Application 1
Plastic recycling

Secondary fuels in the cement industry

Elemental Analysis of Plastic Waste

Challenge

- Not sorted by type, foreign substances (metals, paper, org. Material)
- Fluctuating material flows complicate stable processes
- Faulty workmanship: damage, quality and environmental problems

XRF Solutions

- Rapid screening of raw materials
- Identification of critical components
- Contamination testing of the final product
- Standard-less semi-quantitative analysis

Secundary Fuels for Cement Production

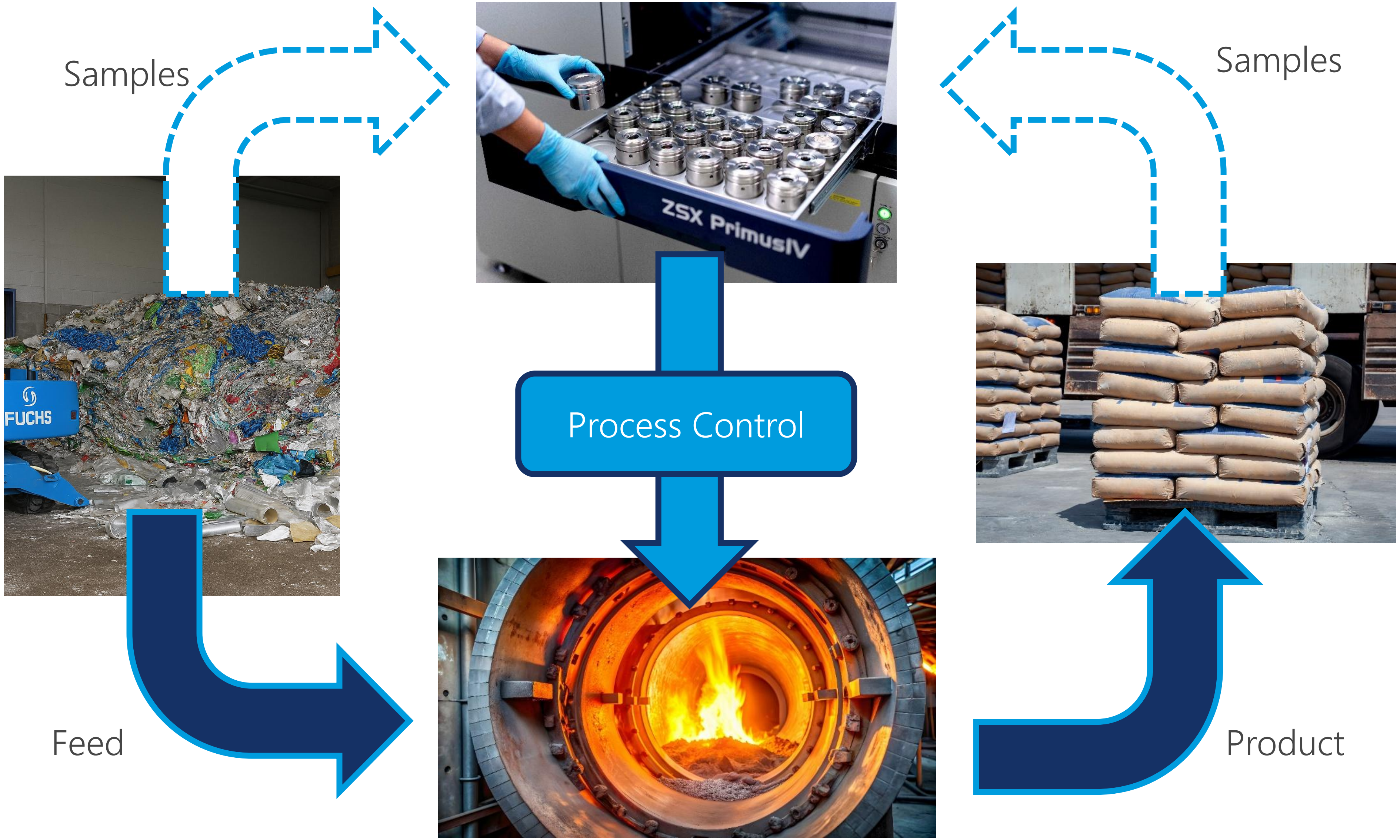
Secondary fuels in the cement industry

- Substitution of fossil fuels
- Cost reduction
- CO_2 reduction (from fossil fuels)

Elements to Monitor

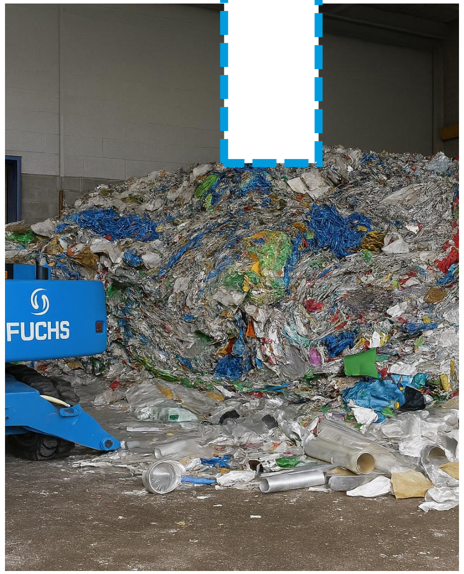
- P: Severe impairment of strength
  made of flame retardants in plastic
- V, Zn, Pb: Increase the reactivity of the clinker
  Additives such as zinc stearates
- Mn, Ti: Interfere with the hydration properties of
  MnO/TiO_2 as pigments or UV stabilizers

Analytics for Process Control



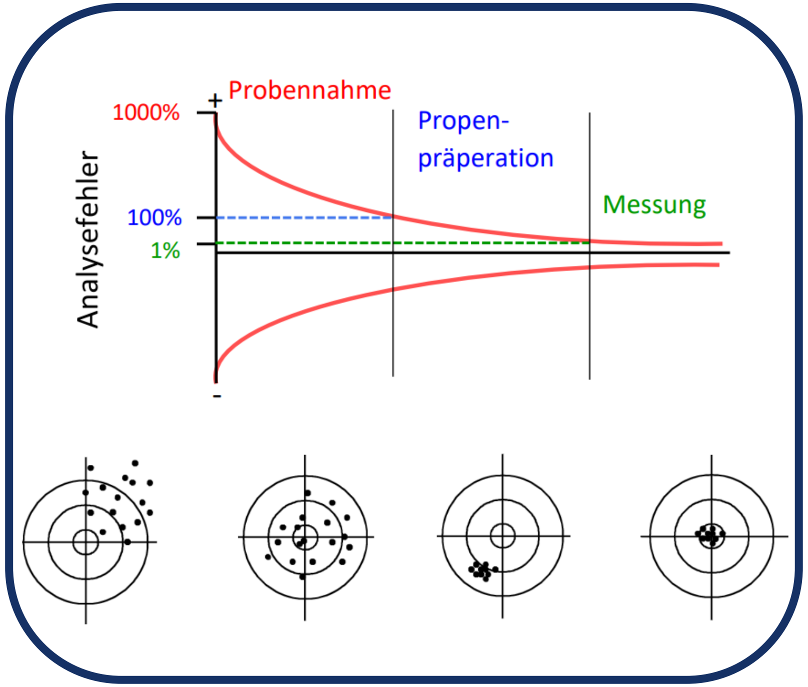
Analytics for Process Control

Samples



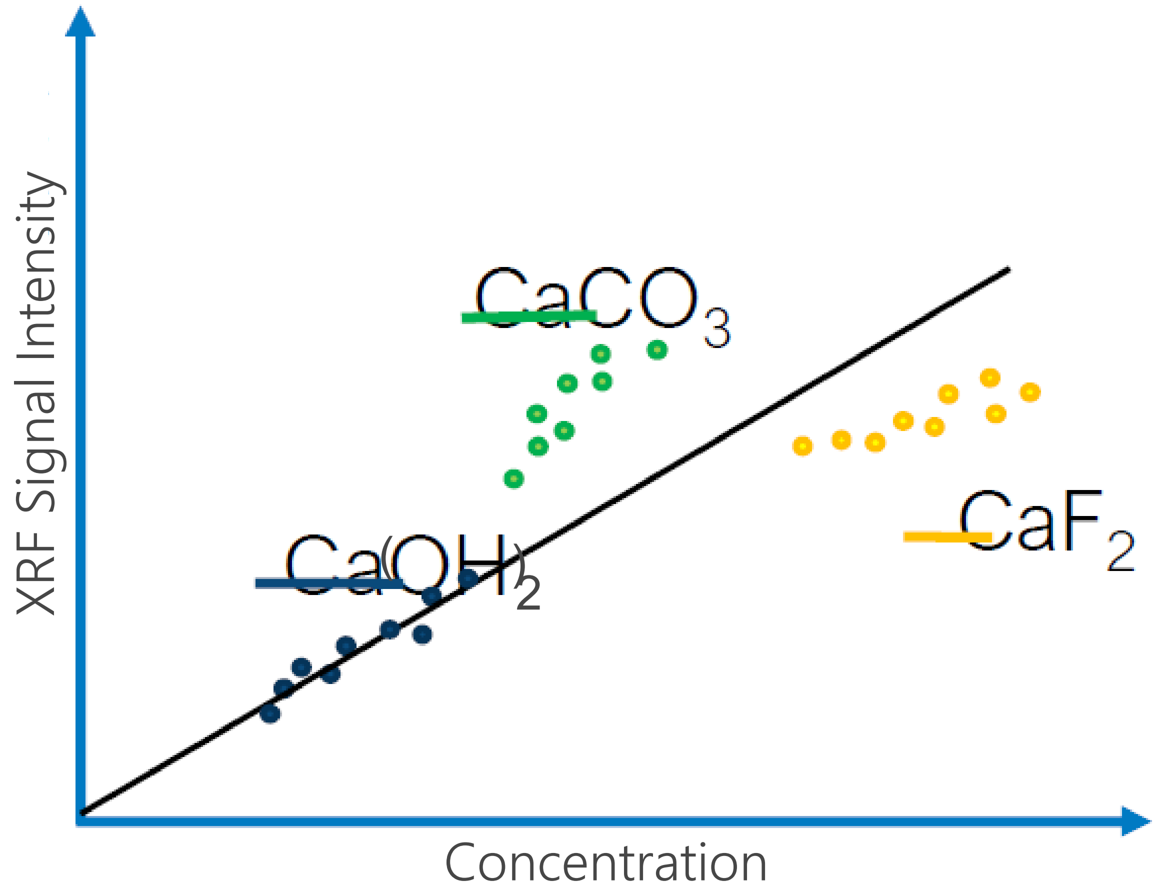
Process Control

Where are the sources of error and what influence do they have?



Matrix matched Calibration

Ca calibration in different matrices



Matrix Customized Calibration

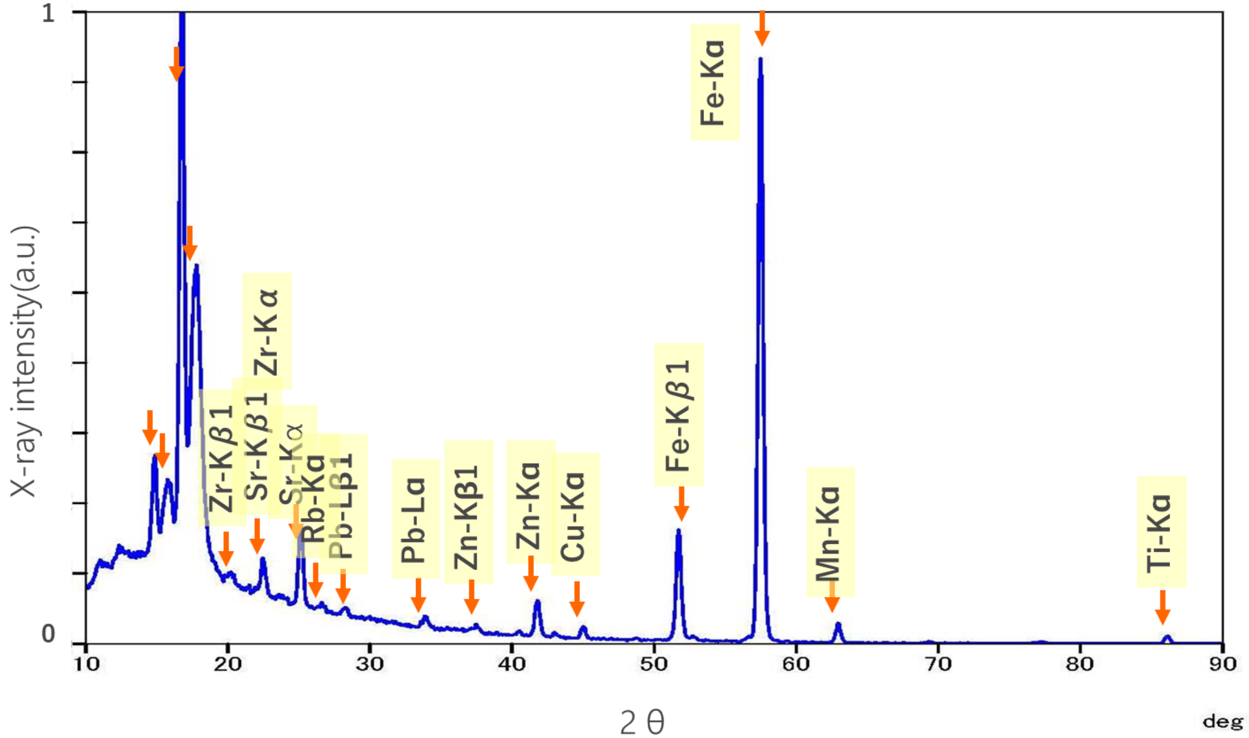
A must for precise analysis results

Strong influence of:

Absorption effects, spectroscopic background and interference

Matrix Compensation Methods on standardization procedures

Standardless semi-quant analysis



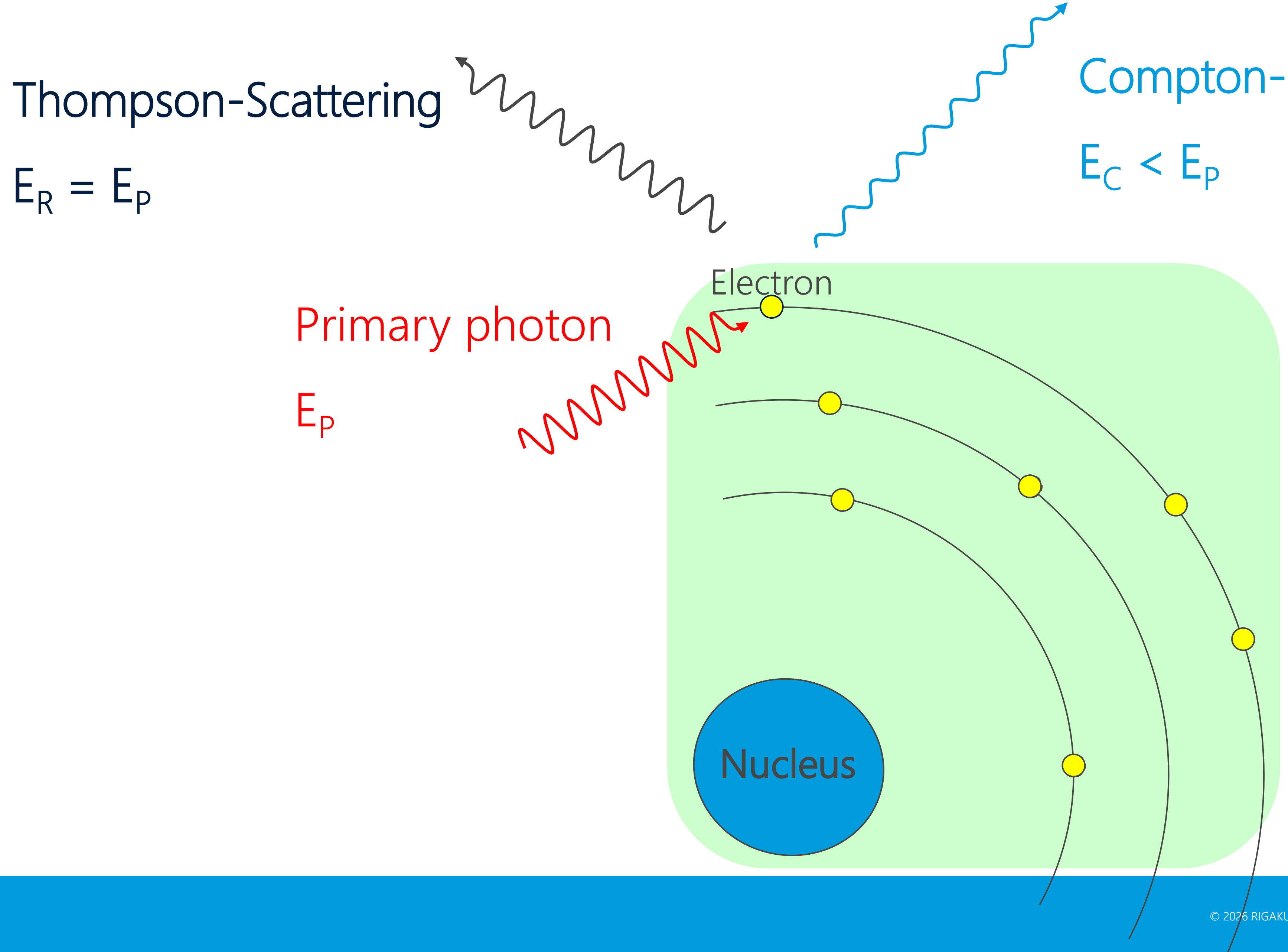
$$C_{i,u} = \left(\frac{C_{i,r}}{I_{i,r}\,(1+\sum_j \alpha_{ij} C_{jr})} \right) . I_{i,u} . \left(1+\sum_j \alpha_{ij} C_{ju} \right)$$

