The Chemistry of Solid-Phase Extraction

or “That’s all there is to it?”

Reverse Phase

Mixed Mode

Normal Phase

Ion Exchange
“And I’ll thank you to wipe that smirk off your phase!”
The force known as solid phase extraction is unusually strong.
Solid Phase Extraction (SPE) is a broad term to describe the digital separation technique where liquids contact sorbents, and organic compounds or ions in the liquid adsorb to the functional group(s) of the sorbent.

- Sorbents are chosen to either retain the components of interest, or selectively release them into a strong liquid phase.
- SPE manufacturers commonly pack these sorbents into cartridges, well plates, dispersive tubes or other convenient devices.
SPE & Sorbents

- SPE is “digital”
- Theoretical plates aren’t used
- SPE is used for extraction, concentration and purification
- Sorbents are available in many forms: Silica based, Polymeric, Alumina, and Carbon(s)
- For all fields of application, **silica based sorbents are the most common sorbents used**
- Silica based sorbents give the greatest number of choices for extraction
- Silica based sorbents are very rugged (Stable over a wide pH and solvent range)
- Silica based sorbents are the most cost effective
Silica Gel Structures

Core: Porous
Pore: Continuous
Shape: Irregular

Microparticulate
Core: Porous
Pore: Continuous
Shape: Irregular
## Particle Size and Pore Diameter

<table>
<thead>
<tr>
<th>Silica Shape</th>
<th>Particle Size Range (µm)</th>
<th>Pore Diameter (in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irregular</td>
<td>5 – 20</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>40 – 60</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>60 – 90</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>90 – 125</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>60 – 200</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>120 – 200</td>
<td>60</td>
</tr>
</tbody>
</table>
Surface Area

- **Surface area** = sum of internal + external surfaces
- **External area** = geometric surface of particles per gram of silica
- **Internal area** = surface area of open pores
- Surface area of bonded silica is approximately 300 m$^2$/g
- 97% of surface area is due to internal porosity
- Surface area depends mostly on pore size & pore volume
- Particle size primarily affects flow characteristics and not surface area
Continuous Pores

Pore Diameter 60 Å

SiOSi

SiOSi
Endcapping

• Bonded phases are manufactured by the reaction of organo-silanes with activated silica.

• During the polymerization reaction of carbon chains to the silica backbone, a very stable silyl ether linkage forms.

• In order to decrease this slight polarity, these hydroxyl sites are deactivated.

• Because there are no hydroxyl sites left, our **endcapped** sorbents are **more hydrophobic** than our unendcapped sorbents.
Unendcapped vs Endcapped
### Types of Solid Phase Extraction

<table>
<thead>
<tr>
<th><strong>Types</strong></th>
<th><strong>Binding Energies</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse Phase</td>
<td>1-5 kcal/mole</td>
</tr>
<tr>
<td>- Nonpolar Interactions</td>
<td></td>
</tr>
<tr>
<td>- Van der Waals Forces</td>
<td></td>
</tr>
<tr>
<td>- π/π Interactions</td>
<td></td>
</tr>
<tr>
<td>- Secondary Interactions</td>
<td></td>
</tr>
<tr>
<td>Normal Phase</td>
<td>3-10 kcal/mole</td>
</tr>
<tr>
<td>- Polar Interactions</td>
<td></td>
</tr>
<tr>
<td>- Hydrogen Bonding</td>
<td></td>
</tr>
<tr>
<td>- Dipole-Dipole Interactions</td>
<td></td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>50 to &gt;100 kcal/mole</td>
</tr>
<tr>
<td>- Cationic Interactions</td>
<td></td>
</tr>
<tr>
<td>- Anionic Interactions</td>
<td></td>
</tr>
<tr>
<td>Mixed Mode</td>
<td>3-100 kcal/mole</td>
</tr>
<tr>
<td>- Combine Ionic, Nonpolar and Polar Interactions</td>
<td></td>
</tr>
</tbody>
</table>
## Covalent Phases

