Solid Phase Extraction: the Good, the Bad, and the Ugly?

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Outline

- General Overview
- SPE: The Beginning?
- Methods
- SPE, the Good, the Bad, and the Ugly
- Data Concerns
- Possible Alternatives?
- Q&A

General Overview

- We do what we do, in part, to:
  - Generate data of known quality
  - Be protective of human health
  - Be protective of ecological health
- Explore some of the SPE data available
- The "pros and cons" of SPE
- Provide "food for thought"

SPE, the Beginning?

- SPE, commercially, began in ~1977 (Waters Associates)
- What was "first" reference in literature to use of SPE?

"So the people grumbled at Moses, saying, "What shall we drink?" Then he cried out to the LORD, and the LORD showed him a tree; and he threw it into the waters, and the waters became sweet." Exodus 15: 24 and 25

Methods

- SPE cited in many methods:
  - EPA Method 525 (SVOCs in DW) – 1988
  - SW-846 Method 3535 – 1996
  - EPA Method 1664 (O&G) – 1999
  - EPA Method 527 (Pesticides and Flame Retardants in DW) – 2005
  - EPA Method 522 (1,4-dioxane in DW) – 2008

Methods, con't.

- EPA Method 537, ver. 1.1 (PFAAs in DW) – 2009
- EPA Method 523 (Triazine pesticides in DW) – 2011
- EPA Method 625.1 (SVOCs) – 2014
- Methods developed by the European Committee for Standardization, European Standards (ENs), etc.

SPE, The Good

- Decreased solvent usage, less waste
- Decrease in analyst exposure
- Cleaner extracts…no emulsions
- Less cost for shipping:
  - Can filter in field (with caveats!)
  - Collect smaller sample volumes
- Cannot deny the apparent cost/benefit

SPE, The Bad?

- Interferences always an issue!
- Breakthrough
- Colloids and particulate cause clogging:
  - Filter or centrifuge first?
- Natural Organic Matter (NOM):
  - Particulate matter (PM)
  - Dissolved organic matter (DOM)/dissolved organic carbon (DOC)

SPE, the Bad?, cont.

- DOM (e.g., humic and fulvic acids and natural plant products) can bind COCs
- Proteins and protein-like materials
- Surfactants
- Dechlorination of OC Pesticides; phthalate esters may hydrolyze
- Many more documented concerns discussed in the literature

SPE, the Ugly?

- Interferences always an issue!
- Are the data valid, meaningful, and usable for their intended purpose(s)?
- If QC limits met, it does not mean data are really of "known" quality
- EPA Method 625.1 limits too wide!
- How can data review adequately identify known issues with SPE?

Data Concerns

- Bias with reduced sample volume noted:
  - Extraction of 100 mLs vs. 1,000 mLs issue
  - Higher recoveries when use lower sample volume, why?
  - Reasons for differences have not be adequately addressed in the literature

Data Concerns, cont.

	Recovery Reagent Water		Recovery SWW	
Fraction	100 mLs	1,000 mLs	100 mLs	1,000 mLs
B/N	~81%	~62%	~80%	~57%
Acid	~81%	~75%	~89%	~77%
OC Pesticides	~76%	~69%	~89%	~61%

Clear decrease in percent recovery in 1,000 mL vs. 100 mL

Results of SPE using 1,000 mL comparable to LLE within ~1 to 5%

Data Concerns, cont.

- Recoveries of isotopically-labeled surrogates compared to unlabeled in spikes:
  - Difference in DI water spikes comparable within about ~ 5% lower
  - Difference in simulated TCLP buffer comparable within about ~ 9% lower
  - Difference in simulated waste water trends~18% lower (matrix effects?)

Data Concerns, cont.

- Difference in other more complex matrices also trends ~20% lower (matrix effects?)
- Difference in a pond water sample also trends ~19% percent lower (matrix effects?)

Data Concerns, cont.

- EPA Method 625.1 QC acceptance criteria is very wide:
  - Only 6 compounds with lower limit ≥ 50%
  - Best lower acceptance limit 60% (2-chloronaphthalene)
- QC limits are so wide, then really never will be a problem, so this is ok?
- Only be concerned if "fatal flaw"?

Data Concerns, cont.

- Appears to systematic negative bias with more complex matrices or larger volumes
- Issues are not adequately addressed in literature because QC limits are met
- How can/should data review address known SPE issues and degree of bias?

Possible Alternatives

- First, should we care?
- Use isotope dilution?:
  - Costly
  - Not optional for 600-series and SW-846 series methods
- Use matrix-matched standards? :
  - Impractical for production lab

Alternatives, cont.

- Solvent modifications (e.g., add MeOH)?
- "Salting Out" Effect
- Tighten control limits?
- Think about moving to micro liquid/solvent extraction (e.g., 40 mL VOAs?)
- Switch to LVI on instruments?
- Just say, current QC limits met, so no problem and forget about it?

Facts do not cease to exist

because they are ignored!

Aldous Huxley- author of Brave New World

We are scientists!

We can all figure this out, right?

References

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- This is a partial list of references. Please see author for additional information.

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Thank you!

Any Questions?

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