SPE for analysis of environmental contaminants in water

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OUTLINE

Extraction Disks
  • ENVI Disks vs. Empore
  • Applications

Carbons
  • ENVI-Carb
  • ENVI-Carb Plus

SupelSelect HLB for extraction of PPCPs
Useful EPA 500 Series (drinking water) Accessories

- Visiprep 5-Port Flask Manifold
- Visiprep Lg. Vol. Sampler
- ENVI-Disk Holder
- ENVI-Disk Holder Manifold
Extraction Disks
ENVI-Disk™ SPE Disk vs. Empore SPE Disk

• **ENVI-Disk SPE Disk**
  • SPE Particles embedded in glass fiber matrix
  • Available in C18 and C8
  • Better flow properties but more resistant to clogging
  • More prone to fines

• **Empore SPE Disk**
  • SPE particles embedded in a PTFE fiber matrix
  • Available in over 9 x different chemistries
  • Minimal fines but more prone to clogging
    • Clogging addressed via Empore Filter Aid
  • Compatible with ENVI-Disk Holder

• Both products written in dozens of EPA & other environmental methods
SPE Disks
3M Empore™ SPE

Reduced SPE bed mass = Reduced solvent & elution volumes
  • Minimizes SPE eluate evaporation time
  • Potentially allows for direct injection of the SPE eluate
Dense & uniform extraction medium = NO channeling/voiding
  • Efficient mass-transfer kinetics allow for faster flow rates

47 mm Disks for Environmental Analysis
Empore SPE Disk Technology

SPE Particles tightly enmeshed in an inert PTFE matrix
- 90% SPE Sorbent; 10% PTFE (by weight)
- Dense particle packing (no void spacing)
- Uniform particle distribution
- Thin membrane, small bed volume
- High Surface Area / No Fines
- Smaller bed weights
- Shorter diffusion paths
- More efficient extractions

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Empore Official EPA Method Applications

• **1664 (Rev. A)** - N-Hexane Extractable Material (HEM; Oil and Grease)
• **506** - Phthalate and Adipate Esters in Drinking Water
• **507** - Nitrogen– and Phosphorus-Containing Pesticides in Water
• **508.1** - Chlorinated Pesticides, Herbicides, and Organohalides in Water
• **512.2** - Chlorinated Acids in Water
• **525.2** - Organic Compounds in Drinking Water
• **549.1** - Diquat and Paraquat in Drinking Water
• **550.1** - Polycyclic Aromatic Hydrocarbons in Drinking Water
• **552.1** - Haloacetic Acids and Dalapon in Drinking Water
• **553** - Benzidines and Nitrogen-Containing Pesticides in Water
• **1613 (Rev.B)** - Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution e.g. in water
• **SW846 Method 3535** - Test Methods for TCLP Leachates
• **QTM - Aqueous Phases Quick Turnaround Methods**
  • PAH
  • Phenols
  • Pesticides & PCBs
Tips to get good performance from extraction disks

Conditioning
- Prepares sorbent to interact with analytes
- Critical to good recovery and reproducibility
- Do not allow disk to go dry

Extraction
- Flow rate is not critical to recovery
- After sample, remove water by pulling vacuum

Elution
- Use multiple aliquots of elution solvent
- Use first aliquot to rinse out sample container
- Soak the disk for one minute with elution solvent prior to pulling vacuum
Application:
Polynuclear Aromatic Hydrocarbons

Method: US EPA 550.1
Disk: 47 mm Empore or ENVI-C18

1. Add 5 mL methanol and IS (if used) to 1 L water sample.
2. Wash disk w/5 mL methylene chloride.
3. Condition disk w/ 5 mL methanol followed by 5 mL dei. water.
4. Process sample through disk at a flow rate of 100 mL/min.
5. Elute the disk with 5 mL acetonitrile and 5 X 5 mL methylene chloride
6. Dry eluate through 3 gm anhydrous sodium sulfate.
7. Concentrate to 0.5 mL and analyze by HPLC

Column: Ascentis Express C18, 15 cm x 2.1 mm ID
Detection: UV, 250 nm
Temperature: 35 °C
Mobile Phase A: 50:50, water:acetonitrile
Mobile Phase B: acetonitrile

