Sample Prep for Chromatographic Analysis of Difficult Matrixes
Real World & Real Samples

Urine Sample without sample prep

Urine Sample with sample prep
Sources of Chromatographic Errors

- Contamination (4%)
- Sample Introduction (6%)
- Columns (11%)
- Chromatography (7%)
- Integration (6%)
- Instrument (8%)
- Operator (19%)
- Calibration (9%)
- Sample Processing (30%)

Time Spend on Analytical Process

Sample Processing (61%)

Data Management (27%)
Collection (6%)
Analysis (6%)

Sample Prep Innovations

- Solid Phase Microextraction (SPME)
- High specificity SPE
- Dispersive SPE
- Silver Ion SPE for FAMEs
- Carbonaceous adsorbents
- Flash chromatography
Solid Phase Microextraction (SPME)

“Sample Prep Made Easy”
Enrichment technique mainly for trace analysis
Developed in collaboration with Janusz Pawliszyn, Univ. of Waterloo
Unique and proprietary to Supelco

Users are...
• GC and GC-MS analysts (HPLC & LC-MS)
• Analyzing compounds in gases, liquids or solids.

Interested in...
• Sample enrichment
• Solventless extraction
• Using existing GC & HPLC systems
• Economical sample prep
• Reducing lab animal sacrifice

Users can expect...
• Highly consistent, quantifiable results from low concentrations of analytes
Odor-Causing Compounds in Water at 2 ppt (GC/MS)

1. 2-Isopropyl-3-methoxypyrazine (IPMP)
2. 2-Isobutyl-3-methoxypyrazine (IBMP)
3. 2-Methylisoborneol (MIB)
4. 2,4,6-Trichloroanisole (I.S. 8ppt)
5. (±) Geosmin
Linearity of Odor-Causing Compounds from Water at ppt Levels (SPME-GC/MS)

Quantitative

- IPMP $r^2=0.9900$, $y_{int}=+0.015$
- IBMP $r^2=0.9959$, $y_{int}=+0.028$
- MIB $r^2=0.9983$, $y_{int}=0.021$
- Geosmin $r^2=0.9988$, $y_{int}=-0.071$

part per trillion vs. Odor Concentration
SPME Overview

Solvent-free extraction technique for nearly any sample or matrix
Alternative to head-space GC and solid phase extraction (SPE) techniques
Directly interfaced with GC analysis
Non-destructive to sample
Reusable (100+ times)
Inexpensive
Fast
The SPME Concept

Click here for animation

Sample Adsorption
Please click on the numbered steps below for an animated sequence of the instruction.

1. Drill down septum piercing needle to avoid breakage
2. Insert needle into container
3. Adjust needle depth for aqueous sampling or headspace sampling
4. Extend plunger to expose fiber
5. Retract fiber before removing to avoid damaging the fiber
6. Drill down septum piercing needle to avoid breakage
7. Remove SPME Device

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An equilibrium is set up between analytes dissolved in the sample (solution or gas phase) and in the liquid coating on the fiber.

The fiber coating consists of:

- GC-type phases
- Particles
Distribution Constant

Concentration of analyte in stationary phase compared to concentration of analyte in solution:

\[ K = \frac{n_s}{V_1 C_2^°} \]

- \( K \): Distribution constant
- \( n_s \): Moles of analyte in stationary phase
- \( V_1 \): Volume of stationary phase
- \( C_2^° \): Final analyte concentration in water
Adsorption Mechanism for SPME

- Analyte Adsorbed
- Silica Rod
- Liquid Polymer
- Aqueous Solution
- Vial

Graph showing the adsorption mechanism over time.
Absorbent vs. Adsorbent Fibers

Absorbent-type fibers (Film-type fibers)
Analytes are extracted by partitioning
• Liquid phase
• Retains by thickness of coating
Analytes do not compete for sites
Fibers can have high capacity

Adsorbent-type fibers (Particle-type fibers)
Physically traps or interacts with analytes
• Porous particles
• High surface area
Analytes may compete for sites
Fibers have limited capacity
### Types of SPME Fiber Coatings