Fundamental parameter model

- Intensities are compared with a sensitivity library
- Inherent matrix correction for absorption and enhancement effects
- Very good matches possible

  e.g. 0.12 % relative deviation for Si in fused beads from geological samples

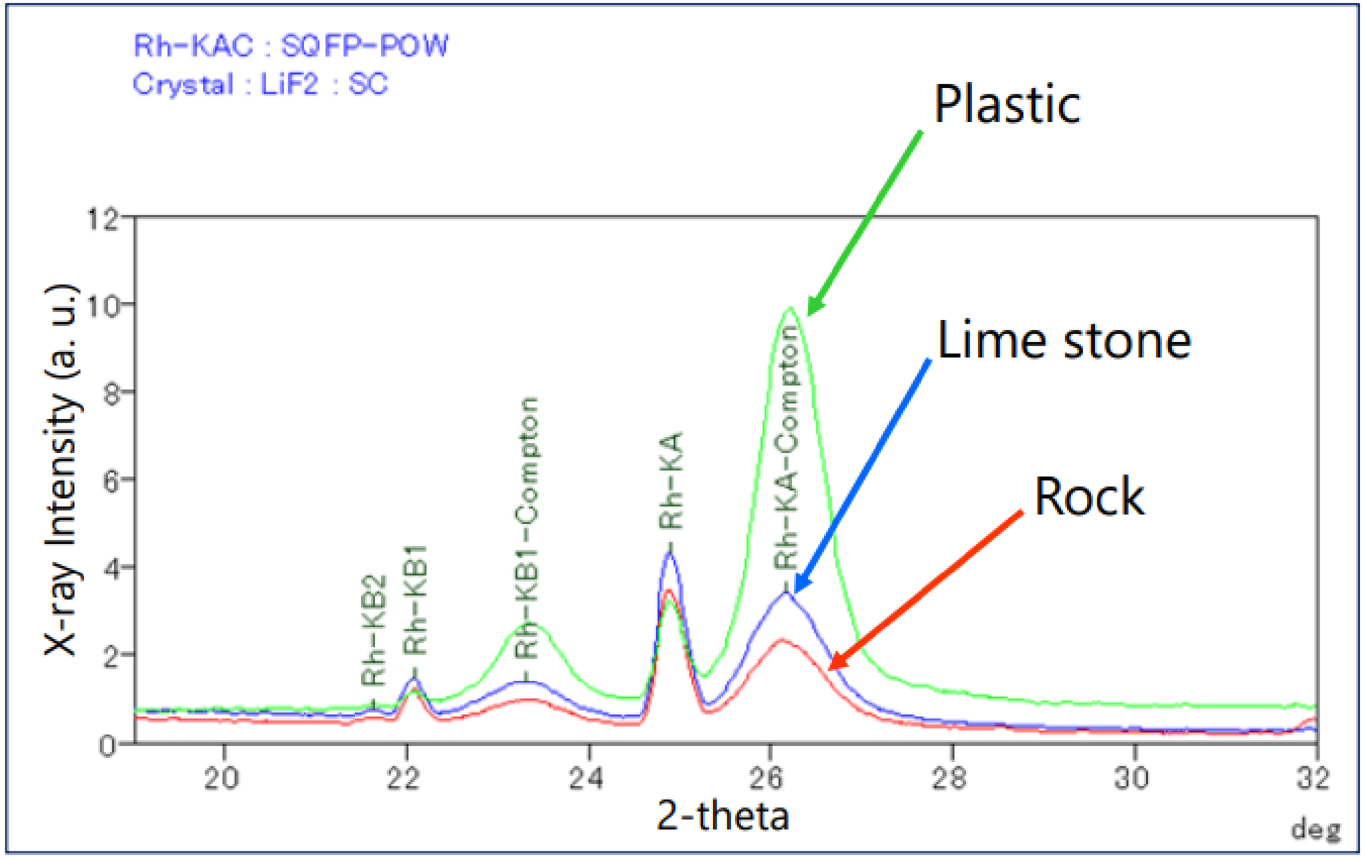
X-ray scattering as a compensating factor



Compton Scattering

With a low atomic number and high photon energy, the probability increases

Determination of the Rh Compton signal



Measurement of Compton Scattering

- Indirect determination of light matrix components such as C, H and N
- Advantage over direct determination: Measurement using high-energy radiation = large penetration depth thus more robust measurement
- Enables good approximations using standard-less semi-quantitative methods

Standardless Semi-Quant Analysis

Problems with elemental quantification in plastics

- Digestions with high material use
- Fluctuating matrix
  makes matrix-matched calibrations difficult

→ High workload and high susceptibility to errors

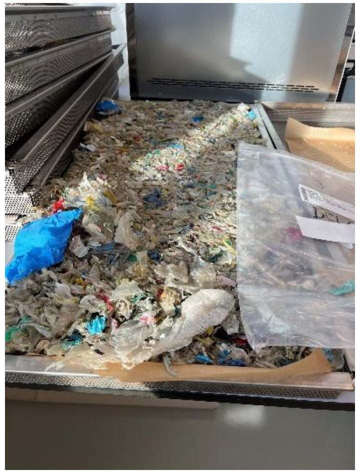
XRF Fundamental Parameter Method

- Minimal sample preparation Measurement of coarse powder pours possible
- Minimal use of materials
- Fast measurement and high flexibility
  Enables higher sample throughput

→ Awareness of the limitations of the method required

Process for a prefect sample

Drying → 1. Grinding SM 300 → 2. Grinding ZM 300 → (Hot) Pressing → Finished sample for XRF analysis



Up to this point, work steps are identical for e.g. ICP

Semi-Quantitative Analysis of Tyres

Tyre Derived Fuel (TDF)

Scrap tyres as secondary fuel in cement production

Pre-cut sample

After cryo-grinding

Heterogeneous sample

Multiple determination necessary
→ A and B Sample

Tyres	Sample A	Sample B
	Mass %	Mass %
Na	0.08	0.19
Mg	0.05	
Al	0.13	0.09
Si	0.21	0.21
P	0.03	
Si	0.84	0.89
Cl	0.24	0.18
K	0.09	
Ca	0.22	0.14
Cr	0.09	0.08
Fe	0.17	0.06
Cu	0.08	
Zn	3.56	2.85
FP Balance	94.21	95.31
Total	100	100

Summary - Plastic waste

Conventional analytical methods:

- Heterogeneous, fluctuating material flows require a high level of analytical effort
- Optimization of sampling and sample preparation

Standard-less semi-quantitative XRF provides

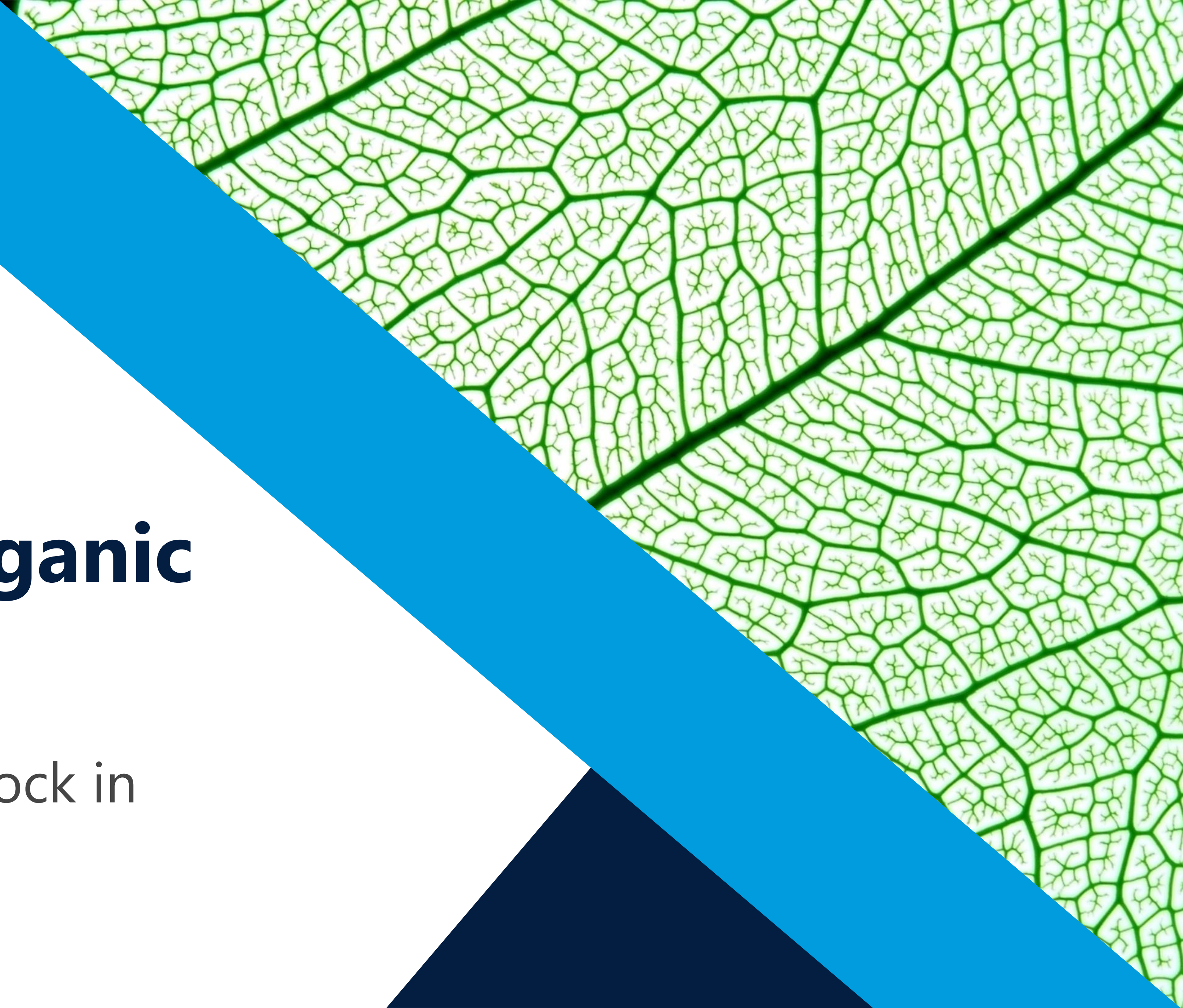
- Flexibility for different matrices
- Time savings in sample preparation
- High throughput

→ More capacity for better screening

Questions to Plastic recycling?

Application 2
Analysis of organic fibers

Straw as green feedstock in industrial applications



Analysis of straw for industrial applications

Application:

Straw and other organic fibers are used in various industrial applications as alternative to fossil feedstocks:

→ BtL Processes: Bio to Liquid

Synfuel or platform chemicals (SynGas)

Challenge

- Humidity adheres well to the fibers
- Agricultural product with strongly varying quality

  → light element concentration influences pyrolysis behaviour
- Multilayer structure

  → Influence on the sample preparation?

XRF Solution

- Easy Analysis from grind biomass
- No combustion, extraction or digestion

Fine grinding: Straw sample – choice of mill

SM 300 Cutting mill

ZM 300 Ultra-centrifugal mill

PM 400 Planetary ball mill

SM 300

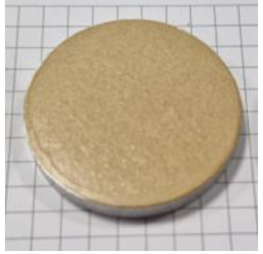
Press

PM 400

Press

ZM 300

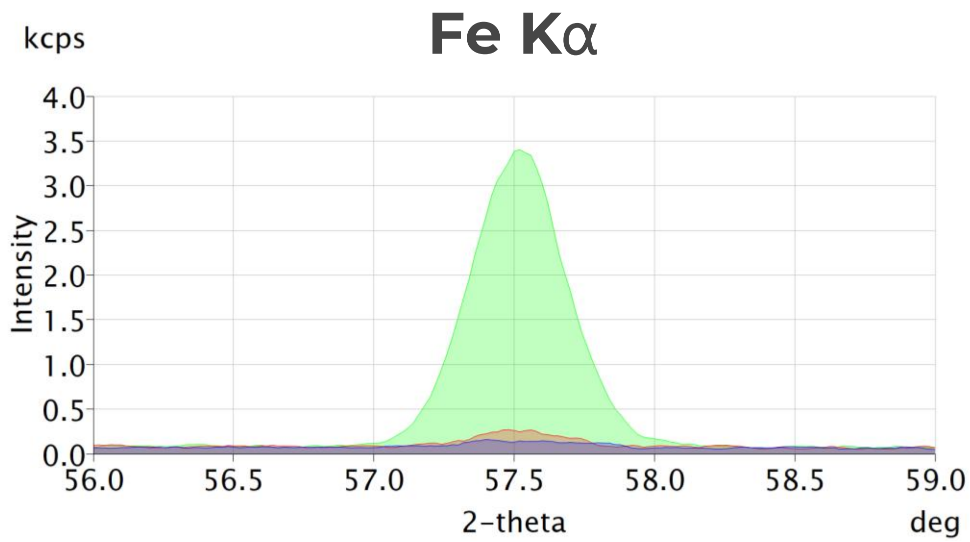
Press



Grinding tools were made from stainless stell

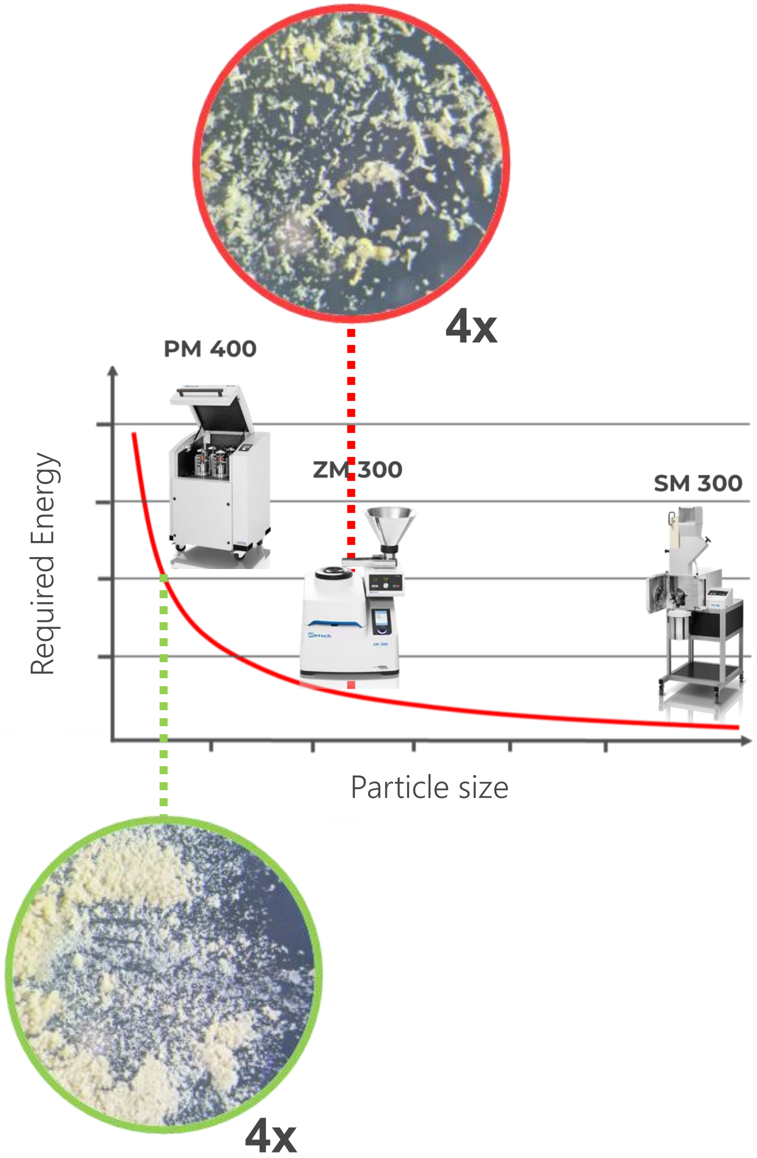
Pressing with Licowax at 15 t on 40mm

Fine grinding: Straw sample – abrasion



Eisenabrieb (Fe)

PM 400	1642 ppm
ZM 300	93 ppm
SM 300	40 ppm



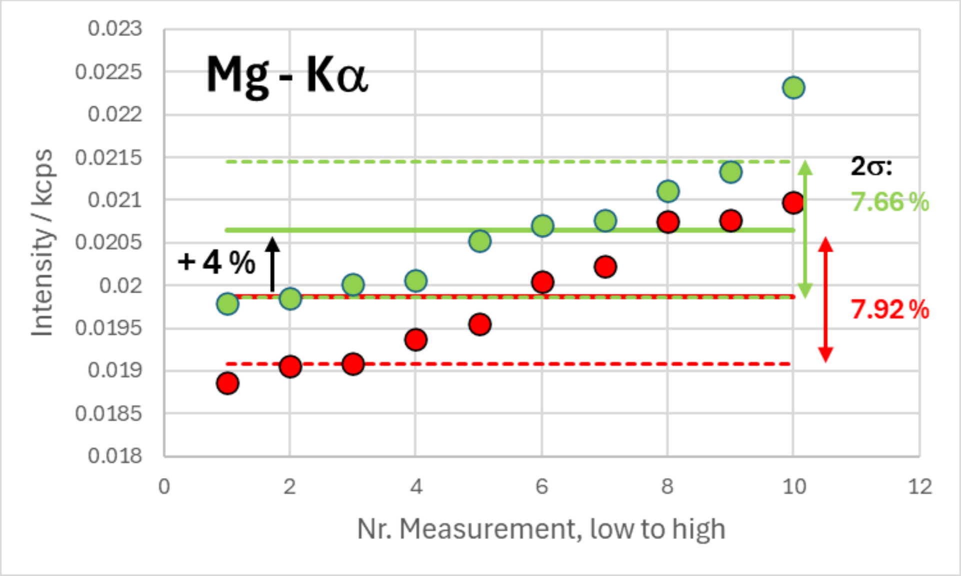
SM 300 Cutting Mill
Coarse crushing, short grinding time, hardly any abrasion