<table>
<thead>
<tr>
<th>Gradient</th>
<th>min</th>
<th>%A</th>
<th>%B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>50</td>
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<td>5</td>
<td>5</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

1. Naphthalene
2. Acenaphthylene
3. Fluorene
4. Acenaphthene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Chrysene
10. Benzo[a]anthracene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Dibenzo[a,h]anthracene
15. Indeno[1,2,3-cd]pyrene
16. Benzo[g,h,i]perylene
**Application:**

**Paraquat and Diquat from Water**

**Method:** US EPA 549.2

**Disk:** 47 mm Empore or ENVI-C8

1. Adjust 250 mL water sample to pH 7-9 using 10% NaOH or 10% HCl
2. Condition the disk as follows:
   1. 10 mL methanol
   2. 2 x 10 mL dei. water
   3. 10 mL conditionin soln. A*
   4. 2x 10 mL dei. water
   5. 20 mL conditioning soln. B*
3. Process sample through disk at a flow rate of 100 mL/min.
4. Add 1 mL methanol to disk; soak for 1 min.
5. Add 4 mL eluting solution* to disk, apply slight vacuum, and soak disk for 1 min.
6. Add 4 mL eluting solution* to disk and draw completely through.
7. Add ion pair reagent concentrate to eluate, adjust final volume (if necessary) and analyze by HPLC/UV

*see method 549.2 for composition of solution

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Fused core column for highly efficient, fast analysis

**Column:** Ascentis Express HILIC, 10 cm x 2.1 mm I.D., 2.7 µm particles (53939-U)

**Mobile Phase:** 20:80; 200 mM TFA NH₃: acetonitrile

**Temperature:** 60 °C

**Flow Rate:** 0.4 mL/min

**Detection:** UV at 308 (diquat) and 257 (paraquat) nm

**Injection Volume:** 1 µL
Application:
Semivolatile organic compounds from water

Method: US EPA 525
SPE: ENVI-18 Cartridge

Results of 5 extractions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Recovery (mean % ± CV)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phthalates (20µg/L)</td>
<td></td>
</tr>
<tr>
<td>Dimethyl phthalate</td>
<td>93 ± 5.9</td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td>97 ± 4.6</td>
</tr>
<tr>
<td>Di-isobutyl phthalate</td>
<td>97 ± 6.8</td>
</tr>
<tr>
<td>Benzyl butyl phthalate</td>
<td>100 ± 5.4</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl)adipate</td>
<td>99 ± 11</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl)phthalate</td>
<td>111 ± 8.3</td>
</tr>
<tr>
<td>Pesticides (8ug/L)</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>87 ± 11</td>
</tr>
<tr>
<td>Lindane</td>
<td>99 ± 13</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>96 ± 12</td>
</tr>
<tr>
<td>Aldrin</td>
<td>94 ± 13</td>
</tr>
<tr>
<td>Hexachlor epoxide</td>
<td>98 ± 13</td>
</tr>
<tr>
<td>Endrin</td>
<td>93 ± 11</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>110 ± 13</td>
</tr>
<tr>
<td>Simazine</td>
<td>89 ± 5.1</td>
</tr>
<tr>
<td>Atrazine</td>
<td>100 ± 5.1</td>
</tr>
<tr>
<td>Polynuclear Aromatic Hydrocarbons (20µg/L)</td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>68 ± 29</td>
</tr>
<tr>
<td>Fluorene</td>
<td>95 ± 7.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>95 ± 8.0</td>
</tr>
<tr>
<td>Anthracene</td>
<td>95 ± 11</td>
</tr>
<tr>
<td>Pyrene</td>
<td>97 ± 7.1</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>94 ± 8.3</td>
</tr>
<tr>
<td>Chrysene</td>
<td>101 ± 8.8</td>
</tr>
<tr>
<td>Benz(a)fluoranthene</td>
<td>103 ± 10</td>
</tr>
<tr>
<td>Benz(k)fluoranthene</td>
<td>103 ± 9.4</td>
</tr>
<tr>
<td>Benz(a)pyrene</td>
<td>94 ± 11</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>102 ± 10</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>104 ± 9.7</td>
</tr>
<tr>
<td>Benz(a)pyrene</td>
<td>101 ± 11</td>
</tr>
</tbody>
</table>

* Extract can be passed through a bed of sodium sulfate, to remove traces of water, before concentration.

