Rigaku Retsch Workshop

Content

XRF Theory and the influence of sample preparation on the analytical results

Particle size effect on the analytical results

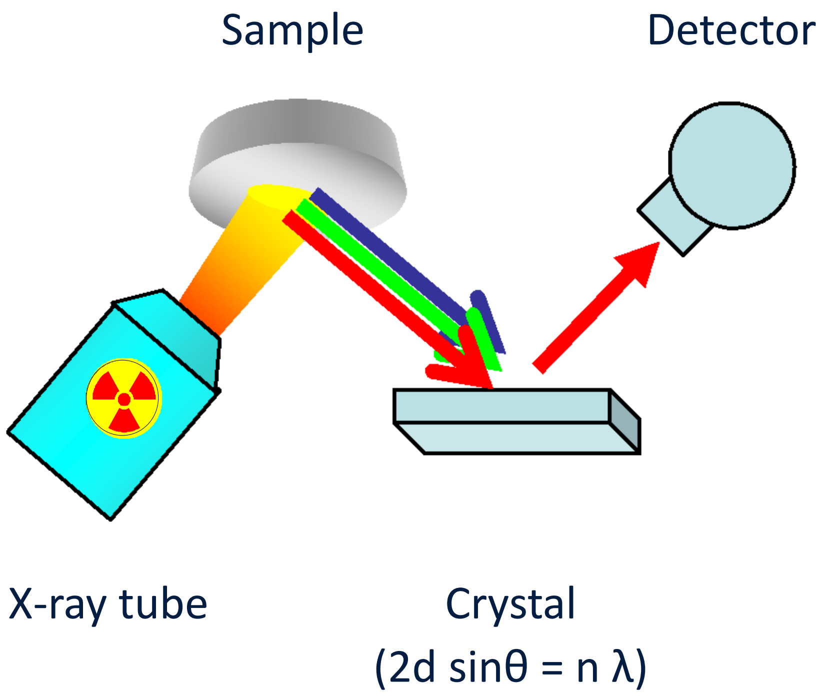
Grain size effect on the accuracy of a calibration

Influence of pressing on the analytical results

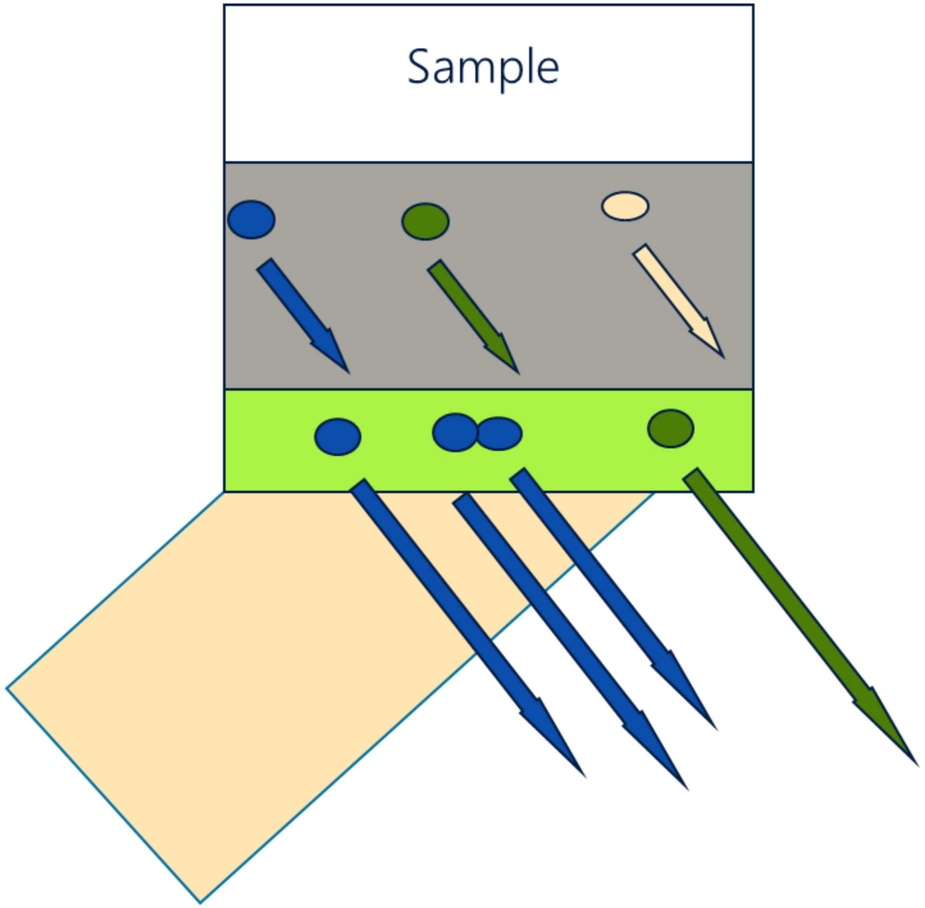
Best practices to ensure the sample preparation is consistent

