# TOPwave®

## Digestion theory

Analytik Jena Sales Tools

# Basics of sample decomposition

- Target
- Decomposition methods
- Liquid digestions
- Digestion in practice
- Summary

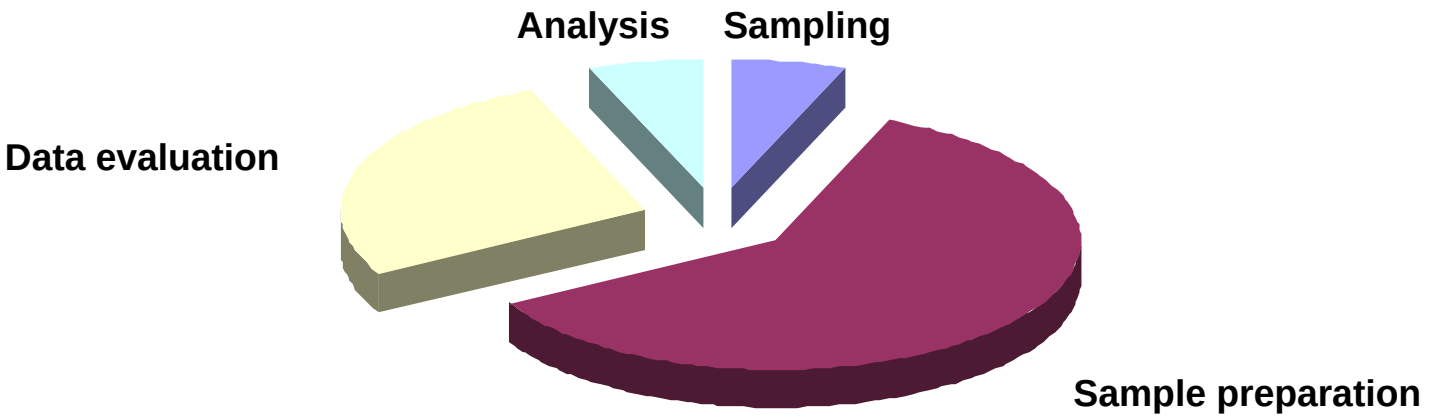
# Target

- Quantitative determination of main and trace components
- Usually spectroscopic analysis

- Total decomposition / extraction
- Destruction of matrix to reduce interferences
- Avoiding analyte loss / contamination