**Mean of 5 extractions.
Semivolatile organic compounds from water

Background from ENVI-18 is low, even when exposed to sample at pH=2

Sample: 1 liter water
Extraction Tube: Supelco ENVI-18, 6mL, 0.5g packing
Cat. No.: 57894
Column: PTE-5 QTm fused silica, 15m x 0.53mm ID, 0.50µm film
Cat. No.: 25366
Inj.: 1µL

Conditions for Figure B2
Sample: 1 liter water
Extraction Tube: Supelco ENVI-18, 6mL, 0.5g packing
Cat. No.: 57894
Column: PTE-5 fused silica, 30m x 0.25mm ID, 0.25µm film
Cat. No.: 24915-U
Cat Temp.: 45°C (1 min) rapid to 160°C (3 min) to 320°C at 6°C/min
Carrier: helium, 33mL/min
Inj.: see Figure A

Figure B1 from method 525.1

GC-FID

GC-MS
Carbon SPE
ENVI-Carb™ and ENVI-Carb™ Plus
Carbon SPE

ENVI-Carb™

- Predominately GCB (graphitized carbon black)
- Unique Selectivity & Ideal for polar compounds
- Non-porous (adsorption) = faster flow rates
- Example Applications
  - Chloroacetanilide and Chloroacetamide Herbicide Degradants (535.1)
  - Non-volatile pesticides (carbamate & thiourea) in drinking water
  - BNA Pesticides in ground water
  - Acidic herbicides in drinking water (515.2)
  - Nitrosamines in drinking water (521)

<table>
<thead>
<tr>
<th>ENVI-Carb Adsorbent</th>
<th>C8- &amp; C18-Modified Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphitized carbon black</td>
<td>silane phase-modified silica gel</td>
</tr>
<tr>
<td>hydrophobic</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>irregular 40-100μm particles</td>
<td>irregular 40-60μm particles</td>
</tr>
<tr>
<td>nonporous</td>
<td>porous (60-300Å)</td>
</tr>
<tr>
<td>surface area: 100m²/g</td>
<td>surface area: 400-600m²/g</td>
</tr>
</tbody>
</table>
Application:
Use of Envi-Carb for pesticides in water

Pesticide Extraction from Drinking Water, Using ENVI-Carb Solid Phase Extraction Tubes

- **SPE Tube:**
  - Superclean ENVI-Carb, 3mL/0.25g packing
- **Tube Conditioning:**
  - 5mL methylene chloride/methanol (80:20)
  - 1mL methanol
  - 10mL 2% acetic acid in water
  - Draw solutions through the packing bed consecutively.
  - Keep packing bed wet until sample is added.
  - **Sample Addition:**
    - 100mL/L liter drinking water (pesticide concentration: 10-50μg/L)
    - Draw sample through packing at a rate of 5mL/min.
    - Accelerated rates do not have an adverse effect on recovery.
- **Drying:**
  - 1 minute, vacuum suction
- **Sample Elution (base-neutral fraction):**
  - 0.8-1mL methanol
  - 2×3.5mL methylene chloride/methanol (80:20)
- **Dry elution under gentle nitrogen purge in a room temperature water bath to approximately 400-500μL.**
  - For best recovery, wash inside wall of recovery vial with methanol, again dry to 400-500μL.
  - Reconstitute samples to a constant volume of 1mL using methanol.
  - Inject 20μL for HPLC analysis. Analysis can be automated.

