or 100 mL...

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 matrix 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?

Survey Says...

- **about 40% say 90%**
- **another 25% say 98%**
- **perhaps 15% say 99%**
- **less than 10% say 107%,**
- **we have heard 45% and 53.5%, which represent a 2X error and answers (A) and (E)**

107%, by the way, is the correct answer.
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

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"

(use for any analysis that is similar)

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) **<u>spiked</u> = 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) **<u>recovered</u> = 133.75**
= C - A = *233.75 - 100*

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

Unspiked sample .246 X 25 = 6.15ug/mL **Spiked sample .346x 25= 8.65 ug/mL**
Unspiked sample Volume 2mL=>50 mL **Total volume 2 mL + 1 mL =>50 mL**

Spike volume 1 mL
Spike Conc. 5 ug/mL

A. Contribution (ug) from the sample in the spike = _____
_____ *ug/mL X (_____ mL - _____ mL) = _____ X ____*

B. The # of ug (of analyte) **spiked = _____**
_____ *ug/mL X _____ mL*

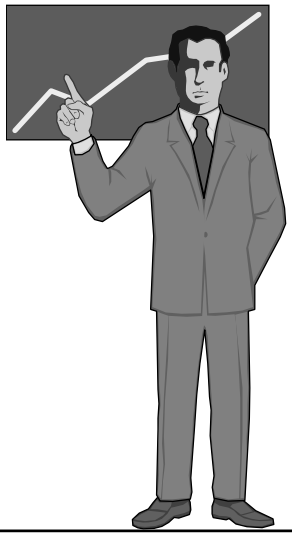
C. The # of ug (of analyte) **in the spiked sample = _____**
_____ *ug/mL X _____ mL*

D. The # of ug (of analyte) **recovered = _____**
_____ - _____

% Recovery = ____%
(_____ / _____) X 100

Example: Phosphorus- hotplate

Control Limit Reminders



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 $\pm$ 2 standard deviations
4. Control limits = Mean $\pm$ 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

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.

The Auditor says your limits are too broad

How do they know that?

- Remember: RPD should be about 20% or less
- 20% RPD means a range that is 1/5 of the mean
- Therefore, your upper control limit should be no more than 20% of your sample mean
  - Effluent Range control limit should be no more than 20% of average effluent concentration
    - Example…Effluent BOD averages 7 ppm Your replicate control limit should not be greater than about 0.2 x 7 = 1.4 ppm
  - Influent Range control limit should also be no more than 20% of average influent concentration

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 <u>out-of-control</u> data!
   Outliers should be excluded, but
   all out-of-control points are **not** outliers.

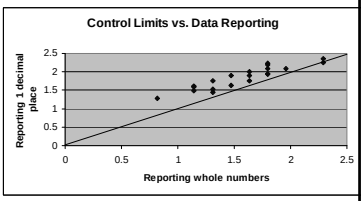
2. Include enough significant figures.
   - If values are whole numbers (e.g., 10, 89%), you can use one or even two decimal points to include some variability (10**.2**, 89**.3**%).
   - This same problem has been observed when a laboratory only reported recoveries to the nearest 5%.

Data Reporting vs. Control Limits

Date	Sample	Replicate	Range	Sample	Replicate	Range
1	10	10	0	9.9	9.6	0.3
2	5	4	1	4.6	3.5	1.1
3	10	10	0	9.6	9.6	0
4	10	10	0	9.5	9.9	0.4
5	8	8	0	7.7	7.9	0.2
6	11	10	1	10.6	9.9	0.7
7	8	7	1	7.5	6.6	0.9
8	11	11	0	10.7	10.7	0
9	6	6	0	5.8	5.5	0.3
10	8	8	0	7.6	7.7	0.1
11	10	10	0	9.6	9.6	0
12	11	11	0	10.6	10.8	0.2
13	11	10	1	10.6	9.8	0.8
14	9	8	1	8.7	7.6	1.1
15	6	6	0	5.6	5.7	0.1
16	8	8	0	7.6	7.9	0.3
17	11	10	1	10.8	9.9	0.9
18	9	8	1	8.8	7.5	1.3
19	5	5	0	4.8	4.9	0.1
20	11	10	1	10.9	9.6	1.3
Sum	**178**	**170**	**8**	**172**	**164**	**10**
Mean	**9**	**9**	**0.40**	**9**	**8**	**0.51**
Warning	2.51	X	1.004	2.51	X 0.505 =	1.26755
Control Limit	3.27	X	1.308	3.27	X 0.505 =	1.65135
Control limit should be no >			1.74			1.68

