Efficient digestion and separation techniques in trace element analysis of difficult sample materials

Guenter Knapp
Graz University of Technology, Graz, Austria
Content

Sample decomposition
  High pressure — high temperature wet digestion
  Microwave assisted UV-digestion
  Microwave assisted combustion

Separation and preconcentration
  Volatilization of the analyte
  Liquid-liquid extraction

Conclusion
Analytical Steps

- Drying
- Homogenization
- Decomposition
- Separation
- Preconcentration
- Determination

G. Tölg, P. Tschöpel
Analyt. Sci. 3 (1987) 199
Decomposition Methods for Element Analysis – an Overview

Fusion
Wet digestion
  In open vessels
    Hot plate techniques with graphite blocks
    Microwave assisted open vessel digestion
  In closed vessels
    Conductive heating ➔ Teflon bombs, High temperature wet digestion
    Microwave heating ➔ Low-, medium- and high-pressure systems
    Microwave assisted UV-digestion
  In flow systems ➔ in development

Combustion
  In open systems
    Dry ashing
    Low temperature ashing with oxygen plasma
  In closed systems
    Flask combustion with oxygen
    Bomb combustion with oxygen
    Microwave assisted combustion
Advantages of Pressurized Wet Digestion

Advantages
+ High temperatures beyond the boiling point
+ Improved dissolution of inorganic samples
+ Powerful oxidation of organic samples just with pure nitric acid
+ No element losses
+ Low reagent consumption
+ Reduced contamination

Disadvantages
- Limited sample weight
- Complicate vessel construction
- Higher equipment costs
High Temperature Pressurized Wet Digestion

High pressure – high temperature wet digestion in quartz vessels up to 320°C

Actual Version of the High Pressure Asher®
Principle of the High Pressure Asher® Pressure Compensation

Reaction Vessel: Sample + Reagents
PTFE-Seal
Lid

N₂ – Pressure (130 bar)

www.anton-paar.com
Scheme of the High Pressure Asher®

- Safety Disk
- Bayonet Lid
- Autoclave
- Gas Connector
- Reaction Vessel
- Heating Block
- Heating Element
- Temp. Sensor

130 bar

320 °C

www.anton-paar.com
# High Pressure Asher® HPA-S Reaction Vessels

<table>
<thead>
<tr>
<th>Number &amp; Type of Vessel</th>
<th>max. sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x Quartz 90 mL</td>
<td>1.5 g</td>
</tr>
<tr>
<td>7 x Quartz 50 mL</td>
<td>0.8 g</td>
</tr>
<tr>
<td>21 x Quartz 15 mL</td>
<td>0.2 g</td>
</tr>
<tr>
<td>6 x Glassy Carbon 20 mL</td>
<td>0.2 g</td>
</tr>
</tbody>
</table>
High Pressure Asher® HPA-S

Typical applications of high temperature wet digestion

Maximum Temperature of High Pressure Microwave Systems

~ 280°C

Maximum Temperature of the High Pressure Asher® HPA-S

320°C
High Temperature Wet Digestion $\geq 300^\circ$C

Typical Application – As and Se in Foodstuffs

Interlaboratory Comparison

- Samples: Egg powder, mussel tissue, brazil nut homogenate
- 25 laboratories in Germany and Switzerland
- Microwave, HPA-S and conventional sample preparation
- Determination by HG-AAS, GF-AAS and ICP-MS

Maximum reaction conditions

- HPA-S: $320^\circ$C / 120bar
- Different microwave systems: $200^\circ$C up to $280^\circ$C
- PTFE – bomb (Tölg): up to $200^\circ$C

Ref.: P. Fecher, 1997, Interlaboratory comparison
High Temperature Wet Digestion $\geq 300^\circ\text{C}$

Typical Application – As and Se in Foodstuffs

Se, As [mg/kg] measured by ICP-MS and Hydride-AAS

- Egg
- Mussel
- Nut
- As in Mussel

HPA, MW, Toelg
High Temperature Wet Digestion \( \geq 300^\circ\text{C} \)