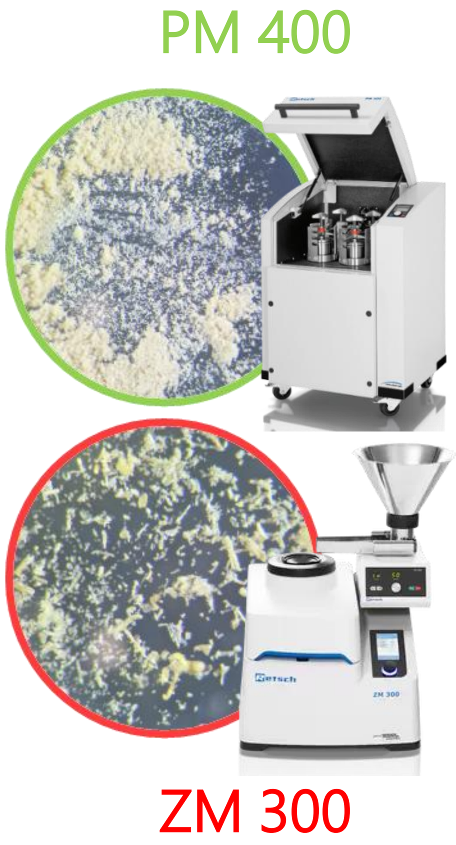
ZM 300 Ultra-Centrifugal Mill
Fast fine crushing, little abrasion, but fibrous powder

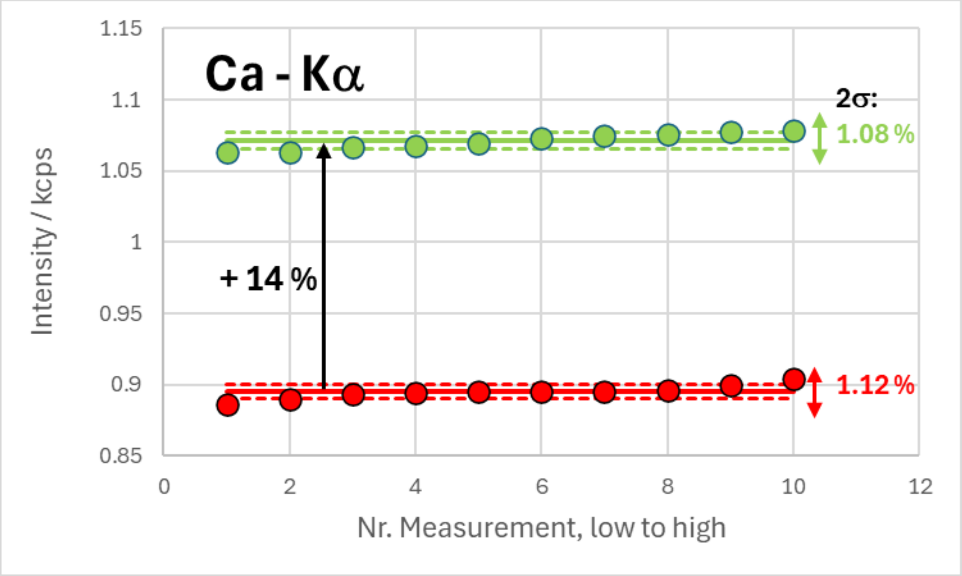
PM 400 Planetary Ball Mill
Long grinding time, with a lot of friction to crush the fibers
High abrasion, fine powder

Fine grinding: Straw sample – signal influence

Measurement: 60 s peak
2 x 30 s underground







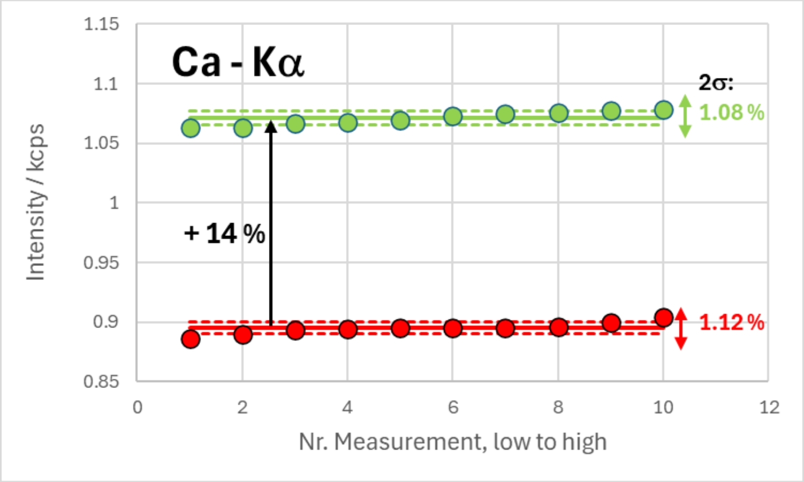
Fine grinding in the PM 400 planetary ball mill leads to better homogeneity of the sample.

Organic fibers are highly structured materials with anistotropic element distribution

Grinding mitigates this

→ Representative signal

Summary – Straw Analysis



Straight forward analysis with XRF?

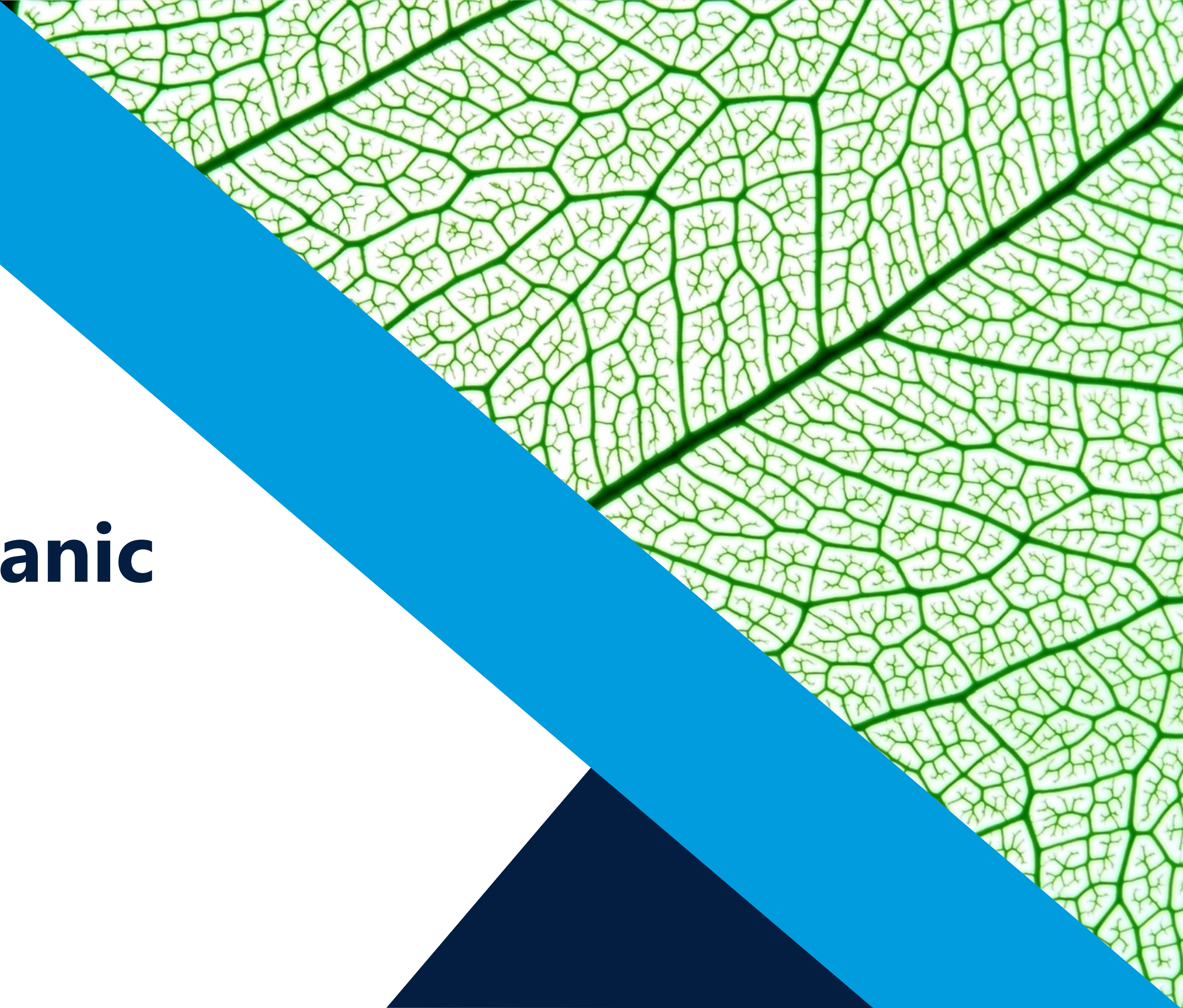
- Initial statement: Easy Analysis from grind biomass

Pitfalls need to be identified and avoided

- Anisotropic bio fibers when ground can smear and not reduce particle size
- High power milling equipment required

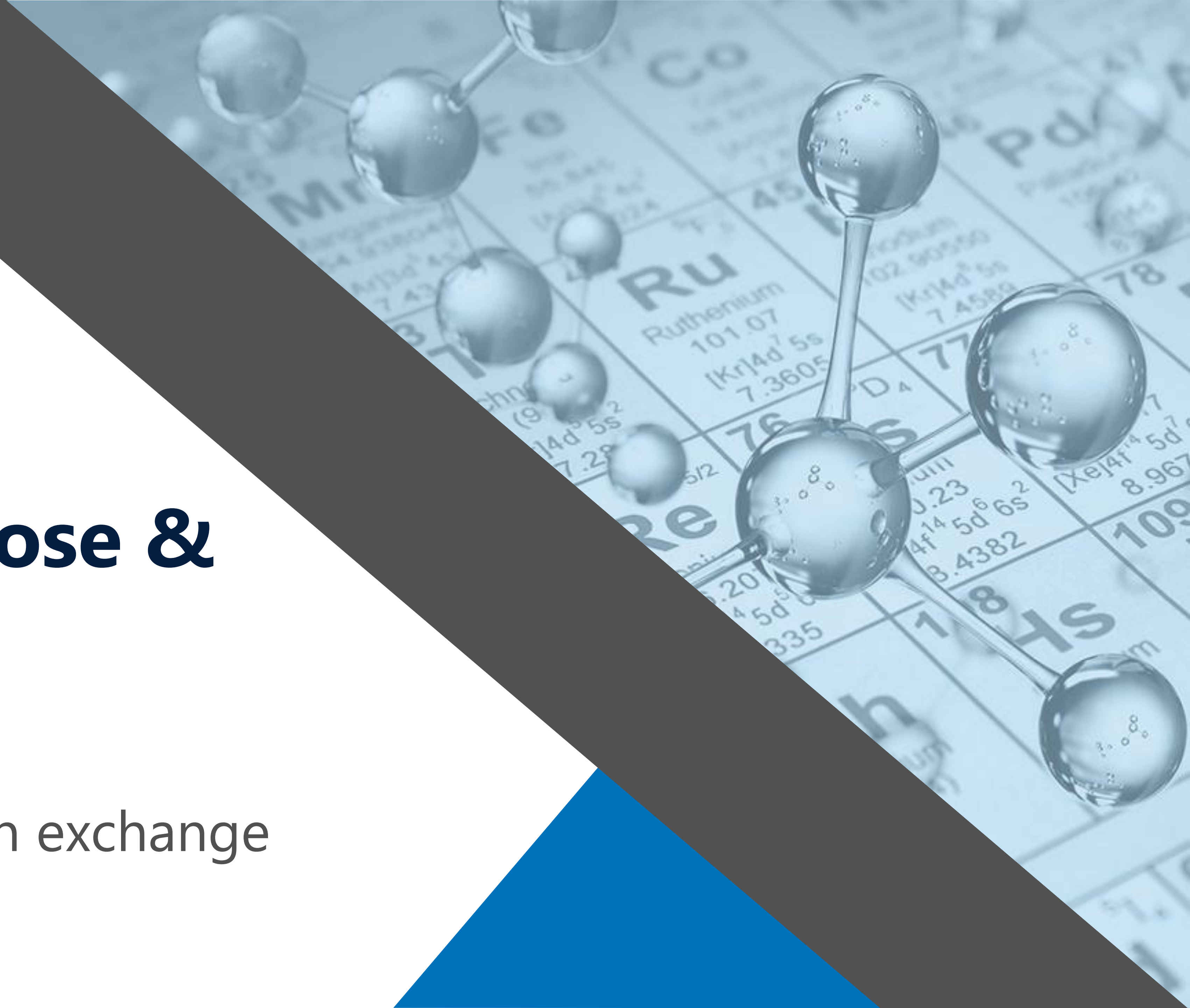
→ More about the importance of sample preparation after the lunch break

Questions to Analysing organic fibers?



Application 3 Calibrating loose & wet powder

On the example of ion exchange resin

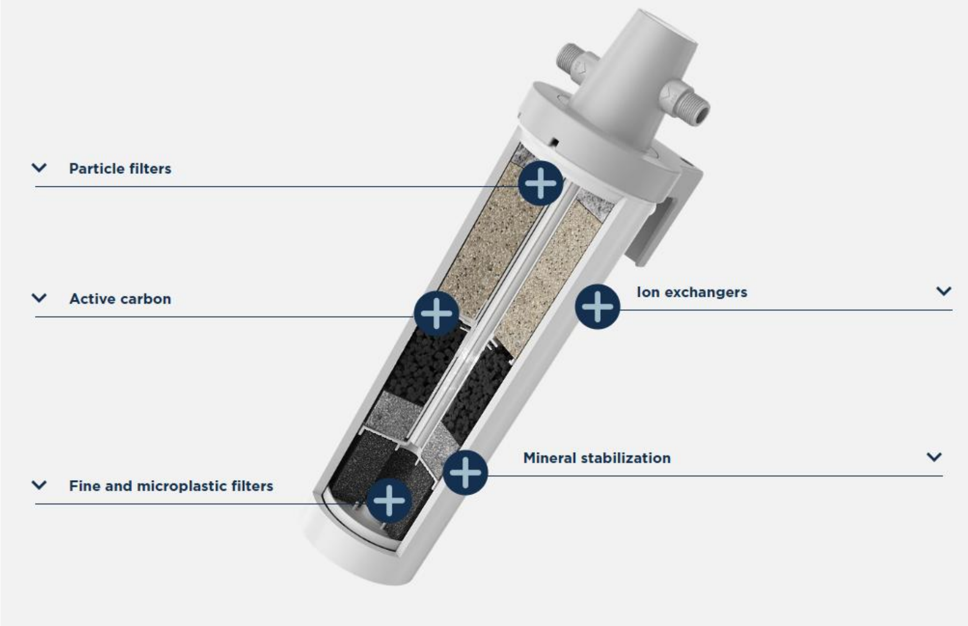


Analysis of Ag+ in Ion Exchange Resin

Application:

Water purification systems are prone to bacterial infestation

Ion exchange resins which release antimicrobial Ag+ ions are used to inhibit bacterial growth



Challenge

- Sample is strongly hydroscopic
- Digestion attempts by the customer failed
- Resin particles are too big to press and too ductile to easily grind down

XRF Solution

- Calibrate for the wet loose powder in a cup

Analysis of Ag+ in Ion Exchange Resin

How should the ideal sample look like:

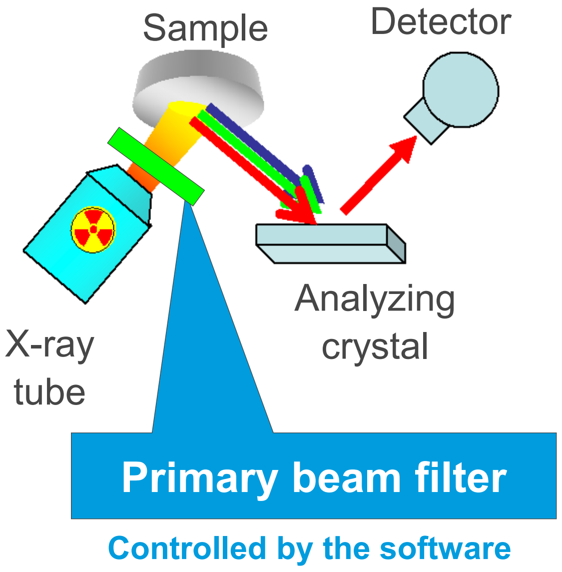
- Homogeneous
- Dry
- Smooth surface / fine particle size
- No air gaps
- Infinitely thick

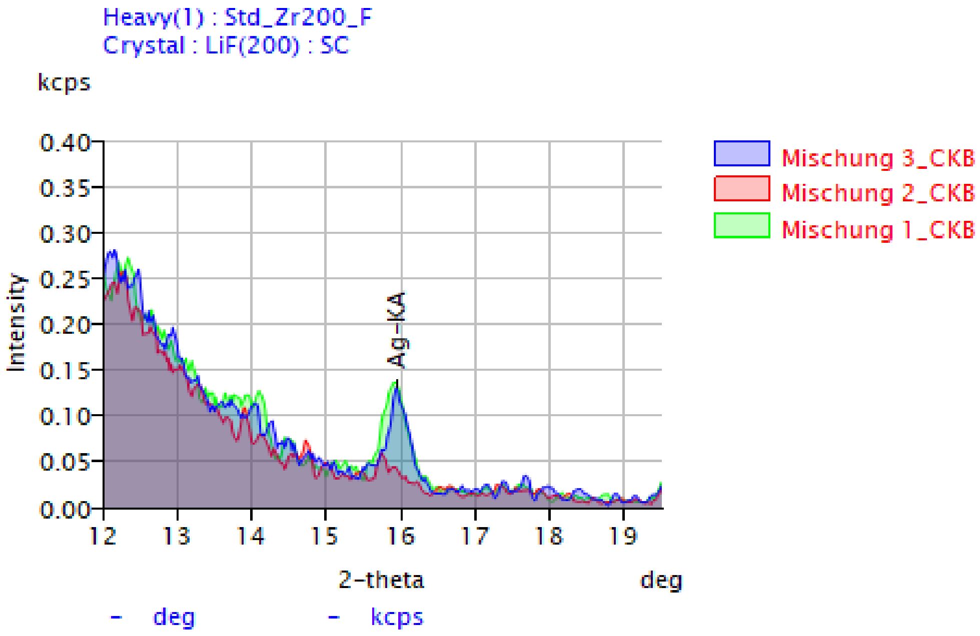
How does the sample look like?