Influence of sample preparation on analytical results

XRF



WDX Spectrometer



Penetration depth

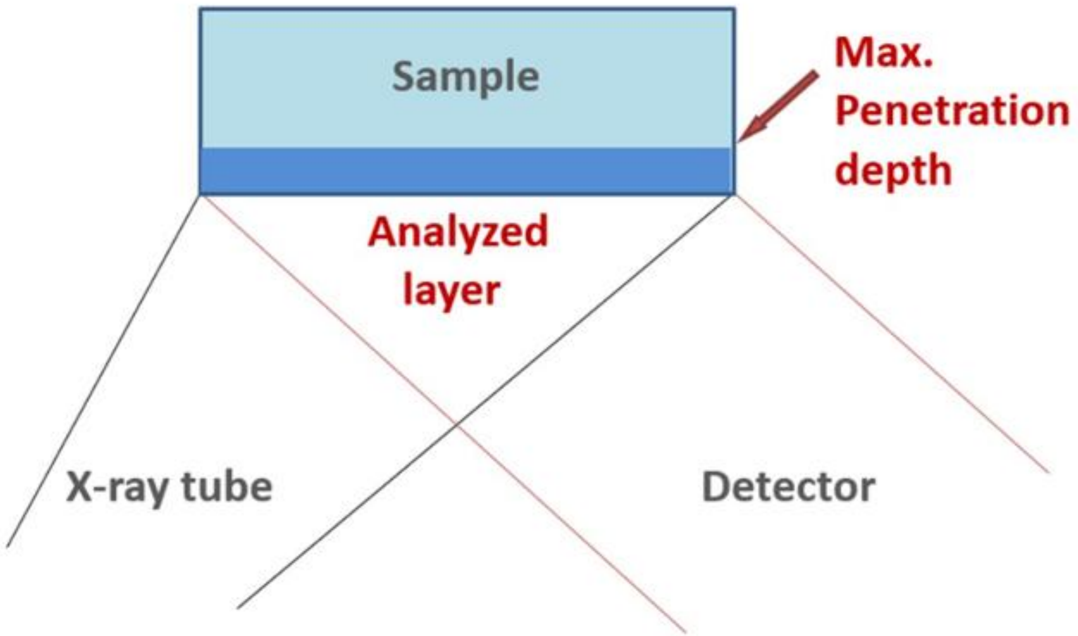


Fig. 34 A maximum penetration depth, depending on the energy of the fluorescence radiation, exists for each element [courtesy of Dr. Reinhold Schlotz].

Table 11 Maximum penetration depth of single elements depending on the sample matrix. Assumption 0.1% intensity rest or penetration is valid for 99.9% intensity .