Typical Application — ICP-MS

Influence of residual carbon on ICP-MS — dilution effect

**Sample:** Caviar (high fat)

**Microwave medium pressure:** about 200°C

**HPA-S method:** \( T = 300^\circ\text{C}, \ t = 120 \text{ min.} \)

<table>
<thead>
<tr>
<th>Element</th>
<th>Microwave</th>
<th>HPA-S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dil. 200x</td>
<td>40x</td>
</tr>
<tr>
<td>Cu</td>
<td>2.1</td>
<td>---</td>
</tr>
<tr>
<td>As</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Se</td>
<td>2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Cd</td>
<td>0.001</td>
<td>0.006</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Ref.: D. Imhof, Kantongales Labor Zürich
High Temperature Wet Digestion $\geq 300^\circ$C
Typical Application – Voltammetry

Influence of residual carbon on voltammetry

Sample: liver, decomposed with HNO$_3$ at 180$^\circ$C
Ref.: M. Würfels, 1987
High Temperature Wet Digestion \(\geq 300^\circ C\)

Typical Application – Voltammetry

Influence of residual carbon on voltammetry

Sample: liver, decomposed with HNO\(_3\) at 300\(^{\circ}\)C
Ref.: M. Würfels, 1987
High Temperature Wet Digestion ≥ 300°C
Typical Application – Voltammetry

Influence of residual carbon on voltammetry and ICP-MS

Determination of zinc, copper, lead and cadmium in some medicinally important leaves by differential pulse anodic stripping analysis.
Jyothi, Nimmagadda Venkata Vijaya, .... ;

Trace analysis of platinum in biological samples: a comparison between sector field ICP-MS and adsorptive cathodic stripping voltammetry following different digestion procedures.
Zimmermann, S., ..... ;
High Temperature Wet Digestion $\geq 300^\circ$C
Typical Application – PGE’s

High pressure asher digestion and an isotope dilution-ICP-MS method for the determination of platinum-group element concentrations in chromitite reference materials CHR-Bkg, GAN Pt-1 and HHH.
Paliulionyte, Vaida, …… ;
Geostandards and Geoanalytical Research (2006), 30(2), 87-96.

Platinum-group element and rhenium concentrations in low abundance reference materials.
Meisel, Thomas, ……… ;
Geostandards and Geoanalytical Research (2004), 28(2), 233-249.

Reference materials for geochemical PGE analysis: new analytical data for Ru, Rh, Pd, Os, Ir, Pt and Re by isotope dilution ICP-MS in 11 geological reference materials.
Meisel, Thomas, ……… ;
Chemical Geology (2004), 208(1-4), 319-338.

Concentration and Distribution of Platinum Group Elements (Pt, Pd, Rh) in Airborne Particulate Matter in Frankfurt am Main, Germany.
Zereini, Fathi, …… ;
Environmental Science and Technology (2004), 38(6), 1686-1692.
High Temperature Wet Digestion $\geq 300^\circ$C

Typical Application – PGE’s and Cr

A simple procedure for the determination of platinum group elements and rhenium (Ru, Rh, Pd, Re, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-line matrix separation in geological and environmental materials.
Meisel, Thomas, .... ;

Precise determination of the platinum-group elements and Os isotopic ratios in low-level rock samples.
Brugmann, Gerhard, ..... ;
Yanshi Xuebao (2001), 17(2), 325-331.

Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples.
Muller, M., ..... ;

Improved chromium determination in various food matrices using dynamic reaction cell ICP-MS.
Hammer, Daniel, ..... ;
Atomic Spectroscopy (2005), 26(6), 203-208.
High Temperature Wet Digestion $\geq 300^\circ$C

Typical Application – Tough Polymers

An evaluation of analytical techniques for determination of lead, cadmium, chromium, and mercury in food-packaging materials.
Perring, L., ...... ;

Producing SI-traceable reference values for Cd, Cr and Pb amount contents in polyethylene samples from the polymer elemental reference material (PERM) project using isotope dilution mass spectrometry.
Vogl, J. ...... ;

Development of an ICP-IDMS method for accurate routine analysis of toxic heavy metals in polyolefins and comparison with results by TI-IDMS.
Diemer, Jurgen, ...... ;
Microwave Assisted Sample Decomposition with Pressurized Oxygen

Requires a microwave system with

- Quartz vessels for high pressure digestion
- Simultaneous pressure measurement in all vessels
- Vessel construction with a valve for loading with gas and pressure release after digestion
- High sophisticated safety facilities

► all this features are fulfilled by the Multiwave 3000® developed in cooperation with Anton Paar (www.anton-paar.com)
MULTI WAVE 3000®