#### Films – Absorption:

<table>
<thead>
<tr>
<th>Coating</th>
<th>Type</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 µm Polydimethylsiloxane (PDMS)</td>
<td>Absorbent</td>
<td>Nonpolar</td>
</tr>
<tr>
<td>30 µm PDMS</td>
<td>Absorbent</td>
<td>Nonpolar</td>
</tr>
<tr>
<td>100 µm PDMS</td>
<td>Absorbent</td>
<td>Nonpolar</td>
</tr>
<tr>
<td>85 µm Polyacrylate (PA)</td>
<td>Absorbent</td>
<td>Polar</td>
</tr>
<tr>
<td>60 µm PEG (Carbowax)</td>
<td>Absorbent</td>
<td>Polar</td>
</tr>
</tbody>
</table>

#### Particles – Adsorption:

<table>
<thead>
<tr>
<th>Coating</th>
<th>Type</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>85 µm Carboxen-PDMS</td>
<td>Adsorbent</td>
<td>Bipolar</td>
</tr>
<tr>
<td>65 µm PDMS-DVB</td>
<td>Adsorbent</td>
<td>Bipolar</td>
</tr>
<tr>
<td>55 µm/30 µm DVB/Carboxen-PDMS</td>
<td>Adsorbent</td>
<td>Bipolar</td>
</tr>
<tr>
<td>15 µm Carbopack Z-PDMS</td>
<td>Adsorbent</td>
<td>Bipolar</td>
</tr>
</tbody>
</table>
PDMS-DVB Fiber SEM

Cross section of the PDMS-DVB fiber. The center is a fused silica core, surrounded by a Stableflex core. The 3-5µm DVB particles are suspended in PDMS and layered over the cores. 275x magnification.

Photomicrograph of SPME fiber provided by Prof. Dan Armstrong, U. Texas Arlington
PDMS-Carboxen Fiber SEM

3000X magnification of the Carboxen PDMS coating. The 3-5µm Carboxen-PDMS particles are suspended in PDMS.

Photomicrograph of SPME fiber provided by Prof. Dan Armstrong, U. Texas Arlington
Carboxen™ Particle – Volume Contribution

Contribution of pore types to total Carboxen pore volume:
- micropores (2-20 Å) = 0.29 mL/g
- mesopores (20-500 Å) = 0.26 mL/g
- macropores (>500 Å) = 0.23 mL/g
### Physical Properties of Divinylbenzene and Carboxen 1006

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m²/g)</th>
<th>Porosity (mL/g)*</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>macro</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>750</td>
<td>0.58</td>
</tr>
<tr>
<td>Carboxen™ 1006</td>
<td>720</td>
<td>0.23</td>
</tr>
</tbody>
</table>

*Macropore = >500Å  
Mesopore = 20-500Å  
Micropore = 2-20Å
Comparison of SPME Fibers for the Extraction of Small Hydrocarbons

(Analytes at 1 ppm in air, extracted for 10 min.)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>100µm PDMS</th>
<th>PDMS/DVB</th>
<th>Carboxen/PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0</td>
<td>0</td>
<td>750</td>
</tr>
<tr>
<td>Propane</td>
<td>0</td>
<td>0</td>
<td>20000</td>
</tr>
<tr>
<td>Butane</td>
<td>0</td>
<td>340</td>
<td>72100</td>
</tr>
<tr>
<td>Pentane</td>
<td>230</td>
<td>2150</td>
<td>108000</td>
</tr>
<tr>
<td>Hexane</td>
<td>460</td>
<td>9280</td>
<td>105000</td>
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</table>

(Absolute area responses)
Molecular Weight Range for SPME Fibers

- Carboxen
- DVB-Carboxen
- DVB
- 100µm PDMS
- 30µm PDMS
- 7µm PDMS

Molecular Weight Range
Area Response vs. Fiber Type

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fiber Types</th>
<th>MW</th>
</tr>
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<tbody>
<tr>
<td>Acenaphthene</td>
<td>30µm PDMS</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>Polyacrylate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PDMS-DVB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxen-PDMS</td>
<td></td>
</tr>
<tr>
<td>Decachlorobiphenyl</td>
<td>30µm PDMS</td>
<td>502</td>
</tr>
<tr>
<td></td>
<td>Polyacrylate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PDMS-DVB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxen-PDMS</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>30µm PDMS</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>Polyacrylate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PDMS-DVB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxen-PDMS</td>
<td></td>
</tr>
</tbody>
</table>
Effects of Fiber Polarity & Coating Thickness