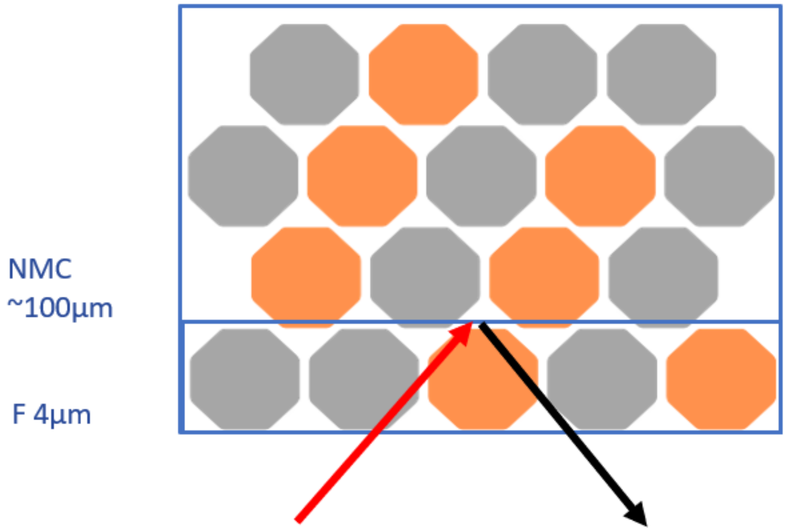
Element line	Graphite	SiO_2	Fe	Pb
B Ka	5 µm	1 µm	0,3 µm	1 µm
Cr Ka	2,2	263	77	10
Mn Ka	2,8	338	96	12
Fe Ka	3,6	430	119	15
Co Ka	4,5	541	146	18
Ni Ka	5,7	675	23	22
Cu Ka	7,1	838	28	26
W La	8,0	949	31	29
Zn Ka	8,7	1 mm	33	32
Au La	1,2 cm	1,5	46	42
Ge Ka	1,3	1,5	48	44
Pb La	1,5	1,9	57	52
Zr Ka	4,4	6,0	176	43
Mo Ka	5,5	8,0	234	47
Rh Ka	7,3	1,2 cm	355	70
Ag Ka	8,5	1,6	460	89
Ba Ka	13,1	4,0	1,3 mm	242

Element	Graphite	SiO_2	Fe	Pb
Si Ka	72µm	40µm	4µm	3µm
Fe Ka	3,6mm	430µm	119µm	15µm
Zr Ka	4,4cm	6,0mm	176µm	43µm

Particle size effects , penetration depth

Loose powder, pressed pellet

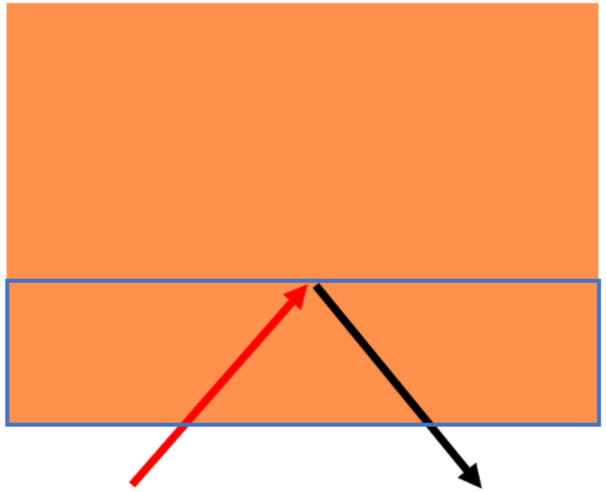
particle size effects…



Black mass particle size ca. 100µm

Fused bead, powder desolved into glass

No particle size effects…



Black mass fused into glass

Penetration depth

Component	Line	Concentration [%]	Energy [keV]	Layer thickness [µm]
Fe2O3	Fe KA1	0.722	6.40	174
MnO	Mn KA1	0.016	5.89	139
TiO2	Ti KA1	0.016	4.51	66
CaO	Ca KA1	30.120	3.69	104
K2O	K KA1	0.103	3.31	77
SO3	S KA1	0.000	2.31	27
P2O5	P KA1	0.004	2.01	19
SiO2	Si KA1	1.130	1.74	13
Al2O3	Al KA1	0.277	1.49	8
MgO	MG KA1	21.030	1.25	7
Na2O	Na KA1	0.029	1.04	4
CO2		46.370		

The following applies particularly to light elements:

Average particle size ≈ layer thickness

(typical particle size varies between 40 – 150 µm)

Layer thickness from which at least 90% of the intensity originate.