Anton Paar, Graz, Austria; www.anton-paar.com
MULTI WAVE 3000®
Rotor for Simultaneous Pressure Measurement and Vessels with Connection Valves for Oxygen Loading

Anton Paar, Graz, Austria; www.anton-paar.com/ap/
Special Sample Decomposition Techniques by means of the Multiwave 3000 System

- Microwave assisted UV-digestion for ultratrace analysis
- Microwave assisted sample combustion for volatile analytes and tough sample materials
Conventional UV-Digestion at Low Temperatures <100°C

Electrically driven UV source symmetrically surrounded by open quartz vessels;

Advantage:
- Low concentration of HNO₃ and H₂O₂
- Low blank levels

Disadvantage:
- Long digestion time
- Only for samples with low DOC


G. Schwedt, J. Petri; *Labor Praxis* (1992) 1223
Microwave-Assisted UV-Digestion at High Temperatures >250°C

Microwaves as energy source
- for simultaneous heating of the reaction mixture
- for generation of UV radiation

Dieter Florian, Günter Knapp; Anal. Chem. 2001, 73, 1515-1520

G. Knapp, US Pat. 6,210,538 B1; Apr. 2001
Microwave-Assisted UV-Digestion with H2O2 and Ozone

- UV source directly immersed in digestion solution in closed vessel.
- Lamp operation initiated and maintained by the oscillating microwave field.
- Immersed UV lamp continuously emits UV irradiation.
Microwave-Boosted UV Lamp

Filled with 0.5mg Cd
5 mbar Ar

Low pressure Cd discharge lamp

Schematic of a MWL.
Microwave-Assisted UV-Digestion
Microwave Assisted UV Digestion Procedure

- **Equipment for high pressure microwave digestion**
  - Multiwave 3000 (Anton Paar Comp. / Perkin Elmer)
  - 80 mL quartz vessel

- **MWL**
  - Low pressure Cd-discharge lamp (Anton Paar Comp.)

- **Sample materials**
  - Phenylalanine, glycine, wheat flour, bovine liver

- **Procedure**
  - 50 – 100 mg sample + 7 mL H2O + 1 mL H2O2 + 0.05 mL HNO3
  - vessel pressurized with 20 bar oxygen
  - digestion 30 Min. at 80 bar (about 250°C)
# Microwave Assisted UV Digestion

## Results

<table>
<thead>
<tr>
<th>Sample material</th>
<th>Sample weight [mg]</th>
<th>Residual carbon [%]</th>
<th>with lamp</th>
<th>without lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylalanine</td>
<td>50</td>
<td>1,9</td>
<td>12,3</td>
<td></td>
</tr>
<tr>
<td>Glycine</td>
<td>50</td>
<td>0,9</td>
<td>19,5</td>
<td></td>
</tr>
<tr>
<td>Bovine liver</td>
<td>100</td>
<td>8,2</td>
<td>24,6</td>
<td></td>
</tr>
<tr>
<td>Wheat flour</td>
<td>100</td>
<td>0,9</td>
<td>5,3</td>
<td></td>
</tr>
</tbody>
</table>
Microwave Assisted UV Digestion

Advantages

- Acceleration of the degradation process owing to high reaction temperature (250 – 280 °C)
- Best efficiency of generated UV-radiation (immersion system)
- Enhancement of reactivity due to simultaneous microwave and UV-irradiation
- Oxidation with H$_2$O$_2$ and Ozone
- Suitable for samples with high DOC (5000-7500 mg/l carbon)
- Digestion technique for ultra trace analysis
Special Sample Decomposition Techniques by means of the Multiwave 3000 System

- Microwave assisted UV-digestion for ultratrace analysis
- Microwave assisted sample combustion for volatile analytes and tough sample materials
Combustion Systems

Combustion of organic samples in closed systems is state of the art

- for the determination of volatile nonmetals
- for decomposition of tough organic materials like cole, coke, some polymers, etc.
Schöniger Flask Combustion
Oxygen Bomb Combustion

a) Steel bomb
b) Lid with valve
c) Electrodes
d) Ignition wire
e) Sample holder

E.g. 500 mL $O_2$-Bomb
Parr Instrument, USA
Multiwave 3000

Microwave assisted oxygen combustion

Microwave Assisted Oxygen Combustion

- Multiwave 3000
- 80 mL quartz vessels XQ80
- 0.3 - 0.4 g organic organic sample pressed to a tablet
- 10 ml absorption solution (mobile phase of ion chromatography)
- Put sample on impregnated filter paper (1 drop of 50% NH₄NO₃)
- Load with 20 bar oxygen
Microwave Assisted Oxygen Combustion