HPLC Analysis

- **Column:** SUPELCO SIL LC-18-DB, 25cm x 4.6mm (5μm particles)
  - (with Supelguard™ LC-18-DB guard column)
- **Cat. No.:** 56335-U
- **Mobile Phase:** A - water/acetonitrile, 90:10, B - acetonitrile
- **Flow Rate:** 1.0mL/min
- **Det.:** UV, 220nm
  - inj.: 20μL extract (see Table 2)

### Pesticide recovery using ENVI-Carb

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Solid Phase Extraction</th>
<th>n=5 Recovery (% ± standard deviation)</th>
<th>n=4 Recovery (% ± standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxamyl</td>
<td>ENVI-Carb Tubes</td>
<td>111 ±9.6</td>
<td>28 ±46</td>
</tr>
<tr>
<td>Methomyl</td>
<td>ENVI-Carb Tubes</td>
<td>105 ±5.0</td>
<td>25 ±44</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>ENVI-Carb Tubes</td>
<td>106 ±6.2</td>
<td>97 ±3.8</td>
</tr>
<tr>
<td>Fluometron</td>
<td>ENVI-Carb Tubes</td>
<td>106 ±5.7</td>
<td>96 ±4.1</td>
</tr>
<tr>
<td>Monuron</td>
<td>ENVI-Carb Tubes</td>
<td>99 ±3.2</td>
<td>98 ±6.2</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>ENVI-Carb Tubes</td>
<td>97 ±3.9</td>
<td>43 ±25</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>ENVI-Carb Tubes</td>
<td>97 ±3.5</td>
<td>90 ±12</td>
</tr>
<tr>
<td>Propham</td>
<td>ENVI-Carb Tubes</td>
<td>95 ±3.2</td>
<td>76 ±23</td>
</tr>
<tr>
<td>Propachlor</td>
<td>ENVI-Carb Tubes</td>
<td>96 ±3.8</td>
<td>90 ±7.5</td>
</tr>
<tr>
<td>Aldicarb</td>
<td>ENVI-Carb Tubes</td>
<td>96 ±3.5</td>
<td>86 ±14</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>ENVI-Carb Tubes</td>
<td>90 ±5.4</td>
<td>99 ±10</td>
</tr>
<tr>
<td>Atrazine</td>
<td>ENVI-Carb Tubes</td>
<td>89 ±5.7</td>
<td>74 ±14</td>
</tr>
<tr>
<td>Diuron</td>
<td>ENVI-Carb Tubes</td>
<td>88 ±5.7</td>
<td>91 ±7.8</td>
</tr>
<tr>
<td>Linuron</td>
<td>ENVI-Carb Tubes</td>
<td>88 ±5.4</td>
<td>94 ±4.1</td>
</tr>
<tr>
<td></td>
<td>C8/C18 Silica*</td>
<td>28 ±46</td>
<td>25 ±44</td>
</tr>
</tbody>
</table>

**100 mL water samples, 10-50 μg/liter (ENVI-Carb extracts) or 20-500 μg/liter (C8/C18 silica), HPLC/UV (ENVI-Carb extracts) or HPLC/MS (C8/C18 silica) analysis.**


Low recoveries for polar pesticides on C18/C8
Application: Use of ENVI-Carb for extraction of acidic herbicides

Extraction procedure  
(automated using Zymark)

1. Condition 6 mL/250 mg ENVI-Carb tube w/ 10 mL water
2. Pass 900 mL sample through tube
3. Rinse tube w/10 mL water
4. Dry tube for 10 min.
5. Elute with 10 mL 80:20 methylene chloride: methanol containing .01% phosphoric acid

Minimal background from ENVI-Carb tube
Acidic herbicide recovery using ENVI-Carb

Results: average recovery of 4 sample replicates spiked at 4-5 ug/L

<table>
<thead>
<tr>
<th>Analyte</th>
<th>% Recovery</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrachloroterephthalic acid</td>
<td>15.7</td>
<td>-</td>
</tr>
<tr>
<td>Picloram</td>
<td>91.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Dicamba</td>
<td>91</td>
<td>3.4</td>
</tr>
<tr>
<td>2,4-D</td>
<td>88.3</td>
<td>7.1</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>78.7</td>
<td>6.2</td>
</tr>
<tr>
<td>2,4,5,-TP</td>
<td>84.7</td>
<td>9.9</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>95.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Dachtal</td>
<td>89.3</td>
<td>4.7</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>69.5</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Lower recovery due to strong retention on carbon