- Wet (hard to dry)
- Wet powders shouldn't be pressed

→ Loose powder calibration required

Analysis of Ag+ in Ion Exchange Resin





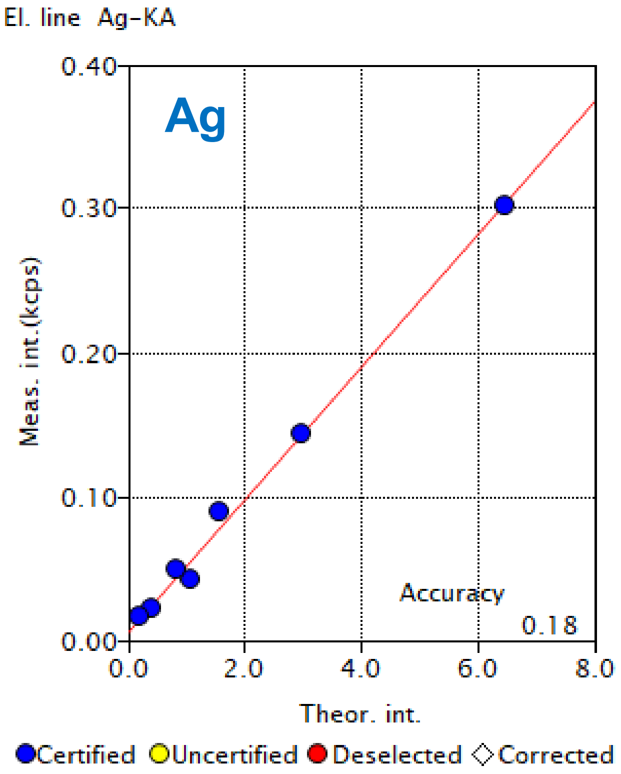
Ag has a direct line overlap with the characteristic lines from the Pd tube

Zr filter (standard) eliminates interfering Pd-K lines and Compton scatter lines from the X-ray tube target. Used for analysis of Cd, Ru, Rh, Pd, Ag, or In.

Good spectral resolution & low background

Calibration loose and wet powders

Regression r^2 0.9974
Slope 2.168e1
Intercept -1.233e-1



Ag-Calibration of loose powders.

- Calibration standards from readily available materials

→ Mixture from fresh resin (100 % Ag) and blank resin (0 % Ag)

- FP Calibration mitigates influence of varying matrix scattering

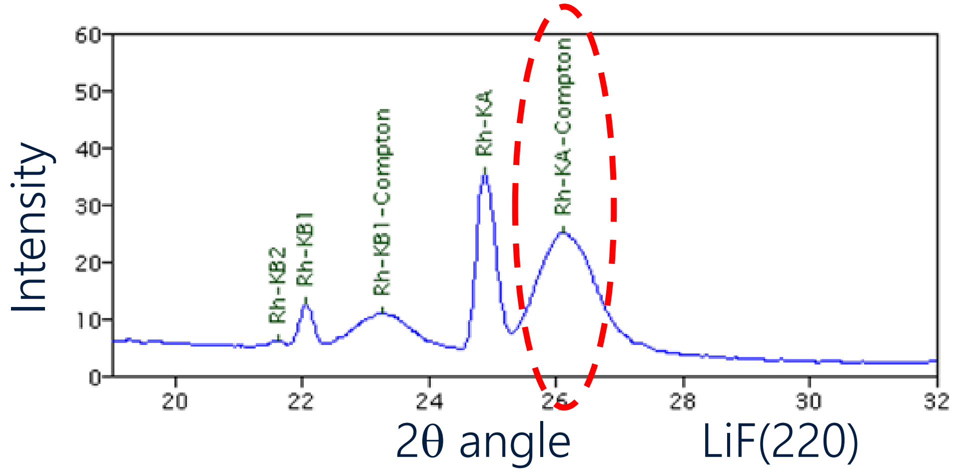
→ Varying water content & particle distribution

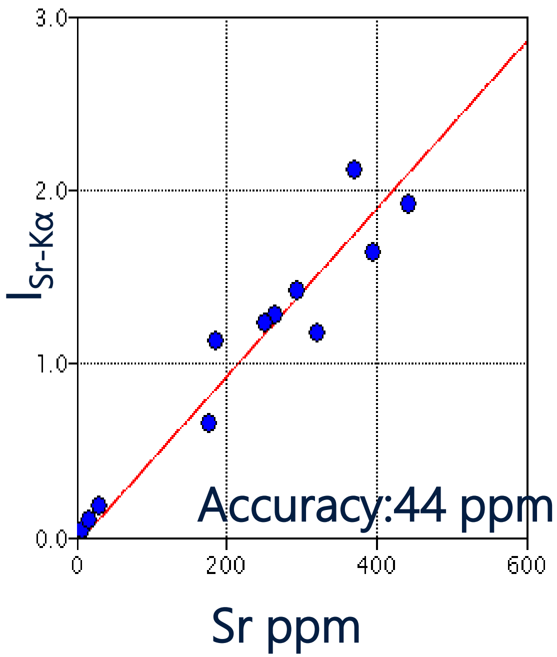
FP Calibration with Compton Ratio Method

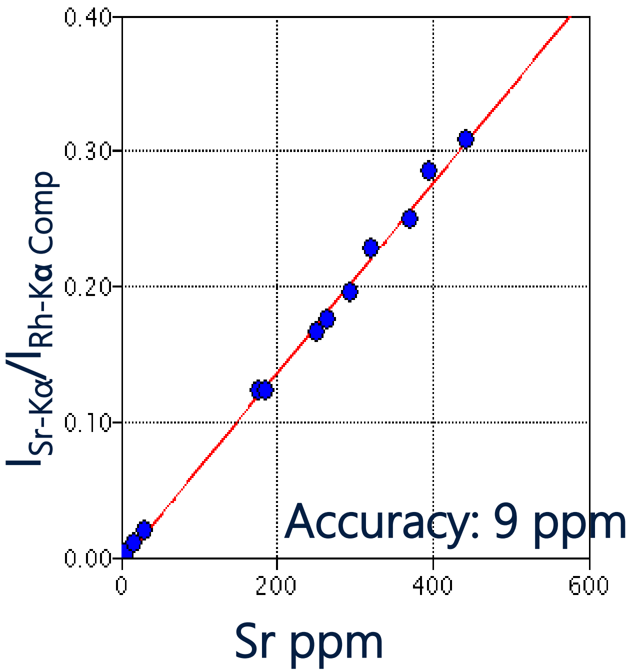
Analysis of Sr in rocks

Calibration equation

$$W_i = CI_R + D \qquad I_R = \frac{I_i}{I_{Rh-K\alpha Compton}}$$

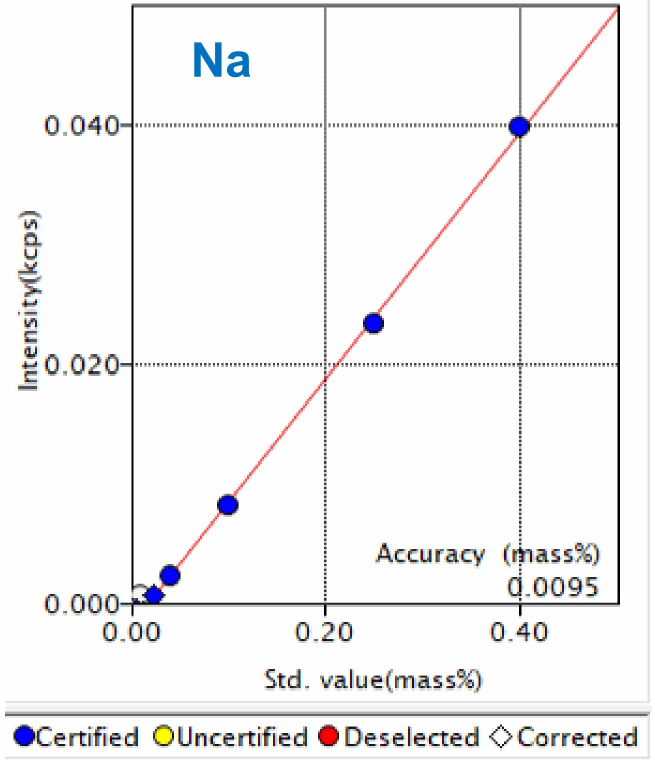






Calibration loose and wet powders

Supermini200



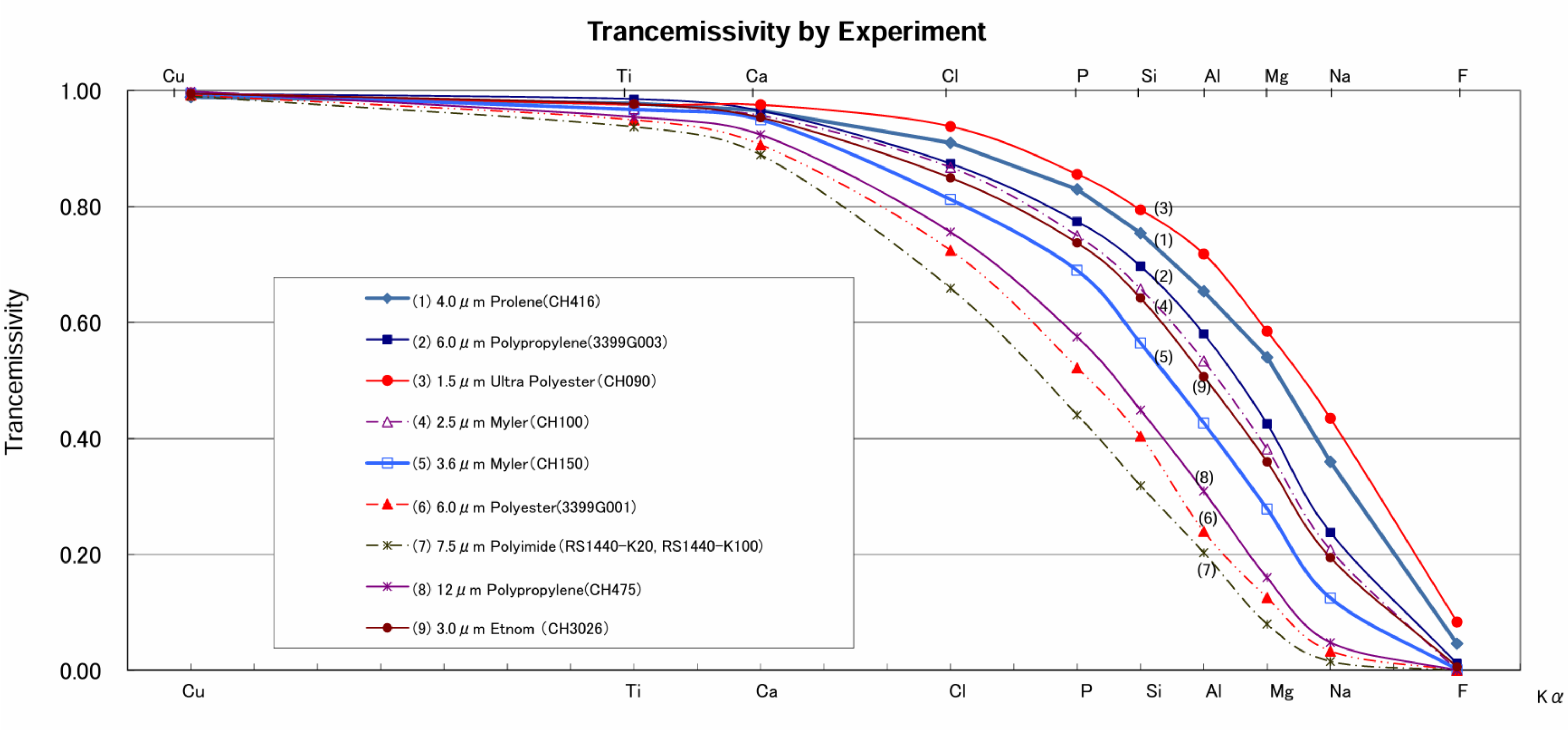
Na-Calibration of loose powders

Low level calibration despite:

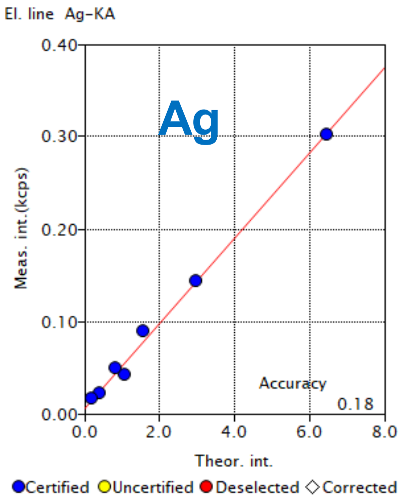
- Not ideal sample form
- Measurement in He atmosphere
- Measurement in a cup with a film

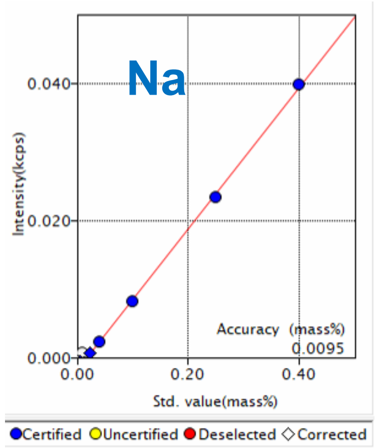
→ absorbs >70 % Na signal

Film transparency



Summary – Calibrating loose & wet powder





- High quality calibration can be achieved even under adverse prerequisites

→ Matrix matching is key

- Certain matrix effects can be compensated

→ ZSX Guidance software with FP package

- Benchtop size, full WD performance

→ Supermini200 for low level Na calibration

Questions to Calibrating loose & wet powder

Application 4 Micro Carry for analysis of aqueous solutions

On the example of kaolin as plant protection agent

Analysis of Kaolin in Water

Application:

Kaolin suspensions are used in agricultural research as inexpensive biocompatible plant protection agents:

- Insect repellant (Drosophila suzukii)
  Used until shortly before harvest
- Reflecting agent to reduce water evaporation in the summer

Application via regular water irrigation systems

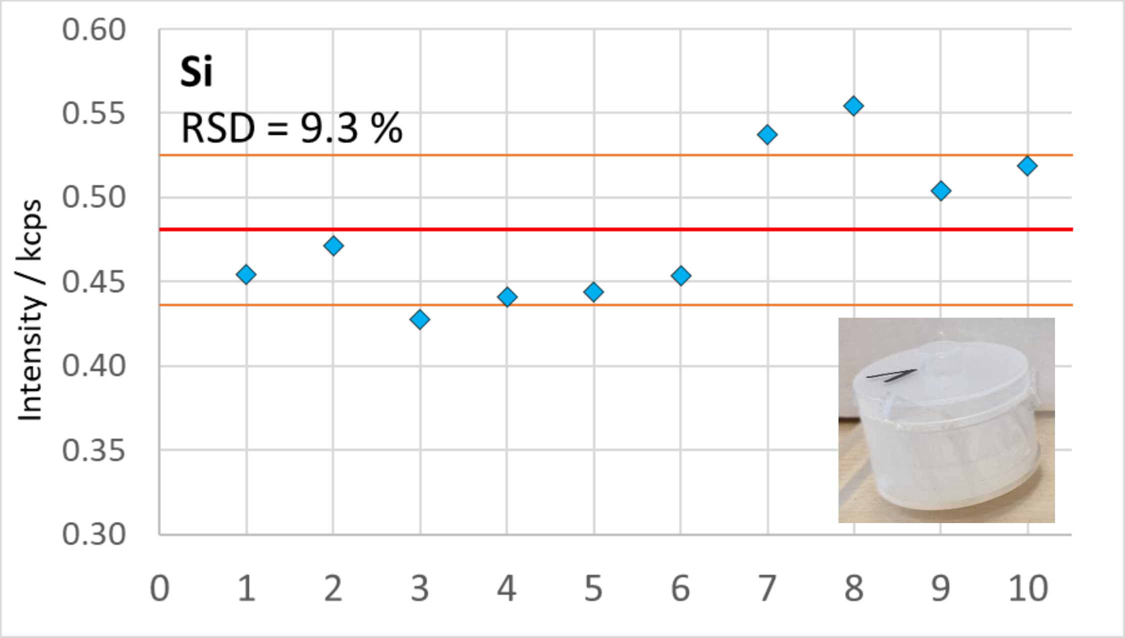
Challenge

- Water spraying tanks need to be checked before regular irrigation
- Kaolin AlSiO(OH) is difficult to digest for ICP analysis
- Suspensions are not stable

XRF Solution

- Measurement via preconcentration on filter materials (Micro Carry / Ultra Carry)

Repeatability 1%/400 for the Si Kα Signal (Cup)

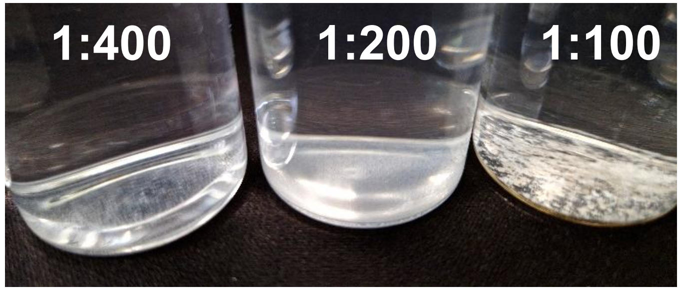


Kaolin suspensions:

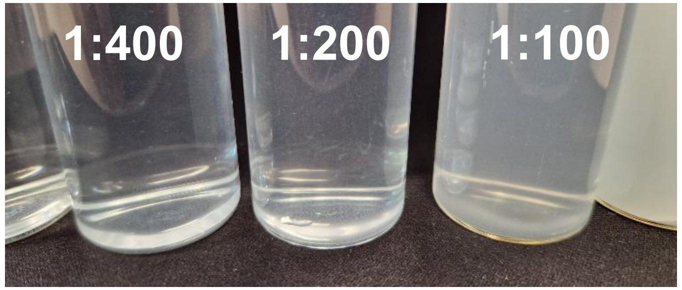
- Sedimentation is an issue for this sample
  → Enrichment in the analytical layer

- Signal intensity dependend on the time between preparation and measurement
  - Each cup prepared on the left was measured twice (see graph)

before homogenizing



after homogenizing

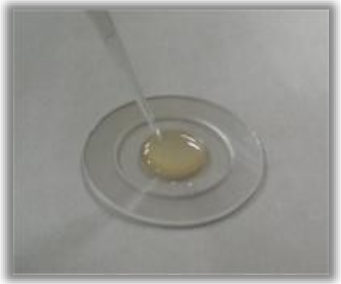


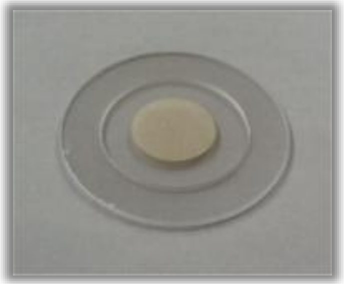
- Poor repeatability

→ Not fit for calibration!