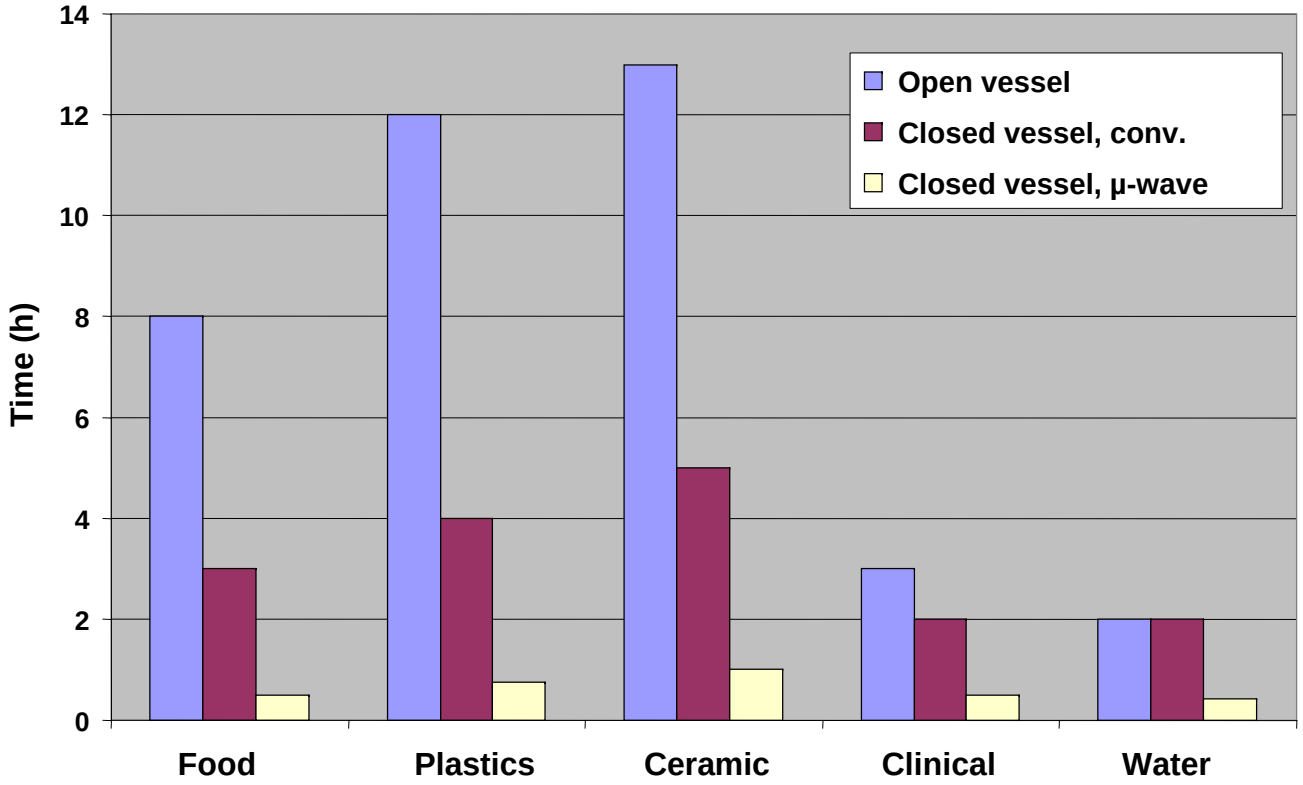
# Target

- Time consumption of analytical procedure



# Target

- Sample throughput



# Deomposition methods

- Melting / flux
  - Acidic (z.B. $KHSO_4$, $LiBO_2$)
  - Alkaline (z.B. NaOH, $Na_2CO_3$)
  - Oxidizing (z.B. $KNO_3$, $Na_2CO_3$, $Na_2O_2$)
  - Reducing (z.B. Na, KCN)
- Advantages:
  - Refractory materials (ceramics, oxides)
  - Simple procedure
- Disadvantages:
  - Excess amount of reagent (blank!)
  - High salt load (matrix effects)
  - Loss of volatile species (high temp.)
  - Risk of contamination (open)

# Deomposition methods

- Wet digestion
  - Acidic (z.B. HCl, $H_2SO_4$, HF)
  - Alkaline (z.B. NaOH, $NH_3$)
  - Oxidizing (z.B. $HNO_3$, $H_2O_2$, $HClO_4$)
  - Reducing (z.B. HI, HBr)
- Advantages
  - Ultra-pure reagents available
  - No additional matrix effects
- Disadvantages
  - Boiling point of acid mixture limits temp.-range (refractories!)
  - Dangerous / toxic reagents (HF, $HClO_4$)

# Deomposition methods

- Decomposition with gases
  - Oxidizing (z.B. $O_2$, $Cl_2$)
  - Reducing (z.B. $H_2$)
- Advantages
  - Fast reaction
- Disadvantages
  - Complex apparatus
  - Practice: organic samples only
  - Difficult dosage of gas (blank!)
  - Difficult quantitative analysis

# Deomposition methods

- Summary
  - Wet digestion is method of choice
    - Flexible selection and dosage of reagents
    - Low risk of contamiation
    - Easy handling
    - Conditions can be controlled

- Different methods
  - Open vessel with reflux (e.g. aqua regia extraction)
  - Closed high temperature vessel
    - Heating plate / -block (conventional heating)
      - Higher pressure and temperature (>300°C, >100bar)
    - Microwave heating
      - Limited to certain vessel materials, limits p / T range

# Wet digestions

- Chemical decomposition of sample matrix
- Temperature accelerates reaction

  Rule of thumb: 10°C temp. Increase = double reaction rate
- Open digestion: max. temperature limited by boiling point
- Closed vessel: pressure increases boiling point
- Pressure has no influence on reaction
- Microwaves have no influence on reaction

# Wet digestions

- Sample preparation

  1. Grinding and homogenizing sample
  2. Weighing of one or more aliquots
  3. Addition of reagents
  4. Energy input

# Wet digestions - reagents

- Nitric acid
  - Oxidizing acid: $(CH_2)_n + 2\ HNO_3 \rightarrow CO_2 + 2\ NO + 2\ H_2O$
  - Often mixed with $H_2O_2$, HCl, HF, ($H_2SO_4$)
  - Boiling point: 122°C ($HNO_3$ 65%)
  - Vapor pressure: ca. 25bar at 220°C
  - Forms soluble nitrates with most elements
    (Exceptions: Au, Pt, Al, B, Cr, Ti, Zr)