- The smaller, more polar herbicides show good recoveries from ENVI-Carb.
- Tetrachloroerephthalic acid and pentachlorophenol are large with more planar structures. These are difficult to remove.
**Carbon SPE**

**ENVI-Carb™ PLUS**

**Spherical Carbon Molecular Sieve**
- Extraction of highly polar compounds from water samples
- > 70% Absolute Recovery from 0.5 L drinking water (1-100 ng/mL)

**Procedure:**
1. Condition w/ 10 mL MeOH & 10 mL DI water
2. Load up to 1 L sample
3. Reverse tube & elute w/ 4-5 mL MeOH in opposite direction

**Example Polar Compounds:**
- Acephate
  - LogP –0.85
- Acrylamide
  - LogP –0.67
- 1,4-dioxane
  - LogP –0.27
- Propylene glycol
  - LogP –0.92
Application: Analysis of Glycols In Water Using ENVI-Carb Plus

Current method requires direct aqueous injection (DAI)

- Water has a high vapor volume
  - Requires low injection volume and/or high inlet pressure to contain vapor cloud
- Poor peak shape
  - Especially early eluting compounds
  - Affects detection and quantitation
- Presence of matrix (such as salt) in a sample could easily foul the GC inlet and/or column.
Analysis of Glycols

Goals of New Method

- Eliminate direct aqueous injection (DAI) of samples for glycol analysis.
- Lower detection and quantitation levels.
- Use solid phase extraction to extract glycols from water matrices.
  - Achieve elution with an organic solvent
  - Inject sample extract in organic solvent into GC
**Glycol SPE Extraction Method Using ENVI-Carb Plus**

<table>
<thead>
<tr>
<th>Extraction Cartridge</th>
<th>ENVI-Carb ™ Plus reversible cartridge, 1 ml/400 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cartridge Conditioning</td>
<td>1 ml methylene chloride, 2 x 2 ml aliquots methanol, 3 ml deionized water</td>
</tr>
<tr>
<td>Sample</td>
<td>5 mL tap water spiked at 10 ug/ml</td>
</tr>
<tr>
<td>Sample extraction</td>
<td>5 ml sample, 5 mm Hg</td>
</tr>
<tr>
<td>Dry time</td>
<td>10 minutes, 10 mm Hg</td>
</tr>
<tr>
<td>Elution</td>
<td>Cartridge in <strong>forward</strong> direction, 2 ml of methanol:methylene chloride, 80:20 (soak cartridge for 1 minutes prior to pulling through)</td>
</tr>
<tr>
<td>Preparation for GC analysis</td>
<td>Added methanol to bring sample to final volume of 2 ml and analyzed directly</td>
</tr>
</tbody>
</table>
Extraction method vs. DAI

Extract of 2 ug/ml spiked tap water

DAI of 2 ug/ml spiked dei. water

Peaks 1 & 2 not detected

Column: SPB-1000, 30 m x 0.25 mm I.D. x 0.25 μm

Oven: 50 °C (1 min. or 2.5 min.), 8 °C/min. to 200 °C (12 min.)

Injector: 220° C

Carrier gas: Helium, 1.5 ml/min, constant flow

Detector: FID, 220 °C

Injection: 1 μL, splitless

Liner: 4 mm ID, focus liner with taper (extracts) & 4 mm ID dual taper liner (DAI)
## Recovery and Reproducibility Evaluation

### Comparison of extraction method with DAI

Absolute recovery from tap water spiked at 2 ug/ml, n=7

<table>
<thead>
<tr>
<th>Compound</th>
<th>DAI Average Recovery</th>
<th>DAI %RSD n=7</th>
<th>Extraction Average Recovery</th>
<th>Extraction %RSD n=7</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methoxyethanol</td>
<td>Not detected</td>
<td></td>
<td>96%</td>
<td>3</td>
</tr>
<tr>
<td>2-ethoxyethanol</td>
<td>34%</td>
<td>30</td>
<td>94%</td>
<td>3</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td>106%</td>
<td>26</td>
<td>95%</td>
<td>6</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>114%</td>
<td>30</td>
<td>53%</td>
<td>16</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>56%</td>
<td>28</td>
<td>99%</td>
<td>6</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>77%</td>
<td>26</td>
<td>98%</td>
<td>7</td>
</tr>
<tr>
<td>Triethylene glycol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High RSDs

