Analysis of Semi-Volatiles in Wastewater Using Stir Bar Sorptive Extraction

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Outline

- Introduction
- Stir Bar Sorptive Extraction (SBSE) Basics
- Round Robin Study Results
- Conclusion
GERSTEL
Company Overview

- Family-owned business
- Founded in 1967
- Headquarters: Mülheim an der Ruhr, Germany
- Subsidiaries:
  - GERSTEL Inc., U.S.A.
  - GERSTEL AG, Switzerland
  - GERSTEL KK, Japan
  - GERSTEL, Brazil
  - GERSTEL, Singapore
- 200+ employees
- ISO 9001 Certified since 1997
- Represented in more than 70 countries

www.gerstelus.com
Techniques – Sample Prep and Intro for LC and GC

MultiPurpose Sampler MPS
MultiFiber EXchange MFX
Twister
Selectable 1D/2D GC/MS
LC/MS Effluent Optimizer LEO
MultiPosition Evaporation Station mVAP
Cooled Injection System CIS
Thermal Desorption System TDS
Dynamic Headspace DHS
Olfactory Detection Port OPD
MPS Workstation
Automated Liner EXchange ALEX
Thermal Desorption Unit TDU
TDU PYRO
Preparative Fraction Collector PFC
Solid Phase Extraction SPE
Solid Phase Extraction SPE
MAESTRO PrepAhead
MAESTRO Software
easy Liner Exchange eLEX
Automated TDU Liner Exchange ATEX
μFlowManager
MultiPurpose Sampler MPS for LC/MS
Disposable Pipette Extraction DPX
www.gerstelus.com
- 1.5cm long magnetic stir bar sealed in glass
- High capacity PDMS phase on glass
- Extremely rugged
- Preconditioned for low background
- Stirs and extracts in one step
- Splitless desorption of stir bar gives low detection limits
Stir Bar Sorptive Extraction (SBSE)

- Same principle as liquid/liquid extraction
  - But with a low amount of immobilized “solvent” (PDMS)
- Extraction is based on sorption
  - Predictable recovery due to proportionality with log $K_{o/w}$
  - No displacement effects
- PDMS
  - Very inert
  - Retains no water
  - Selectivity eliminates polar matrix interferences
- Desorption with TDS or TDU
  - Fast and mild
  - Extremely low detection limits (ppt to ppq)
Extremely Easy to Use

- Add stir bar to vial
Extremely Easy to Use

- Add stir bar to vial
- Stir 1hr to overnight
Add stir bar to vial
Stir 1hr to overnight
Remove stir bar with forceps and rinse briefly in distilled water
Add stir bar to vial
Stir 1hr to overnight
Remove stir bar with forceps and rinse briefly in distilled water
Dry with lint-free tissue
Add stir bar to vial
Stir 1hr to overnight
Remove stir bar with forceps and rinse briefly in distilled water
Dry with lint-free tissue
Place in a thermal desorption tube
Thermal Desorption Unit - TDU

Cooled Injection System - CIS

TDU Tube

No Transfer Line!
Predicting Twister Extraction Results

- Extraction is assumed to be an equilibrium process
- Predictions are based on the assumption that the PDMS:water partition coefficient (unknown) is similar to the octanol:water partition coefficient (extensive published tables)
Distribution of Analytes Between Water and PDMS

\[
\frac{m_s}{m_o} = \frac{k_{o/w}}{\beta} \left( \frac{k_{o/w}}{\beta} \right) + 1
\]

- \( m_s \): Amount of Analyte in PDMS
- \( m_o \): Amount of Analyte in Water
- \( K_{O/W} \): Octanol/Water Distribution Coefficient
- \( \beta = \frac{V_w}{V_s} \): Phase Ratio
- \( V_w, V_s \): Sample-, PDMS-Volume

*Baltussen et al.*

www.gerstelus.com
### Example: Atrazine in Water

\[
\log K_{o/w} \text{ Atrazine} = 2.61 \quad (K_{o/w} = 407.4) \\
\text{Sample Volume: 10 ml}
\]

<table>
<thead>
<tr>
<th>SBSE</th>
<th>SPME</th>
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<tbody>
<tr>
<td><strong>Twister:</strong></td>
<td><strong>Fiber:</strong></td>
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<tr>
<td>24 µl PDMS</td>
<td>0.5 µl PDMS</td>
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<tr>
<td>Phase Ratio:</td>
<td>Phase Ratio:</td>
</tr>
<tr>
<td>0.0024</td>
<td>0.00005</td>
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\[
\frac{0.0024 \times 407.4 \times 100}{0.0024 \times 407.4 + 1} \quad \text{49.4 %} \\
\frac{0.00005 \times 407.4 \times 100}{0.00005 \times 407.4 + 1} \quad \text{2.0 %}
\]
Phase Volume (µL)

