Solvent Emission Reduction in the Modern Environmental Laboratory

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Outline

- Clean Air Act, Title V Permits
- Solvent Reduction Backgrounder
- Reducing Solvent Emissions
  - Reduce Sample Size
  - Increase Detection Sensitivity
  - Reduce Solvent Consumption
  - Employ Solvent Recovery
- LLE to SPE
- Solvent Recovery
- Conclusions
Solvent Reduction Background

- **Clean Air Act, Title V Permits**
  - Emissions of Hazardous Air Pollutants (HAP) has a stated potential limit of 10 tons per year and a combined HAP potential maximum of 25 tons per year.

- **Individual State Regulations**
  - Most states have adopted Title V amounts but others have implemented their own limits.
  - MA requires a single HAP potential emission of 1 ton per year.

- **Environmental Analysis Labs**
  - A major concern is Dichloromethane (DCM) among other HAP solvents.

- **Extremely Small HAP Emitters**
  - No permit is required if they are not at risk of exceeding the individual state limits.
Penalties for Exceeding HAP Emission Limit

- In 2014, four labs in Massachusetts were fined for exceeding the HAP emission limit, without a valid permit.
- The fine was $350K per site.
- The concern is that other states will become more stringent. In which case, a reduction in solvent use and/or more effective recovery would be required.
Liquid-Liquid Extraction

- Water sample (1 Liter)
- Extract at basic pH with 60 mL of DCM three times
- Extract at acid pH with 60 mL of DCM three times
- Dry extract over sodium sulfate
- Evaporate over 360 mL DCM down to 1 mL
- Add Int. Std. and transfer to GC vial
- Inject 1 µL into GC/MS, with split

• Over 360 mL DCM per sample
• 1 ton DCM ~ 1895 samples (~ 7 samples/day for year)
How to Reduce Solvent Emissions?

- Reduce sample size collected
- Reduce extraction solvent needs
- Recover solvent used
1-L sample size set decades ago based on:

- Sample homogeneity
- Analytical instrument sensitivity

- Sample homogeneity has been shown to be less of a concern than originally thought
- Analytical instrument sensitivity has dramatically increased
- Benefit of lower sample shipping costs and reduced hazard
- Possible to do additional sampling at a lower cost
EPA methods are acknowledging smaller samples as they are updated:

- **Method 521 (2004)**
  - Nitrosamines in Drinking Water, specifies 500 mL of water sample size

- **Method 535 (2005)**
  - Chloroacetanilide and other Acetamide Herbicide Degradates in Drinking Water, specifies 250 mL water sample size

- **Method 522 (2008)**
  - 1,4-Dioxane, specifies 100 or 500 mL water sample size, depending upon the SPE adsorbent chosen

- **Method 3511 (2002)**
  - Microextraction for Selected Compounds, approximately 35 mL sample size

- **Method 625 (2014)**
  - flexible sample volume based on the detection limits needed for compliance
Manufacturers have improved sensitivity over the past few decades
- Split can be changed to improve sensitivity
- SIM can be used, especially now that scanning can be used simultaneously
- Triple quad?
- Large-volume injection becoming more common, inject up to 50 µL sample
Smaller samples require less solvent for extraction
Solid-phase extraction (SPE) requires less solvent for analyte elution

Summary:
- Water is passed through the SPE disk and analytes are retained
- Analytes are eluted with a small volume of solvent
- Depending on sample complexity 80-180 mL of solvent are needed for elution compared to 360 for a typical acid/base neutral liquid-liquid extraction
## US EPA Methods Specifying SPE for Drinking Water (1 of 2)

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<thead>
<tr>
<th>Number</th>
<th>Title</th>
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<tr>
<td>508.1</td>
<td>Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid-Solid Extraction and Electron Capture Gas Chromatography</td>
<td>1995</td>
<td>Pesticides (45)</td>
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<td>Determination of Nitrosamines in Drinking Water by SPE and GC with Large Volume Injection and Neg Chem Ionization MS/MS</td>
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<td>Atrazine and Simazine by SPE and GC/MS</td>
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<td>Atrazine and Simazine (2)</td>
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<td>SVOAs in DW by SPE and GC/MS</td>
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<td>Selected SemiVOAs using SPE and GC/MS</td>
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<td>Acetochlor to nitrobenzene and 2,4,6-trichlorophenol (11)</td>
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<td>527.0</td>
<td>Determination of Selected Pesticides and Flame Retardants in DW by SPE and GC/MS</td>
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<td>Atrazine to Malathion to Vinclozolin (26)</td>
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## US EPA Methods Specifying SPE for Drinking Water (2of 2)

