Alternative Approaches to Collecting and Interpreting Matrix Spike Data

There has to be a better way ...

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27th Annual EPA Conference on Managing Environmental Quality Systems

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Why Do We Analyze Matrix Spike Samples?

- One hallmark of data of "known quality" is an assessment of the bias and precision of the measurement process
- Usually assess this by preparation and analysis of field samples spiked with the analytes of interest
- These "matrix spike" samples have been incorporated into many EPA programs and methods since the 1970s
- Purpose is to demonstrate how well the method applies to the sample matrix

Three aspects have remained largely the same for over 30 years

- Frequency at which spiked samples are to be analyzed
- Equation used to calculate the recovery of the spiked analytes
- Spiking levels used

Problems can arise with any or all of these.

Matrix Spike Frequency

- Most commonly used frequency is 5%, (1 in 20 samples of the same type)
- Matrix spikes alone are used for analytes that routinely occur in the environment, such as metals, with duplicate analyses used to assess precision
- Matrix spike/matrix spike duplicate pairs are used for analytes that rarely occur, such as organics and provide data on both bias and precision
- 5% frequency balances the need for performance data against cost
- Other frequencies may be appropriate — 5% is simply a common default value, not a magic number

Equation

A common form of the equation is:

$$\%R = \frac{X_s - X_u}{K} \times 100$$

where:

%R = percent recovery of the spiked analyte

X_s = measured value for spiked sample

X_u = measured value for unspiked sample

K = known value for the spike in the sample

Equation (cont.)

- **The form of the common equation amounts to:**

$$\frac{\text{The increase you expect to occur from spiking}}{\text{The amount you spiked}}$$

- **Problems occur when:**
  - **Parent sample isn't homogenous, or can't be made homogeneous (e.g., samples for volatile organics can't be vigorously stirred)**
  - **Amount of analyte spiked is low, relative to the background concentration. Uncertainty in measurement of the unspiked sample may exceed the absolute amount of the spike**
  - **Can result in negative recovery values – a physical impossibility that violates the law of conservation of mass**

What Do Data Users Do?

- Scratch their head
- Blame the lab
- Try to explain what happened
- Keep blaming the lab
- Give up and ignore the lack of useful data on method performance in the matrix
- Reject the data and start all over, because it obviously was all the lab's fault …

What *Should* Data Users Do?

- Understand the purpose of the matrix spike analysis
  - It's NOT a measure of laboratory performance
  - Rather, it's a demonstration of how well the overall method performs in the sample matrix in the particular application

What *Should* Data Users Do? (cont.)

- Focus on making the best of a bad situation
  - Maybe the method specified for the project wasn't the best choice
  - Maybe the sampling approach was not ideal

What *Should* Data Users Do? (cont.)

- Use an alternative equation that eliminates the possibility of negative recovery values and provides a better picture of what is really happening
- Empower the laboratory to do a better job

Alternative Equation

- **A simple rearrangement of the terms eliminates the chance of negative values**
- **The alternative equation is:**

$$\%R = \frac{X_s}{X_u + K} \times 100$$

with the meanings of all the terms staying the same

Alternative Equation (cont.)

- **Eliminating the subtraction operation from the numerator means that there can never be a negative value**
- **The alternative equation amounts to:**

$$\frac{\text{What you found in the spiked sample}}{\text{What you expected to find}}$$

Example Data - Matrix Spike Recoveries for Metals in Sludge, Calculated in the Traditional Fashion and with the Alternative Equation

Analyte	Recovery (%)									
	MS1	ALT1	MS2	ALT2	MS3	ALT3	MS4	ALT4	MS5	ALT5
Aluminum	177.7	102.4	334.5	104.2	68.8	98.5	400	114.9	443.9	107.9
Antimony	44.3	45.7	41.1	43.7	75.7	75.7	41.5	42.0	46.4	47.4
Arsenic	102	101.8	102	101.7	101.5	101.4	111.1	110.6	101.6	101.5
Barium	99.2	99.7	98.8	99.5	101.9	101.0	96.3	98.2	117.5	105.7
Beryllium	108.7	108.3	99.7	99.7	102.3	102.3	112.4	112.0	101.2	101.2
Boron	105.1	103.5	106.5	105.9	110.6	108.4	110.6	108.9	103.7	103.0
Cadmium	110.7	105.9	117.4	108.6	112.9	111.5	121.8	119.6	110.7	107.9
Chromium	93.9	98.8	113.7	105.0	110.5	106.9	118.8	110.5	118.1	102.4
Cobalt	101.1	101.0	102.9	102.7	107.6	107.3	116.3	115.7	115.7	104.0
Copper	83.2	98.5	59.7	96.7	79.5	97.9	40	95.2	173.3	104.7
Iron	-203	98.0	1543.8	111.3	-71.4	96.5	265	103.4	156.2	100.8
Lead	111.3	104.4	108.3	103.0	111.1	108.6	118.9	113.6	109.5	105.7
Manganese	78.2	97.9	135.9	108.1	91.7	99.7	81	95.1	101.3	100.4
Molybdenum	103	102.6	108.7	105.7	111.5	110.0	110.3	110.0	107.5	106.9
Nickel	101.7	101.3	105.5	103.8	105.6	105.1	118.3	114.7	102.5	102.2
Phosphorus	-101.5	96.9	-123.5	91.2	-203.9	90.1	-46	91.7	-41.8	96.0
Selenium	102.3	102.0	101.4	101.3	102.8	102.6	112.9	112.2	103.5	103.2
Silver	68	90.7	93.8	98.2	103.3	101.4	83.1	92.3	101.8	101.1
Thallium	104.8	104.7	106.2	106.2	107.4	107.4	108.9	108.8	108.4	108.4