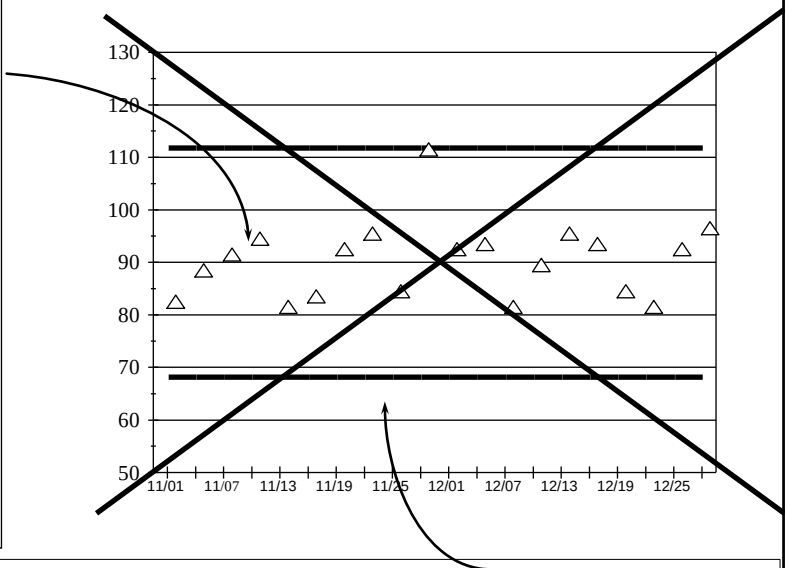
25% increase in control limi

- 19 of 20 runs: control limits higher without rounding
- Sample range 4-10 ppm
- 1 ppm max range
- correlation 0.922
- average percent increase was 18%
- Range was -1% to +44%



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%**

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)

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

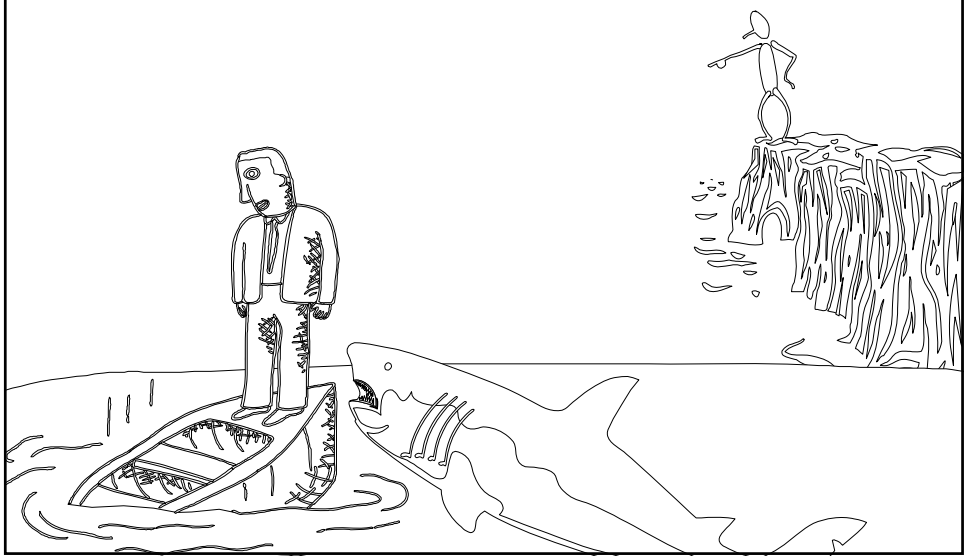
4. Discard outliers; re-calculate mean and SD

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?