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<td>Determination of Explosives and Related Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS).</td>
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<td>535.1</td>
<td>Measurement of Chloroacetanilide and Other Acetamide Herbicide Degradates in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry</td>
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<td>Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS).</td>
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<td>Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection</td>
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# SPE Development Efforts in Waste Water

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## 8270 ANALYTES & PERFORMANCE

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<td>1/10th sample volume lower cost disk, lower solvent consumption</td>
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1 Liter Sample Volume with SPE (applied to EPA Method 625)

1 μL is injected (10/90 split mode) into the GC-MS.

**EZ Flow Disk Holder**
- 6x more filtering surface area for 47 mm disk
- Uses 100 mm pre-filters (1 and 5 μm)

- **200 mL Extract Volume**
- **1 ton DCM ~ 3410 samples (~ 13 samples/day for a year)**
100 mL Sample Volume with SPE (applied to EPA Method 625)

- 1 μL is injected (unsplit) into the GC-MS.
- This maintains the same mass loading as the 1 Liter Sample Method.

- 80 mL Extract Volume
- 1 ton DCM ~ 8526 samples (~ 33 samples/day for a year)
Solvent Recovery

- The less solvent that needs to be evaporated to obtain the sensitivity needed in the analytical step, the less that might be emitted.
- Recovery of evaporated solvent is the last step to consider in the full process.
- Consider the potential for recovery when purchasing evaporators.
- Evaporators that combine water vapor with solvent vapor will make recovery challenging.
Closed Evaporation System

- **DryVap Evaporation System**
  - Evaporate up to 6 samples at once

- **SolventTrap\textsubscript{SVOC} Condensing Kit**
  - The cooled glass column condenses more than 95% of a variety of solvents

- **LLE’s**
  - 1 ton DCM ~ 7 samples/day for a year without solvent recovery
  - Or ~ 146 samples/day for a year with solvent recovery
Recovery of DCM

Experimental Conditions

- 1200 mL DCM Total
- 200 mL per Evaporation Tube

Operating Conditions

- Heat Power 5
- Vacuum -5 in Hg
- Chiller @ 0°C
- Nitrogen Sparge @ 0 psig during heat state
- Nitrogen Sparge @ 20 psig during Sparge state
- Sparge Heat enabled
- Evaporate to 0.9 mL endpoint

Run time under 50 minutes

- 97.4% Recovery of DCM
- Std. Dev. of 0.270
- 5 runs spanning 2 days with 2 operators
Benefits of Solvent Recollection

The SolventTrap SVOC System allows facilities to:

- Prevent harmful solvent vapors from being released to the atmosphere
- Collect solvents for proper disposal or potential redistillation and reuse
- Protect workers from exposure to harmful solvent vapors
What to Do with the Collected Solvent?

- Disposal through proper channels
- Redistill to the quality required by the lab
- Sell to another facility for different use requiring less quality (such as metal finishing, etc..)
SolventTrap_{SVOC} Operation
Advantages of the system include:

- Typical solvent volumes of 180-200 mL of DCM can be evaporated in 50-60 minute run times
- The end point can be automatically detected and the process ended when the endpoint is reached
- The sample can be evaporated directly into GC autosampler vials, eliminating transfer from the evaporation vessel
- Excellent solvent recovery for disposal or re-use
Real Samples – Soil Extracts

Excellent Solvent Recoveries
Analyte Recovery 8270 Spike

Average of n=6

50 µg spike into 200 mL DCM
DryVap/ SolventTrap svoc
Advances have been made that allow the reduction of solvent use in the laboratory

- Smaller sample sizes
  - Less solvent needed for efficient extraction
  - More sensitive analytical techniques reduce the need for large samples

- Solid-phase extraction reduces the solvent needed for effective extraction of small or larger samples (1L)

- Solvent recollection is feasible and instrumentation has been developed to recollect more than 95% of many solvents

- The trend of using less solvent will continue until the limit of feasibility is reached