But Seriously …

- **We could put up dozens of tables in tiny type, but let's start a few select examples**
- **Phosphorus in sewage sludge:**

X_s (mg/kg)	X_u (mg/kg)	K (mg/kg)	Rec %	Alt Rec %
271	317	189	-24.3	53.6

53.6% recovery isn't great, but -24.3% recovery makes no sense at all. The likely culprit is an inhomogeneous sample.

More Examples

- **bis(2-Ethylhexyl)phthalate in sewage sludge:**

X_s (µg/kg)	X_u (µg/kg)	K (µg/kg)	Rec %	Alt Rec %
140,000	170,000	419	-7160	82.2

82% recovery is quite reasonable in contrast. The original recovery is likely a function of the high dilution factor needed, a low spike amount and an inhomogeneous sample.

- **Sertraline in fish tissue:**

X_s (µg/kg)	X_u (µg/kg)	K (µg/kg)	Rec %	Alt Rec %
733	545	40	468	125

The effect of the low spike amount is eliminated here.

Still More Examples

- **2-methylnaphthalene in sewage sludge:**

X_s (µg/kg)	X_u (µg/kg)	K (µg/kg)	Rec %	Alt Rec %
479	29	489	92.02	92.47

Rounded to the nearest percent, the two recoveries are indistinguishable.

This is not surprising, since the original equation works well when there is little or no background, or the spike amount is much greater than the background.

No, its not cherry picking!

- In the 2006-2007 National Sewage Sludge Survey, the lab analyzed 15 MS samples spiked with 25 metals (n = 375). Many recoveries were acceptable, but the alternative equation:
  - Converted all 18 negative values to recoveries from 56% to 96%
  - Reduced 22 recoveries between 150% and 1500% to values between 90% and 110%
  - Reduced 12 recoveries between 200% and 2100% to values between 190% and 450%
- Also worked well for dozens of other analytes in that survey and in various other studies involving fish tissues and sediments

What It Does

- Uses the same measurement results, so it simply illustrates the performance in a more appropriate fashion
- Addresses those cases where the sample is not homogeneous, such as soils, sediments, and tissues
- Helps where the spike level is simply too low to make a dent in the background concentration

What It Doesn't Do

- Can't make up for a poor choice of method for a given matrix
- Won't solve all the problems of blindly spiking samples

The Perils of Blindly Spiking Samples

- Without knowledge of the background concentration, labs are forced to guess at what concentration to spike
- Often under pressure to turn results around quickly, regardless of the quality of the data
- Often spike with the same stock solution for every sample, based on a method default or recommendation

The Perils of Blindly Spiking Samples (cont.)

- Lab gets blamed, no matter what
- Data users are so used to getting illogical data that they are reluctant to talk to the lab or give them the tools to try to do better
- In the end, no one really knows if the method performs well in the matrix

The Solution — Empower the Lab

- Let the lab analyze the unspiked sample first, then choose an appropriate spiking level
  - Runs afoul of the *assumption* that the spiked sample must be prepared in the same batch as the original sample
  - But the MS/MSD is designed to provide information about matrix, not the prep batch
  - Some methods already describe how to choose an appropriate spiking level

The Solution (cont.)

- **Decouple the spiked sample from the batch frequency and prepare the spiked samples after the results for the unspiked sample are known**
  - **Requires a change in thinking by labs and their clients**
  - **Those changes begin in the planning stages, as you develop a QAPP and SAP**
  - **Specify it in the QAPP and it becomes a requirement**

Decoupling Works Best in Long-term Projects

- **Samples analyzed early in the project can be used to prepare matrix spike samples for later batches, avoiding blind spiking**
- **Time lag minimized if the lab examines results as soon as possible**
- **Spiked samples come from your project, not someone else's, where the matrix may not be similar**
- **Lab and data user gain knowledge of what to expect as time goes on and changes can be made to the sampling and analysis plan**
- **User ends up with helpful information on method performance**
- **Better data can lead to better decisions**

Where Decoupling Works Less Well

- Compliance monitoring situations where only one sample is analyzed and the results must be submitted to a permitting authority on a set schedule
  - –You get what you pay for. Shopping for lowest price every time means that the lab can't gain experience with your matrix and background levels.
  - – Giving the lab knowledge of past results can help (e.g., ranges of concentration of the analytes they could expect to find)
  - –It can still work if the lab examines the original sample results as soon as possible

Where Decoupling Works Less Well (cont.)

- There's no free lunch. If you aren't willing to pay for the matrix spike on your sample, then you have to accept recovery data from whatever sample the lab chooses
- Not likely to affect permit reporting because the permitting authority rarely sees anything other than the compliance sample results. Matrix spike and other QC data are usually kept on file by the permittee or the lab

You Choose:

- **Better data and better decisions?**
- **Or the "convenience" of doing a consistently bad job time and time again?**

Tough choice, eh?