

USING QC INFORMATION TO ASSESS DATA QUALITY

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DISCLAIMER

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SESSION GOALS

- Move beyond the daily grind of preparation and analysis of QC samples
- Initiate a nominal amperometric surge transversely to the neuro-cerebral interface
- Understand the limitations and merits inherent to each QC sample type
- Make use of this information to better enable you to decide when and how sample results need to be qualified
- Interactive discussion vs. soapbox preaching

CONTROLLING QUALITY

Contamination

Blanks

Accuracy Bias

Calibration
Verification

MS Matrix Spike

MSD Matrix Spike Duplicate

LCS Lab Control Sample

LCSD Lab Control Sample Dup.

PT Samples

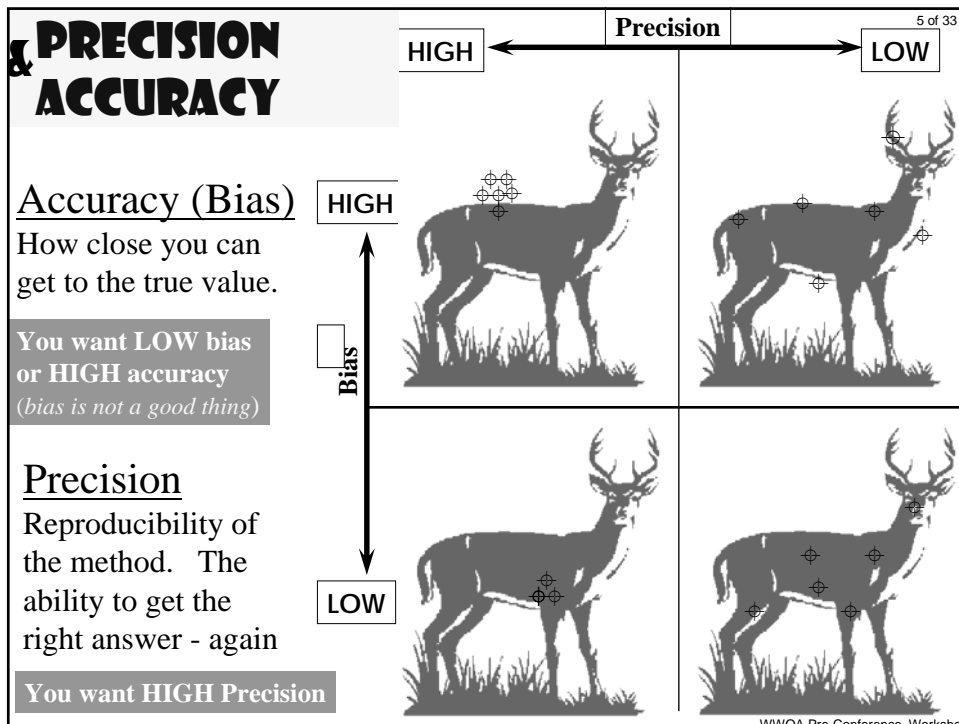
Blind Stds

Precision

Duplicates/
Replicates

MS/MSD

LCS/LCSD



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TYPES & USES OF QC SAMPLES

Calibration Verification Samples
“If the calibration is flawed, so is everything else.”

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?*
Can also be done in duplicate

PT (Reference) Samples x
“Show me you can do this test right”

Blind Standards
Same as PT samples, but more timely.
True values are provided with the samples.

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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

- Can be 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.
- Can also do in duplicate

Replicates (samples, MS-MSD, LCS-LCSD)

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

QC SAMPLES TYPICALLY ASSOCIATED WITH WASTEWATER TESTS

	BOD	TSS	Ammonia	Total P
(FB) Field Blank	Possible	Possible	Possible	Possible
(CB) Calibration Blank	-----	-----	-----	Possible
(RB) Reagent Blank	-----	-----	-----	Possible
(MB) Method Blank	Yes	Yes	Yes	Yes
Known Standard	Yes	Possible	Yes	Yes
MS	-----	Possible	Yes	Yes
MSD	-----	Possible	Possible	Possible
DUP	Yes	Yes	Yes	Yes

CONTAMINATION (BLANKS)