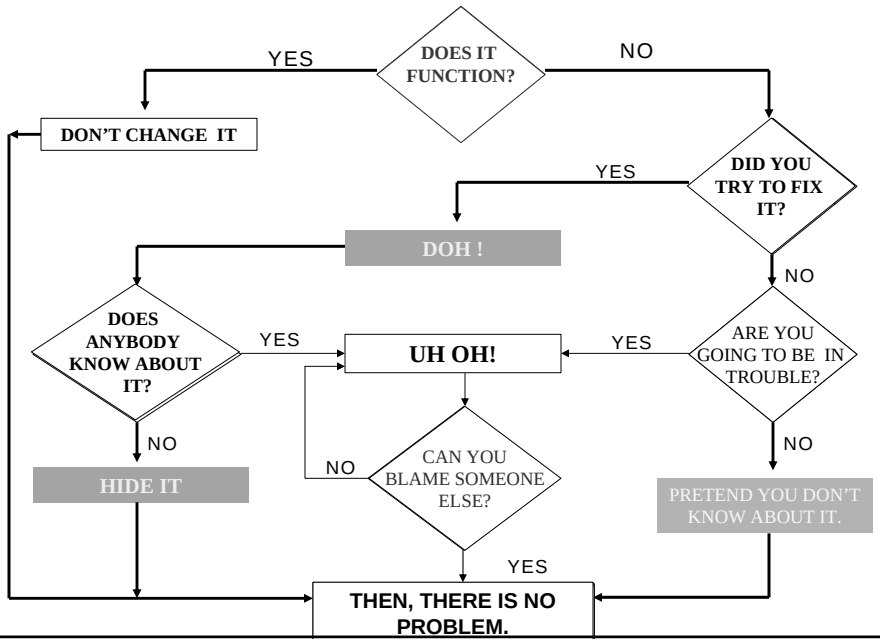
- In a nutshell, Corrective Action is anything done in response to an out-of-control situation.
- It MUST, however, be designed to identify the reason for the failure, and then correct it.
- There should also be a plan to quickly verify that the action taken has the desired effect.

What IS NOT Corrective Action?

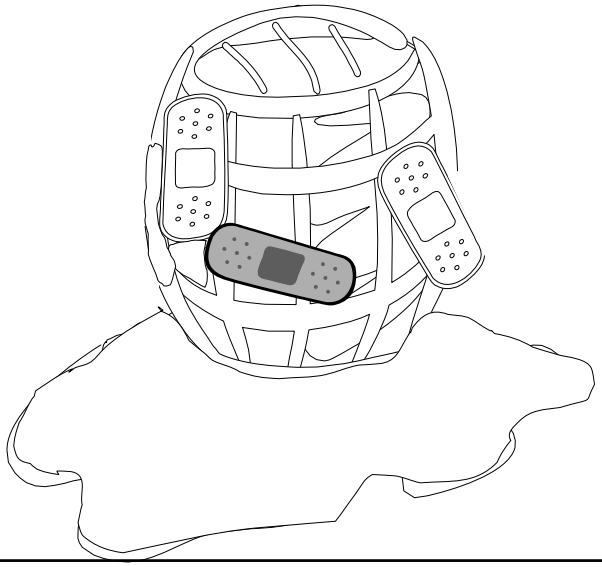
- Inaction
- A limited repertoire of fixes
- Addressing the effect vs. the cause
- Failure to ensure resolution

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

ACME Labs' Corrective Action Flowchart



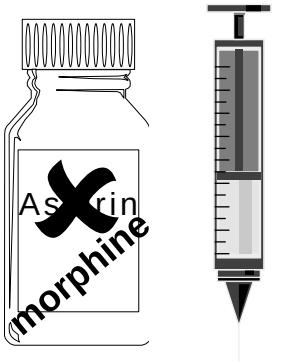
You need more than band-aids...



Getting past the Symptoms; Determining & Treating the Illness

If you're **not** prone to headaches, and suddenly develop a major migraine...