Fiber Polarity
- Analyte selectivity
- Better recovery of polar analytes
- PEG
- Polyacrylate

Coating Thickness
- Analyte selectivity
- Extraction time
- Sample capacity
- Desorption time and carryover
Effects of Phase Coating Thickness of PDMS on Analyte Recovery Relative to Chrysene*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>%Relative Recovery</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>100µm</td>
</tr>
<tr>
<td>Benzene</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td>5</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>13</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>37</td>
</tr>
<tr>
<td>Anthracene</td>
<td>49</td>
</tr>
<tr>
<td>Pyrene</td>
<td>69</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>105</td>
</tr>
<tr>
<td>Chrysene</td>
<td>100</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>119</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>61</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>61</td>
</tr>
</tbody>
</table>

*Absolute response of chrysene set to 100%
Factors Affecting Extraction Recovery

Salts and pH
Headspace vs. direct extraction
Inlet liner volume
Stirring (sample) & agitation (fiber)
  • Increases precision
  • Reduces time to reach equilibrium
  • Must be consistent for all analyses
  • Required for analytes with high distribution constants
  • Sonication may increase temperature
Effects of Salt and pH

Salt usually increases analyte uptake
Use 25-30% NaCl to salt-out samples
Salt is not necessary for large non-polar analytes, such as PAHs and large hydrocarbons, and may reduce recovery
Lower pH to extract acidic compounds
Raise pH to extract basic compounds
Beware of stability of analytes at different pH levels
The Effect of Salt and pH on Extraction of Phenols by SPME

<table>
<thead>
<tr>
<th>Phenol</th>
<th>No Salt Neutral</th>
<th>No Salt pH = 2</th>
<th>Salt Neutral</th>
<th>Salt pH = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>810</td>
<td>1003</td>
<td>6425</td>
<td>6150</td>
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<tr>
<td>Methylphenol</td>
<td>761</td>
<td>882</td>
<td>5485</td>
<td>7434</td>
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<tr>
<td>2-Nitrophenol</td>
<td>422</td>
<td>474</td>
<td>311</td>
<td>2315</td>
</tr>
<tr>
<td>2,4-Dimethylphenol</td>
<td>1344</td>
<td>1476</td>
<td>15000</td>
<td>20710</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>5396</td>
<td>8138</td>
<td>19803</td>
<td>61664</td>
</tr>
<tr>
<td>2,4,5-Trichlorophenol</td>
<td>3115</td>
<td>11097</td>
<td>24270</td>
<td>96333</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>0</td>
<td>11</td>
<td>765</td>
<td>1182</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td>626</td>
<td>730</td>
<td>6536</td>
<td>11438</td>
</tr>
<tr>
<td>2,3,4,6-Tetrachlorophenol</td>
<td>3108</td>
<td>27683</td>
<td>33938</td>
<td>70440</td>
</tr>
<tr>
<td>2-Methyl-4,6-dinitrophenol</td>
<td>55</td>
<td>47</td>
<td>920</td>
<td>1685</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>2305</td>
<td>40582</td>
<td>22056</td>
<td>143905</td>
</tr>
</tbody>
</table>
Headspace vs. Direct Immersion

Analytical considerations:

• Volatility of sample
• Extraction time concerns
• Sample matrix
• Selectivity of analytes

Headspace extraction

Liquid or solid sample

Direct immersion extraction

Liquid sample
Inlet Liner Volume: Comparison for Analysis of Gaseous VOCs by SPME

Standard Splitless Liner, 2mm ID 50ppb

- 1. Chlormethane
- 2. Vinyl chloride
- 3. Bromomethane
- 4. Chloroethane
- 5. Freon 11

0.75mm ID Inlet Liner 50ppb

- 1. Chlormethane
- 2. Vinyl chloride
- 3. Bromomethane
- 4. Chloroethane
- 5. Freon 11
SPME Automation

Compatible with common GC autosamplers (Gerstel MPS, CTC Combi PAL, etc.)