- Nitric acid + hydrogen peroxide
  - Increases oxidizing potential: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$
  - Re-oxidation of NO to $NO_3^-$ (reduces nitrous oxides)
  - Typical mixture: $HNO_3 : H_2O_2 = 4 : 1$

# Wet digestions - example

- Digestion of milk powder

Sample: 300mg milk powder

Reagent: 5mL $HNO_3$ 65% + 2mL $H_2O_2$ 30%

Temperature program:

| Step | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Temp. [°C] | 145 | 170 | 190 | 100 |
| Ramp [min] | 2 | 5 | 2 | 1 |
| Hold [min] | 5 | 10 | 15 | 10 |

Result: clear solution

# Wet digestions - reagents

- Hydrochloric acid
  - Not oxidizing
  - Boiling point: 84°C (HCl 32%)
  - Vapor pressure: ca. 25bar at 205°C
  - Forms soluble chlorides with many elements
    (Exceptions: AgCl, HgCl, TiCl, $PbCl_2$)
  - Dissolves salts of weak acids (carbonate, phosphate, borate)
  - Dissolution of Fe-alloys and -oxides
  - Complexes many elements (e.g. $[AuCl_4]^-$, $[AgCl_2]^-$ etc.)
  - Some elements form volatile chlorides (open vessel!)
  - Some metal oxides are insoluble in HCl

# Wet digestions - reagents

- Aqua regia
  - HCl : $HNO_3$ = 3 : 1 (v:v, both conc.)
  - Forms NOCl, 2 NOCl → 2 NO + $Cl_2$
  - Vapor pressure: ca. 25bar at 200°C
  - Dissolution of precious metals, geology
  - Must be prepared freshly!

# Wet digestions - example

- Aqua regia extraction of a sediment

Sample: 1g sediment

Reagent: 3mL $HNO_3$ 65% + 9mL HCl 37%

Temperature program:

| Step | 1 | 2 |
|---|---|---|
| Temp. [°C] | 175 | 100 |
| Ramp [min] | 1 | 1 |
| Hold [min] | 10 | 10 |

Result: clear solution with white $SiO_2$-precipitate

# Wet digestions - reagents

- Hydrofluoric acid
  - Not oxidizing
  - Decomposes silicates: $SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$
  - Excess required to avoid volatile fluorides ($BF_3$, $SiF_4$, $GeF_4$, $SeF_4$)
  - Boiling point: 108°C (HF 40%)
  - Vapor pressure: ca. 25bar at 240°C
  - Mostly mixed with other acids
  - Decomposition of minerals, ores, soil
  - Decomposition of refractory ceramics and oxides (Ti, Al, Si...)
  - Complexation: $B(OH)_3 + 4\ HF \rightarrow HBF_4 + 3\ H_2O$
  - F-AAS: High concentrations → Teflon-coated impact bead!

# Wet digestions - example

- Total dissolution of glass and quartz

Sample: 500mg glass

Reagent: 4mL $HNO_3$ 65% + 4mL HF 40%

Temperature program:

| Step | 1 | 2 |
|---|---|---|
| Temp. [°C] | 200 | 100 |
| Ramp [min] | 5 | 1 |
| Hold [min] | 15 | 10 |

Result: clear solution

# Wet digestions - reagents

- Sulphuric acid
  - Oxidizing at high temperatures
  - Attracts water from organic compounds (wet ashing)
  - Boiling point: 340°C ($H_2SO_4$ 98%)
  - Vapor pressure: negligible
  - Increases boiling point (=working range) in open digestions
  - Mostly disliked in closed vessel digestions
  - Usually mixed with other acids
  - Digestion of plastics, geology
  - Insoluble sulphates of Ba, Sr, Pb, (Ca)
  - GF AAS: Graphite corrosion
  - CS AAS: $SO_2$- and CS- molecular bands

# Wet digestions - example

- Decomposition of plastics

Sample: 250mg Plastic

Reagent: 1.5mL $HNO_3$ 65% + 1.5mL $H_2SO_4$ 98%

Temperatur program:

| Step | 1 | 2 | 3 |
|---|---|---|---|
| Temp. [°C] | 190 | 220 | 100 |
| Ramp [min] | 5 | 1 | 1 |
| Hold [min] | 20 | 15 | 10 |

Result: clear solution

# Wet digestions - reagents

- Perchloric acid
  - Strongest oxidizer
  - Boiling point: 203°C ($HClO_4$ 72%)
  - Vapor pressure: ca. 25bar at 200°C
  - Explosive decomposition at 240°C !!!
  - Usually mixed with other acids
  - Open digestion: Oxidation of org. residue
  - Closed vessel: unwanted and unnecessary
  - Forms insoluble $KClO_4$
  - Risk of explosion! Exceptional use! Special fume hood required!