Pressed powder without a binder

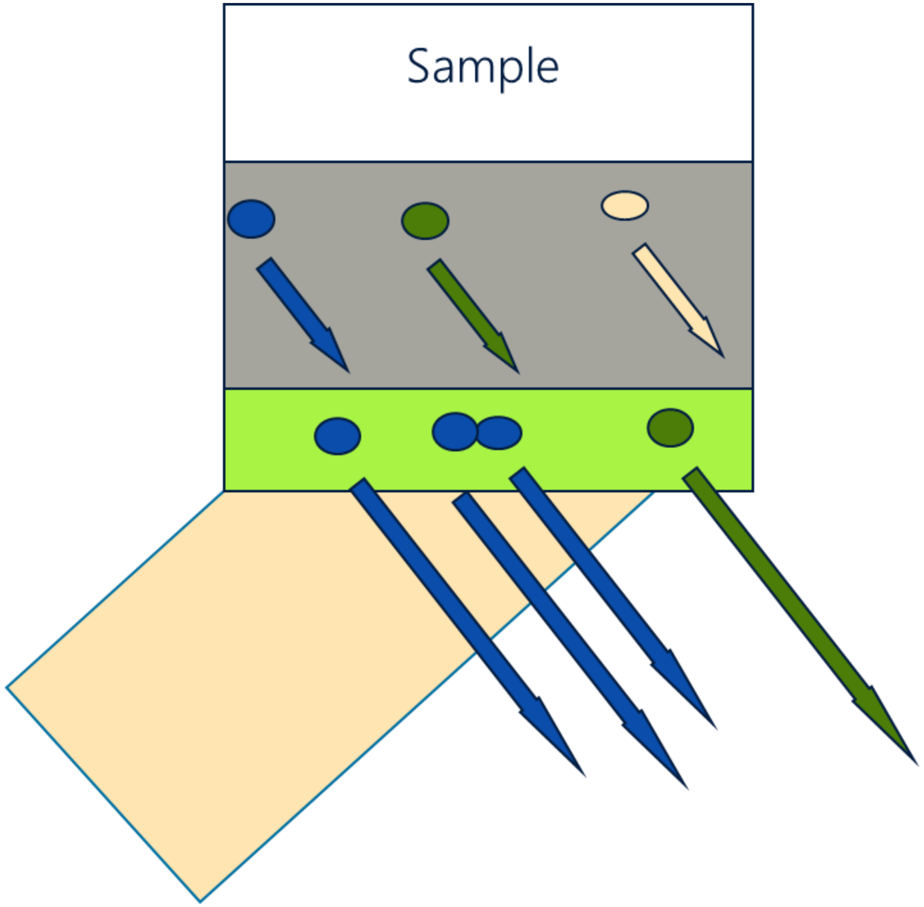
CRM STD NBS 88b Dolomite

XRF

Pressed powder

- Sample surface analyzed
  - Information depth depends on sample matrix & element
  - nm to µm to cm

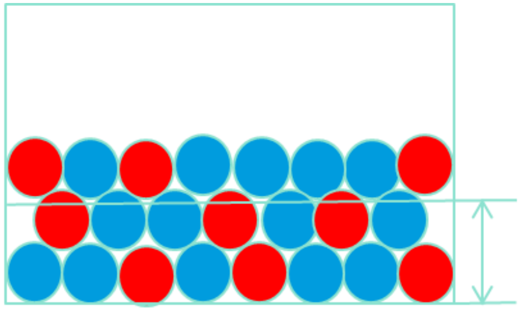
Homogenous sample needed

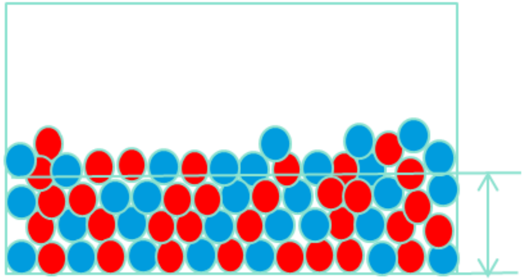


XRF

Pressed powder

- XRF is a relative method
    - Calibration needed
- Focus on powder samples
- Intensities depend on particle sizes