FAT uses Stable Al Metal disk

Micro / Ultra Carry sample preparation



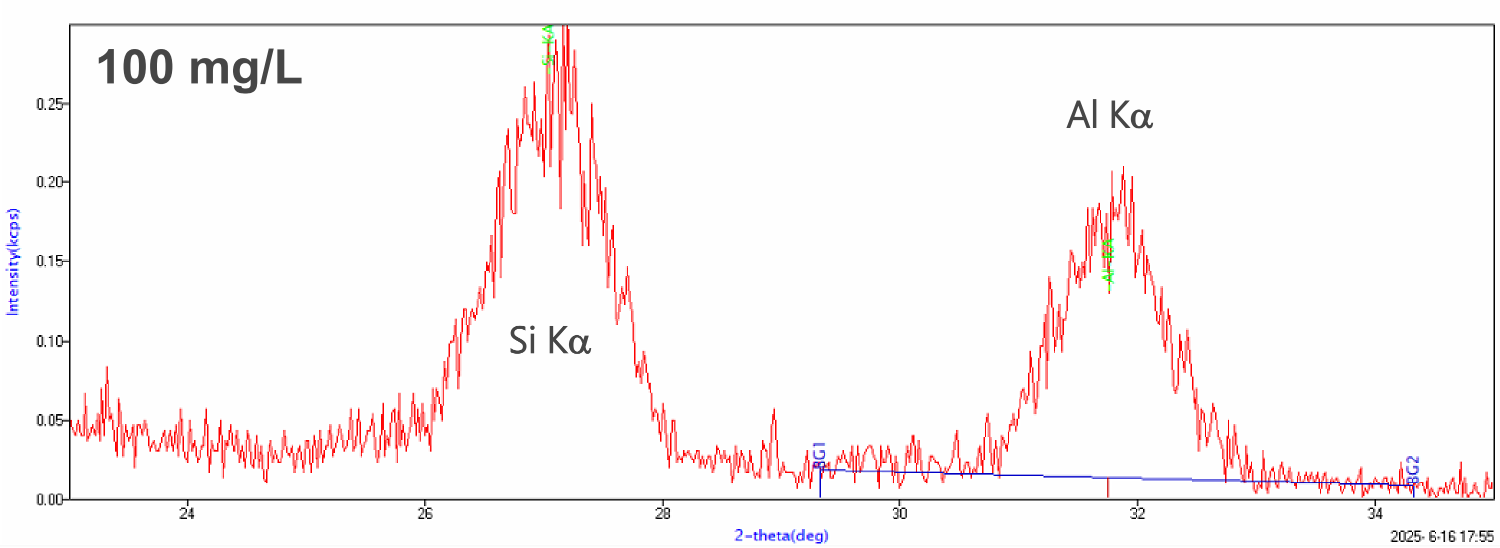


Take a representative sample → Pipette 10 to 500 µL on the filter → Dry at 45° C ideally under vacuum → Place in sample holder and analyze

Supermini200

- MicroCarry (≤200 µL) and UltraCarry (≤500 µL) allow precise analysis of small sample volumes
- High precision with low limits of detection
- Undesirable matrix is removed by drying
- Left over is a near perfect sample thin homogeneous layer on the surface of the filter
- No film needed → high sensitivity of light elements
- ICP standards for calibration

MicroCarry Calibration



MicroCarry Calibration

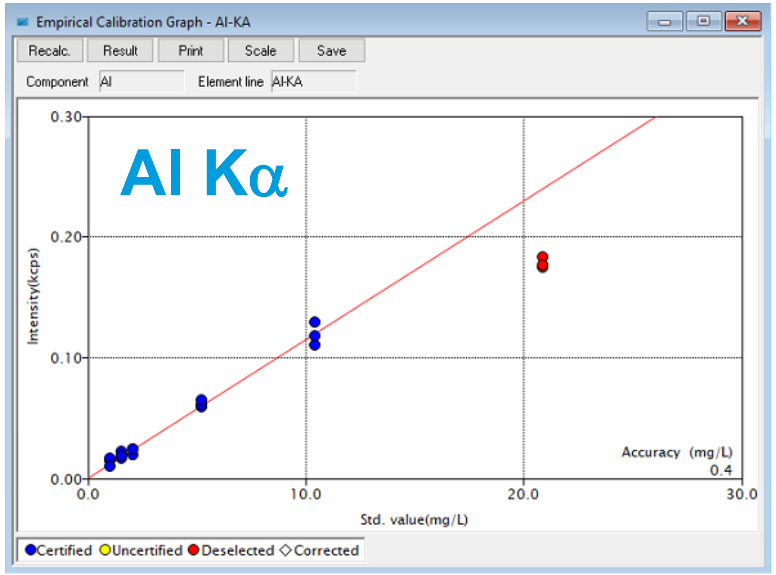
Calibration method:

- Empirical calibration on stock solutions of defined kaolin content
- 3 samples per standard
  → minimal spread

→ Here: accuracy for Kaolin: 1.9 – **2.1 mg/L**

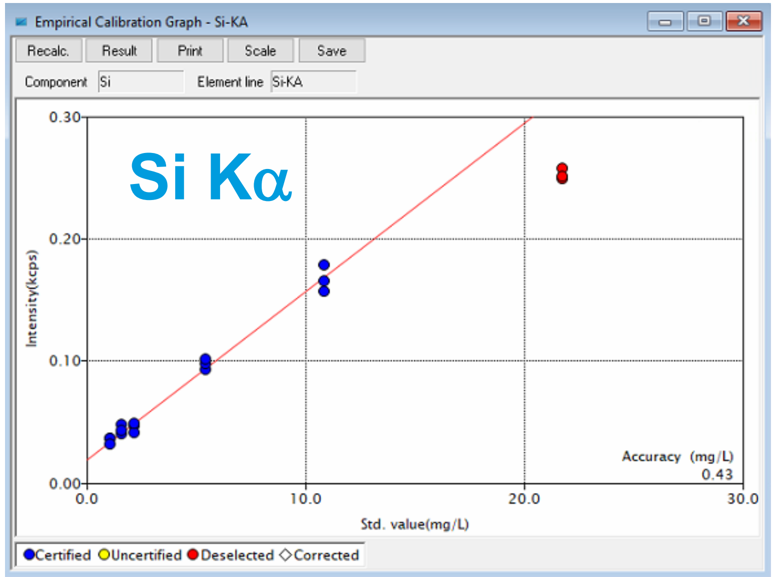
→ LOD (Kaolin) = 0.6 – 0.7 mg/L

Further standards and longer measuring times can further improve LOD and accuracy



Al

Standard 6 not considered
Corr. Factor 0.994
Accuracy ±0.40 mg/L
LOD (Al) ~0.13 mg/L



Si

Standard 6 not considered
Corr. Factor 0.994
Accuracy ±0.43 mg/L
LOD (Si) ~0.17 mg/L

MicroCarry Repeatability

For the dilution of 1:400 the Al concentration converts to

c(Kaolin) = 25.83 ± 0.29 mg/L

vs. the standard value given at 25 mg/L

The conversion of Al Ka and Si Ka signal intensity to Kaolin concentration can be done automatically by the software (as two independent values)

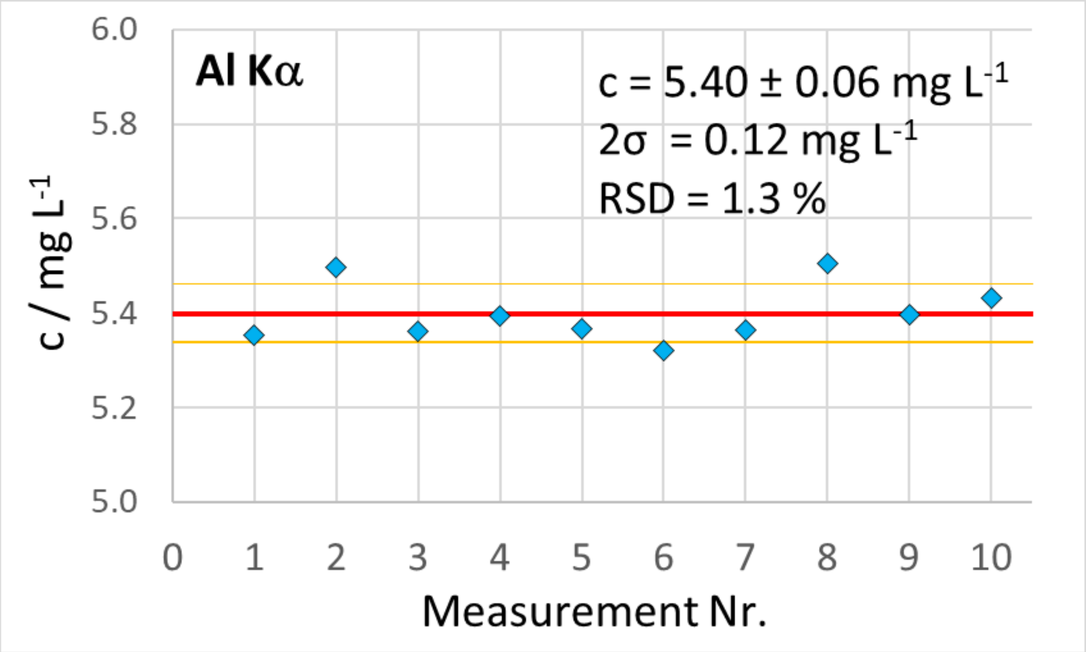
→ High accuracy provided by the instrument

→ High precision

can be further improved with more standards,

improved preparation, maybe certification

Standard	4(a)
Dilution	1:400
c(Kaolin)	25 mg/L
c(Al)	5.23 mg/L



Summary: MicroCarry

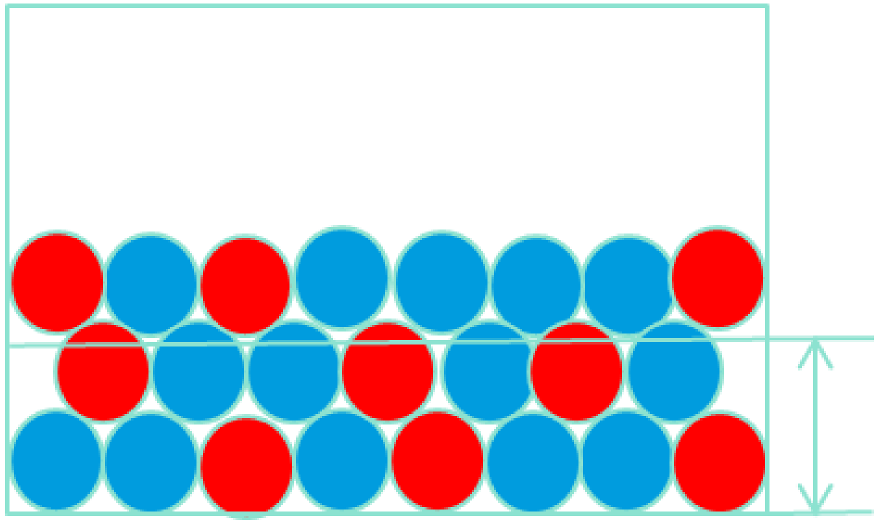
- Excellent for low limits of detection in samples with volatile matrix
- Low sample volumes for scarce sample materials
  e.g. Enzyme quantification in life science
- No need for digestions
- Easy Calibration & cheap consumables

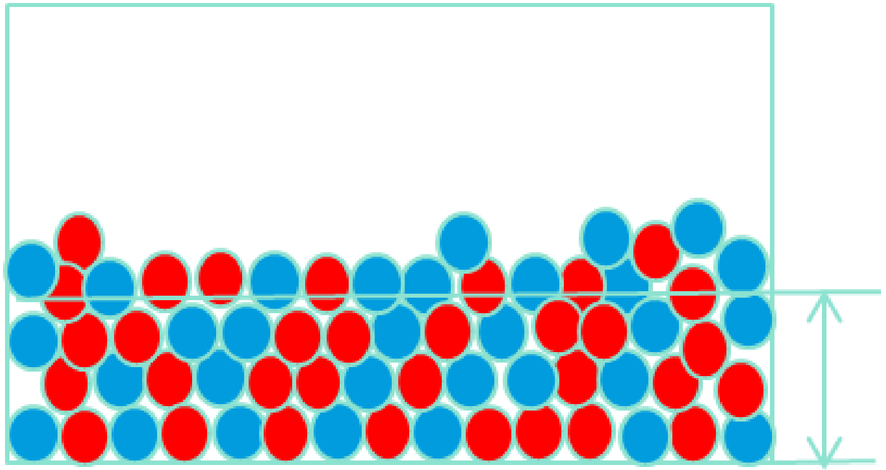
Questions to Analysing with the Micro Carry filter?

Influence of particle size on the XRF result

On the example of lime stone

Why is sample preparation / grind important?



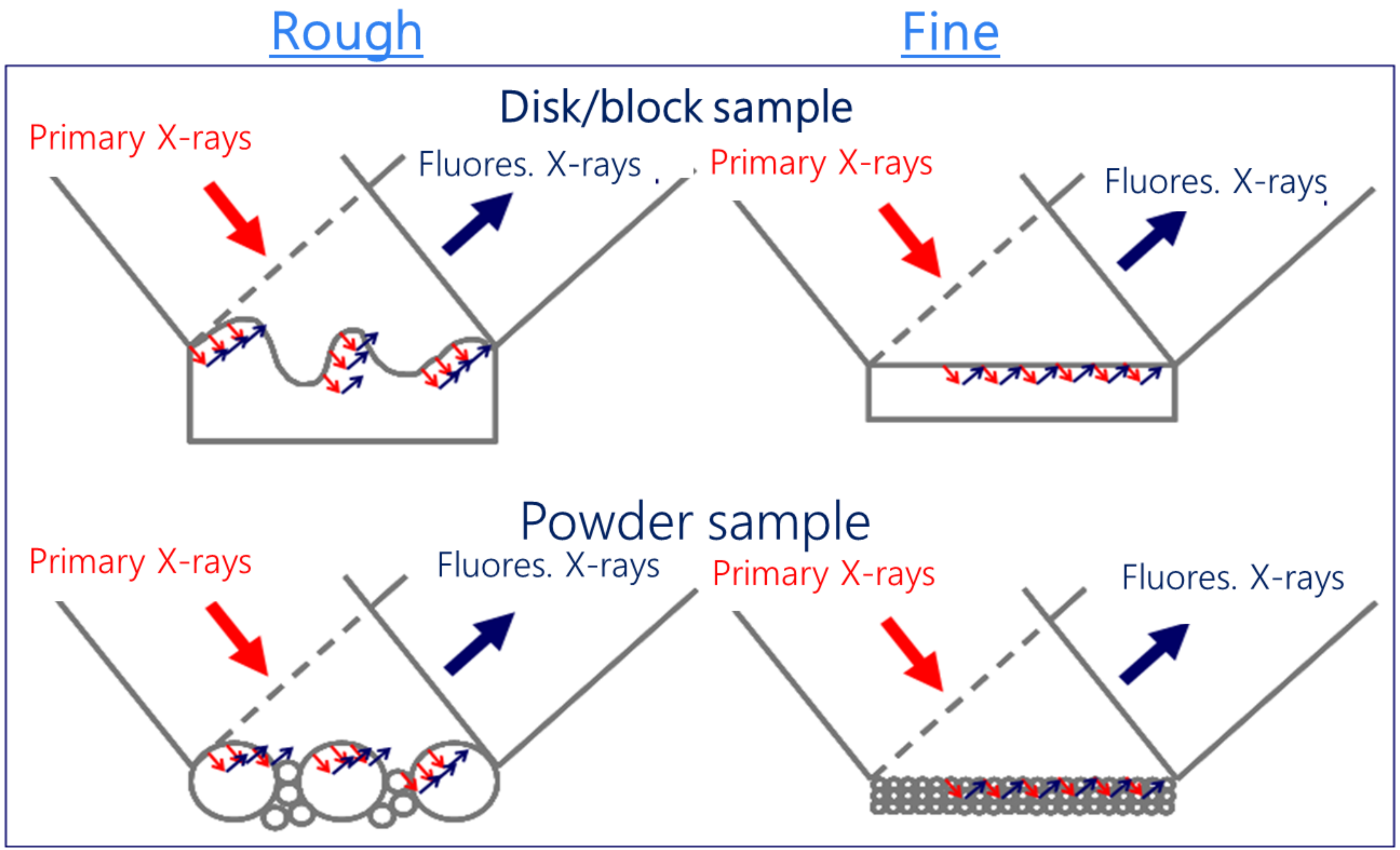


- The required particle size is directly correlated with the thickness of the analytical layer
- If the particles are too coarse, the analyzed layer may no longer be representative
- Reduction of particle size leads to a denser, more homogeneous and more representative layer

- XRF is a relative method, the intensity must be correlated with the concentration

→ Matrix-matched calibration is required

Influence of the sample surface on the XRF signal



Disadvantages of rough surfaces

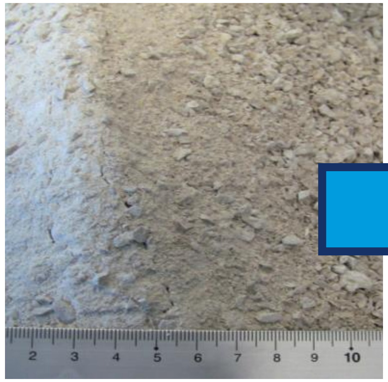
- Absorption effects, especially with light elements
- Irregular Scattering
- Orientation effects

- Especially disadvantageous when the surface finish fluctuates

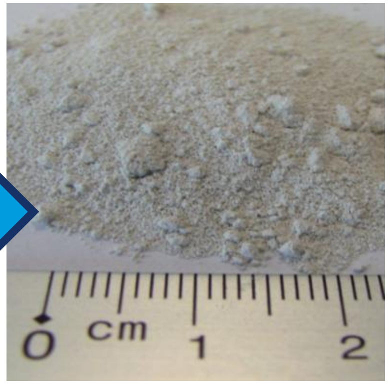
Sample types and their applications

Loose Powder	Pressed Powder	Fused Beads
		
Qualitative and Semi-quantatative applications	Quantitative Process Control Matrix matched calibrations	Reference method Matrix independent calibrations