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>EPX</td>
<td>-Si-(CH$_2$)$_3$ O - CH$_2$ - CH - CH$_2$</td>
</tr>
<tr>
<td>Aldehydic</td>
<td>ALD</td>
<td>-Si-(CH$_2$)$_4$CHO</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>ICN</td>
<td>-Si-(CH$_2$)$_3$NCO</td>
</tr>
<tr>
<td>Thiopropyl</td>
<td>THX</td>
<td>-Si-(CH$_2$)$_3$SH</td>
</tr>
</tbody>
</table>

- Forms Schiff Base with amines
- Used to filter out primary amines, hydrazines, reducing agents, and other nucleophiles
- Covalent bonding for proteins, enzymes and other bioactive molecules
Retention Mechanisms

**Reversed Phase**
- Hydrophobic (nonpolar)
  - Load un-ionized
  - Elute non-polar solvent
- Secondary interactions of amines with unreacted silanols on bonded silicas
  - Elute with polar to moderately polar solvent

**Ion Exchange**
- Strong and weak ionic attraction
  - Load as ionized
  - Elute in acid or base

**Mixed Mode**
- Both reversed phase and ionic attraction
  - Load as ionized
  - Elute as un-ionized non-polar solvent
Activated Carbon

• Activated – refers to high surface area allowing many surfaces to adsorb simultaneously

• Surface area as high as 1500 m²/g

• Retention Mechanisms
  – Van der Waal and London dispersion forces
  – pi-pi structure of substrate bonding to oxygen

• Liquid chromatography – Not SPE, bed height critical
Graphitized Carbon Black (GCB)

Retention mechanism – carbon/hydrogen interaction “ring-on-ring”
• Very high surface areas are available

• Positively charged and can adsorb like ion-exchange

• \( \pi: \pi \) interactions between sheets

• planar molecules trapped between sheets

• electron lone pair repulsion (valence shell repulsion theory)
Polystyrene Divinylbenzene

Retention mechanisms - Van der Waals/dispersion forces and ring structure, resonance, ππ
## Non-Polar or Hydrophobic

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8 octyl</td>
<td>C08</td>
<td>-Si-(CH(_2))(_7)CH(_3)</td>
</tr>
<tr>
<td>C18 octadecyl</td>
<td>C18</td>
<td>-Si-(CH(<em>2))(</em>{17})CH(_3)</td>
</tr>
<tr>
<td>C30 tricontyl</td>
<td>C30</td>
<td>-Si-(CH(<em>2))(</em>{29})CH(_3)</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>CYH1</td>
<td>-Si –Hex</td>
</tr>
<tr>
<td>Phenyl</td>
<td>PHY1</td>
<td>-Si –Ben</td>
</tr>
</tbody>
</table>
Non-Polar Extractions

- Also called hydrophobic or reverse phase
- Interactions between sorbent C-H bonds and analyte C-H bonds
- Involves van der Waals / dispersion forces
- Applications - PCBs, flame retardants, pesticides, PAHs, petroleum products
- Analytes - protonated / neutral state, aromatics & alkyl chains
- Matrix - biologicals, water, aqueous buffers
Example of a Hydrophobic Bonding

Sorbent

Compound
For best hydrophobic retention, the analyte and sorbent should be uncharged.

Elution solvents - typically non-polar to moderately polar
### Hydrophilic or Polar Phases

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>SIL1</td>
<td>-SiOH</td>
</tr>
<tr>
<td>Diol</td>
<td>DOL1</td>
<td>-Si-(CH$_2$)$_3$OCH$_2$CHOHCH$_2$OH</td>
</tr>
<tr>
<td>Cyanopropyl</td>
<td>CNP1</td>
<td>-Si-(CH$_2$)$_3$CN</td>
</tr>
<tr>
<td>Florisil®</td>
<td>FLS</td>
<td></td>
</tr>
<tr>
<td>Alumina, Acidic</td>
<td>ALA</td>
<td></td>
</tr>
<tr>
<td>Alumina, Neutral</td>
<td>ALN</td>
<td></td>
</tr>
<tr>
<td>Alumina, Basic</td>
<td>ALB</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>CARB</td>
<td></td>
</tr>
</tbody>
</table>

