Accelerated Solvent Extraction
ASE
ASE

- Pressurized fluid extraction (PFE)
- Pressurized liquid extraction (PLE)
- Performed at elevated temperature (50-200 °C) and pressure (1500-2000 psi)
- Dionex Corp. SFE → ASE
  - Overcome limitations of SFE (matrix dependent, organic modifier)
Solubility and Mass Transfer Effect

High Temperature

- Faster diffusion rate
- Improves mass transfer

- Increases the capacity of solvent to solubilize analytes

- Increases extraction rate
Disruption of Surface Equilibria

- **Temp**
  - Disrupts solute-matrix interactions
  - Decreases viscosity
  - Improves penetration on matrix
  - Improves extraction

- **Pressure**
  - Solvent remains liquefied above their boiling point
  - Enhances extraction within the matrix
Load sample
Fill cell with solvent
Heated and pressurized cell
Hold sample at P and T
Pump clean solvent
Purge with N₂
Extract for ready analysis

Temp. ~ 200 °C
Pressure ~ 500 – 3,000 psi

Schematic of ASE
ASE System

ASE 100

ASE 200

ASE 300
# ASE Saves Solvent, Time & Money

<table>
<thead>
<tr>
<th>Method</th>
<th>Average solvent used per sample</th>
<th>Average extraction time per sample</th>
<th>Average cost per sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soxhlet</td>
<td>200-500 mL</td>
<td>4 - 48 hr</td>
<td>$27</td>
</tr>
<tr>
<td>Automated Soxhlet</td>
<td>50-100 mL</td>
<td>1 - 4 hr</td>
<td>$16</td>
</tr>
<tr>
<td>Sonication</td>
<td>100-300 mL</td>
<td>30 min – 1 hr</td>
<td>$24</td>
</tr>
<tr>
<td>SFE</td>
<td>8-50 mL</td>
<td>30 min – 2 hr</td>
<td>$23</td>
</tr>
<tr>
<td>ASE</td>
<td>15-40 mL</td>
<td>12 – 18 min</td>
<td>$14</td>
</tr>
</tbody>
</table>
ASE Method Development

- Pressure and temperature
- Static time
- Number of static cycles
- Flush volume
Application

- Environmental, i.e., EPA SW-846
- Food
- Polymer
- Pharmaceutical
Microwave Assisted Extraction

Microwave Assisted Acid Digestion
Microwave

- Electromagnetic wave
- $\lambda = 0.3 \text{ mm} - 1 \text{ mm}$
- $\nu = 100 \text{ GHz} - 300 \text{ MHz}$
- Operate at 2.45 GHz
Microwave Generator - Magnetron

Anode block inside a magnetron

Side view of the magnetron
Clockwise motion of electrons in the anode block

Cloud of electrons and the induced current
Microwave chamber
Convective vs. Microwave Heating

- **Convective Heating**
  - Flame
  - Hot plate
  - Heating mantles
  - Oven
  - Heating block
  - Sample independent

- **Microwave heating**
  - Directly heat
  - Dipole rotation
  - Ionic conduction
  - Heated above BP possible
  - Sample dependent
    - Microwave absorbing characteristic
Heating Using Microwave

► Ionic conductance
  • Electrophoretic migration of ions when an electromagnetic field is applied

► Dipole rotation
  • Realignment of dipoles with the applied field
  • At 2.45 GHz, dipoles align ~5 billion times/sec

HEAT
Microwave Oven (To heat food)

Typical microwave oven

Microwaves

Fan

Magnetron

Wave guide

Fan

Cooling chamber

Glass window with metal screen

Door

Controls

Door release

High voltage power supply
Interaction between water molecule and microwave
Microwave – Sample Preparation

- Electromagnetic radiation to desorb analytes from their matrices
- Microwave energy as a heating source
- Open vessel microwave heating system
  - Like automated Soxhlet
- Closed vessel microwave heating system
Extracting Solvent Mechanism

- Sample immersed in a single solvent or mixture of solvents that strongly absorb microwave energy
- Sample extracted with both high and low dielectric losses in various proportions
- Samples that have a high dielectric loss extracted with a microwave transparent solvent
Open-Vessel MAE
Open-Vessel MAE

- Atmospheric pressure microwave
- Focused microwave
- Microwave assisted soxhlet extraction

Closed-Vessel MAE System

Closed vessel microwave heating system

- Vessel; PTFE, quartz
- Outer body; PP
- Temperature control
- Indirect heating
- Stirring
- Solvent safety features
Multiwave MAE system
Multiwave 3000
Microwave transparent materials

Reflux action

# Solvent Boiling Point and Closed Vessel Temperature comparison

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point (°C)</th>
<th>Closed Vessel Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>56.2</td>
<td>164</td>
</tr>
<tr>
<td>Acetone-cyclohexane 7:3 (v/v)</td>
<td>52</td>
<td>160</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>81.6</td>
<td>194</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>39.8</td>
<td>140</td>
</tr>
<tr>
<td>Hexane</td>
<td>64.7</td>
<td>162*</td>
</tr>
<tr>
<td>Methanol</td>
<td>68.7</td>
<td>151</td>
</tr>
</tbody>
</table>

*Using carbon black filled fluoropolymer heating insert*
Indirect Heating

- Acetone
- n-Hexane with insert
- n-Hexane

Temperature (°C)

Time (min)
Microwave – EPA Method

► EPA SW-846

- Method 3015 (acid digestion of aqueous sample)
- Method 3051 (acid digestion of sediments, sludges and soils)
- Method 3052 (acid digestion of organic based matrices)
- Method 3546 (organic extraction)
Method Development

- Pretreatment
- Choice of solvent
- Solvent volume
- Temperature
- Extraction time
- Matrix characteristic and water content
- Additional clean-up
# Comparison of Extraction Methods for Solid Sample Preparation