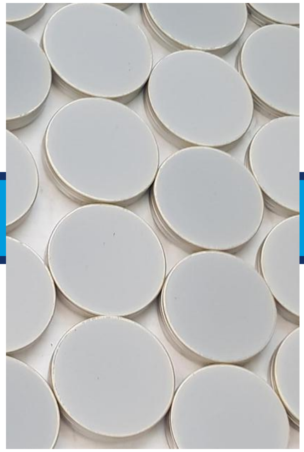
Influence of grinding time



Beispieldarstellung



Beispieldarstellung



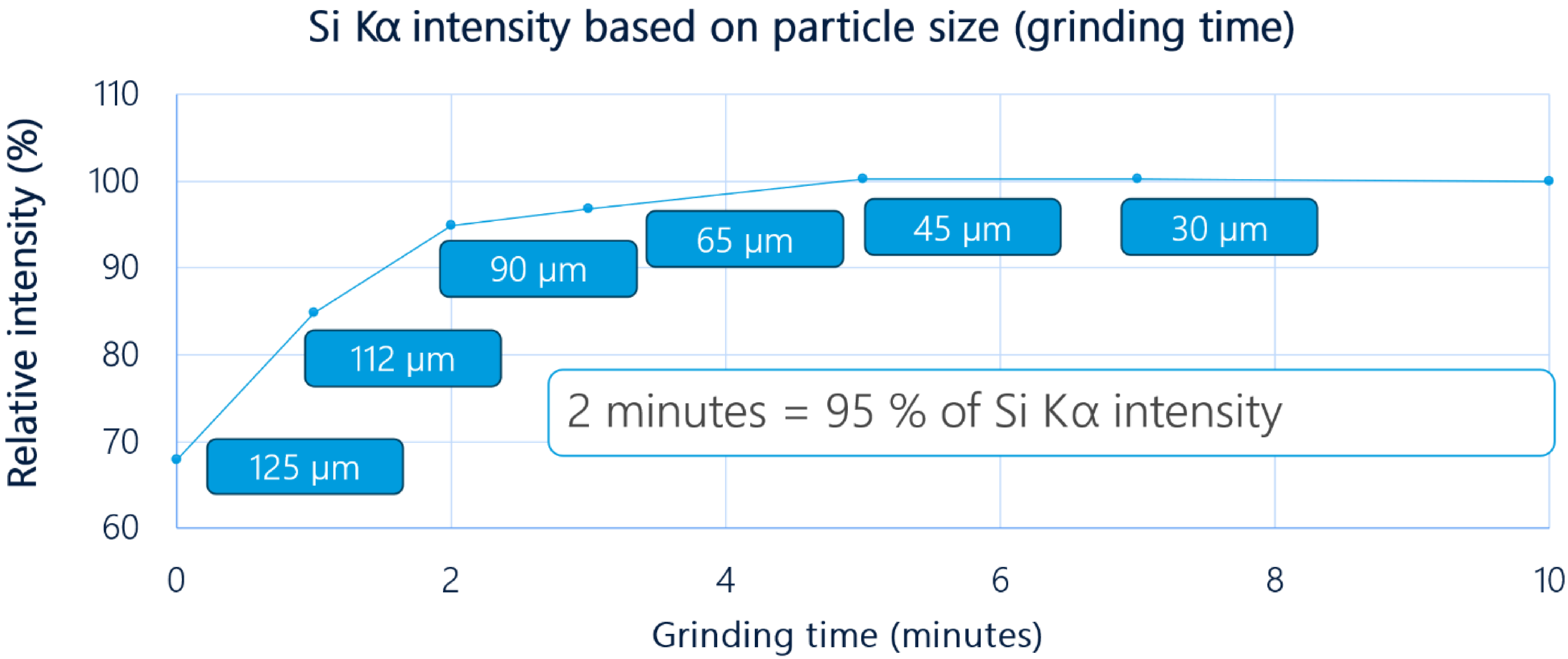
- Sample limestone powder
- Element Si

  Line Kα
- Disc Vibrating Mill with Tungsten Carbide Vessel

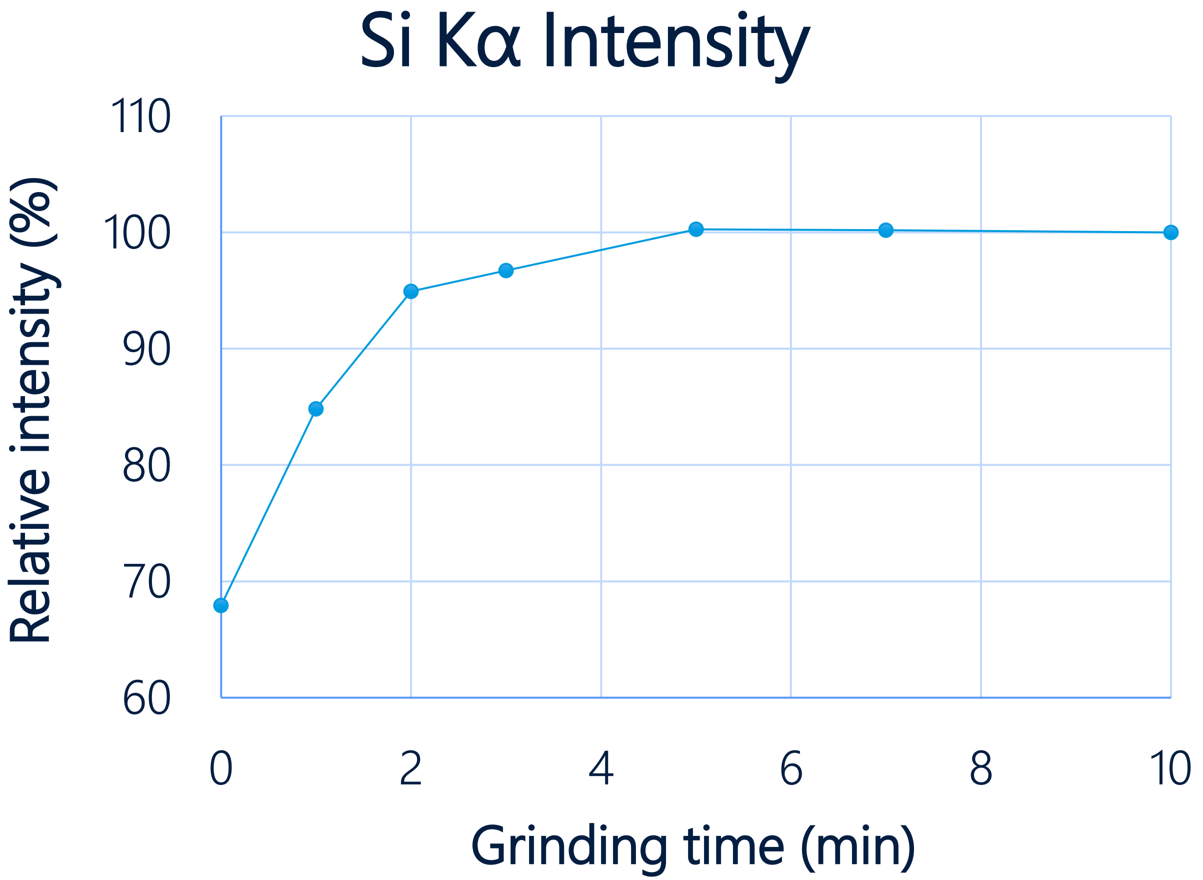
- **Grinding time 1 to 10 minutes**

- Constant pelleting parameters
- Constant XRF Parameters

Influence of grinding time



Influence of grinding time



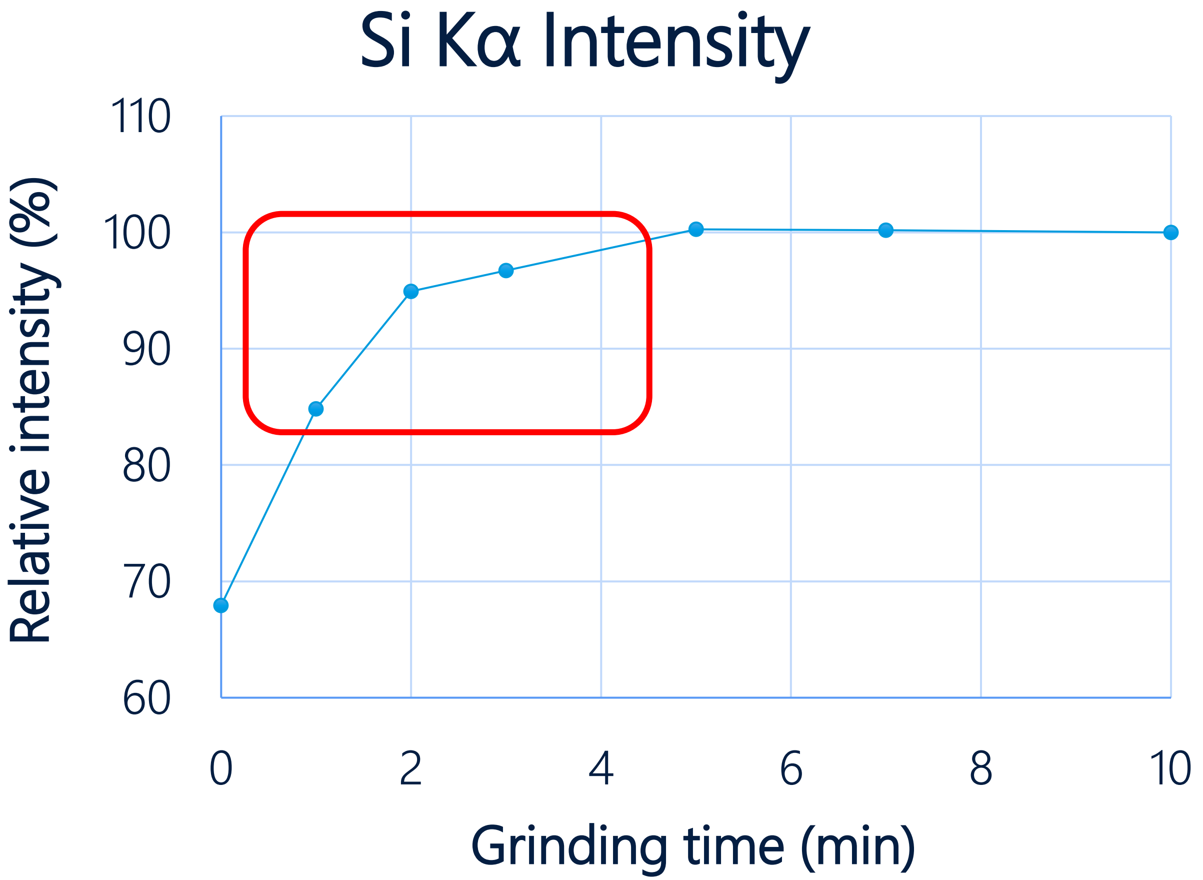
Observation

From 0 min to 10 min, the intensity increases by about half

The plateau (100 % relative int.) is reached after 5 minutes

Grinding too short can lead to a loss of intensity, after 1 min only 85 % relative Int. is reached

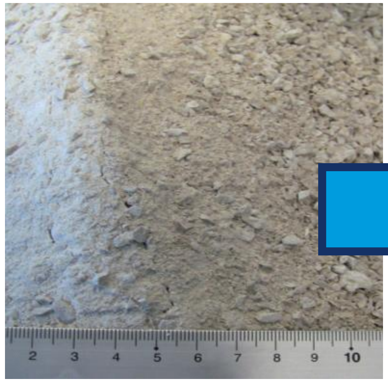
Influence of grinding time



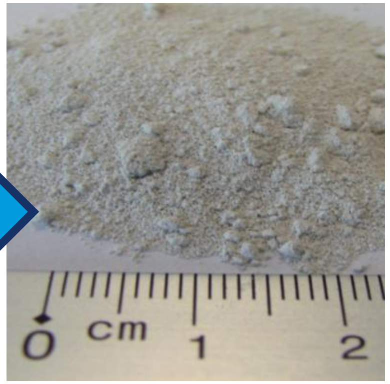
Recommendation

- Grind as long as necessary and as short as possible here 5 min
- Constant / Reproducible grinding time
  → Routine samples and calibration standards
- New sample preparation?
  → new calibration
- Use of programmable mills increases reproducibility

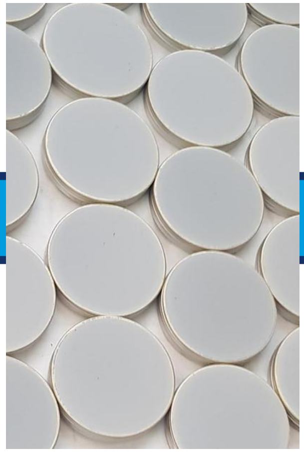
Influence of pressing pressure



Beispieldarstellung



Beispieldarstellung



- Sample limestone powder
- Element approx

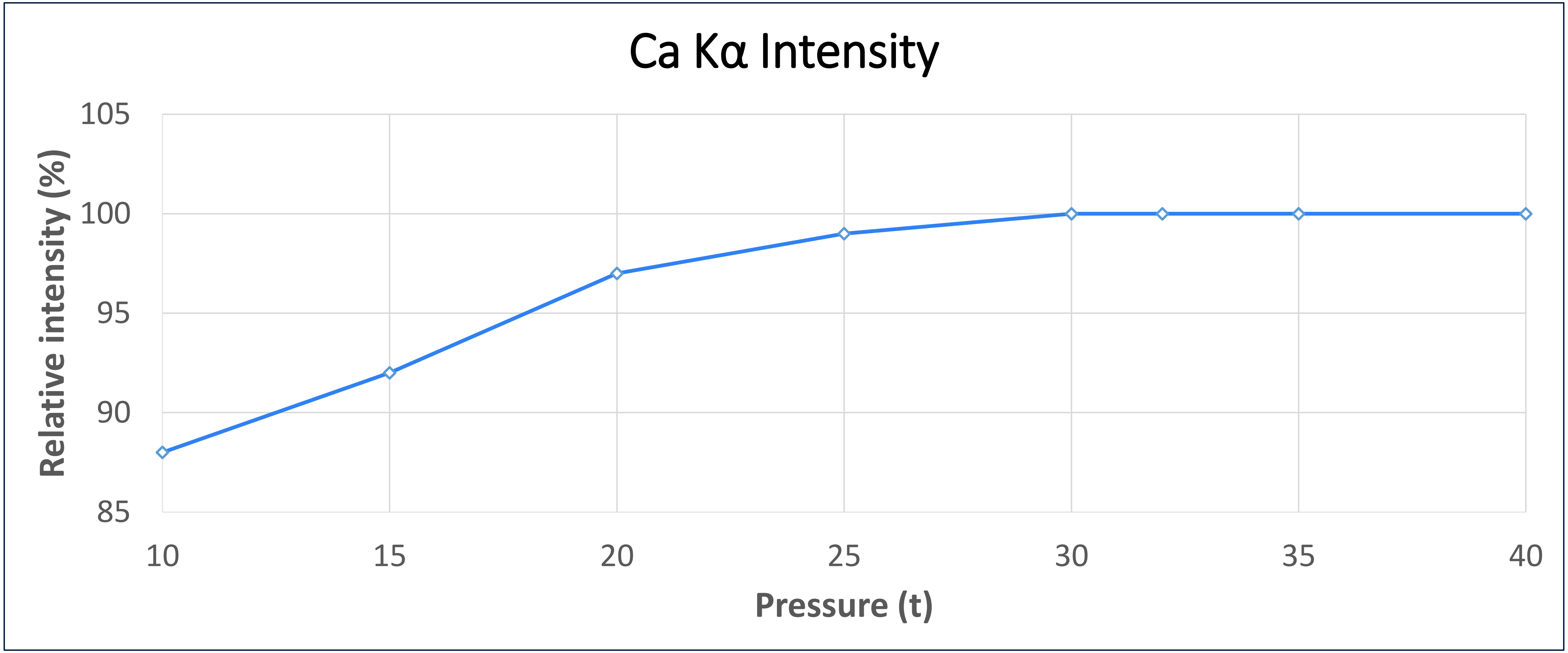
  Line Kα
- Disc Vibrating Disk Mill with Tungsten

