Basic Digestion Principles
From Samples to Solutions
Direct Analytical Method

Mech. Sample Preparation (Grinding, Sieving, Weighing, Pressing, Polishing, ...)

Solid Sample Autosampler

Solid Sample

Multielement Analysis Arc/sparc OES, XRF, INAA

Problems:

- Homogeneity
- Representativity
- Calibration
- Reference Materials
- Matrix Interferences
**Combined Analytical Method**

**Problems:**
- Time consumption
- Handling steps
- Error sources

"Weakest link"
Decomposition ...

... is the transfer of a solid or liquid sample into a soluble or dissolved state for subsequent analytical characterization of its major, minor, and trace constituents.
Why Decomposition?

- Conversion from solids into liquids
- Destruction of matrix
- Separation of interfering substances
- Isoformation of sample and standard
- Homogenization
- Preconcentration of analytes

Is there a direct analytical technique?
Decomposition: Pros and Cons

Pros:

• Leads to a representative sample
• Reduces problems in the measurement step
• Easy to standardize

Cons:

• Labor intensive cost factor
• Bottle neck in the analytical process
• Risk of contamination or losses of analyte
Decomposition must be...

- Analytically accurate
- Economically efficient
- Safe and easy to perform
Analytical Accuracy

- No contamination
- No loss of elements
- Complete decomposition
- Small number of working steps
- Reliable equipment

Reproducible analytical results
Economic Efficiency

- Low consumption of chemicals
- Ease of handling
- Low investment costs
- Low operating costs
- Automation

Costs of faulty analytical results
Assumption: microwave digestion with a three fold dilution step and ICP-OES multielement analysis with three replicates.
Safety

- Low amounts of hazardous chemicals
- Simple handling
- Spontaneous reactions
- Protection from operator error
- Instrument safety (design & manufacture)
Sample Digestion ...

- influences analysis time and quality
- is an important economic factor in the analytical lab
- has to be optimized with respect to the measuring technique
- is trending towards automated, closed systems which require minimal amounts of samples and reagents
Trends in Sample Preparation

- Improve quality
- Improve productivity
- Reduce systematic handling errors
- High degree of automation at minimum costs
- Push for one-pot or on-line techniques
- Reduce head counts in the laboratory
Survey of Decomposition Methods
Digestion Method Development

- Identify sample and matrix
- Identify analyte(s)
- Determine analysis instruments
- Determine extent of digestion needed
- Establish trial digestion
- Modify to improve method
- Test accuracy and precision
As much as necessary, as little as possible!

- **Total mineralization**
  - Determination of total element contents
  - Max. requirements (temperature, pressure)
  - Max. accuracy

- **Leaching**
  - Determination of soluble contents
  - Standardized procedures (EPA, DIN, EN, ...)
  - Reproducibility

Matrix, analyte, standard procedure, analytical method, laboratory equipment?
Factors of Influence

- **Matrix**
  - Sample matrix type
  - Reactivity
  - Homogeneity
  - Sample size

- **Analyte**
  - Element(s) of interest
  - Concentration
  - Molecular interactions
  - Analytes final form and instrument compatibility

- **Reaction properties**
  - Reagent interactions at specific temperatures
  - Solubility and volatility of analyte & matrix components

- **Instrumentation**
  - Instrument(s) used
  - Sample throughput
  - Detection limit
  - Sample introduction system
  - Clean chemistry facilities
Decomposition Methods

Wet Digestion
- Open Vessel
  - Conv. Heating
  - Microwave
  - UV-Digestion
- Closed Vessel
  - Conv. Heating
  - Microwave
- Flow System
  - Conv. Heating
  - Microwave

Combustion
- Muffle Furnace
- Wickbold Comb.
- Plasma Ashing
- Schoeniger Comb.
- Oxygen Bomb
- Dynamic System

Fusion
- Basic
- Oxidic
**Wet Digestion**

- **Open systems**
  - Hot plate / block techniques
  - Microwave heating
  - UV digestion

- **Closed systems ("bombs")**
  - Conventional heating
  - Microwave heating

- **Flow systems**
  - Conventional heating
  - Microwave heating
Open Wet Digestion

- Simple equipment
- High number of samples
- Large sample weight

- High reagent consumption
- Reagent blank
- Contamination (dust)
- Evaporation of analyte
- Supervision required
- Limited Temperature
- Long decomposition time
Decomposition Reagents