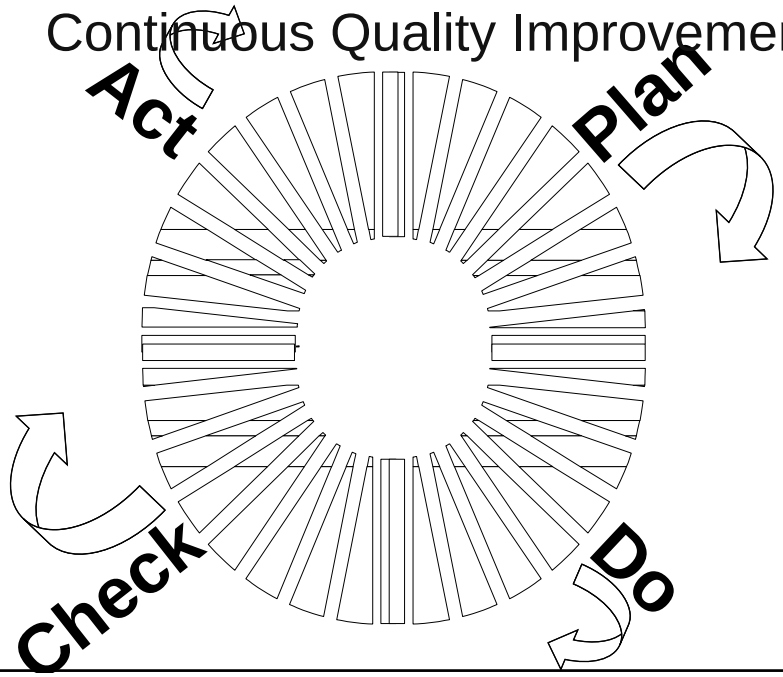
…how would you feel if the doctor simply prescribed ...?



Sure… it might work, but as the one with the problem, YOU don't want to waste time with "maybe" solutions

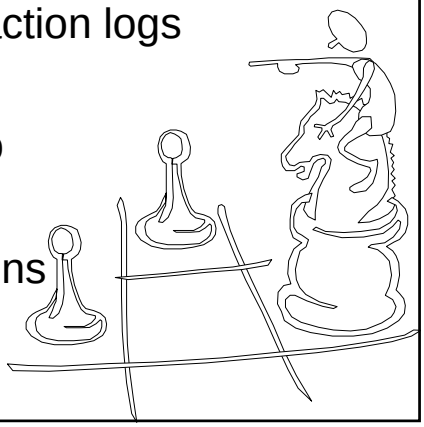
The first step in Corrective Action is to identify the cause of the problem at hand

Corrective Action = Continuous Quality Improvement



Plan

- ✓ Really think about potential causes
- ✓ Two heads are better than one…consult others
- ✓ Maybe check corrective action logs
  (*we'll discuss those later*)
- ✓ Identify a plan of action to address the problem
- ✓ Collect data or observations
- ✓ Establish a timetable for follow-up



Do

- ✓ Implement the plan--on a small scale
- ✓ Try to incorporate routine variables
- ✓ Don't commit to wholesale changes at this stage
- ✓ Most important…do not assume your plan is the ultimate solution…or even a viable one

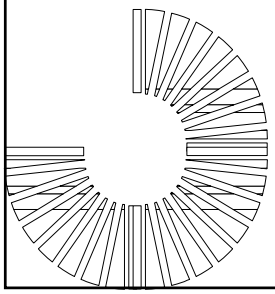
Think you have it covered?

- You've carefully thought out all the angles.
- You've done it a thousand times.
- It comes naturally to you.
- You know what you're doing, its what you've been trained to do your whole life.
- Nothing could possibly go wrong, right ?

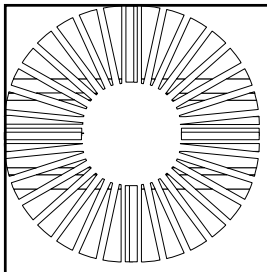
Think Again

Check

- Time to evaluate results
- Did the action correct the problem?
- Did it work under most routine situations?
- What did you learn?



Be sure to document each and every step along the way



Act

- ✓ Decision Time!
- ✓ If your plan seems to have corrected things, consider full-scale implementation
- ✓ Alternatively, consider other options

Corrective Action Form

QC failures

What QC type failure is involved:

___blank ___known standard ___calibration ___matrix spike ___replicate ___blind ___o

Blank: what is the LOD? _____ What level was detected in the blank? _____

Spikes/replicates: What are the acceptance criteria? _____ Your result? _____

If a matrix spike: Is this a matrix interference? ____ How do you know that?_____

_____

Known standards/blinds: True Value: _____ Acceptance criteria? _____ Your result? _

Other pertinent information_____

_____

Corrective Action Form -2

Other problems (equipment malfunctions, etc.)

Symptom(s) (how did you know something was wrong?):_____

_____

_____

_____

_____

_____

Corrective Action Taken

List any activities or checks you performed to identify the source and resolve the problem.