**HILIC** – **Hydrophilic Interaction Liquid Chromatography**

- mobile phase more polar than sorbent

*Florisil is a registered trade mark of US Silica*
Polar Extractions
(HILIC)

- Also called hydrophilic or normal phase
- Unequal distribution of electrons
- Involves hydrogen bonding, pi-pi and dipole/ dipole interactions
- Sorbents - silica, diol, diethylamino,
cyanopropyl, carbon, Florisil, alumina, zwitterionic
- Applications - oil additives, carbohydrates, phenols, oil soluble vitamins
- Analytes - amines, hydroxyls, carbonyls,
aromatic rings, heteroatoms (O, S, N, P)
- Matrix - non-polar, organic
- Elution solvents - medium to high polarity

Example of a Hydrophilic Phase

- Silica Backbone
- Hydrophilic Chain
Example of Hydrophilic Bonding

Sorbent

Compound
“It’s time we face reality, my friends… We’re not exactly rocket scientists.”
## Ion Exchange Phases

### Anion Sorbent

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminopropyl (1° amine)</td>
<td>NAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9.8</td>
</tr>
<tr>
<td>N-2 Aminoethyl (1° &amp; 2° amine)</td>
<td>PSA1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;NH(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.1, 10.9</td>
</tr>
<tr>
<td>Diethylamino (3° amine)</td>
<td>DAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.6</td>
</tr>
<tr>
<td>Quaternary Amine Chloride</td>
<td>QAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>always charged</td>
</tr>
<tr>
<td>Quaternary Amine Hydroxide</td>
<td>CHQAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; CH&lt;sub&gt;3&lt;/sub&gt;CO&lt;sup&gt;-&lt;/sup&gt;</td>
<td>always charged</td>
</tr>
<tr>
<td>Quaternary Amine Acetate</td>
<td>CAQAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>always charged</td>
</tr>
<tr>
<td>Quaternary Amine Formate</td>
<td>CFQAX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; CHO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>always charged</td>
</tr>
<tr>
<td>Polyimine</td>
<td>PAX</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;-R-[NHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;x&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>

### Cation

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic Acid</td>
<td>CCX1</td>
<td>-Si-CH&lt;sub&gt;2&lt;/sub&gt;COOH</td>
<td>4.8</td>
</tr>
<tr>
<td>Propylsulfonic Acid</td>
<td>PCX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Benzenesulfonic Acid</td>
<td>BCX1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;─[O]─SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>always charged</td>
</tr>
<tr>
<td>Benzenesulfonic Acid High Load</td>
<td>BCXHL1</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;─[O]─SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>always charged</td>
</tr>
<tr>
<td>Triacetic Acid</td>
<td>TAX</td>
<td>-Si-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;NH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;N(CH&lt;sub&gt;2&lt;/sub&gt;COOH)&lt;sub&gt;2&lt;/sub&gt; CH&lt;sub&gt;2&lt;/sub&gt;COOH</td>
<td></td>
</tr>
</tbody>
</table>
**Copolymeric (Multifunctional Phases)**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminopropyl + C8</td>
<td>NAX2</td>
<td>-Si-(CH$_2$)$_3$NH$_2$ &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Quaternary Amine + C8</td>
<td>QAX2</td>
<td>-Si-(CH$_2$)$_3$N+(CH$_3$)$_3$ &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Carboxylic Acid + C8</td>
<td>CCX2</td>
<td>-Si-CH$_2$COOH &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Propylsulfonic Acid + C8</td>
<td>CX2</td>
<td>-Si-(CH$_2$)$_3$SO$_3$H &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Benzenesulfonic Acid + C8</td>
<td>BCX2</td>
<td>-Si-(CH$_2$)$_2$—[O]—SO$_3$H &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Cyanopropyl + C8</td>
<td>CNP2</td>
<td>-Si-(CH$_2$)$_3$CN &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
<tr>
<td>Cyclohexyl + C8</td>
<td>CYH2</td>
<td>-Si—[O] &amp; -Si-(CH$_2$)$_7$CH$_3$</td>
</tr>
</tbody>
</table>
Ion Exchange Mechanisms

