

# Uses (and Abuses) of Reference Materials for Environmental Analyses

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# Disclaimer

- The authors are a couple of old EPA contractors (emphasis on “old”). We did not ask anyone at EPA for permission to present this material and we don't presume to speak for our EPA clients.

# Definitions

(from NIST.gov)

- **Reference material:** Material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.
  - Generic term
  - Properties can be quantitative or qualitative, e.g. identity of substances or species.
  - Uses may include the calibration of a measurement system, assessment of a measurement procedure, assigning values to other materials, and quality control.

# Definitions

## (continued)

- There are several “flavors” (our word) of reference materials:
  - Certified Reference Material (CRM)
  - NIST Standard Reference Material<sup>®</sup> (SRM)  
*(NIST has registered the term as a trade name)*
  - NIST Reference Material (not certified)
  - NIST Traceable Reference Material<sup>™</sup> - a commercially-produced reference material with a well-defined traceability linkage to existing NIST standards for chemical measurements

# Definitions

*(ours, for the purposes of this presentation)*

- **Reference material:** Something you buy from a vendor that has known properties or characteristics and that usually comes with some certificate as to what it contains.
- **Reference matrix:** A clean example environmental matrix type (e.g., aqueous, solid, tissue).

# Practical Aspects

- Reference materials should be:
  - Readily available
  - Stable under reasonable storage conditions
  - Affordable
  - Well characterized, in terms of both contaminant levels and other properties of the material (e.g., particular size distribution of a soil, conductivity of an aqueous material)

# Practical Aspects (continued)

- Reference matrices should be:
  - Readily available or easily prepared in the lab in large quantities
  - Reproducible
  - Affordable
  - As free of “contaminants” as practical
- Common examples include reagent-grade water, Ottawa sand, ASTM synthetic wastewater

# Uses of Reference Matrices

- Reference matrices are used every day to prepare:
  - Method blanks
  - Laboratory control samples
  - Diluted samples
- Less frequent uses include:
  - Initial demonstrations of capability
  - Method detection limit studies

# Challenges for Reference Matrices

- They need to be “clean,” and as new methods become more sensitive, or address new environmental contaminants, local production of matrices such as reagent water has to keep pace.
- Many common uses require that the reference matrix be spiked with analytes of interest, thus spiking protocols and solvents become important considerations.

# Challenges for Reference Matrices (continued)

- Meeting these challenges sometimes means “outsourcing” production by purchasing matrices from commercial sources.
  - Ottawa sand is easy to buy from multiple vendors
  - Some labs use “bottled water” from local, but large-scale sources

# Uses of Reference Materials

- Reference materials are used for:
  - Method development projects
  - Method modification testing
  - “Intercalibration” exercises among laboratories
- Less frequent uses include:
  - “Routine” quality control purposes
  - “Remedial” performance testing samples in response to laboratory performance concerns

# Challenges for Reference Materials

- Balancing cost versus intended use.
  - High-cost materials should be reserved for less frequent uses
  - Lower-cost materials must be available if they are to be used more frequently
- Relevance! The reference material has to be reasonably similar to the environmental samples being analyzed.

# Challenges for Reference Materials (continued)

- Relevance involves:
  - The original sample matrix, which governs the sample preparation techniques used
  - The final form of the stable reference material
    - Is it freeze-dried, air-dried, or does it contain preservatives?
    - Are the environmental samples of interest treated similarly?
  - The levels of the analytes, compared to those in the samples of interest

# Abuses of Reference Materials

- For all of the appropriate uses of reference materials from recognized sources, there is some small percentage of uses that are inappropriate, or actual abuses of the materials and concepts behind these materials.
- What follows are some famous and some lesser known such abuses.

# “You’re Wrong”

- Perhaps one of the most significant “abuses” of a reference material dates back to when NIST was still known as the National Bureau of Standards (NBS).
- Organizers of a “round robin” study of lead in a biological reference material and in “natural waters” decided that the data from Clair Patterson’s lab at Cal Tech were “outliers” well below the range of all of the other study participants, and therefore invalid.

## “You’re Wrong” (continued)

- After years of haggling, in 1976, Patterson and Settles finally conclusively demonstrated that their data were correct and that all of the other participants had in fact been measuring the background levels of lead in their “dirty” laboratories.
- Ultimately, these results and other work by Patterson lead to the formal development of “clean techniques” for metals analyses.

# Which of these things is not like the others?

- A large-scale sediment remediation effort involved analyses of dioxins and furans by two laboratories: one under contract to EPA and one working for the “potentially responsible party” (PRP).
- Overall, the results for the two laboratories disagreed by about a factor of two, with EPA’s lab consistently producing higher results.