# Wet digestions - reagents

- Selection of reagents
  - Organic matrices
    - Oxidizing acids / mixtures (usually $HNO_3$, $H_2O_2$)
    - Pressure generated by $CO_2$
    - Low sample weight, high pressure vessels
  - Inorganic matrices
    - Complecation more important than oxidation ($HNO_3$, HCl, HF)
    - Pure and precious metals: HCl, aqua regia, HCl / HF
    - Refractory oxides: $H_2SO_4$ / HCl, $HNO_3$ / HCl / HF
    - High temperature often required
    - Pressure increase usually only by carbonates (open pre-reaction)

# Wet digestions - theory

- Critical parameters
  - Temperature
    - High temperature accelerates reaction
    - Limited by vapor pressure of reagents + reaction gas
    - P / T specification of vessels
  - Cycle time
    - Short cycle time increases throughput
    - Slow ramp avoids spontaneous reactions
    - Moderate conditions extend life time
  - Chemical properties of reagents
    - Must be selected according to samle / analytes
    - Reactions among reagents

# Wet digestions - theory

- Pressure build-up in a closed vessel

  $p(total) = p(CO_2) + p(acid)$

  $CO_2$-pressure depends on sample amount and C-content

  $p(CO_2) = 6.9 * m(C)\ [g] * T/V\ [K/mL]$

  Example:
  V = 30mL, m(C) = 0.2g, T = 200°C → $p(CO_2)$ = 22bar
  V = 80mL, m(C) = 0.2g, T = 200°C → $p(CO_2)$ = 8bar
  → $CO_2$-partial pressure depends on vessel volume !

# Wet digestions - theory

- Pressure build-up in a closed vessel

  p(acid) depends on vapor pressure of components (incl. $H_2O$!)

  Independent from vessel volume !
  (Assuming that acid concentration remains constant)

  → Acid volume must be adapted to vessel volume.

# Wet digestions - theory

- Example for pressure build-up

  60mL – vessel at 200°C

  500mg C generates 930mL $CO_2$
  → Partial pressure: 26bar

  Vapor pressure $HNO_3$ at 200°C: ca. 10bar

  **→ Total pressure: ca. 36bar**

# Wet digestions - theory

- Digestion time
  - Short time = high throughput
  - More vessels = higher throughput (?)
  - Ramp must be adapted to sample reactivity
  - Excessive p / T shortens life time
  - Fast heating by µ-waves: direct heating of sample
  - Cooling: Air flow inside oven or in fume hood, water bath (external)

# Wet digestions - theory

## Sample throughput (2 sets of vessels)

| Samples per run | Manual work[1] | Run time + pre-cooling[2] | External cooling[3] | Max. samples per day[4] |
|---|---|---|---|---|
| 1 | 4 min. | 45 min. | 15 min. | 11 |
| 4 | 16 min. | 45 min. | 15 min. | 43 |
| 8 | 32 min. | 45 min. | 15 min. | 85 |
| 10 | 40 min. | 45 min. | 15 min. | 107 |
| 12 | 48 min. | 45 min. | 15 min. | 120 |
| 16 | 64 min. | 45 min. | 15 min. | 120 |
| 24 | 96 min. | 45 min. | 15 min. | 120 |
| 40 | 160 min. | 45 min. | 15 min. | 120 |

1 Estimated time per sample: Weighing 1.5 min.; Acid addition: 0.5 min.; Fill-up: 1 min.; Vessel cleaning: 1min.
2 Digestion and cooling inside oven
3 Cooling outside oven
4 Base: 8h labour day