EG, smallest, most hydrophilic – difficult to retain on SPE
Application: Extraction of 1,4-Dioxane from water using ENVI-Carb Plus

• US EPA Method 522 describes several different sorbents for extraction, including ENVI-Carb Plus.
• Flow through design of cartridge allows it to be connected directly to a continuous flow pump.
• ENVI-Carb Plus cartridges can be reversed (if necessary) for efficient elution of analytes.
Analysis of 1,4-dioxane from water, extracted using ENVI-Carb Plus

Column: SPB-624; 30 m x 0.25 mm I.D. x 1.4 µm
Inj. temp.: 200°C
Oven: 30°C (1 min.), 13°C/min. to 90°C,
20°C/min. to 200°C (15 min.)
MS interface: 220°C
Carrier: helium, 1 mL/min constant

1. THF-d8 (I.S.)
2. 1,4-Dioxane-d8 (Surr.)
3. 1,4-Dioxane

<table>
<thead>
<tr>
<th></th>
<th>1,4-dioxane-d8 (surrogate)</th>
<th>1,4-dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spike level (ug/L)</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>Avg. % Recovery</td>
<td>102</td>
<td>83</td>
</tr>
<tr>
<td>%RSD, n=9</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>
Supel™-Select HLB
Supel™- Select HLB

- Hydrophilic modified styrene-based polymer
- Can retain lipophilic and hydrophilic compounds
- Wide pH compatibility range (0-14)
- Imparts minimal extractables to samples
- Described in US EPA Method 1694 for the extraction of personal care and pharmaceutical compounds from water
- Very reproducible lot-to-lot performance

Optical microscope picture of Supel-Select HLB resin
Cleanliness of Supel-Select HLB-Rat Plasma Extracts

LC-MS Analysis
scan masses 100-600
Extraction of Pharmaceutical & Personal Care Products (PPCPs) from Water using SupelSelect HLB

- US EPA Method 1694
- Method uses solid phase extraction (SPE) and LC-MS-MS for analysis of >70 PPCPs
- SPE used is hydrophilic/lipophilic balance (HLB)
  - Supel-Select HLB SPE

Extraction – based on method 1694

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction Cartridge</td>
<td>Supelco Select HLB SPE Tube, 500 mg/6 mL</td>
</tr>
<tr>
<td>Sample</td>
<td>500 mL of drinking water spiked with Group 1 compounds, adjusted to pH=4 with 6M HCl</td>
</tr>
<tr>
<td>Tube Conditioning</td>
<td>20 mL of methanol, 6 mL of water, 6 mL of water at pH 2 (with 6 M HCl)</td>
</tr>
<tr>
<td>Sample extraction</td>
<td>10 mL/min through tube</td>
</tr>
<tr>
<td>Dry time</td>
<td>5 min</td>
</tr>
<tr>
<td>Elution</td>
<td>12 mL, 50:50 methanol:acetonitrile</td>
</tr>
<tr>
<td>Dry down</td>
<td>40 °C, under nitrogen stream</td>
</tr>
<tr>
<td>Reconstitution</td>
<td>To final volume of 2 mL using mobile phase</td>
</tr>
</tbody>
</table>

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**LC-MS/MS Analysis**

- **Column:** Ascentis Express C18, 10cm x 2.1 mm, I.D., 2.7 µm (53823-U)
- **Mobile Phase:**
  - **A:** 0.1% formic acid and 0.1% ammonium formate
  - **B:** 50:50 methanol:acetonitrile
- **Temp.:** 40 °C
- **Det.:** ESI (+), MS/MS
- **Injection:** 5 µL
- **Sample:** CS-5 Concentrations from EPA method 1694

<table>
<thead>
<tr>
<th>Gradient</th>
<th>min</th>
<th>mL/min</th>
<th>% A</th>
<th>% B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.15</td>
<td>95</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>95</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>0.30</td>
<td>12</td>
<td>88</td>
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<tr>
<td>23</td>
<td>0.30</td>
<td>0</td>
<td>100</td>
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<tr>
<td>26</td>
<td>0.30</td>
<td>0</td>
<td>100</td>
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</tr>
<tr>
<td>26.5</td>
<td>0.15</td>
<td>95</td>
<td>5</td>
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</tr>
</tbody>
</table>