  Carbide Vessel

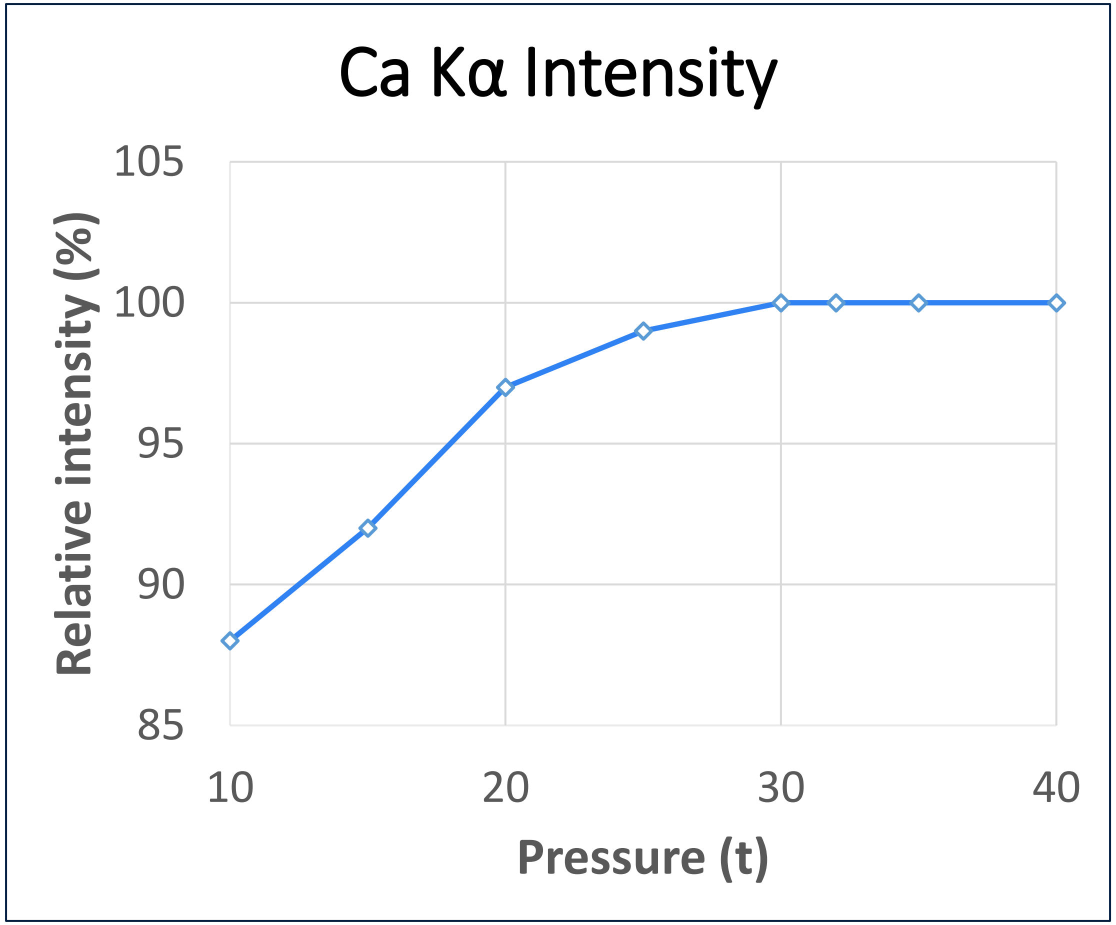
- **Press pressure 10 – 40 t**

- Constant grinding parameters
- Constant XRF Parameters

Influence of pressing pressure



Influence of pressing pressure



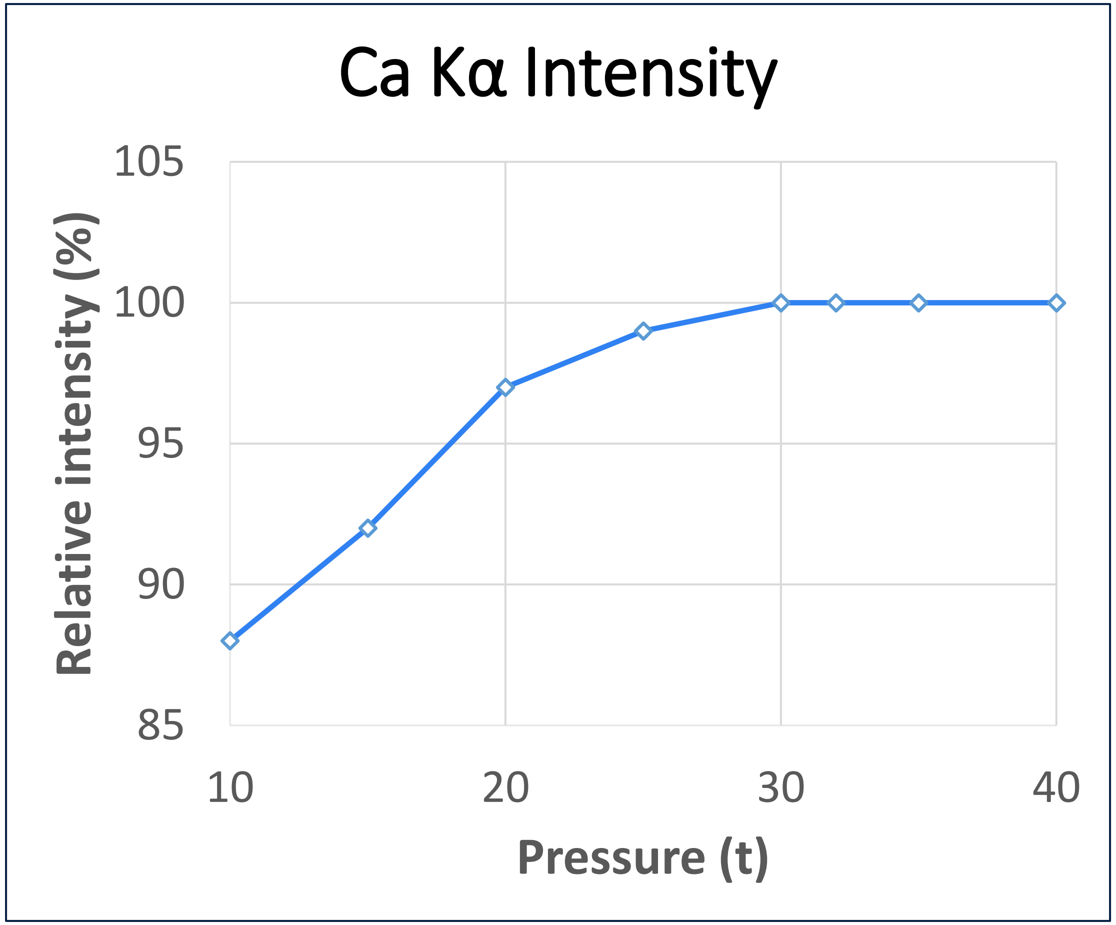
Observation

From 10 t to 40 t, the intensity increases by 12 % points

The plateau (100 % relative int.) is reached at 30 t

Pressing at too low a pressure can lead to a loss of intensity

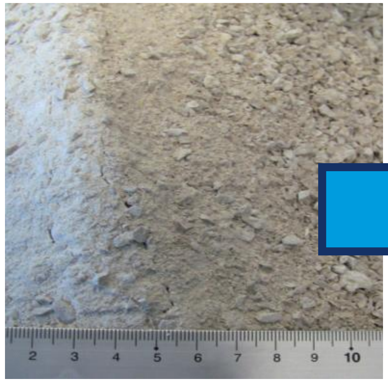
Influence of pressing pressure



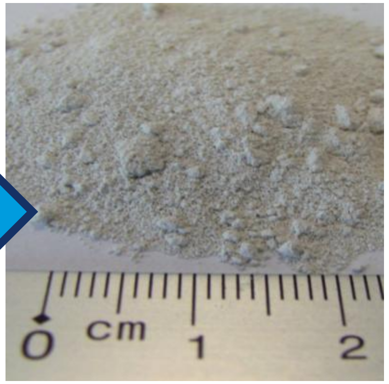
Recommendation for action

- Urgent consideration of pelleting parameters in method development
- When only a smaller press is available, reproducibility is even more important
- Use of programmable presses increases reproducibility

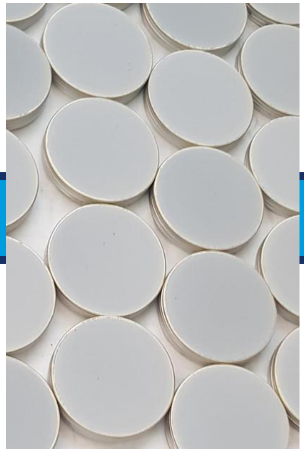
Influence of particle size on calibration



Beispieldarstellung



Beispieldarstellung



- Sample clay
- Element Al as Al2O3

  Line Kα
- Disc vibrating mill with

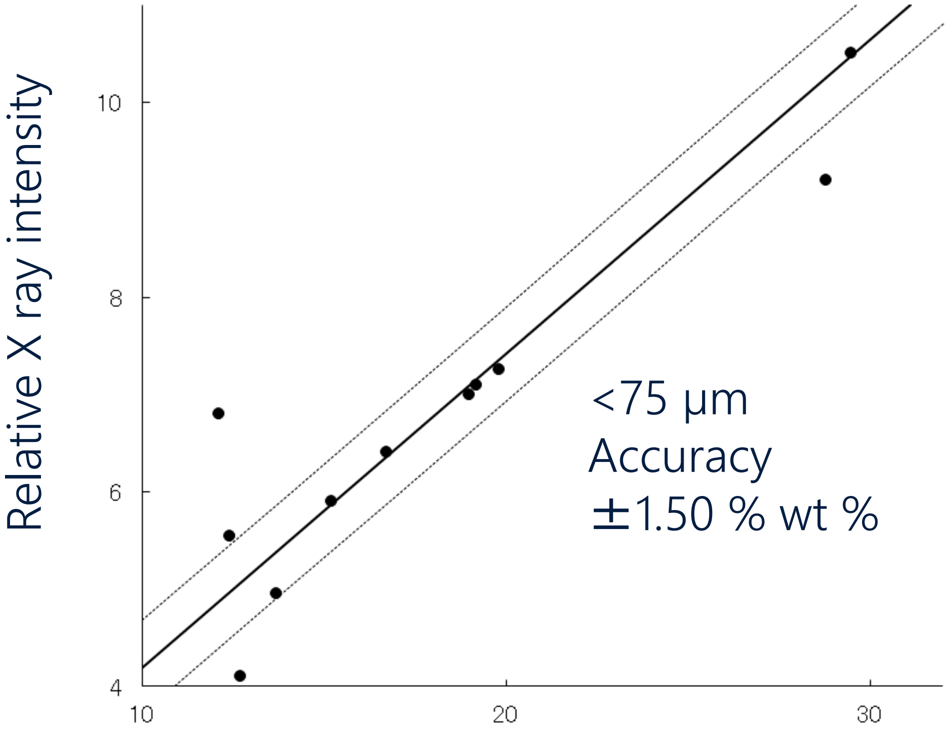
- **Standard Set A < 75 µm**

  Standard Set B < 44 µm

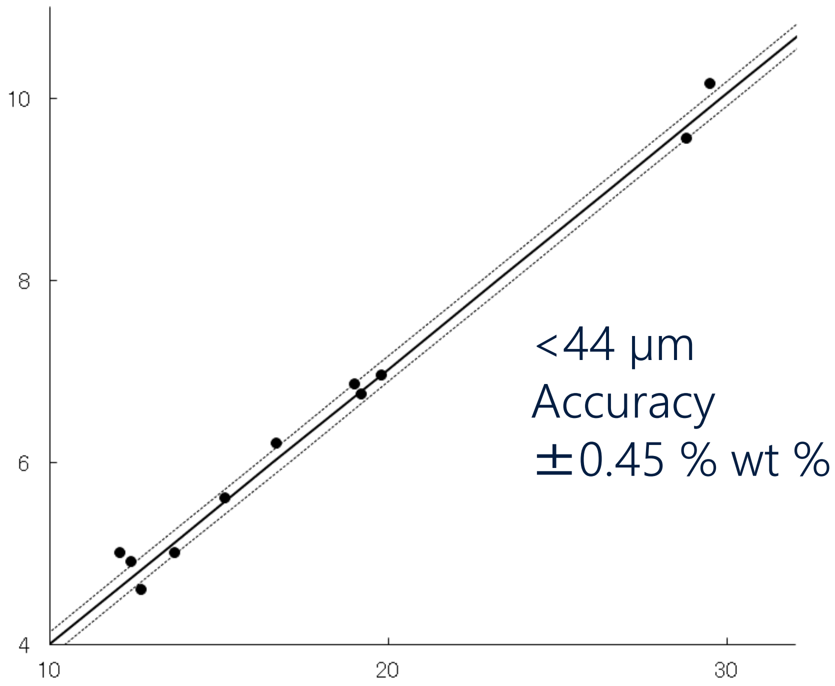
- Constant pelleting parameters
- Constant XRF Parameters

Influence of particle size on calibration

Standardset A

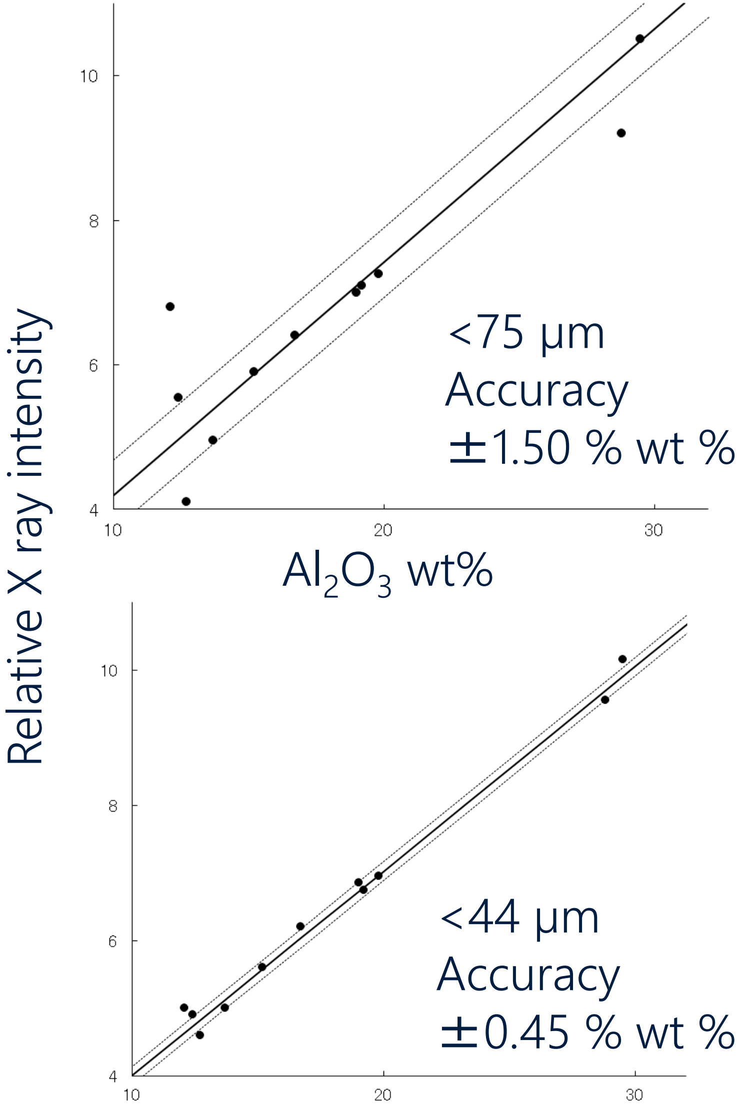


Standardset B



Al_2O_3 wt%

Influence of particle size on calibration



Observation

The dispersion of the calibration standards depends largely on the particle size

Recommendation for action

Optimizing the grind size can drastically improve the accuracy of a method

→ Shorter XRF measurement time possible

Summary – Grind & XRF

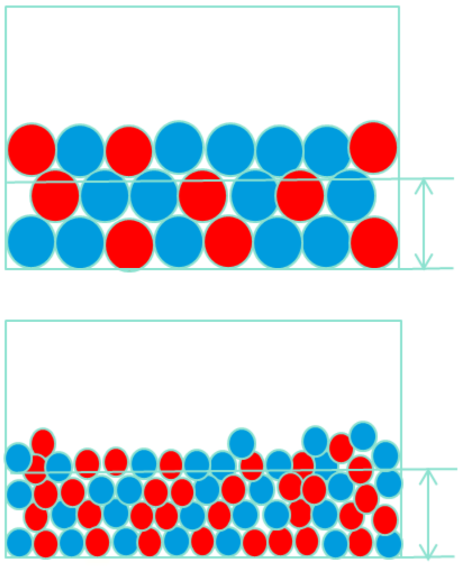
- The shape of the sample influences the measurement result

  particle size (and distribution), preparation, etc.

- Method parameters include sample preparation

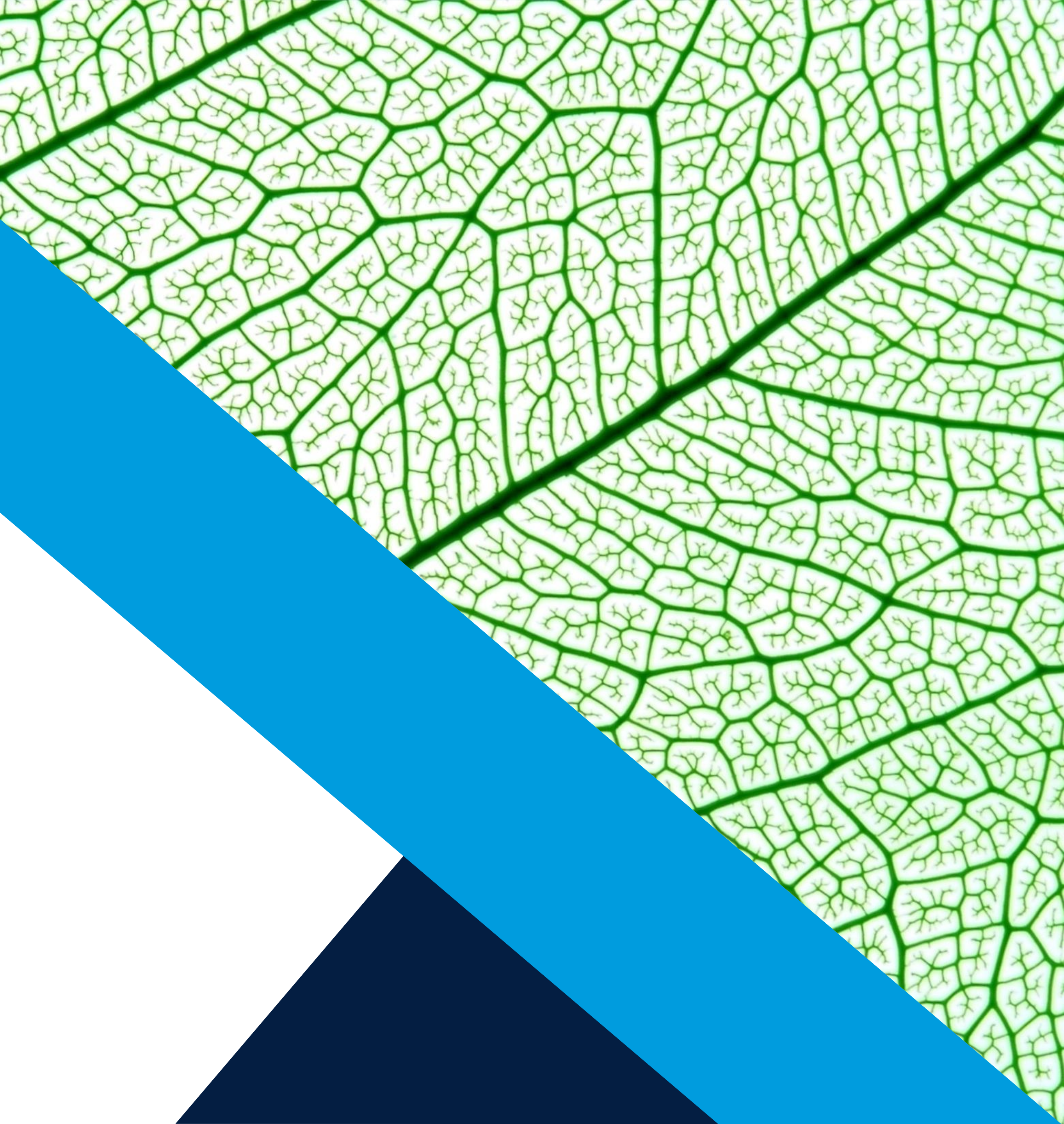
- Parameter optimization in sample preparation means recalibration