Action/Check Performed	What did you conclude?	Initials	Date

Corrective Action Form -3

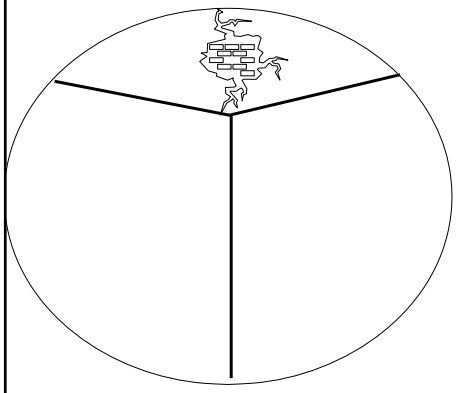
Resolution **Date:** _____

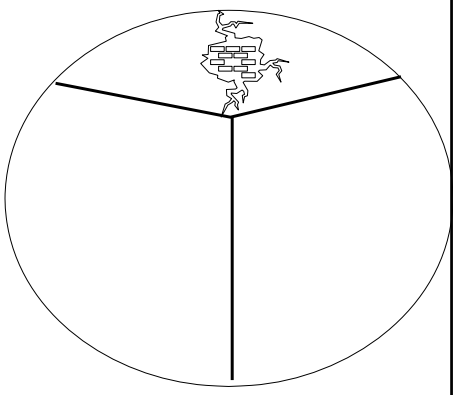
Briefly document how you know this problem has been corrected. What changes have you made to prevent it from recurring?

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?

Corrective Action?





Or Taking the
<u>Correct</u> Action?

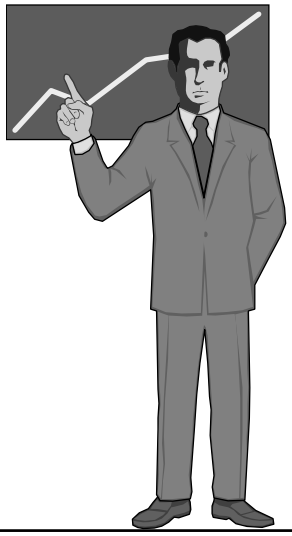
Corrective Action means changing roles

Time to STOP being the scientist….

Summary: Corrective Action

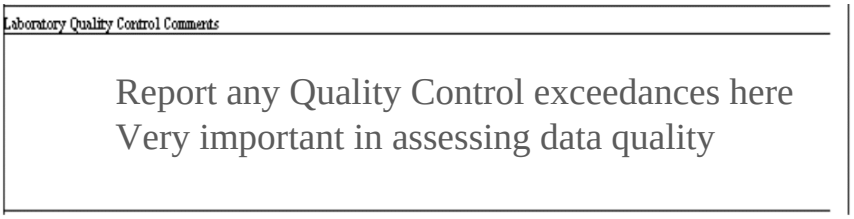
- *Identify the source of the problem*
- *Look beyond the effects…find the cause*
- *Develop a Game **Plan** to address the problem*
- *Implement the plan on a trial basis (**Do**)*
- *Evaluate the results of the change (**Check**)*
- *Decide whether or not the problem is solved (**Act**)*
- *Develop a documentation protocol*
  (trail of bread crumbs)
- *Qualify any affected data*

Qualifying Data



DMR: Laboratory QC Comments Box

This box is reserved for comments SPECIFICALLY related to laboratory QA/QC problems



Laboratory QA/QC Comments Box

Failure to report QC exceedances here is a weakness we are seeing during audits

Historically, reporting anything here has been perceived as a “black mark” against the facility

Time to change history!

(1) You are required to report this information

(2) If engineers do NOT see information here, we cannot assist you in resolving laboratory problems

The Truth About Qualified Data

Qualified data are NOT <u>necessarily</u> “bad” data.

ALL this means is that the data user (i.e., the DNR) needs to take into consideration the nature of the situation surrounding the qualification when interpreting the results.

Checking with Mr. Webster

qual·i·fy (kwŏl′ə-fī′)
v. **qual·i·fied, qual·i·fy·ing, qual·i·fies.**
v. tr.

1. To describe by enumerating the characteristics or qualities of; characterize.

4. To modify, limit, or restrict, as by giving exceptions.
5. To make less harsh or severe; moderate.

Qualifying Data - Considerations

- Make sure your comments are meaningful and understandable to the end user.
- Provide enough information so that the DNR can assess the data quality.
- Remember to include qualifiers from subcontract labs!
- Attach comments on a separate sheet if necessary. Write "see attachment" in the QC Comments box.