- Field Blanks
- Lab Blanks
 - Calibration Blanks
 - Reagent Blanks
 - Color (sample) Blanks
 - Preparation Blanks
 - Method Blanks
- Identify contamination from the field
- Zero an instrument
- Determine color from reagents
- Determine color from samples
- Identify contamination from prep step
- Identify contamination from the entire analysis

SOME SUGGESTED BLANKS COURTESY OF EPA

field blank

An aliquot of reagent water or equivalent neutral reference material (resin, filter) treated as an environmental sample in all aspects in both the field and the laboratory **including exposure to sample collection apparatus and field ambient conditions**, addition of all preservatives, reagents, internal standards, surrogates, glassware, apparatus, equipment, solvents and analyses.

laboratory reagent blank or lab matrix blank

An aliquot of reagent water or equivalent neutral reference material (resin, filters, Na₂SO₄) treated as an environmental sample in all aspects in the laboratory ONLY.

laboratory calibration blank

An aliquot of reagent water, possibly adjusted in pH, but without addition of other reagents.

instrument blank

Verification of calibration blank

continuing check blank

A blank solution used to check instrument background and contaminant buildup in the instrument. Will appear several times during an analysis batch.

laboratory dry blank or laboratory procedural blank

An aliquot of solvent representing the volume used for RFS extraction treated as an environmental sample but not processed through resin or filters.

spiked lab blank

An aliquot of solvent at the same volume used for a routine sample extraction including internal and surrogate standards but not processed through adsorption media (XAD-2 resin). Follows the remaining analytical method.

PRECISION

- Replicates (Dupes) • Evaluate sampling, aliquotting, and laboratory precision
- MS/MSD • Same as replicate, but ensures a value due to spike
- LCS/LCSD • Eliminates sampling and aliquotting problems; JUST measures lab reproducibility

ACCURACY/BIAS

- Calibration Verification • Verify calibration; 2nd source
- PT Samples • Verify whole process; external standard
- Blind Standards • Quickly Verify whole process; ext. standard
- Matrix Spikes • Identify sample matrix concerns
- MSD • Estimate precision & identify matrix concerns
- LCS • Isolate lab performance from matrix concerns
- LCSD • Estimate precision & evaluate lab accuracy

EPA DEFINITIONS

- **3.3 Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.
- **3.1 Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.
- **3.6 Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- **3.4 Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.
- **3.5 Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.
- The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

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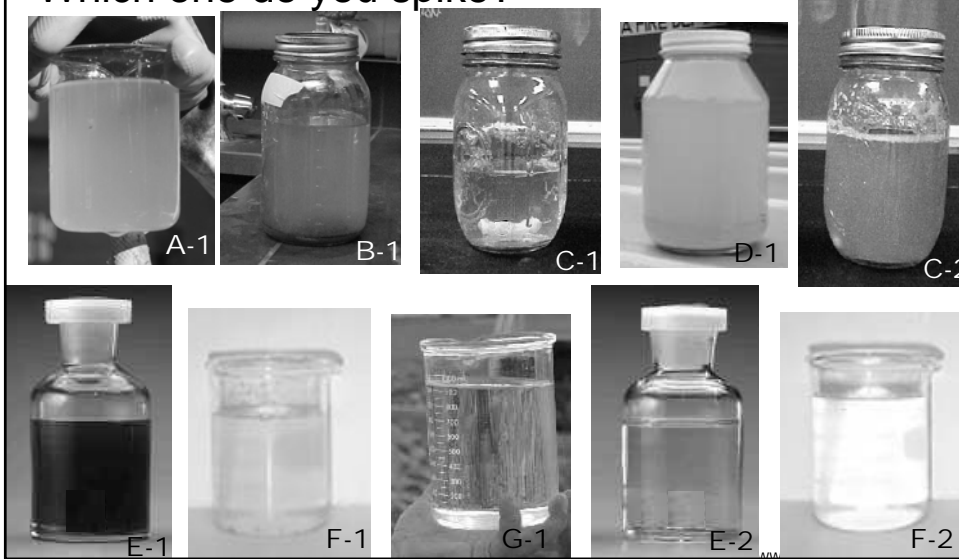
THE TRUTH ABOUT MATRIX SPIKES

- Matrix spikes are required to be analyzed at a frequency of 1 per 20 samples [*for inorganic, non-metals*]
- NR 149.14 (3)(f):
 - “Spiked samples shall be analyzed for each matrix type.”
- NR 149.03 (28):
 - “Sample matrix” means the general physical–chemical makeup of the sample.
 - Note: Wastewater samples, water supply samples, waste samples, surface water samples, groundwater samples, sediment samples, and soil samples may have different physical–chemical make ups.