Improves reproducibility by automating important variables:
- Heating
- Agitation
- Equilibration time

SPME automation video (~2 mins.)
Peppermint Oil in Chocolate Cookie Bar

1. Solvent
2. Internal standard
3. cis-Menthone
4. trans-Menthone
5. Menthol

SPME Fiber: 100µm PDMS
Sample: 4g peppermint cookie bar
Extraction: headspace, 1 min, 45°C
Desorption: 5 min at 250°C
Column: PTE™-5, 30m x 0.25mm ID, 0.25µm film
Detector: FID, 250°C
Injector: Splitless (3 min), 250°C
Milk Sample Off-Flavors by SPME-GC/MS

SPME Fiber: 75 µm PDMS/Carboxen
Sample: 3g of 2% milk + 10µL internal standard solution, (20µg/mL 4-methyl-2-pentanone) (9mL GC vial)
Column: Supel-Q™ PLOT, 30m x 0.32mm ID
Det.: GC/MS ion trap, m/z = 33-300

Prior to Exposure to Sunlight

After 1-Hour Exposure to Sunlight

1. Acetone
2. 2-Butanone
3. 3-Methylpentane
4. Pentanal
5. Dimethyldisulfide
6. Hexanal
IS. 4-Methyl-2-pentanone

Chromatogram provided by Ray Marsili, Dean Foods Technical Center, Rockford, IL, USA.
Residual Solvents in Commercial Ibuprofen

Brand “A”
1. Acetaldehyde
2. Ethanol
3. Acetonitrile
4. Acetone
5. 2-Propanol
6. 2-Methylpentane
7. 3-Methyl pentane
8. Hexane
9. Ethyl acetate
10. 2,2-Dimethylpentane
11. 2,4-Dimethylpentane
12. Methylcyclopentane

Brand “B”
10ppb Nitrosamines in Water: SPME-GC/MS

Sample: analytes in (water + 25% KCl, pH 10)
SPME Fiber: 65µm PDMS-DVB
Extraction: immersion, 15 min (rapid stirring)
Desorption: 270°C, 1 min
Column: PTA-5 (amine deactivated, 30m x 0.32mm ID, 0.5µm film)
Oven: 50°C (1 min) to 250°C at 10°C/min, hold 2 min
Carrier: helium, 30cm/sec
Det.: GC/MS (quadrupole, SIM)
Inj.: splitless, 250°C (0.75mm ID liner)

1. Nitrosodimethylamine
2. Nitrosodiethylamine
3. Nitrosomethylethylamine
4. Nitrosodipropylamine
5. Nitrosopiperidine
6. Nitrosodibutylamine
7. Nitrosodiphenylamine
New Development: Biocompatible Fiber Pipette Tips for Solvent Extraction
Single Use Biocompatible Fiber Probes for *in vivo* Analysis
Comparison of SPME *in-vivo* PK Study of Carbamazepine from Mice Whole Blood to Extracts of Plasma Removed from Mice

Slide Courtesy of Ines de Lannoy-NoAb BioDiscoveries
SPME fiber Holder with Automated DESI-1D Source

Courtesy of Joseph Kennedy of Prosolia
Solid Phase Microextraction (SPME) Products

Fibers

Holders
  • Manual
  • For autosamplers

Accessories

Instructions

Applications on CD

sigma-aldrich.com/spme
Sample Prep Innovations

- Solid Phase Microextraction (SPME)
- High specificity SPE (SupelMIPs)
- Dispersive SPE
- Silver Ion SPE for FAMES
- Carbonaceous adsorbents
- Flash chromatography

Users are...
- Analytical chemists (LC, LC-MS, GC...)