- Ignite impregnated filter by means of microwave power
- Program:
  - 1400W / 1 min
  - Cool 15 min at level 2
- Up to 8 combustions simultaneously
- Absorption time 1 hour
- Analysis of absorbed ions
  - IC for Cl^-, Br^-, I^- and S (sulfate)
  - Ion selective electrode for F^-
Microwave Assisted Oxygen Combustion
Results

<table>
<thead>
<tr>
<th></th>
<th>Cl (µg/g)</th>
<th>S (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Certified</td>
<td>measured</td>
</tr>
<tr>
<td>BCR 60</td>
<td>10</td>
<td>9.3 ± 0.8</td>
</tr>
<tr>
<td>Aquatic plant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCR 61</td>
<td>2.3</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>Aquatic plant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCR 63</td>
<td>9.94 ± 0.3</td>
<td>10.1 ± 1.0</td>
</tr>
<tr>
<td>Milk powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCR 100</td>
<td>1.49 ± 0.06</td>
<td>1.55 ± 0.1</td>
</tr>
<tr>
<td>Peach leaves</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCR 186</td>
<td>9.4</td>
<td>9.5 ± 0.5</td>
</tr>
<tr>
<td>Pig kidney</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MAC — Results

<table>
<thead>
<tr>
<th>BCR 151 Milk powder</th>
<th>Element</th>
<th>Certified (µg/g)</th>
<th>Measured (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C~50%)</td>
<td>Ca</td>
<td>-</td>
<td>12890±191</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>5.23±0.08</td>
<td>5.26±0.21</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>50.1±1.3</td>
<td>48±0.3</td>
</tr>
<tr>
<td></td>
<td>Hg (ng/g)</td>
<td>101±10</td>
<td>104±7</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>-</td>
<td>1272±22</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>(0.223)</td>
<td>0.264±0.01</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>-</td>
<td>5467±195</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>2.002±0.026</td>
<td>1.97±0.22</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>(50)</td>
<td>48.5±4</td>
</tr>
<tr>
<td></td>
<td>DOC</td>
<td>-</td>
<td>&lt; 0.2%</td>
</tr>
</tbody>
</table>
# MAC – Results

<table>
<thead>
<tr>
<th>BCR 185 Bovine liver</th>
<th>Element</th>
<th>Certified (µg/g)</th>
<th>Measured (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C~50%)</td>
<td>Ca</td>
<td>(131)</td>
<td>151±5</td>
</tr>
<tr>
<td></td>
<td>Cd (ng/ g)</td>
<td>298±25</td>
<td>325±22</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>189±4</td>
<td>165±2,6</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>214±5</td>
<td>195±2,5</td>
</tr>
<tr>
<td></td>
<td>Hg (ng/ g)</td>
<td>44±3</td>
<td>45±2</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>(634)</td>
<td>622±12</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>9,3±0,3</td>
<td>9,2±0,14</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>11700</td>
<td>12170±223</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>142±3</td>
<td>146±3,5</td>
</tr>
<tr>
<td></td>
<td>DOC</td>
<td>-</td>
<td>&lt; 0,2%</td>
</tr>
</tbody>
</table>
Microwave Assisted Oxygen Combustion Demonstration

- Combustion of 0.3 g Coal
- MULTI WAVE 3000®
- 80 mL Quartz vessel
- Loaded with 20 bar oxygen
Separation and Preconcentration

Volatilization
- hydride generation
- halogen volatilization

Liquid-liquid extraction

Coprecipitation

Sorption
- of ions
- of metal-chelates
- of organic compounds
Separation and Preconcentration

Multimode sample introduction system – MSIS for hydride generation and nebulization
R.L.J. McLaughlin, I.D. Brindle U.S. Patent no. 6.891.605
Separation and Preconcentration – MSI S
Separation and Preconcentration – MSIS