- $\text{HNO}_3$  Nitric Acid
- $\text{H}_2\text{SO}_4$  Sulfuric Acid
- $\text{H}_2\text{O}_2$  Hydrogen Peroxide
- $\text{HCl}$  Hydrochloric Acid
- HF  Hydrofluoric Acid
- $\text{H}_3\text{PO}_4$  Phosphoric Acid
- $\text{H}_3\text{BO}_3$  Boric Acid
## Dissolution of Organic Matter

<table>
<thead>
<tr>
<th></th>
<th>HNO₃</th>
<th>HCl</th>
<th>H₂SO₄</th>
<th>HClO₄</th>
<th>H₂O₂</th>
<th>Remark</th>
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<td>2</td>
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<td>✔</td>
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<td>✔</td>
<td></td>
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<td>✔</td>
<td>✔</td>
<td>Increase oxidation potential</td>
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<tr>
<td>5</td>
<td></td>
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<td>✔</td>
<td></td>
<td>✔</td>
<td>Charring &amp; oxidation</td>
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<tr>
<td>6</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
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<td>Requires temp. control</td>
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This table is only a guide, it is not exhaustive!

1 ... 4: Typ. closed vessel methods  
5, 6: Typ. open vessel methods
## Dissolution of Inorganic Matter

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<th>HNO₃</th>
<th>HCl</th>
<th>HF</th>
<th>H₃PO₄</th>
<th>H₂SO₄</th>
<th>HClO₄</th>
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<td>✓</td>
<td>✓</td>
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</table>

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Open vs. Closed Vessels

The graph shows the temperature change over time for both open and closed vessels.

- **Open Vessels**: The temperature increases rapidly initially and then levels off.
- **Closed Vessels**: The temperature increases more gradually and continues to rise over a longer period.

The graph indicates that closed vessels maintain a higher temperature for a longer duration compared to open vessels.
TOC in Open & Closed Vessels

- **Sewage sludge**
- **Soil**

**Reaction Temperature °C**
- 100
- 120
- 140
- 160
- 180
- 200
- 220

**Total organic carbon [%]**
- 60
- 50
- 40
- 30
- 20
- 10
- 0

**open vessels**

**pressure digestion**
Closed Vessel Wet Digestion

- High temperature
- Short reaction time
- No volatilization
- Less reagents
- Less contamination

- Limited sample weight
Preferred Vessel Materials

Quartz glass
- High temperature stability
- Pure and inert
- No diffusion (preferred for Hg and hydride-forming elements)
- Chemical limitations (HF)

PTFE-TFM
- Universal resistance
- Sintered $\rightarrow$ Porosity
- Temperature $< 250^\circ$C

Glassy carbon
- High temperature
- HF-applications
- Prone to oxidation
Microwave Assisted Chemistry

- Basic microwave theory
- Reaction control
- Safety considerations
Why Microwave Digestion?

- Sample Preparation is simplified
- Contamination is minimized
- Retention of volatiles is assured
- Complete digestion usually possible
- Reproducible results
- Sample preparation time is reduced
Conventional vs. Microwave

- Conduction
- Convection

Conductive Heating

- Dipole rotation
- Ion conduction

Microwave Heating
MW-Assisted Sample Preparation

- Wet chemical decomposition
  - Closed vessel systems
  - Open vessel decomposition & Kjeldahl systems
  - Flow systems
- Sample drying
- Evaporation / concentration of solutions
- Organic solvent extraction
- MW muffle furnace (dry ashing)
Interaction with Microwaves

**Conductor**
- Reflective
- e.g. metals, do not heat

**Insulator**
- Transparent
- e.g. plastics, do not heat

**Dielectric**
- Absorptive
- e.g. polar liquids, heat
Microwave Principles

Same Principle as a Pressure Cooker

No MW absorption

Little MW absorption

Strong MW absorption

Cool

70°C Gas

Vapor

Liquid 180°C

Hot
Closed Microwave Systems

**Advantages**
- High temperatures
- Simple chemistry
- Fast method
- Complete mineralization
- Minimum reagents
- No loss of analyte
- Minimum contamination

**Disadvantages**
- Limited sample weight
- Pressure peaks
- Higher equipment costs
- More handling steps
- Two-step procedures are time-consuming