Interested in...
- Very selective extraction
- Analysis at extremely low concentrations (ppb, ppt)
- Increasing specificity of sample prep from complex matrixes

Users can expect...
- More rigorous washing to remove matrix
- Detect at lower levels
High Specificity Sample Prep

The specific innovation we will describe: SupelMIP Molecularly Imprinted Polymers
- SPE tubes
- 96-well plates
The Molecular Imprinting Process

Molecularly imprinted polymers (MIPs) are polymers that have been prepared by polymerizing either pre-formed or self-assembled monomer-template complexes together with a cross-linking monomer. After removal of the template molecule, a polymer with binding sites for the template is obtained.
The MIP Binding Site

Graphical representation of the MIP binding site, which contains a cavity of the right size and attractive molecular features that can bind to the target molecule(s).
SupelMIP Chloramphenicol: Analysis in Honey

Chloramphenicol is an antibiotic that is monitored in honey.

Background from honey sample cleaned by SupelMIP SPE and LLE for Chloramphenicol analysis

Comparison of ion suppression effect between different clean-up methods for honey. Samples were post-spiked with CAP prior to analysis.
Overview of a Typical SupelMIP SPE Procedure

Very simple methods. Full protocols are included with each MIP product. Protocols may require optimization depending on the sample matrix.
SupelMIP Products

- **PAHs** in edible oils
- **Nitroimidazoles** in milk, eggs and other foods
- Nonsteroidal anti-inflammatory drugs (NSAIDS) in wastewater and other matrices
- **Fluoroquinolones** in bovine kidney, honey and milk
- **Amphetamines** and related compounds in urine
- **Chloramphenicol** in plasma, urine, milk, honey and shrimp
- **NNAL** - nitroso compound in urine
- **TSNAs** - tobacco specific nitrosamines in urine and tobacco
- **β-agonists** and **β-blockers** in tissue, urine and wastewater
- **Clenbuterol** in urine
- **Triazines** in water
- **Riboflavin** in milk

[sigma-aldrich.com/supelmip]
Topics: Sample Prep Innovations

- SPME (solid phase microextraction)
- High specificity SPE (SupelMIP)
- Dispersive SPE
- Silver Ion SPE for FAMEs
- Carbonaceous adsorbents
- Flash chromatography

Users are...
- Food safety analysts

Interested in...
- Multi-residue pesticide analysis in food and agricultural products

Users can expect...
- Quick, easy, inexpensive extraction method
Dispersive SPE (dSPE or QuEChERS) Multi-residue Pesticide Method

Multi-residue (100’s) pesticide analysis
Retains/removes key interferences in food samples
Analytes are un-retained

**Quick** (~30 min./6 samples)
**Easy** (no laborious steps)
**Cheap**
**Effective** (wide scope, low consumption)
**Rugged** (minimal sources of errors)
**Safe** (solvents and techniques)
Dispersive SPE Procedure

**Procedure:**
1. Food initially extracted with aq. miscible solvent (e.g. ACN)
2. High amounts of salts (NaCl, Mg-sulfate) and buffering agents added to induce phase separation and stabilize acid/base labile pesticides
4. Transfer supernatant to centrifuge tube. Add bulk SPE phase(s) and salts. Shake/vortex. Centrifuge and analyze supernatant.

Standard dSPE product line configured for:
- CEN Standard Method EN – 15662
- AOAC Method 2007.01

Full details of the simple protocol is included with the product.
GC-MS of Pesticides from Oranges Following Extraction with dSPE

column: SLB-5ms, 30 m x 0.25 mm I.D., 0.25 µm (28471-U)
oven: 100 °C (1 min.), 10 °C/min. to 300 °C (5 min.)
 inj.: 250 °C
 MSD interface: 300 °C
 scan range: selected ion monitoring (SIM), 7 monitoring groups used
carrier gas: helium, 1 mL/min constant
injection: 1 µL, pulsed (20 psi until 0.20 min.), splitless (1.0 min.)
liner: 4 mm I.D., single taper

2. Dichlorvos 12. Dichlofluanid 22. cis-Chlordane
3. Acephate 13. Chlorpyrifos 23. Imazalil
4. Propoxur 14. p-Dichlorobenzophenone 24. 4,4'-DDE
5. Ethoprophos (L.S.) 15. Cyprodinil 25. Dieldrin
7. γ-BHC 17. Tolyfluanid 27. Dicofol
Dispersive SPE Products

Centrifuge tubes containing pre-determined amounts of salts and SPE sorbents to support the most common method configurations used today