- Ionic interactions occur between charged sorbent & analyte of opposite charge
- pH is manipulated to ionize analytes functional group
- Ionic bonds are strong & retain analyte
- Hydrophobic interferences washed away with organic solvents
- Polar interferences removed with aqueous or weak aqueous / organic washes
- Elute by changing pH
Example of Anion Exchange Binding

Example of Cation Exchange Binding
pKa\textsubscript{dissociation constant}

pH at which the analyte is 50% ionized (equilibrium)
pKa - dissociation constant

**Acids:**
- pH > pKa promotes ionization
- pH < pKa suppresses ionization

**Bases:**
- pH < pKa promotes ionization
- pH > pKa suppresses ionization
The most important number in ion exchange
THE MAGIC NUMBER IS 2

% of Compound in Ionic State

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Ionization State</th>
<th>2&lt;</th>
<th>1&lt; at pKa</th>
<th>1&gt;</th>
<th>2&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Anion (-)</td>
<td>1</td>
<td>9</td>
<td>50</td>
<td>91</td>
</tr>
<tr>
<td>Base</td>
<td>Cation (+)</td>
<td>99</td>
<td>91</td>
<td>50</td>
<td>9</td>
</tr>
</tbody>
</table>
Load the Analyte on the Sorbent

Fully Charge the Ion

Base

pKa

pH 14

2 pH units

Neutral pH

pKa

pH 1

Acid
Remove Charge and Elute

Base

pKa

pKa

Acid

pH 1

pH 14

2 pH units

Neutral pH
### Relative Counter ion Selectivity

#### Strong Cation Exchanger

- **Benzenesulfonic Acid (BCX)**

#### Strong Anion Exchanger

- **Quaternary Amine (QAX)**

<table>
<thead>
<tr>
<th>Cations</th>
<th></th>
<th>Anions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba²⁺</td>
<td>8.7</td>
<td>Benzene Sulfonate</td>
<td>500</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>7.6</td>
<td>Salicylate</td>
<td>450</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>7.5</td>
<td>Citrate</td>
<td>220</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>7.2</td>
<td>I⁻</td>
<td>175</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>5.3</td>
<td>Phenate</td>
<td>110</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>4.9</td>
<td>HSO₄⁻</td>
<td>85</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3.9</td>
<td>ClO₃⁻</td>
<td>74</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>3.0</td>
<td>NO₃⁻</td>
<td>65</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>2.9</td>
<td>Br⁻</td>
<td>50</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>2.9</td>
<td>CN⁻</td>
<td>28</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>2.8</td>
<td>HSO₃⁻</td>
<td>27</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>2.7</td>
<td>BrO₃⁻</td>
<td>27</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>2.7</td>
<td>NO₂⁻</td>
<td>24</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>2.6</td>
<td>Cl⁻</td>
<td>22</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.5</td>
<td>HCO₃⁻</td>
<td>6.0</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>2.5</td>
<td>IO₃⁻</td>
<td>5.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.5</td>
<td>HPO₄⁻</td>
<td>5.0</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>2.3</td>
<td>Formate</td>
<td>4.6</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.9</td>
<td>Acetate</td>
<td>3.2</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.5</td>
<td>Propionate</td>
<td>2.6</td>
</tr>
<tr>
<td>H⁺</td>
<td>1.0</td>
<td>F⁻</td>
<td>1.6</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.8</td>
<td>OH⁻</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Cation exchange counter ions**

**Anion exchange counter ions**
Counter Ion Effects

- Ions in the sample solution compete with the analyte for sorbent binding sites.

- Poor recovery of analyte can occur if these counter ions have a greater affinity for the sorbent than does the analyte.

- This occurs in two ways: high counter concentrations (ionic strength) and high counter ion chemical affinity for the bonded phase (high counter ion selectivity).