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample size (g)</th>
<th>Solvent volume (mL)</th>
<th>Temperature (°C)</th>
<th>Pressure</th>
<th>Time (hr)</th>
<th>Number of samples</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sofhlet</td>
<td>10-20</td>
<td>200-500</td>
<td>40-100</td>
<td>Atm</td>
<td>12-24</td>
<td>1 (serial)</td>
<td>Very Low</td>
</tr>
<tr>
<td>Automate Sohlet</td>
<td>10-20</td>
<td>50-100</td>
<td>40-100</td>
<td>Atm</td>
<td>1-4</td>
<td>6 (batch)</td>
<td>Moderate</td>
</tr>
<tr>
<td>SFE</td>
<td>5-10</td>
<td>10-20</td>
<td>50-150</td>
<td>2000-4000 psi</td>
<td>0.5-1.0</td>
<td>44 (serial)</td>
<td>High</td>
</tr>
<tr>
<td>ASE</td>
<td>1-30</td>
<td>10-45</td>
<td>50-200</td>
<td>1500-2000 psi</td>
<td>0.2-0.3</td>
<td>24 (serial)</td>
<td>High</td>
</tr>
<tr>
<td>Closed vessel MAE</td>
<td>2-5</td>
<td>30</td>
<td>100-200</td>
<td>1500-2000 psi</td>
<td>0.1-0.2</td>
<td>12 (batch)</td>
<td>Moderate</td>
</tr>
<tr>
<td>Open vessel MAE</td>
<td>2-10</td>
<td>20-30</td>
<td>Ambient</td>
<td>Atm</td>
<td>0.1-0.2</td>
<td>6 (batch)</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Sample Preparation for Metal Analysis
Metal Determination

Bulk Sample Preparation
  Sieving/Grinding
  Dividing bulk sample to obtain proper size sample

Dissolution or extraction of analyte

Concentration if too dilute for analytical system

Measurement by selected analytical procedure
  FAAS, GFAAS, ICP, ICP/MS, IC, XRF
Sample Preparation

- Dissolution of the entire sample producing a clear solution
  - Wet acid digestion: dissolve by heating in a strong oxidizing acid solution
  - Dry ashing: moist samples, destroy organic matters
  - Extraction: water samples, chelating agent, complex of metals

- Prevention of sample contamination
Wet Digestion Methods

- Total matrix dissolution
- All the metals are in the same form
- Destroy information about the species originally present
  - Acid digestion – Wet ashing
  - Microwave digestion
## Reagents used for digestion

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Sample type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Soluble salts</td>
</tr>
<tr>
<td>Dilute acids</td>
<td>Dry ashed sample residues, easily oxidized metals and alloys, salts</td>
</tr>
<tr>
<td>Concentrated acid (e.g., HNO₃)</td>
<td>Less readily oxidized metals and alloys, steels, metal oxides</td>
</tr>
<tr>
<td>Concentrated acid with added oxidizing agent (H₂O₂)</td>
<td>Metals, alloys, soils, particulates from air, refractory minerals, vegetable matter</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>Silicates and other rock samples</td>
</tr>
</tbody>
</table>
Acid Digestion

5-10% HNO₃ may be added

Solution becomes clear and light colored

Hot plate

Watch glass

5-10% HNO₃
H₂O₂ may be added

Analyte may loss due to the retention of metals in the silica residues
Microwave Digestion

► Closed vessel microwave system
► Polymer container (PTFE)
► Eliminate airborne dust contamination
► Reduce evaporation, less acid solution
► Eliminate volatile metal species
► Reproduce digestion conditions
► Reduce operator attention
Dry Ashing

- For samples contain much organic matter which are being analyzed for nonvolatile metals; nutritional elements in food
- Crucible; silica, porcelain, platinum
- Ignited in a muffle furnace (400-500 °C)
- Loss due to volatilization
- Air borne dust contamination
- Irreversible sorption into the wall of the vessel
- Additives: H₂SO₄, Mg(NO₃)₂, Na₂CO₃, MgO
Extraction

- A soluble form is of concern
- Metal chelates, metal-organic complexes, ion-pairing
- LLE, SPE, SLM
- Chelating agents

- Ammonium pyrrolidine dithiocarbamate
- Cupferron
- 8-hydroxyquinoline
- Dithizone (Diphenylthiocarbazone)
Extraction of chelated metal

\[ K_4 = \frac{[MA_n]_{\text{org}}}{[MA_n]_{\text{aq}}} \]

\[ K_1 = \frac{[HA]_{\text{org}}}{[HA]_{\text{aq}}} \]

\[ K_2 = \frac{[H^+]_{\text{aq}}[A^-]_{\text{aq}}}{[HA]_{\text{aq}}} \]

\[ K_3 = \frac{[MA_n]_{\text{aq}}}{[M^{n+}]_{\text{aq}}[A^-]^n_{\text{aq}}} \]

\[ D = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}} \]
Others

► Precipitation method

► Sample slurries
  ▪ Distribution of fine particles in a liquid

► Hydride generation method
  ▪ As, Se → Na₄BH

► Colorimetric method
  ▪ Oxidation state: color forming reagent

► Metal speciation
  ▪ Identification and determination of individual physical-chemical forms → total concentration in a sample
Metal Speciation

- Range of chemical forms, solid and dissolved phases
- Hydrated ion, inorganic and organic complexes, heterogeneous colloidal dispersions, organometallic
- Sorbed with particles or organic solid
- Bound with minerals
- Present in more than one valence state
Metal Speciation information

- Toxicity: effect on living organism
- Mobility: transport of element to environment
- Bioavailability, bioaccumulation: influence of species on animals and plants, susceptibility