24  63  47  126

Sample Information

Sample Size (ml): 10
CAS Number: 001912-24-9
log K_{o/w}

Results

log K_{o/w} 2.61
Name Atrazine
Formula C_{8814CL1N5}

Twister Recovery Calculator

Twister Volume (µL)

24 47 63 126

Twister Recovery

10mm x 0.5mm  10mm x 1.0mm  20mm x 0.5mm  20mm x 1.0mm

Recovery

49.4%  72.0%  65.7%  83.7%
CAS Number: 1512-24-9
SMILES : n(c(nc(n1)NC(C)C)NC)c1Cl
CHEM : 1,3,5-Trisamin-2,4-diamine, 6-chloro- N-ethyl-N'-(1-methylethyl)-
MOL FOR: C8 H14 Cl1 N5
MOL WT : 215.69

-- EPI SUMMARY (v4.1G) -----------------------------

Physical Property Inputs:
Boiling Point (deg C) : ------
Melting Point (deg C) : ------
Vapor Pressure (mm Hg) : ------
Water Solubility (mg/L) : ------
Henry LC (atm·m3/mole) : ------

Log Octanol-Water Partition Coef (SPC):
Log Kow (KOWWIN v1.68 estimate) = 2.82
Log Kow (Exper. database match) = 2.61
Exper. Ref: HANSCH, C ET AL. 1977

Boiling Pt, Melting Pt, Vapor Pressure Estimates (MPBPVP v1.43):
Boiling Pt (deg C): 313.03 (Adapted Stein & Brown method)
Melting Pt (deg C): 113.31 (Mean or Weighted MP)
Sample Volume

Liquid Sampling

- Standard 1 cm Twister typically used for 10-40 mL liquid samples
- Standard Headspace or VOA vials
- Larger 2 cm Twister used for larger volumes (50-200 mL)
- Extraction vessel must have flat bottom surface for smooth stirring
Extraction Time

Liquid Extraction

- Extraction kinetics are slow and depend strongly on sample volume
- Use high stirring speeds (1000 rpm)
- 10 mL samples stir 60-90 min
- 40 mL samples stir 3-4 hrs
- 200 mL samples stir 16 hrs
Extraction Temperature

- Most Twister extractions are performed at room temperature.
- Practical temperature range (0-60 °C) has minimal effect (+/- 20%) on most compounds.
- Effect can be positive or negative depending on compound.
Matrix Effects

- Samples in water behave most ideally.
- Presence of competing organics (nonpolar solvents, fats) or significant levels (>20%) of polar solvents (i.e., ethanol, acetonitrile) can reduce extraction efficiency, particularly of polar analytes.
- Sample pH can strongly influence extraction of ionizable species.
- Salting out can be used to enhance extraction efficiency.
Twister Precision and Storage

2 mL Balsamic Vinegar + 8 mL of H₂O: SBSE for 1 Hour
Results

No Interference from acetic acid
Ester Peaks show good precision, Average RSD = 3.1%
Two samples stored at room temperature for 4 days show minimal loss of apolar compounds. Ethyl acetate ($\log K_{o/w} = 0.86$) shows a 16% loss.
Twister Reconditioning

Thermally condition for 2 hours at 300 °C
Dry Nitrogen 50-100 mL/min
For simultaneous conditioning of 10 tubes up to 40 Twisters

GERSTEL TC-2: Tube Conditioner

www.gerstelus.com
Round Robin Study

Host Organization: Independent Laboratories Institute
Title: Solid Phase Extraction (SPE) Protocol Validation Study
Purpose: Update to EPA Method 625

Participants: SPE Manufacturer’s, Commercial Environmental Labs, and Government Laboratories, 24 Laboratories

GERSTEL Twister accepted as an “SPE Material”

GERSTEL Applications Lab
Government Lab
Academic Lab
SBSE Protocol

- Add 10.0 mL of sample to 10 mL vial
- Add 8.0 mL of sample + 2.0 mL of acetonitrile to a 10 mL vial
- Add internal standard to each vial
- Add a conditioned stir bar to each vial
- Extract at 1000 rpm for 60 minutes
- Remove stir bars with forceps, rinse in water, dry on tissue
- Place the stir bar from the acetonitrile extract in the TDU tube first
- Analyze the Twisters by thermal desorption GC/MS
- N = 3 Replicates
- Sample Spike Range 0-200 ppb