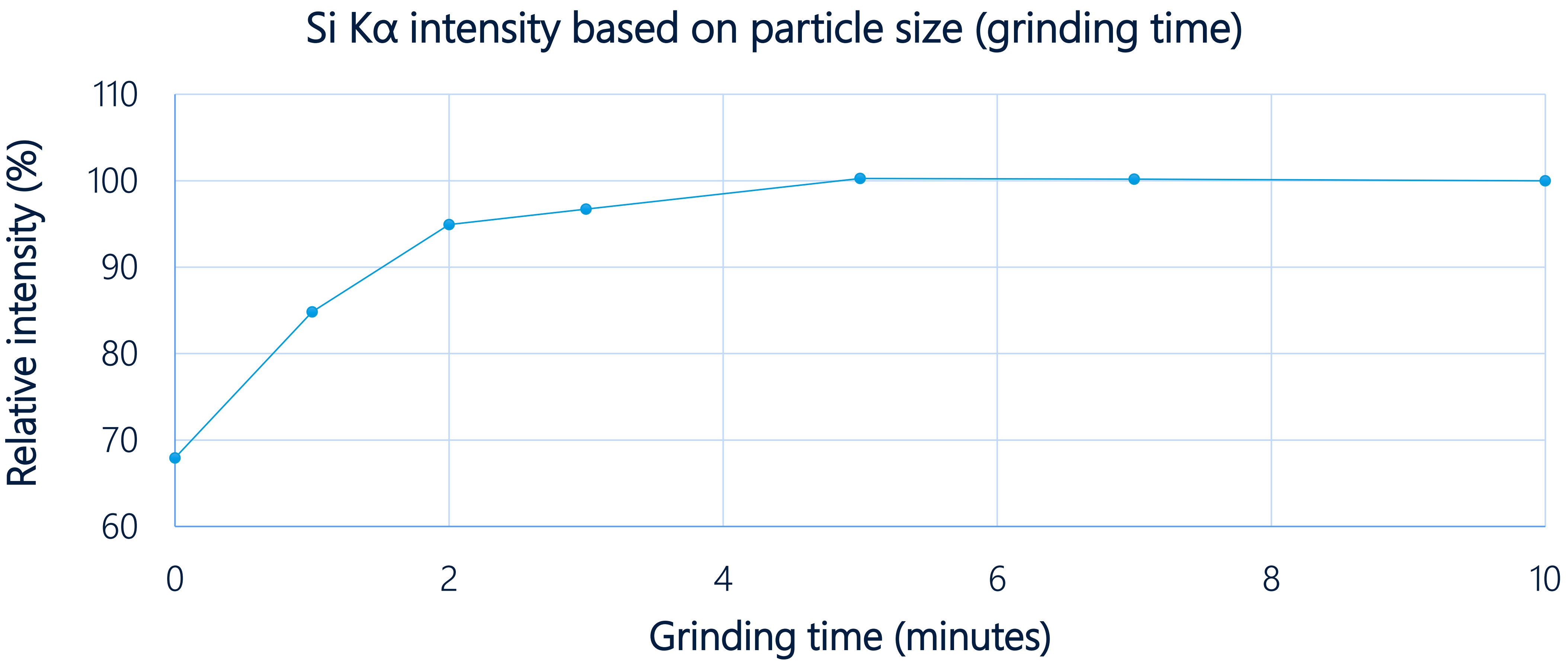
XRF

Example – particle size effects

- Sample Limestone powder
- Element Si Kα
- Vibratory disc mill- tungsten carbide vessel
- grinding times 1 to 10 minutes
- Constant pelletizing parameters
- Constant XRF parameters
- Relative intensities