Qualifying Data - Reference Sample Failures

NR 149.13 (4) PROCEDURE FOR CORRECTING UNACCEPTABLE REFERENCE SAMPLE RESULTS.

(a) *All test categories, except category 18– safe drinking water tests.* After 2 consecutive reference sample failures the laboratory shall…

2. Qualify all test results of the analytes in the test or test categories which the laboratory has failed to meet acceptance limits on 2 consecutive reference samples

Example - Reference Samples

Situation: You have failed your BOD reference sample for the 2nd consecutive round of testing.

Resolution:

1. Order a 3rd reference sample ASAP
2. Identify and correct the problems
3. Pass the remedial reference sample!
4. Qualify any BOD results on the DMR until you pass a reference sample

Qualifying Data - QC Failures

NR 149.14 (3)(h) If the results of

- known standards,
- spiked samples,
- method blanks, or
- replicates

exceed the quality control limits,

<u>corrective action</u> shall be taken by the laboratory.

The laboratory shall

- reanalyze the affected samples or
- qualify the results *back to the last acceptable quality control check <u>of the same type</u>*

unless the laboratory determines that sample results are unaffected.

Qualifying Data - the "HOWs"

Code definition...
NR 149.04 (21m) "Qualify" means to place a written statement accompanying the test results which identifies anomalies encountered in generating the data.

Reference Sample failures (2 consecutive)...
NR 149.13 (4)(a) 2. Laboratories shall qualify test results by placing a statement in their analytical report [*i.e. the DMR*] stating that the laboratory has failed 2 consecutive reference samples for this analyte or analyte group.

QC Exceedances...
NR 149.14 (3)(h) The results are qualified by reporting that the laboratory analysis was not within the acceptance limits for this test.

QC Examples - Blanks

Situation: Your BOD blank depletions have been unacceptable for the past week. You traced the problem to a new bottle of "Cowboy Bob's" distilled water.

- ~~BOD blank failed~~.

- 5/10/01 to 5/17/01 - BOD blank depleted more than is allowed (0.2 mg/L). Blank depletions ranged 0.6 to 1.1 mg/L. Traced to new bottle of water.

QC Examples - Known Standard

Situation: Your BOD glucose-glutamic acid (GGA) exceeded acceptance criteria. You used a new lot of GGA standard the next day and results were fine.

- ~~GGA exceeded acceptance criteri~~a.
- 5/7/01 - GGA analyzed this day (235 mg/L) exceeded criteria (198 ± 30.5). Repeated GGA with new lot on 5/12/01. Result was 202 mg/L.

QC Examples - Replicates

Situation: Your influent TSS replicate on 5/17/01 exceeded upper control limit.

- ~~Replicate failed for TSS.~~
- 5/17/01 - Replicate result (5.5 mg/L) for TSS on influent exceeded upper control limit (1.9 mg/L). Replicates are done weekly, so data since 5/10/01 are affected. Heavy rains caused TSS levels to be 3 times typical levels. Did another replicate next day and it passed.

QC Examples - Spikes

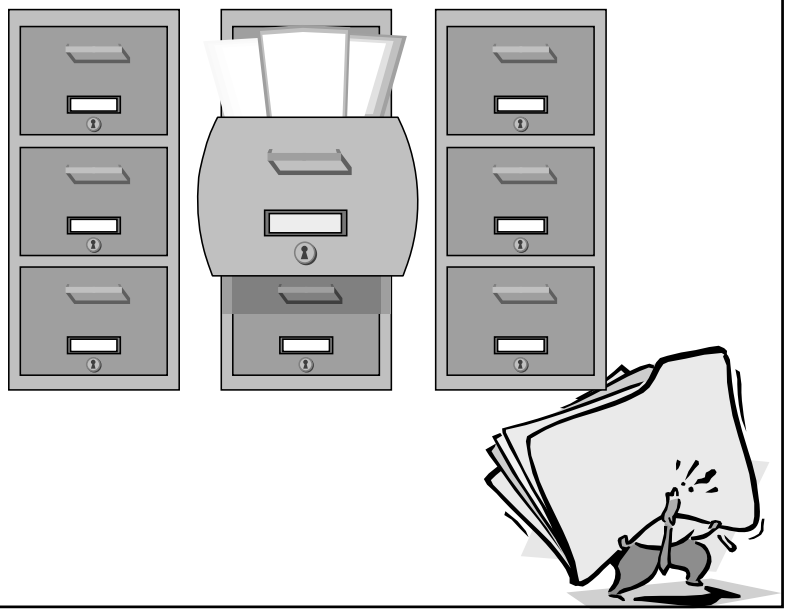
Situation: Your phosphorus effluent spike on 5/17/01 exceeded control limits.