Determination of hydride elements in high alloy steels and nickel alloys

- Plasma power: 1300 W
- Cooling gas: 15.0 L min\(^{-1}\)
- Nebulizer gas: 0.75 L min\(^{-1}\)
- Nebulizer: Mira Mist
- NaBH\(_4\): 30 g L\(^{-1}\)
- Tartaric acid: 400 g L\(^{-1}\)
- L-Cystein: 400 g L\(^{-1}\)
Separation and Preconcentration – MSI S

Determination of hydride elements in high alloy steels and nickel alloys

<table>
<thead>
<tr>
<th>Element, nm</th>
<th>IDLs, mg/kg</th>
<th>MDLs, mg/kg (in Ni)</th>
<th>LOQ, mg/kg (in Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As 189,042</td>
<td>0,1</td>
<td>0,1</td>
<td>0,6</td>
</tr>
<tr>
<td>Bi 190,241</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
</tr>
<tr>
<td>Sb 206,833</td>
<td>0,1</td>
<td>0,6</td>
<td>2,0</td>
</tr>
<tr>
<td>Se 196,090</td>
<td>0,1</td>
<td>0,4</td>
<td>1,2</td>
</tr>
<tr>
<td>Sn 189,991</td>
<td>0,1</td>
<td>5,5</td>
<td>19,3</td>
</tr>
<tr>
<td>Te 214,281</td>
<td>0,1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Separation and Preconcentration

Volatilization of halogens

Determination of Cl, Br and I with ICP-OES
## Oxidation of Chloride, Bromide and Iodide to the Elements

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$E^\circ$ (V)</th>
<th>Oxidation to the element</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{S}_2\text{O}_8$</td>
<td>+2.12</td>
<td>$\text{S}_2\text{O}_8^{2-} + 2 \text{X}^- + 2 \text{H}^+ \Rightarrow \text{X}_2 + 2 \text{HSO}_4^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>+1.77</td>
<td>$\text{H}_2\text{O}_2 + 2 \text{X}^- + 2 \text{H}^+ \Rightarrow \text{X}_2 + 2 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{PbO}_2$</td>
<td>+1.69</td>
<td>$\text{PbO}_2 + \text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{X}^- \Rightarrow \text{X}_2 + \text{PbSO}_4 + 2 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{KMnO}_4$</td>
<td>+1.51</td>
<td>$2 \text{MnO}_4^- + 10 \text{X}^- + 16 \text{H}^+ \Rightarrow 5 \text{X}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{KBrO}_3$</td>
<td>+1.42</td>
<td>$2 \text{BrO}_3^- + 10 \text{X}^- + 12 \text{H}^+ \Rightarrow 5 \text{X}_2 + \text{Br}_2 + 6 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{K}_2\text{Cr}_2\text{O}_7$</td>
<td>+1.23</td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 6 \text{X}^- + 14 \text{H}^+ \Rightarrow 3 \text{X}_2 + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{NaNO}_2$</td>
<td>+0.96</td>
<td>$2 \text{NO}_2^- + 2 \text{I}^- + 4\text{H}^+ \Rightarrow \text{I}_2 + 2 \text{NO} + 2 \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

| +0.54       | $\text{I}_2 + 2 \text{e}^- \Rightarrow 2 \text{I}^-$          |
| +1.07       | $\text{Br}_2 + 2 \text{e}^- \Rightarrow 2 \text{Br}^-$        |
| +1.36       | $\text{Cl}_2 + 2 \text{e}^- \Rightarrow 2 \text{Cl}^-$        |
| (+2.87)     | $\text{F}_2 + 2 \text{e}^- \Rightarrow 2 \text{F}^-$          |

**References:**
2. D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press Inc., Boca Raton, Florida (1993);
Reduction of Iodate (IO$_3^-$) to the Element with H$_2$O$_2$

\[
\begin{align*}
\text{H}_2\text{O}_2 & \Rightarrow 2 \text{H}^+ + \text{O}_2 + 2 \text{e}^- \quad \text{E}^\circ = +0,68 \text{ V} \\
2 \text{IO}_3^- + 10 \text{e}^- + 12 \text{H}^+ & \Rightarrow \text{I}_2 + 6 \text{H}_2\text{O} \quad \text{E}^\circ = +1,19 \text{ V}
\end{align*}
\]

Reference:
Separation of the Volatile Halogens by means of a Gas-Liquid-Separator