- Retention of analyte is improved by loading the sample in a buffer or solvent system of the proper pH at low ionic strength (<0.010 M) buffer comprised of low selectivity ions.
Anion Exchange Extractions

- Anion exchange sorbents positively charged
- Acidic analytes manipulated to carry negative charge
- Opposites attract forming strong bonds

Sorbents
- PSA, pka 10.1, 10.9
- Aminopropyl (weak), pka 9.8
- Quaternary amine (strong)
- Diethylamino (weak), pka 10.6

Applications include phosphates, organic acids, fatty acids, sugars

Analytes
- Phosphates
- Carboxylic acids
- Sulfonic acids (cations)

Matrix - aqueous

Acidic elution solvents to neutralize analyte
Example of a Anion Exchange Phase

\[ \text{Silica Backbone} \]

\[ \text{Anion Exchanger} \]
Cation Exchange Extractions

- Cation exchange sorbents negatively charged
- Basic analytes manipulated to carry positive charge
- Opposites attract forming strong bonds

**Sorbents**
- Benzenesulfonic acid (strong)
- Propylsulfonic acid (strong) $\text{pka} < 1$
- Carboxylic acid (weak) $\text{pka} 4.8$

**Applications include basic drugs, catecholamines, pharmaceuticals**

**Analytes**
- Amines
- Pyrimidines (cations)

**Matrix - aqueous**

**Basic elution solvents to neutralize analyte**
Example of a
Cation Exchange Phase

[Chemical structure image]

Silica Backbone
Anion Exchanger
Hydrophobic & ionic retention mechanisms
Reverse phase sorbent with cation or anion exchange
Acidic, basic & neutral analyte applications
Matrix - aqueous
Selective washes
Elution solvents mixture of organics with acid or base
Superior sample clean up
Example of a Copolymeric Phase

Silica Backbone
Hydrophobic Chain
Ion Exchanger
Example of Copolymeric Bonding

(CH₂)ₙ NH₃⁺ → O−C

Sorbent Compounds
Choosing the Sorbent

- Identify the functional groups present in the analyte
  - Look up the structure (Merck Index or Internet)
- Understand how an analyte behaves in response to changing extraction conditions (sample pH, % organic, etc.)
- Determine pKa if possible
- Manipulate the conditions to meet defined method objectives
  - Polar or nonpolar
  - Ionic or nonionic
  - Analyte solubility
    - Rule of thumb: Aqueous solubility >200 mg/L difficult to extract using reverse phases
Select sorbent chemistry that encourages B to interact strongly with A, weakly with C.

1. Analyte must adsorb to SPE medium
2. Analyte residence time must be sufficient
3. Analyte must be removed from SPE medium
Choosing the Sorbent
A simple rule: “Like attracts like”

Non-polar analytes
- Alumina, Silica, Florisil®, Diol, Carbon

Polar analytes
- Carbon

Ionic analytes
- Ion Exchange

Increasing solubility
- C8, C18, C30, DVB, CYH, PHY
SPE Steps

- Prepare sample
- Condition sorbents
- Apply sample
- Wash interferences
- Dry sorbent
- Elute analyte
- Concentrate
- Derivatize (if necessary)
**SPE as a Filter**

ex. Florisil Clean-up

- **Apply Sample**
  - A = Analyte
  - M = Matrix

- **Wash Solvent**
  - M = Matrix

- **Collect**
  - A = Analyte
SPE as a Selective Adsorption Tool

A = Analyte
M = Matrix

1. **Apply sample**
2. **Wash solvent**
3. **Elution solvent**
Common SPE Errors:

- Testing pH of deionized water with paper
- Absorption of analyte on glass, plastic, or filters
- Aggressive extract concentration
- Weak or incorrectly prepared elution solvent
• Reverse Phase
  – Needs a neutral charge
  – Sorbent must be dried
  – Extract must be dried
  – Sample loaded too quickly
Ion Exchange

- Sample loaded and/or eluted too quickly

Analysis Errors

- Calibrate in same solvent as extract

Normal Phase

- Sample loaded too quickly
- Sorbent compromised by environment
- Extract eluted at wrong polarity
“Do or do not... there is no try.”
This man’s job is to help you.

Contact him with any questions or issues. dshelly@unitedchem.com