Trace Organics in MST using Micro Extraction with LVI GC/MS

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Objective & Challenge

- Develop an Organic Analysis method that is quick and economical and can be used to support microbial analysis in tracking waste water intrusion into storm water pathways.

- Given the nature of organics analysis, a thorough review of the process was required to create a viable method.

Extraction Options

Problems w/Current Techniques

- **Method 3520 Liquid-Liquid:**
  - 18-20 hour extraction process, uses significant solvent, and must compete with routine samples for the limited number of extraction setups currently available.
- **Method 3535 S.P.E.:**
  - physical extraction problems with filters (i.e. plugging with debris), compound recoveries can be variable, and the cartridges are expensive.
- **Method 3510 Separatory Funnel:**
  - **l**abor intensive, uses significant solvent, and requires capital investment for equipment.
- **All the above techniques require one - 1 liter container per sample. In addition, each QC sample requires 2 additional 1 liter containers. Furthermore, there is no recourse for reanalysis unless additional sample volume is collected.**

Solution:

Method 3511 Micro extraction:

- An EPA approved modified version of 3510. This technique uses smaller sample volumes, minute amounts of solvent and can generally be extracted and ready for analysis in day.

This procedure requires only one 250 mL container for each sample-sufficient volume to perform all required organics analysis, QC, and potential reanalysis on any given sample.

Analysis Technique

Large Volume Injection with GCMS detection.

- Two distinct advantages:
- An increased injection volume gives a proportional lowering of detection limits. 1uL injection vs. 5, 10, 15, or 20uL using LVI. Instrument detection in the low to mid part per billion range.
- The increased sensitivity allows for full scan MS detection that is more definitive and allows for TIC processing – Tentatively Identified Compound.

Compounds of Interest:

Selected because they have historically been detected in influent samples, they have desirable analytical properties, the standards are readily available, and they have been used by other agencies for similar purposes....

- Caffeine -

- Triclosan -

- Cholesterol & Coprostanol -

Caffeine

- *Advantages:*
  - Good Chromatography.
  - Calibrates well.
  - Reliably extracts and quantitates in the sample matrixes we have analyzed thus far.
  - Excellent instrument response resulting in low limits of detection (relative to the other measured compounds).
- *Limitations:*
  - Hits are a good indicator of intrusion but it must be associated with the presence of other compounds to confirm. More experience is needed to determine the relationships.
  - Caffeine can be introduced from other sources such as storm runoff of surface streets. Field samples of clean water streams to establish a baseline would be appropriate, at least initially.

Triclosan

- *Advantages:*
  - Calibrates well
  - Good Chromatography
  - Reliably extracts and quantitates in the sample matrixes we have analyzed thus far.
  - Good instrument response resulting in fairly low limits of detection (relative to the other measured compounds).
  - It is generally believed to be specific to influent streams and therefore an excellent indicator of sewage intrusion.
- *Limitations:*
  - Even though the detection of Triclosan is excellent indicator of intrusion its concentration relative to Caffeine is low in waste water streams. Triclosan may vary in concentration depending on the wastewater sources (i.e. residential, industrial, etc.).

Coprostanol & Cholesterol

- *Advantages:*
  - Excellent indicators of intrusion as they are almost exclusively related to human activity.
  - Calibrates well, but Continuing Calibration Verifications fall off quickly.
  - Recent literature suggests that the ratio of these two compounds can be a clue to intrusion from sewage wastewater (faecal material) as opposed to other environmental sources (cattle, sheep, birds).
- *Limitations:*
  - Less reliable quantification due to its sensitivity to instrument conditions.
  - High limit of detection relative to Caffeine and Triclosan and QC recoveries tend not to adhere to normal limits. Most likely have to qualify hits with a “J” or “JG” flag.

Summary:

- First, confirmation based on a tiered approach. Follow up analysis triggered by microbial results. We may need to analysis more samples at least initially to establish the “trigger value”.
- Second, new compound may be added if they exhibits the same characteristics as the current analytes. However, increasing the analyte list increases the data processing time which in turn increases cost.
- Third, TIC analysis will have to be evaluated very carefully to ensure that we are identifying unknown compounds that reside in the sample and not from the extraction process. A specialized TIC library my provide useful information in the future and cut down on data reduction time.
- Fourth, the reduction in the number and size of containers makes field sampling less cumbersome and more efficient.
- Fifth, QC still need to be refined. The laboratory recommends a MB, SB, LD, and MS. Limits will be wide until performance based limits can be established.
- Finally, cost will be estimated at 1.0 hour per sample. Ten samples are optimal , and cost will increase with fewer samples. Recommended TAT is 30 days.

Acknowledgements

- Evaluation of the behavior of caffeine in fresh watersheds and as a tracer of sewage contamination, James McConaghie author – www.enviroment.yale.edu/hixon.
- http://en.wikipedia.org/wiki/Coprostanol.
- http://www.epa.gov/oppsrrd1/REDs/factsheets/triclosan_fs.
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- PAH, Phthalates, and Pentachlorophenol in Water: Preparation and Analysis, Andrey Biryukov City of Portland Bureau of Environmental Science.
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