# Wet digestions - Practice

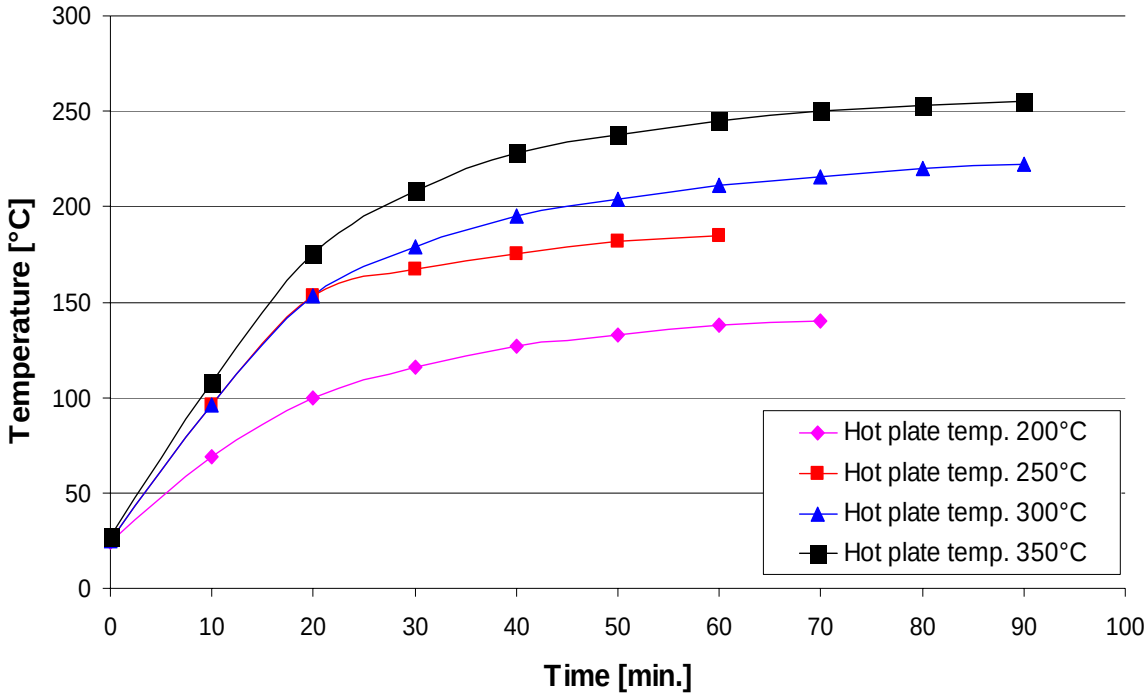
- Open-vessel digestion with reflux
  - Working temperature limited by boiling point of acid mixture $H_2SO_2$ / $H_3PO_4$ to increase b.p.
  - Large amount of sample possible
  - Often insufficient quality of decomposition due to limited temperature range
  - Loss of volatile elements
  - Contamination from dust
  - Often used for geological samples (extraction with aqua regia or buffer)

# Wet digestions - Practice

- Conventionally heated pressure digestion
  - Working range up to ca. 200bar and 300°C
  - Duration: 2h – several days
  - Vessel liner: PTFE-TFM, high stability, low contaminations
  - Different vessel sizes for different sample types / amounts
  - High quality of decomposition
  - No loss of volatile elements
  - Low risk of contamination
  - High safety level, easy handling
  - No process control
  - Slow heating / cooling behaviour

# Wet digestions - Practice

- Heating behaviour - conventional



# Wet digestions - Practice

## Open vessel digestion

- Temperature limited by boiling point
- High acid consumption
- Large sample amount possible
- Quality of decomposition not always sufficient
- Loss of volatile species
- Slow heating
- No process control

## Closed vessel pressure digestion

- Max. temperature: 260-300°C
- Low acid consumption (blank!)
- Small sample amount (<1g)
- High quality of decomposition
- No loss of volatile species
- Fast heating / cooling (µ-wave)
- Pressure and temperature monitoring for reaction control

→ Acceleration of reaction by higher temperature

→ Time saving by fast heating / cooling

→ Process control by p / T based adaptive power control

. Provides safety for reactive samples and reproducible conditions

# Wet digestions - Practice

- Properties of microwave digestions
  - Fast, direct heating of sample
  - Parallel processing of up to 24 samples
  - Advantages of a closed-vessel digestion

- Critical points
  - Homogeneous distribution of µ-waves (oven geometry)
  - Temp.- / pressure resistance of vessels
  - Transparency for µ-waves
  - Measurement and control of process parameters p, T, P
  - Venting of vessels