<table>
<thead>
<tr>
<th>Product #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>55227-U</td>
<td>Dispersive SPE (dSPE) Citrate Extraction Tube, pk of 50</td>
</tr>
<tr>
<td>55237-U</td>
<td>Dispersive SPE (dSPE) Citrate/Sodium Bicarbonate Extraction</td>
</tr>
<tr>
<td></td>
<td>Tube, pk of 50</td>
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<tr>
<td>5524-U</td>
<td>Dispersive SPE (dSPE) MgSO₄ Extraction Tube, pk of 50</td>
</tr>
<tr>
<td>55228-U</td>
<td>Dispersive SPE (dSPE) PSA SPE Clean Up Tube 1, pk of 50</td>
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<tr>
<td>55229-U</td>
<td>Dispersive SPE (dSPE) PSA/C18 SPE Clean Up Tube 1, pk of 50</td>
</tr>
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<td>55230-U</td>
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<td></td>
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<td>55233-U</td>
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<td></td>
<td>of 50</td>
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</table>

Also available:
- Sample packs
- Custom tubes and packing materials

sigma-aldrich.com/spe
Topics: Sample Prep Innovations

- SPME (solid phase microextraction)
- High specificity SPE (SupelMIP)
- Dispersive SPE
- **Silver Ion SPE for FAMEs (Discovery Ag-Ion)**
- Carbonaceous adsorbents
- Flash chromatography

Users are...
- Food analysts

Interested in...
- Measuring cis/trans fats or degree of unsaturation

Users can expect...
- To fractionate FAME samples prior to GC analysis, simplifying analytical chromatography and improving method accuracy
Discovery Ag-Ion SPE for FAME Fractionation

Silver ion anchored onto SCX SPE support
Ag+ forms a charge transfer complex with unsaturated FAME double bond
- Ag+ = electron acceptor; double bond = electron donor
Cis configuration offers greater steric accessibility = stronger retention
Strength of interaction increases with no. of double bonds
Overview Discovery Ag-Ion SPE Procedure

1) Fatty acids (FA) extracted from food sample
2) FA converted to FAMEs using BF$_3$
3) FAMEs are extracted into hexane
4) Hexane sample applied to Discovery Ag-Ion SPE cartridge
5) FAMEs separated using different mixtures of hexane:acetone to extract from cartridge
   • Increasing % acetone disrupts retention of strongly retained FAMEs (cis and higher number of double bonds)
6) Fractions analyzed by GC
Cis/Trans Fractionation of FAMEs from Potato Chips with and without Ag-Ion SPE
Discovery Ag-Ion SPE Products

<table>
<thead>
<tr>
<th>Description</th>
<th>Qty.</th>
<th>Cat. No.</th>
</tr>
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<tbody>
<tr>
<td>Discovery Ag-Ion SPE</td>
<td>30</td>
<td>54225-U</td>
</tr>
<tr>
<td>750 mg/6 mL SPE Tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>750 mg/1 mL Rezorian™ Cartridge</td>
<td>10</td>
<td>54226-U</td>
</tr>
</tbody>
</table>

http://tinyurl.com/agionspe
Topics: Sample Prep Innovations

• SPME (solid phase microextraction)
• High specificity SPE (SupelMIP)
• Dispersive SPE
• Silver Ion SPE for FAMEs
• Carbonaceous adsorbents (ENVI-Carbs)
• Flash chromatography

Users are...
• Analytical chemists, HPLC, GC doing sample prep

Interested in...
• Extraction of highly polar compounds from water samples, and many others...

Users can expect...
• High extraction efficiency
# Structural Classification of Carbons

<table>
<thead>
<tr>
<th>Carbon Class</th>
<th>C–C Distance (nm)</th>
<th>Layer Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous (hexagonal)</td>
<td>0.139</td>
<td>—</td>
</tr>
<tr>
<td>Turbostratic</td>
<td>0.142</td>
<td>0.365</td>
</tr>
<tr>
<td>Graphitic</td>
<td>0.142</td>
<td>0.335</td>
</tr>
<tr>
<td>Diamond (cubic)</td>
<td>0.155</td>
<td>—</td>
</tr>
</tbody>
</table>