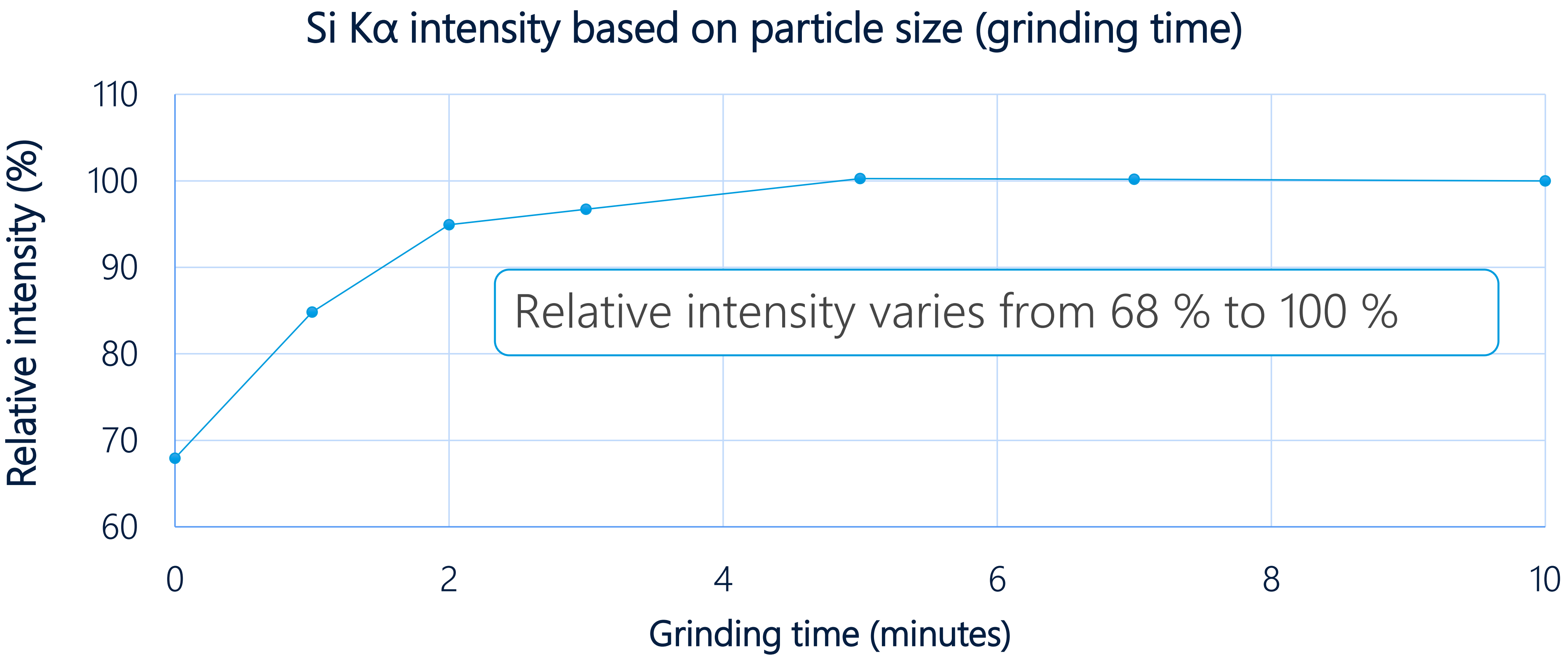
Influence of Sample preparation

Example – particle size effects



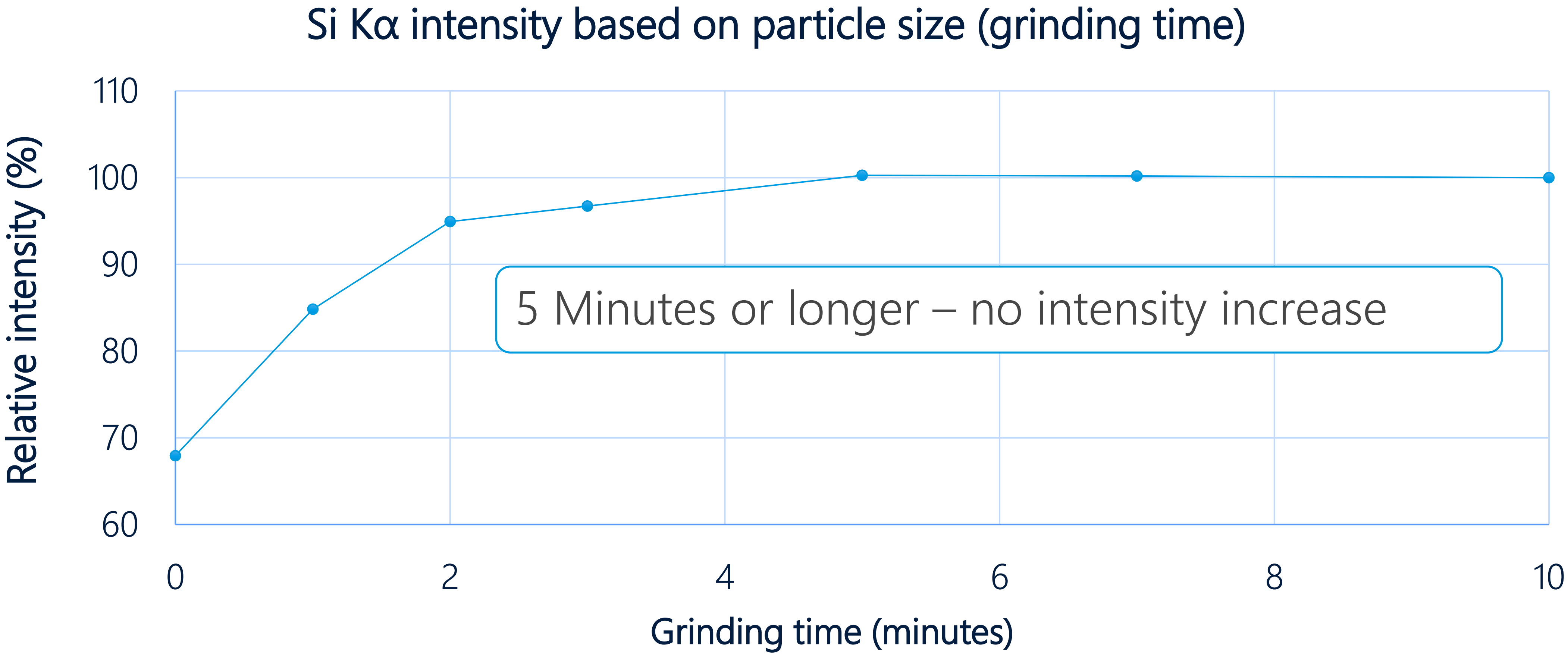