# Wet digestions - Practice

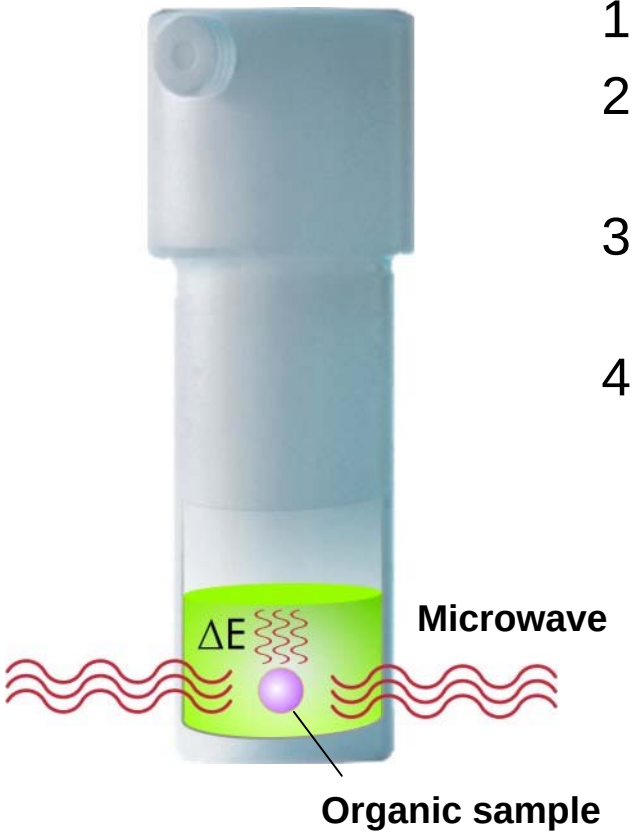
- Pressure vessels made of PTFE-TFM
  - Low contaminations, easy cleaning
  - Transparent for microwave radiation
  - Different pressure- and temperature ranges
  - Highest decomposition quality for most applications
  - Shortest cycle times by fast heating and cooling (10-60 min)
  - Over-pressure protection by rupture disc
  - Opening / closing without any tools
  - Gas collection system and easy venting

# Microwave physics

- Different behaviour of materials
  - Metal reflects µ-waves (oven)
  - Plastics, glass, ceramics are transparent (vessels, pressure jackets)
  - Dipolar and ionic compounds absorb µ-waves (acid / sample / $H_2O$)

- Absorption behaviour
  - Blank digestions absorb less radiation, final temperature is lower
  - Amounts of acid and sample influence temperature
  - Homogeneous distribution of radiatrion necessary (oven, rotor)

# Reaction control in real time




1. Solution is heated by microwaves
2. Activation energy for reaction:
   $CH_2 + 2\ HNO_3 \rightarrow CO_2 + 2\ NO + 2\ H_2O$
3. Exothermic reaction generates additional heat
4. Microwave power is reduced to avoid overheat

# Pressure vessels AJ TOPwave

- Massive PTFE-TFM vessels
  - PH 30 — 30 mL / 80 bar (12-position rotor)
  - PM 60 — 60 mL / 40 bar (12- position rotor)
  - PL 100 — 100 mL / 25 (40) bar (12- position rotor)
  - PM 40 — 40 mL / 40 bar (24- position rotor)
  - CX 100 — 100 mL / 100 bar (8- position rotor)
  - CX 17 — 17 mL / 130 bar (liner for PL 100 / CX 100)
  - QX 20 — 20 mL / 100 bar (liner for PM 60 / PL 100)

  - Multi-vial (MT-) system as insert for CX 100:
    3 x 10mL vials per CX 100

# Temperature measurement

- Temperature is the most important digestion parameter
- Reaction rate / completeness of decomposition
- Internal temperature depends on sample type and amount

→ Temperature monitoring in all vessels
→ Measurement by contactless mid-IR measurement
→ Vessel material is transparent in used IR range

# Summary

- Requirements to a digestion system
  - Reaction temperatures up to >250°C
  - Sample weights up to 1000 mg
  - Temperature monitoring in real-time in all vessels
  - Option: Pressure monitoring in one or more vessels
  - Process control by p / T – adapted power control
  - Recording and storage of all process parameters

## Summary

- Liquid digestion always method of choice
- Closed vessels improve decomposition quality due to higher temperature.
- Adaptive process control allows reproducible conditions and safe operation
- Microwave technology accelerates cycle and allows high sample throughput
- Conventionally heated digestion bombs for most difficult samples

# Summary

- AJ TOPwave decomposition system
  - Up to 24 simultaneous digestions
  - Pressure vessels up to 100 mL / 100 bar
  - Temperature up to 260°C
  - Remote temperature monitoring RTM
  - Remote pressure monitoring RPM
  - Power control with SMART-Algorithm
  - Touchscreen – Controller with USB and Ethernet connectors