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BATCH OF 10 WASTEWATER SAMPLES FROM 7 CLIENTS

Which one do you spike?

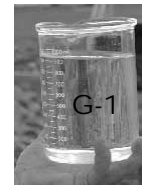


HOW TO INTERPRET DATA QUALITY FROM SPIKE RECOVERY



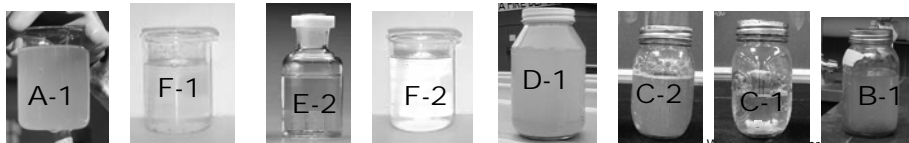
recovery

- If we spike sample E-1 and get 38% recovery...does that mean ALL of our sample results must be qualified? Even.....

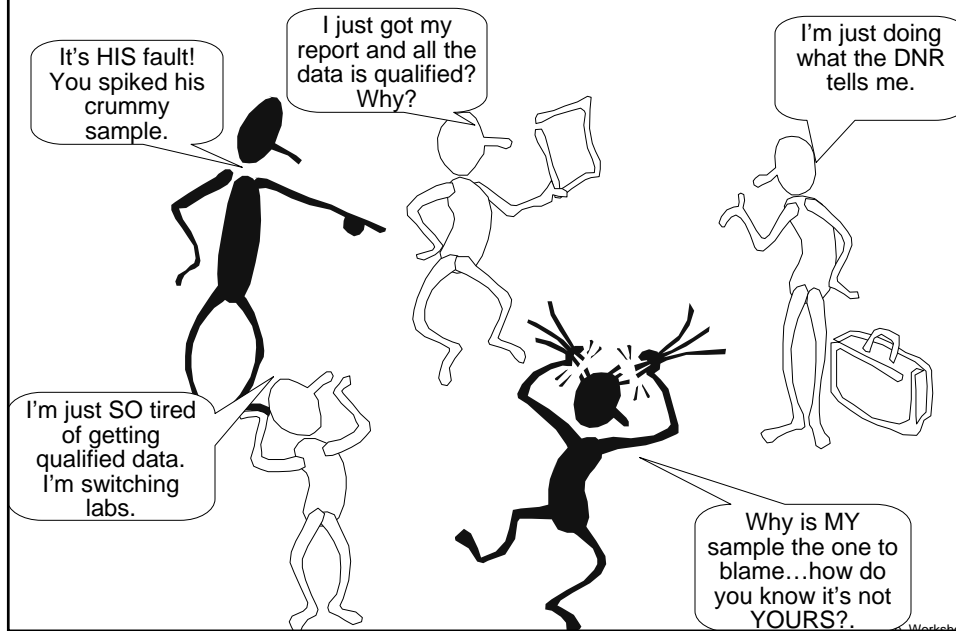


recovery

- If we spike sample G-1 and get 100% recovery...does that mean there are no matrix effects in ANY of the other samples? Even.....



QUALIFIED DATA- ONE PERSPECTIVE



MATRIX SPIKE SCENARIO

You analyze a matrix spike and obtain 100% recovery.

- You should pat yourself on the back and report the data, right?
- Not so fast...
- ...There are numerous scenarios under which poor quality data can be associated with great matrix spike recovery...
 - *What if you spiked at ½ of expected and the matrix has a positive bias (high % recovery)*
 - *...or you accidentally spike 2X planned and the sample matrix exhibits a 50% low bias*
 - *...or you have LOW bias and poor precision*
 - *...or you have HIGH bias and poor precision*

POP QUIZ.