- ~~Phosphorus spike exceeded control limit~~
- 5/17/01 - Spike for phosphorus on final effluent (35%) exceeded criteria (79-128%).
  Final is spiked every two weeks, so data back to 5/3/01 is affected. High phosphorus this day (1.2 mg/L) and the spike amount was too low (0.1 mg/L). I raised the spike amount to 0.5 mg/L, made up a spike the next day and it passed.

Qualifying Data - Final Words

- There is a significant level of QC required in testing, and thus - statistically speaking- you are going to exceed something each month.
- Even a lab doing only BOD and TSS 3x/week can generate up to 24 QC samples/ month.
- Add in ammonia & phosphorus, and the number increases to more than 75/month
- Consequently, it's almost an expectation that something will be qualified each month.
- With qualifiers, "less" is not more.

Documentation



Operating Principles

If you didn’t document
it, you didn’t do it!

If you did the work…
take credit for it!

Simple Approach to Co
Reagent Docume

Pre-print labels for new chemica

General convention: MM/YY means the FIRST day of the month

New Chemical or Reagent Label

Date received: ***4/2/01*** Date Expires: ***6/03***
Received by: ***J. Smith*** Date Opened: ***4/12/01***
Required Storage: ***Room temperature, away from light***
Chemical or Reagent: **Ascorbic Acid**

New Working Standard Label

Standard: *Phosphorus, 5 μg/mL* Std. Code: *100-3*
Date Prepared: *8/5/01* Prepared by: *A. Smith*
Date Expires: *9/5/01* Storage: *4°C*
Stock Std Code: *50-25*

Reagent and Standard Control Records

- Full traceability of reagents and standards to the original lot in a logbook

  Remember….traceability is in the "eye of the beholder"

- Traceable record of standards and regents used directly on the analysis record (bench sheet)

- Person preparing the reagents or standards, preparation and expiration dates on all reagents and standards

Reagent and Standard Control Records Continued

- Storage conditions
- Certification records provided by the manufacturer with a direct link to the calibration standards

Remember to record the standard code on the certificate so there is a link to the standards logbook!

The Not-so-obvious Things that Need to be Documented

Items that are often overlooked!

- Corrective actions taken

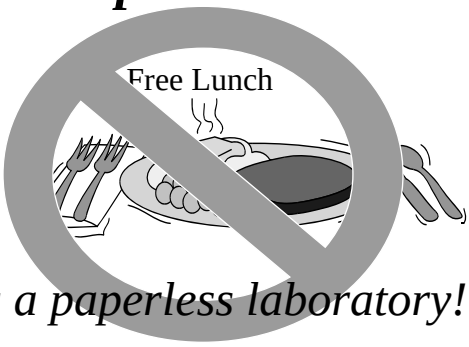
  Remember…you need to be able to ***show*** *auditors or courts what was done ….not just tell them!*

- Historical QC limits

  You may need to defend data 3-4 years old. Could you tell the courts what the QC limits were when the tests were done?

- Performance on blind samples and reference samples

Paperless laboratories - Reality or Pipe Dream?



….and no such thing as a paperless laboratory!!!

Automating and using electronic recording keeping process just means….

less Paper less

Recommended Practices when using Electronic Record-Keeping Processes

- Automated audit trail when ever records are changed
- Limit records access to a few authorized individuals
  e.g., Systems Administrator, Lab Director, etc.
- Implement a process to document any changes by the systems administrator
- Back-up data daily and use a media that will allow retrieval years later

e.g., Optical storage has a longer life than magnetic media

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

Summary

- ☑ Formulated a gameplan [*your QA manual*]
- ☑ Fine-tuned your detection limits
- ☑ Reviewed spike calculations
- ☑ Reviewed control limits and outliers
- ☑ Reviewed PROPER corrective action
- ☑ Discussed what qualifying data means
- ☑ Discussed required documentation

Questions?

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