## Which of these things is not like the others? (continued)

- In response, samples were sent to a third laboratory. Their results more or less agreed with those of EPA's laboratory.
- Both sides wanted to know why.
- All three laboratories made what they considered minor changes to the sample preparation and extraction procedures, under the allowance for flexibility in the "performance-based" method.

## Which of these things is not like the others? (continued)

- EPA's original laboratory had extensive data supporting their method modifications.
- The third laboratory had some data.
- The PRP's laboratory (with the lower results) relied solely on analyses of an NIST SRM for river sediments to show that their extensive modifications worked.

## Which of these things is not like the others? (continued)

- The problem was that the SRM was a freeze-dried powder and the actual field samples were river sediments containing 50% to 90% moisture.
- The method started by extracting a wet sample with an organic solvent.
- However, the SRM was extracted as received - as a dry powder! Thus, the SRM had little relevance to the samples.

# Reference Matrices

- Because they are used every day, there are bound to be more “abuses” of reference matrices than actual reference materials.
- Some may be minor, like using reagent water intended for metals analyses in place of “organic-free” reagent water.
- Others are more serious, such as failing to check for Teflon parts in the reagent water system when gearing up for PFC analyses.

# So, What's in Your Water?

- In 1990, the North Carolina Department of Environmental Health laboratory in Mecklenburg County, NC, had a problem.
- One of their analysts could not produce acceptable results for drinking water QC samples.
- The QC samples and blanks were all contaminated with benzene.

# So, What's in Your Water?

## (continued)

- Despite cleaning the GC/MS and everything else he could think of and rerunning the IDC, the contamination remained.
- After an extensive internal review, the laboratory determined that their reagent water was contaminated.
- They were using ...

# You guessed it!



# Why?

- Rather than make their own reagent water, the laboratory found it cheaper to buy bottles of Perrier from a nearby supermarket.
- The laboratory reportedly used no more than a dozen bottles of water in a year.
- “We go to the grocery store and buy two or three bottles at a time. It's a good source of organic-free water.” (*NY Times* 2-17-1990)

# Tissue Reference Matrix

- In the mid-1990s, EPA's Office of Water embarked on an extensive effort to develop the 1600-Series "Clean Metals" methods.
- The effort was partly in response to a USGS study that indicated that much of USGS's ambient monitoring data for metals was flawed due to contamination.

# Tissue Reference Matrix (continued)

- EPA built on the work by Patterson noted earlier, as well as extensive research by oceanographers measuring metals in open ocean waters.
- EPA also wanted to expand the effort to tissue samples, particularly for mercury, given the human health concerns related to fish consumption.

# Tissue Reference Matrix (continued)

- As part of the statement of work for the single-lab development and validation studies from a certain EPA contractor, the laboratory was required to prepare QC samples associated with tissue sample analyses using a “clean reference matrix.”
- Chicken breast was suggested as a readily available matrix.

# Tissue Reference Matrix (continued)

- At some point, someone specifically suggested that “organic” chicken breast should be used.
- The laboratory purchased chicken breast at a local supermarket that was labeled “organic” and ran some method blanks using it as the reference matrix.

# Tissue Reference Matrix (continued)

- The method blank results all contained mercury at levels higher than anyone expected.
- After further review, it seems that the chicken breast was not only “organic,” but it came from “free range” chickens.
- Those chickens peck at the ground and ingest mercury from the soil ...

# Tissue Reference Matrix (continued)

- In contrast, “regular” chicken breast, presumably from chickens raised indoors, had much lower mercury content and could be used as a suitable tissue reference matrix.

# So What?

- Why bring all this up?
- Isn't all of this obvious?
- As a retired former client at OSW was fond of saying “Any good chemist knows that ...”
- So why are we wasting your time here today?

# Because ...

- It is not so obvious.
- There are all too few “good chemists” working at the bench level in many environmental laboratories these days.
- Too few methods or other documents even discuss these issues.
- Auditors and data validators often do not understand the issues either.

# Partial Solutions

- Education – Talk about the issues, just as we are here today
- Make sure that recommendations or requirements for reference materials *and* reference matrices in methods, QAPPs, SOWs, and other documents raise the issue of relevance.

# Office of Water

## 2016 New Method Protocol

“The relevance of the matrix of the reference material to the field sample matrices to which the method is to be applied cannot be emphasized enough. For example, performance in a freeze-dried sewage sludge reference material is only relevant when the new method includes freeze-drying of solid samples before extraction or digestion, but that performance sheds little light on the new method’s performance in a wet sludge, and has no relevance to wastewater.”



**Questions?**

**If so, then see you in the bar  
right after this session, and  
you're buying...**