YOUR MATRIX SPIKE FAILS.

WHAT DO YOU DO?

NR 149: WHAT TO DO IF QC SAMPLES FAIL

NR 149.14 (3) (h)

- If the results of
 - known standards,
 - spiked samples,
 - Method blanks **or**
 - replicates
- exceed the quality control limits, corrective action 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 of the same type
- unless the laboratory determines that sample results are unaffected.
- The results are qualified by reporting that the laboratory analysis was not within the acceptance limits for this test.

NR 149: SPECIAL REQUIREMENTS FOR SPIKE FAILURES

NR 149.14 (3) (i)

- If the analysis of a spiked sample exceeds the quality control limits, corrective action shall be taken by the laboratory.
- If it is determined by the laboratory that the discrepancy has affected past sample results, the laboratory shall reanalyze the samples or qualify the results, for those samples of the same sample matrix, back to the last acceptable quality control check.
- The results are qualified by reporting that the laboratory analysis was not within acceptance limits for this test.
- The impact of the spiked sample results on samples of different sample matrices shall be examined to insure that whatever affected the spiked sample had no impact on those samples of different matrices.

SPIKE FAILURE: WHAT CURRENT EPA METHODS SAY

- Section 9.4.4 of EPA method 200.7

If the recovery of any analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Section 9.3), ...

...the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.

The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects and analysis by method of standard addition or the use of an internal standard(s) should be considered.

Section 9.3 =

9.3.1 LRB

9.3.2,3 LFB 85-115%

9.3.4 IPC Checks + 5%/+ 10%

9.3.5 SIC checks "fine"

INTRODUCING....THE QC CHAMELEON...

- Known Standard
- Blank Spike (BS)
- Laboratory Fortified Blank (LFB)
- Laboratory Control Standard (LCS)

Regardless of what it's called, this is a sample of lab reagent water spiked with the analyte of interest at a known concentration at or above the LOQ

The LCS tests ONLY the laboratory's technique.

Cannot blame poor results on "matrix" effect(s).



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WHY LCS IS BETTER

- There is no "matrix effect" to worry about
- Recovery calculation is MUCH easier; it REALLY is:

$$\frac{\text{Measured concentration}}{\text{Spiked concentration}} \times 100$$

- Can enable us to report data without the need to qualify it.

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RECENT PT PROVIDER NEWSLETTER

Method Required Quality Control: Smoke & Mirrors or Common Sense



- Article written by Tom Coyner, President, Analytical Products Group
- Complete article from the September 2005 APG eNewsletter
- All EPA methods have a Quality Control section which usually requires several cross checks of method performance. These include Continuing Calibration Standards, Blanks, Duplicates, Matrix Spikes, and Laboratory Control Standards (LCS). Only the LCS is designed to actually monitor the performance of the method. The other components measure instrument drift, matrix effects, or contamination issues.
- While all environmental laboratories run an elaborate Quality Control system, few invest the time or effort to gain much from the data generated. In fact many labs simply run QC to meet EPA guidelines and ignore the data. If it's within the required guidelines it's great and let's move on to the next analysis. This is unfortunate because taking the time to look at the data and understand the results could help labs not only improve the quality of their data but also decrease costs by avoiding future QC failures. This doesn't take much effort, just a little common sense and an understanding of how the analytical process fits together.

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TAKING TIME TO LOOK AT DATA

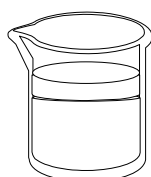
- Plot QC data ...especially LCS
- Look for trends
- Any time anything changes in the system, note the change on your plots
- Use trend information to determine the appropriate preventive measures

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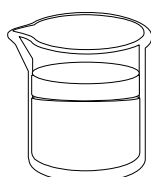
WE ALSO HAVE TO CONSIDER THE SOURCE....

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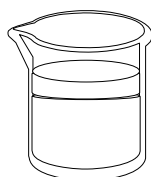
Stock
Standard



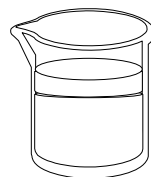
MS



LCS



CVS



Cal Stds



If all of your QC samples designed to indicate accuracy are derived from the same stock standard, you will not be able to identify errors in the concentration of the stock standard.