Only 18 mL of Sample Used !!
The heated zone of the TDU is 20 mm, so 2 Twisters can be desorbed in a single tube.
Analysis Conditions

**Thermal Desorption**
- Pneumatics mode: splitless
- Sample mode: sample remove
- Temperature: 30°C; 720°C/min; 300°C (5.0 min)
- Transfer Heater temp.: 300°C

**CIS**
- Liner type: quartz wool
- Carrier gas: helium
- Pneumatics mode: solvent venting
- Vent flow: 100 ml/min
- Vent pressure: 7.07 psi until 0.00 min
- Split flow: **100 ml/min @ 0.01 min**
- Temperature: -70°C (0.0 min); 12°C/sec; 300°C (3 min)
Analysis Conditions

**Gas Chromatograph**
Agilent 7890  
Column: Rxi-5 MS (Restek); 30 m x 0.25 mm x 0.25 µm (Catalog #13423)  
Mode: Constant Flow: 1 mL/min  
Temp.: 40°C (2 min), 8°C/min; 284°C (0 min); 15°C/min; 310°C (7 min)

**Mass Selective Detector**
Agilent 5977  
EI, Scan mode 35-450 amu

Transferline temp. 280°C  
Source temperature 230°C  
Quad temperature 150°C
Internal Standards

SV Internal Standard Mix (Restek #31006)

1,4-dichlorobenzene-d4
Naphthalene-d8
Acenaphthalene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12
Surrogates

OLC 03.2 SVOA Deuterated Monitoring Compounds (DMC) (Restek #31810)

16 Compounds:

- Acenaphthylene-d8
- Benzo(a)pyrene-d12
- 4-Chloroaniline-d4
- 2,4-Dichlorophenol-d3
- 4,6-Dinitro-2-methylphenol-d2
- 4-Methylphenol-d8
- 2-Nitrophenol-d4
- Phenol-d5
- Anthracene-d10
- Bis-(2-chloroethyl)ether-d8
- 2-Chlorophenol-d4
- Dimethylphthalate-d6
- Fluorene-d10
- Nitrobenzene-d5
- 4-Nitrophenol-d4
- Pyrene-d10
Calibration

Semivolatiles Megamix, EPA method 625 (Restek #31829) (54 Compounds)
Organochlorine Pesticide Mix AB #3 (Restek #32415) (20 Compounds)

Calibration Standards at 0, 2.5, 5.0, 10.0, 50.0 and 100.0 ng/mL
Calibration Standards in Water (Aquafina)
One CCV and 2 LCS spiked at 10 ng/mL run with Samples
Surrogates at 50 ng/mL
Matrices

Phase 1
- Water
- ASTM D5905-98 Wastewater – Mix of Water, Kaolin, Beer, Flour, Ocean Salts (Instant Ocean), and Surfactant (Triton X-100)

Phase 2
- Acetate Buffer pH = 6
- Water (Optional)
Full Scan TIC for 5 ng/mL Standard
EIC (m/z = 77) for 50 ng/mL Standard
Log Ko/w = 1.85 (15%)
100:1 Split Introduction
# Phase 1 Results

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Twister Water</th>
<th>Waste Water</th>
<th>All SPE Water</th>
<th>Waste Water</th>
<th>EPA 625 Criteria</th>
<th>Actual Value</th>
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<td><strong>62.1</strong></td>
<td><strong>63.5</strong></td>
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## Phase 2 Surrogate/LCS Results

### LCS Data (10 ppb):

- **Average Recovery** = 106%
- **RSD** = 15%
- **Range** = 5.9-15.3

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<thead>
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<th>Surrogate</th>
<th>Percent Recovery</th>
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<tbody>
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# Phase 2 Results

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<th>Twister</th>
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### Phase 2 Results

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<th>Analyte</th>
<th>Twister Water</th>
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<th>SPE Water</th>
<th>Waste Water</th>
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<th>Actual Value</th>
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Conclusion

- Solid Phase Extraction is a suitable substitute for LLE
- Twister is an excellent choice for a subset of the 625 List
- Further optimization is required for phenols
- Phthalates can be problematic

- Eliminates solvent extraction steps
- Eliminates most non-volatile and polar matrix interference
- Allows parallel sample preparation minimizing instrument run time
- Stir bars are reusable

- Analytes are stable for days on stir bar allowing field sampling
- Extremely low detection limits possible (low ppt)
- Excellent bar-to-bar reproducibility
- Analyte recovery is predictable
GERSTEL Website

- On-Line Store and Catalog
- Product Information
- Application Bibliography
- GERSTEL Solutions

"Vielen Dank für Ihre Aufmerksamkeit"

Questions??

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