- **Advantage**
  - 10 to 50 times higher transport efficiency than a pneumatic nebulizer
  - no matrix constituents interfere with the measurement

- **Disadvantage**
  - memory effects
  - extended rinse time
Optimum Gas-Liquid-Separator

Optimized gas-liquid-separator for our purposes:

- Optimized size and diameters to prevent foaming
- Optimized frit \(\rightarrow\) pore width, hydrophobic surface; the glass frit is silanated to prevent penetration of the reaction solution, which leads to memory effects and increased rinse time.
- Attached reaction coil for oxidation or reduction
Optimum Gas-Liquid-Separator

Influence of the pore size of the frit:

<table>
<thead>
<tr>
<th>Porosity</th>
<th>Pore width</th>
<th>Max. gas flow without interfering aerosol formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2</td>
<td>40-90 µm</td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>15-40 µm</td>
<td>0.9 L/min.</td>
</tr>
<tr>
<td>G4</td>
<td>9-15 µm</td>
<td>0.5 L/min.</td>
</tr>
</tbody>
</table>

- the lower the pore width the higher the transport efficiency of the halogens;

- the lower the pore width the higher the formation of aerosols with transportation of matrix constituents into the plasma;
An Optimum Gas-Liquid-Separator

Gas-liquid-separator connected to a SPECTRO CIROS VISION ICP-emission spectrometer;
Measurement of Cl$^-$ and Br$^-$ with ICP-OES Spectro Ciros Vision

*Chloride and bromide are measured with the same instrument parameters and the same oxidation reaction*

<table>
<thead>
<tr>
<th>Instrument parameters:</th>
<th>Wavelength: Cl 134.724, Br 154.065</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plasma power 1450W</td>
</tr>
<tr>
<td></td>
<td>Pump speed 3</td>
</tr>
<tr>
<td></td>
<td>Cooling gas 12L/min</td>
</tr>
<tr>
<td></td>
<td>Plasma gas 0.9L/min</td>
</tr>
<tr>
<td></td>
<td>Nebulizer gas 0.4L/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peristaltic pump:</th>
<th>Sample tube orange/orange (3.3mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reagent tube yellow/green (0.6mL/min)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample solution 6M H$_2$SO$_4$</th>
<th>Reagent 0.1M KMnO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD Cl 0.3μg/L</td>
<td>Br 0.5μg/L</td>
</tr>
<tr>
<td>LOQ Cl 1.0μg/L</td>
<td>Br 2.0μg/L</td>
</tr>
</tbody>
</table>
### Measurement of I$^-$ and IO$_3^-$ with ICP-OES Spectro Ciros Vision

**Iodide and iodate are measured with different reagents.**

<table>
<thead>
<tr>
<th>Instrument parameters:</th>
<th>Wavelength: I 178.276</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plasma power 1450 W</td>
</tr>
<tr>
<td></td>
<td>Pump speed 4</td>
</tr>
<tr>
<td></td>
<td>Cooling gas 12L/min</td>
</tr>
<tr>
<td></td>
<td>Plasma gas 0.9L/min</td>
</tr>
<tr>
<td></td>
<td>Nebulizer gas 0.6L/min</td>
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<tr>
<td></td>
<td>Reagent tube yellow/green (0.6mL/min)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample solution</th>
<th>Iodide</th>
<th>Iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent</td>
<td>0.1M HNO$_3$</td>
<td>2M HNO$_3$</td>
</tr>
<tr>
<td></td>
<td>NaNO$_2$ 0.05M + HNO$_3$ 0.5M</td>
<td>H$_2$O$_2$ 30%</td>
</tr>
</tbody>
</table>

| LOD  | I 0.2 µg/L | I 0.5 µg/L |
| LOQ  | I 0.7 µg/L | I 2.0 µg/L |
Separation and Preconcentration

Automated liquid-liquid extraction of heavy metals
Introduction

- Determination of trace heavy metal impurities (< 10 mg/kg)

- Matrix: High alloy steel and Ni super alloy
- Matrix composition varies: eg. <1 - >50% Ni; <1 - >20% Cr
Introduction: Analyte Extraction

- $\text{Ag, Bi, Cd, Pb, Sb, Se, Sn, Zn}$ form iodide complexes $\rightarrow$ extraction with organic solvents

- Reagent: KI in large excess

- Organic extractions: Determination of the analyte concentration via ICP-OES* or F-AAS**