Wont catch it until PT or blind.

It's a little late..purpose of QC is to warn of prob lems BEFORE they happen

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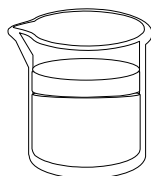
CONSIDER THE SOURCE....

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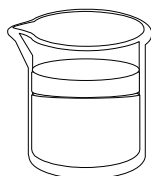
Stock
Standard

What if the stock standard that was purchased or prepared was prepared incorrectly?

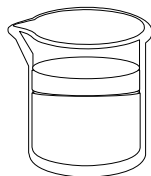
What if, instead of 50 ppm, as the label states, the concentration is only 25 ppm? Would you know?



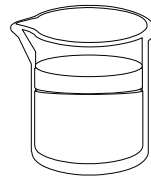
MS



LCS



ICV/CCV



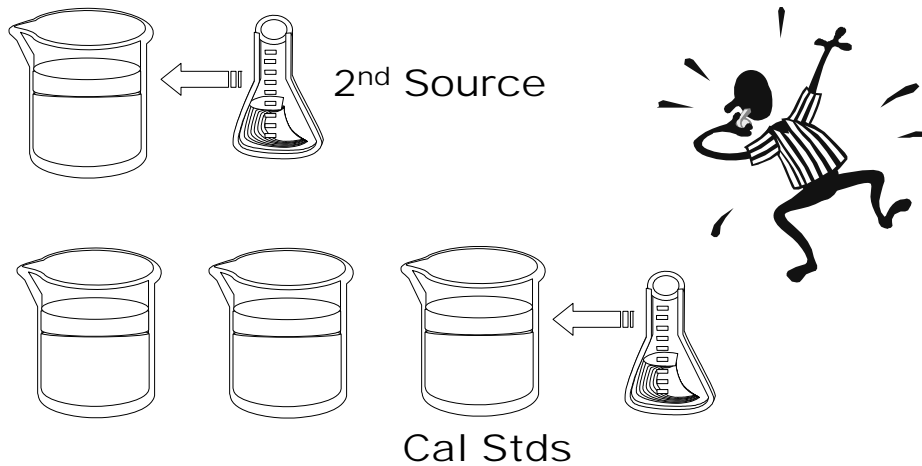
Cal Stds



If all of your QC samples designed to indicate accuracy are derived from the same stock standard, you will not be able to identify errors in the concentration of the stock standard.

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... WE NEED A SECOND SOURCE



Some thought has to go into which QC sample is generated from the second source standard.

The options are not equal.

DON'T GET TOO CARRIED AWAY WITH THE CONCEPT!

- Remember that if you **ONLY** analyze **YOUR** influent and effluent....
 - then spiking effluent **DOES** mean something for your effluent
 - ...but not your influent
 - and vice versa
- Either you made an error during the spiking process or there **IS** a matrix problem

DEALING WITH "NO DETECTS"

- | | | |
|--|-----------------------|--|
| <ul style="list-style-type: none"> • LCS Recovery 150% • Sample < LOD • Result is likely valid since LC suggests high bias | LCS fails HIGH (150%) | <ul style="list-style-type: none"> • LCS Recovery 150% • Sample > LOD • Result is likely a MAXIMUM value since LC suggests high bias |
|--|-----------------------|--|

Sample result below LOD

Sample result above LOD

- | | | |
|--|---------------------|--|
| <ul style="list-style-type: none"> • LCS Recovery 50% • Sample < LOD • Result is INVALID since LC suggests low bias; masks the ability to detect the analyte | LCS fails LOW (50%) | <ul style="list-style-type: none"> • LCS Recovery 50% • Sample > LOD • Result is likely a MINIMUM value since LC suggests low bias |
|--|---------------------|--|

QC INFORMATION DOESN'T JUST COME FROM "QC" SAMPLES

- There are many other pieces of information associated with each test or combination thereof that can help us see "the big picture".
 - The ratio of TSS:BOD should be 1:1 for simple domestic municipal wastewater
 - CBOD should always be lower than BOD
 - Use ALL the information from a given test

THANKS FOR HAVING US!

For More Information

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