- Reproducibility of sample preparation is a priority



Influence of particle size on the XRF result

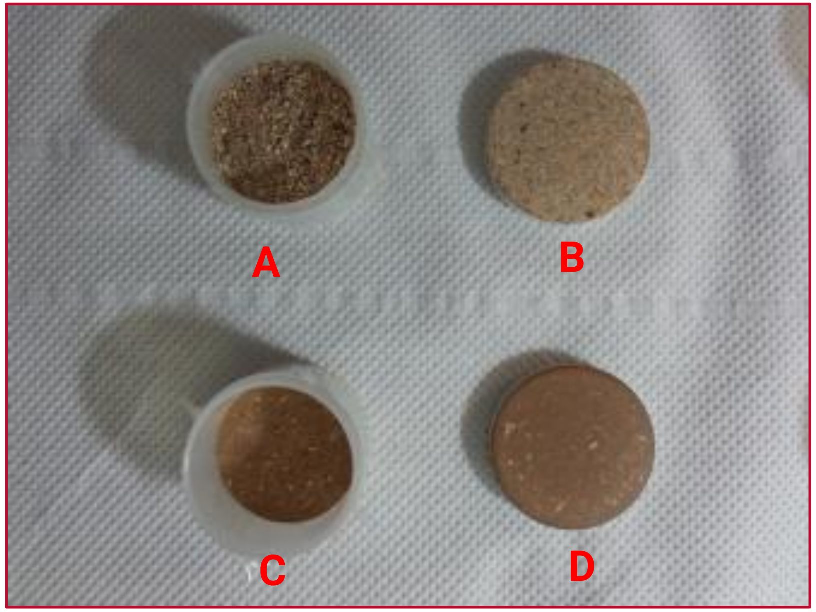
On the example of waste wood

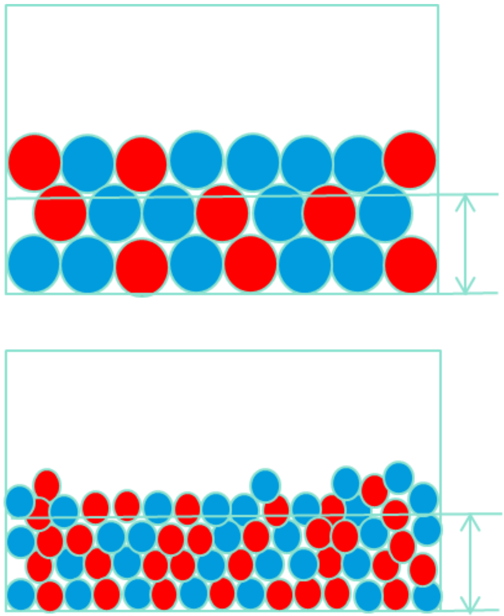


Analysis of wood samples

SM 300

PM 400





(A) Powder pouring after 1st grinding (e.g. SM 300)

(B) Pellet from powder of the 1st grinding step

(C) Powder pouring after 2nd grinding (e.g. PM 400)

(D) pellet made of powder of the 2nd grinding step

Always dry biological samples well and store them in a dry place!

- Water absorbs and scatters
- Strength of pellets impaired

Analysis of wood samples

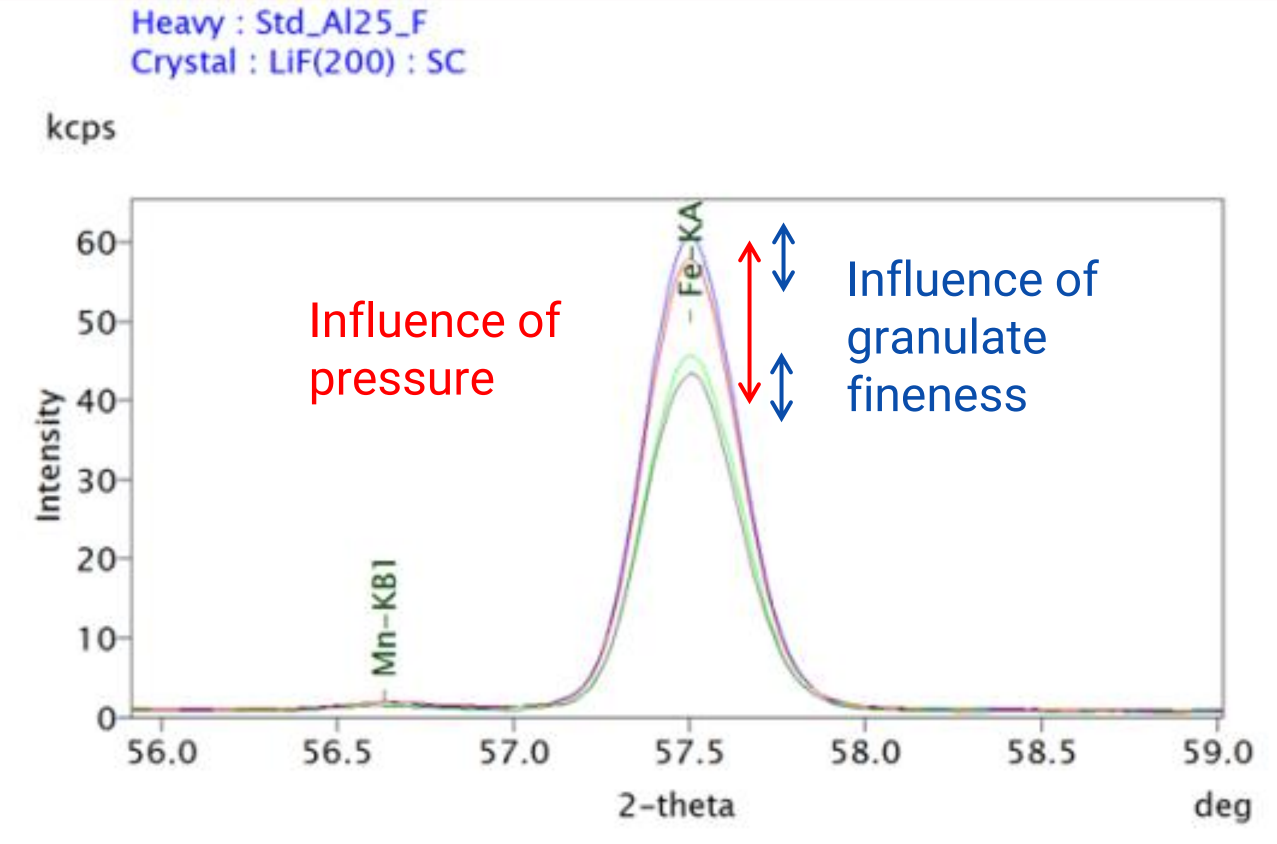
Heavy element (Fe)

(D) Pellet fine

(B) Pellet coarse

(C) Powder fine

(A) Powder coarse



Analysis of wood samples

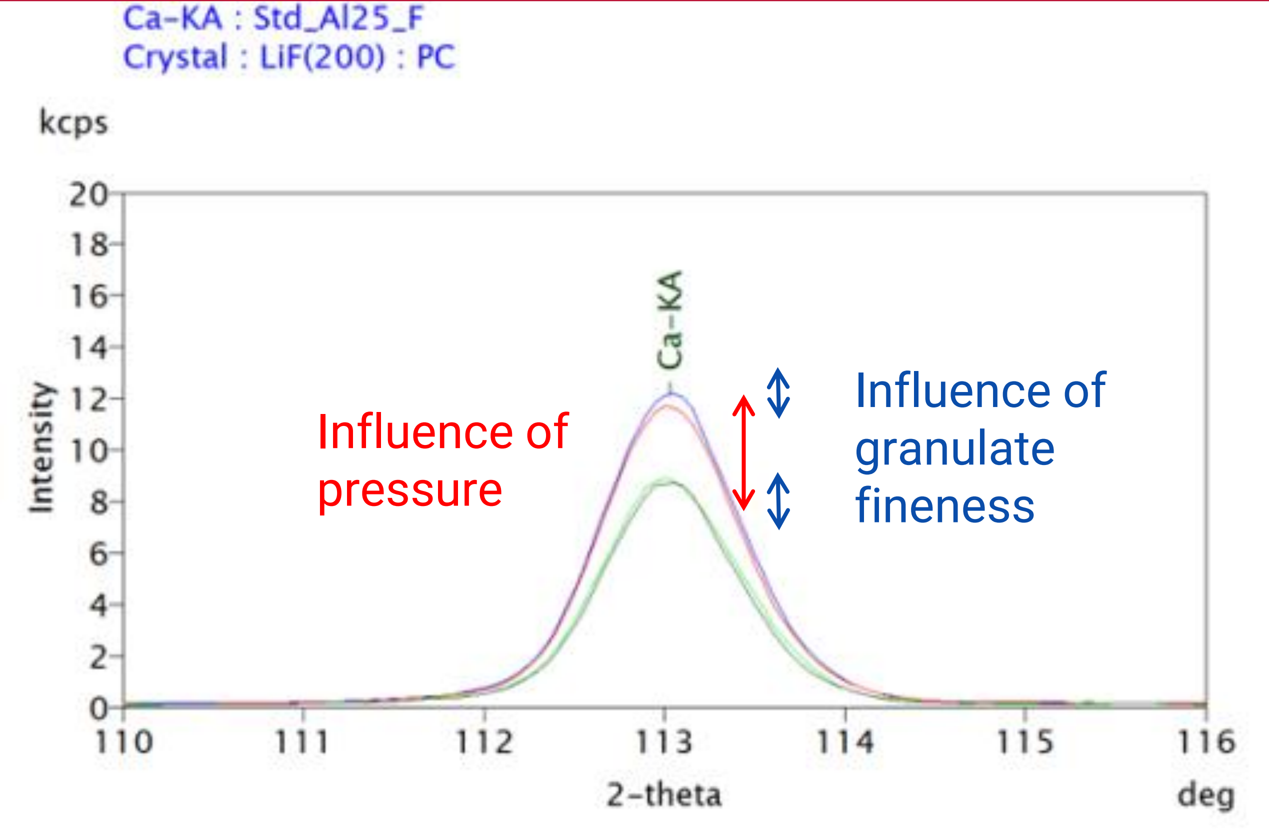
Medium element (Ca)

(D) Pellet fine

(B) Pellet coarse

(C) Powder fine

(A) Powder coarse



Analysis of wood samples

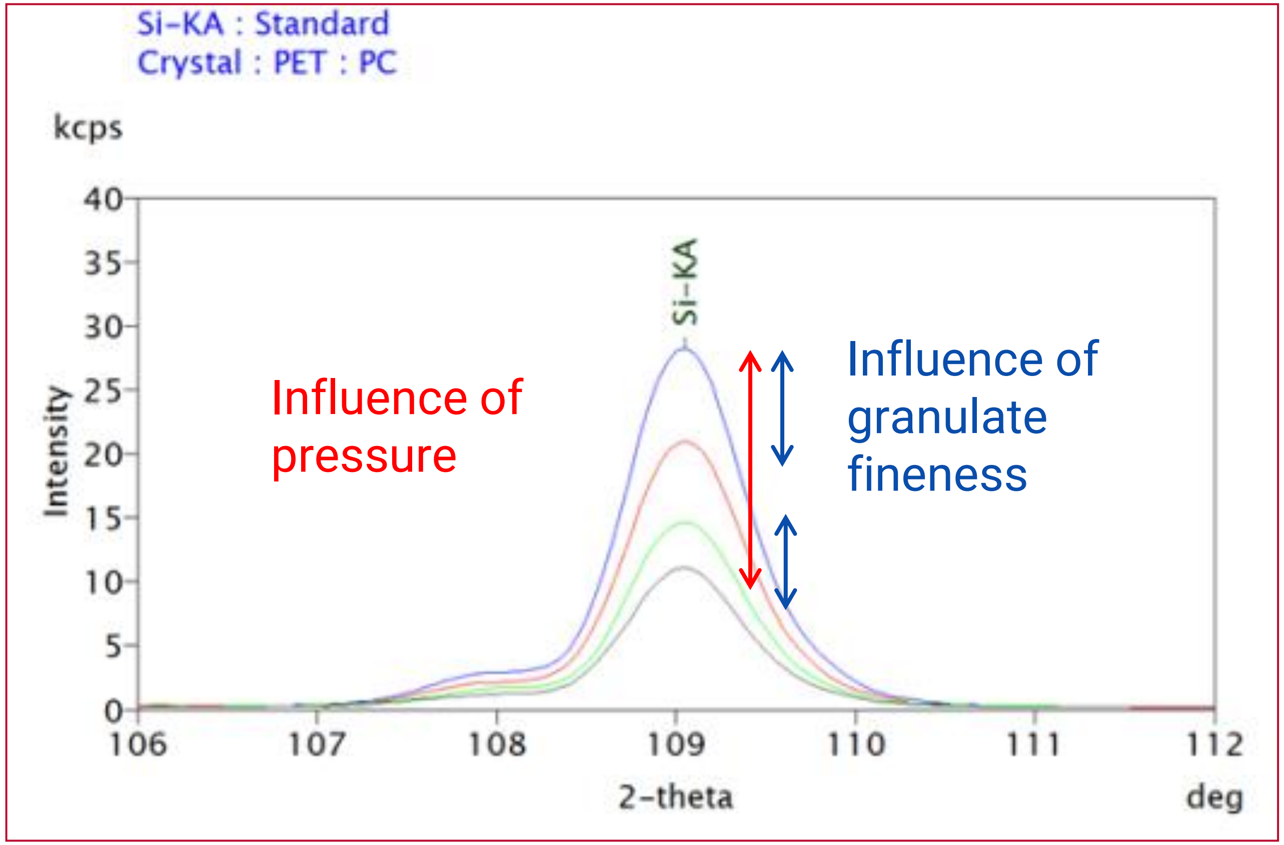
Light element (Si)

(D) Pellet fine

(B) Pellet coarse

(C) Powder fine

(A) Powder coarse



Analyse of wood chips

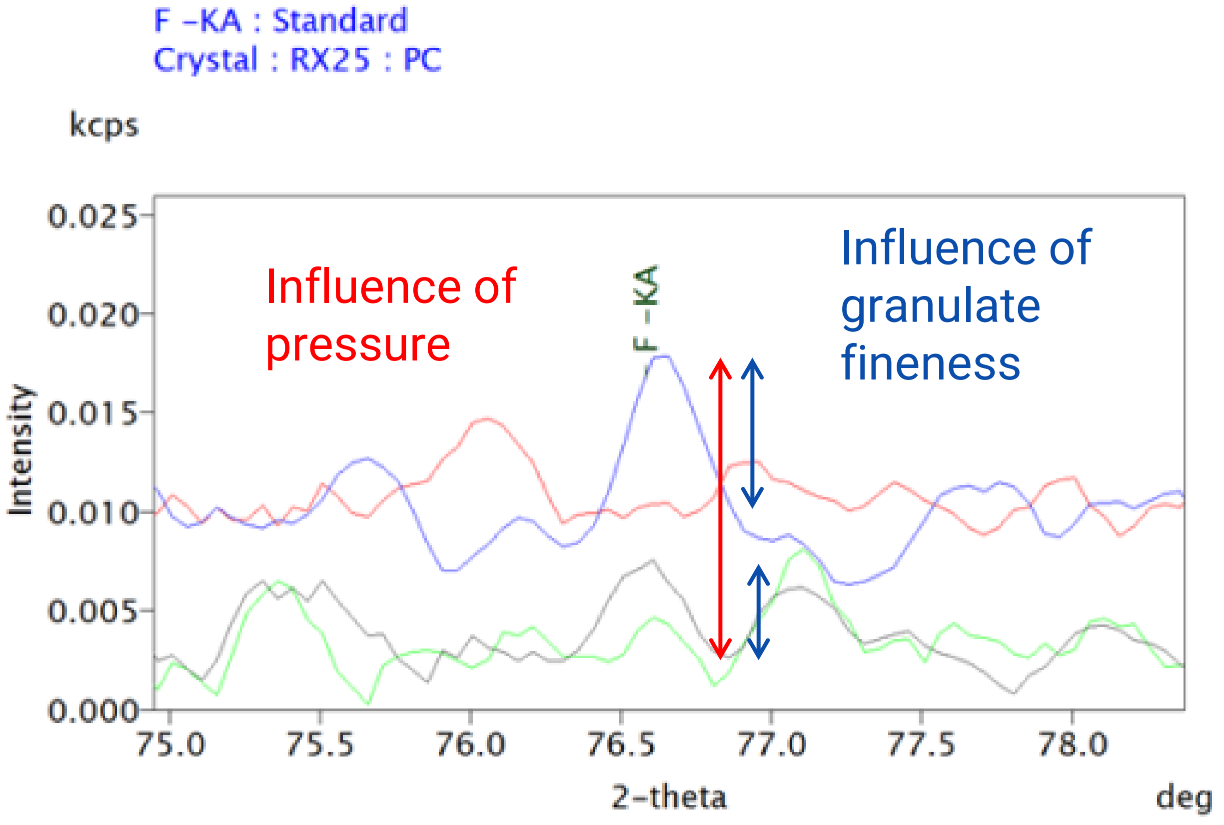
Very light element (F)

(D) Pellet fine

(B) Pellet coarse

(C) Powder fine

(A) Powder coarse



Summary – Organic Fiber Materials

Signal intensity

- Fine powder & compact pellets, high signal intensity
- For lower detection limits, see F-analysis
- Reproducibility is a priority

Abrasion

- Finer powder = more intensive grinding = more abrasion
- Hard metal phases can reduce abrasion
- Which abrasion is the least interfering

→ Abrasion is unavoidable

Questions to the Influence of particle size?