* Ciros Vision EOP, Spectro
** ContrAA, Continuum source AAS, www.analytic-jena.com
Automated liquid liquid extraction

- Flow extraction: Constant flow of samples and reagents
- Batch extraction: “Automated separating funnel”
Flow Extraction Systems: Principle
Flow Extraction Systems: Phase separator
Flow Extraction Systems: Extraction Coil

Disadvantage:
• Low contact between aqueous /organic phase
• Low extraction efficiency (< 20 %)
Flow Extraction Systems: Stirrer

- Magnetically stirred
- Good contact between aqueous / organic phase
Flow Extraction Systems

Without stirring

With stirring
Flow Extraction Systems: Extraction efficiency

<table>
<thead>
<tr>
<th>Element</th>
<th>Extraction efficiency*, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>97 ± 3</td>
</tr>
<tr>
<td>As</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>Bi</td>
<td>101 ± 7</td>
</tr>
<tr>
<td>Cd</td>
<td>55 ± 1</td>
</tr>
<tr>
<td>Pb</td>
<td>70 ± 3</td>
</tr>
<tr>
<td>Sb</td>
<td>39 ± 1</td>
</tr>
<tr>
<td>Se</td>
<td>60 ± 7</td>
</tr>
<tr>
<td>Sn</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>Tl</td>
<td>22 ± 4</td>
</tr>
<tr>
<td>Zn</td>
<td>52 ± 1</td>
</tr>
</tbody>
</table>

*For aqueous solutions without steel matrix
Batch Extractor: Principle
Batch Extractor: Automation

Characteristics:
- magnetically stirred
- no carry over between the samples
Batch Extractor: Automation
Batch Extractor: Automation

1) Sample
2) + KI
3) Mix
4) + Organic solvent
5) Extraction
6) Phase separation
## Batch Extractor: Extraction efficiency

<table>
<thead>
<tr>
<th>Element</th>
<th>Extraction efficiency*, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>95 ± 2</td>
</tr>
<tr>
<td>As</td>
<td>17 ± 4</td>
</tr>
<tr>
<td>Bi</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>Cd</td>
<td>73 ± 2</td>
</tr>
<tr>
<td>Pb</td>
<td>91 ± 2</td>
</tr>
<tr>
<td>Sb</td>
<td>55 ± 6</td>
</tr>
<tr>
<td>Se</td>
<td>73 ± 4</td>
</tr>
<tr>
<td>Sn</td>
<td>87 ± 1</td>
</tr>
<tr>
<td>Tl</td>
<td>53 ± 6</td>
</tr>
<tr>
<td>Zn</td>
<td>81 ± 2</td>
</tr>
</tbody>
</table>
**Comparison Flow Extractor — Batch Extractor**

<table>
<thead>
<tr>
<th>Flow Extractor</th>
<th>Batch Extractor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>+</strong></td>
<td><strong>-</strong></td>
</tr>
<tr>
<td>• Simple</td>
<td>• Expensive</td>
</tr>
<tr>
<td>• Low cost</td>
<td>• Integration into ICP-OES requires additional software</td>
</tr>
<tr>
<td>• Easy to integrate into ICP-OES: between autosampler and spray chamber</td>
<td></td>
</tr>
<tr>
<td>• Memory effects</td>
<td></td>
</tr>
<tr>
<td>• Slow</td>
<td>• Fast; limited only by data acquisition</td>
</tr>
<tr>
<td></td>
<td>• No memory effect</td>
</tr>
</tbody>
</table>
Comparison FAAS — ICP-OES

**Advantage FAAS**

- Higher nebulization efficiency of organic solvents improves DL’s
- No solvent induced spectral interferences
- No structured background from organic solvent
- Low operation costs
- Fast sequential analysis of the extracted analytes is an alternative to ICP-OES \( \rightarrow \) **HR-CS-AAS**
Conclusion

- High temperature wet digestion at $\geq 300^\circ$C can solve some analytical problems, which cannot be solved with microwave assisted wet digestion

- Microwave assisted UV-digestion and microwave assisted combustion are powerful new methods in trace element analysis

- Separation and preconcentration techniques are still necessary in trace element analysis despite of powerful measurement techniques
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27. June – 01. July 2010
Seggau-Castle / Styria
AUSTRIA

www.trisp07.at