![Illustration of carbon structures](image)
Carbon Sorbents for Sample Prep

Packed SPE tubes:

- **Supelclean™ ENVI-Carb PLUS** – spherical carbon molecular sieve for extraction of highly polar compounds from water samples
- **Supelclean ENVI-Carb-II/PSA SPE** – multilayer SPE tubes for multiresidue pesticide analysis in foods
- **Supelclean ENVI-Carb-II SPE** – isolation/removal of pigments (e.g., chlorophyll and carotenoids) and sterols commonly present in fruits, vegetables, and other natural products
- **Supelclean ENVI-Carb-II/SAX/PSA SPE** – additional ion exchange capability
- **Supelclean PSA SPE** – polymerically bonded, ethylenediamine-N-propyl phase that contains both primary and secondary amines

http://tinyurl.com/carbonspe

Dual Layer Supelclean ENVI-Carb-II/PSA SPE Tube
Supelclean ENVI-Carb PLUS

**Spherical Carbon Molecular Sieve**
- Extraction of highly polar compounds from water samples
- > 70% Abs 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

**Examples of polar compounds:**
- Acephate: log P -0.85
- Acrylamide: log P -0.67
- 1,4-Dioxane: log P -0.27
- Oxamyl: log P -1.2
GC-MS Analysis of 1,4-dioxane in water extracted using ENVI-Carb Plus

- THF-d8 (Int. Std.)
- 1,4-dioxane-d8 (surrogate)
- 1,4-dioxane

Column: SPB-624, 30 m x 0.25 mm I.D., 1.4 µm
Oven: 30 °C (1 min.), 7 °C/min. to 90 °C, 20 °C/min. to 200 °C (3 min.)
Inj: 200 °C
Carrier: helium, 1 mL/min constant flow
Injection: 2 µL, splitless
MS interface: 220 °C
Scan range: SIM
Topics: Sample Prep Innovations

• SPME (solid phase microextraction)
• High specificity SPE (SupelMIP)
• Dispersive SPE
• Silver Ion SPE for FAMEs
• Carbonaceous adsorbents (ENVI-Carbs)

• Flash Chromatography

Users are...
• Synthetic, organic chemists
• Medicinal chemists

Interested in...
• Purification of relatively large samples from reaction mixtures or other samples

Users can expect...
• Fast, simple, inexpensive purifications
• High N (spherical particles)
Performance of Spherical vs. Irregular Silicas in Flash Application

Higher efficiency of spherical particles translates to narrower bands for more concentrated fractions and faster isolations.

samples: 5-hydroxy-DL-tryptophan and DL-tryptophan
cartridges: 53 mm x 23 mm I.D.
mobile phase: methanol:water (90:10)
detection: UV 254 nm
flow rate: 20 mL/min.

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Total Volume</th>
<th>Fraction 1 Volume</th>
<th>Fraction 2 Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical silica</td>
<td>120 mL</td>
<td>25 mL</td>
<td>40 mL</td>
</tr>
<tr>
<td>Irregular silica</td>
<td>400 mL</td>
<td>80 mL</td>
<td>260 mL</td>
</tr>
</tbody>
</table>
VersaFlash Support Literature & Products

Silica & C18 Cartridges
  • Particle size options
  • Cartridge size options
  • Cartridges can be coupled
  • Reversible
  • Compatible with other systems

All system components
Summary

Solid Phase Microextraction (SPME) [http://www.sigma-aldrich.com/spme]
High specificity SPE (SupelMIPs) [http://www.sigma-aldrich.com/supelmip]
Dispersive SPE for pesticide extraction [http://www.sigma-aldrich.com/spe]
Silver Ion SPE for FAMEs (Discovery Ag-Ion SPE) [http://tinyurl.com/agionspe]
Carbon adsorbents for polar compounds (ENVI-Carbs) [http://tinyurl.com/carbonspe]
Flash chromatography [http://www.sigma-aldrich.com/versaflash]
Acknowledgements/Collaborators

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Joseph Kennedy, Prosolia (DESI)
Supelco and Fluka R&D Teams

For more information on the subjects presented here, please contact techservice@sial.com or your regional sales team.