Fused core column for efficient, fast analysis
Recoveries of some PPCPs from spiked water samples - extracted using Supel-Select HLB SPE

<table>
<thead>
<tr>
<th>Compound</th>
<th>MRM Transition</th>
<th>SPE Spiking Level (µg/L)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azithromycin</td>
<td>749.9-591.6</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td>Caffeine</td>
<td>195.0-138.0</td>
<td>10</td>
<td>129</td>
</tr>
<tr>
<td>Carbadox</td>
<td>263.2-231.2</td>
<td>1</td>
<td>123</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>332.2-314.2</td>
<td>3,5</td>
<td>105</td>
</tr>
<tr>
<td>Clinafloxacin</td>
<td>366.3-348.1</td>
<td>4</td>
<td>48</td>
</tr>
<tr>
<td>Digoxigenin</td>
<td>391.2-355.2</td>
<td>4</td>
<td>128</td>
</tr>
<tr>
<td>Digoxin</td>
<td>781.5-113.1</td>
<td>10</td>
<td>136</td>
</tr>
<tr>
<td>1,7-Dimethylxanthine</td>
<td>181.2-124.0</td>
<td>100</td>
<td>86</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>256.8-168.1</td>
<td>0,4</td>
<td>122</td>
</tr>
<tr>
<td>Enrofloxacin</td>
<td>360.0-316.0</td>
<td>2</td>
<td>83</td>
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<tr>
<td>Lomefloxacin</td>
<td>352.2-308.1</td>
<td>2</td>
<td>106</td>
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<tr>
<td>Miconazole</td>
<td>417.0-161.0</td>
<td>1</td>
<td>74</td>
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<tr>
<td>Norfloxacin</td>
<td>320.0-302.0</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>362.2-318.0</td>
<td>1</td>
<td>83</td>
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<tr>
<td>Ormetoprim</td>
<td>275.3-259.1</td>
<td>0,4</td>
<td>128</td>
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<tr>
<td>Oxolinic acid</td>
<td>244.1-216.1</td>
<td>0,4</td>
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<tr>
<td>Sarafloxacin</td>
<td>386.0-299.0</td>
<td>9,12</td>
<td>100</td>
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<tr>
<td>Thiabendazole</td>
<td>202.1-175.1</td>
<td>1</td>
<td>119</td>
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</tbody>
</table>
Key SPE Literature

SPE Brochure T402150D

SPE Methodology Wall Poster T409088

Empore SPE Flyer T407075

Supel Select HLB Brochure T408148

Dioxin & PCB Analysis

Environmental Sampling & Analysis Guide T412043
Associated Supelco Publications

1. Extract Polynuclear Aromatic Hydrocarbons from Water, Using Solid Phase Extraction Disks: Application Note 54 (T394054A).
2. Extraction of Paraquat and Diquat from Water, Using ENVI™-8 DSK Solid Phase Extraction Disks: Application Note 60 (T394060A).
3. ENVI™-18 SPE Tube Ensures Low Background from Monitoring Organic Compounds in Drinking Water by EPA Method 525: Application Note 65 (T395065A).
4. Extract Nonvolatile Pesticides from Drinking Water, Using a Graphitized Carbon Adsorbent: Application Note 27 (T394027B)
5. Solid Phase Extraction/HPLC Analysis of Acidic Herbicides in Drinking Water: Application Note 100 (T396100).
7. Santasania, C.T.; Stenerson, K.K.; Aurand, C.; Trinh, A.; Shirey R.E. Using Bonded Silica Solid Phase Microextraction Fibers as a Screening Tool for Pharmaceuticals and Personal Care Products in Drinking Water (T409139)
References

1. Methods for the Determination or Organic Compounds in Drinking Water Supplement 1; EPA/600/R/4-90/020
2. Methods for the Determination of Organic and Inorganic Compounds in Drinking Water Volume 1; EPA 815-R-00-014
Dziękuję za uwagę!