Influence of Sample preparation

Example – particle size effects



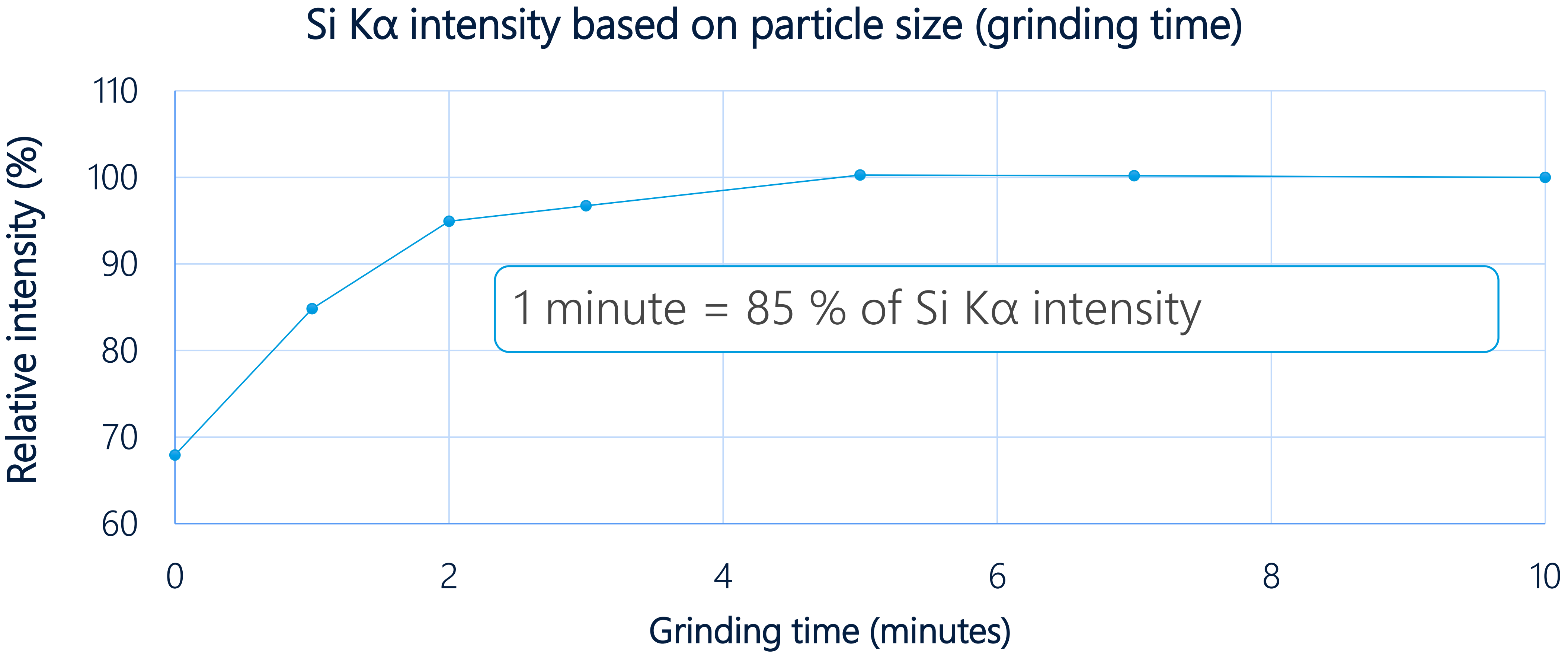
Influence of Sample preparation

Example – particle size effects



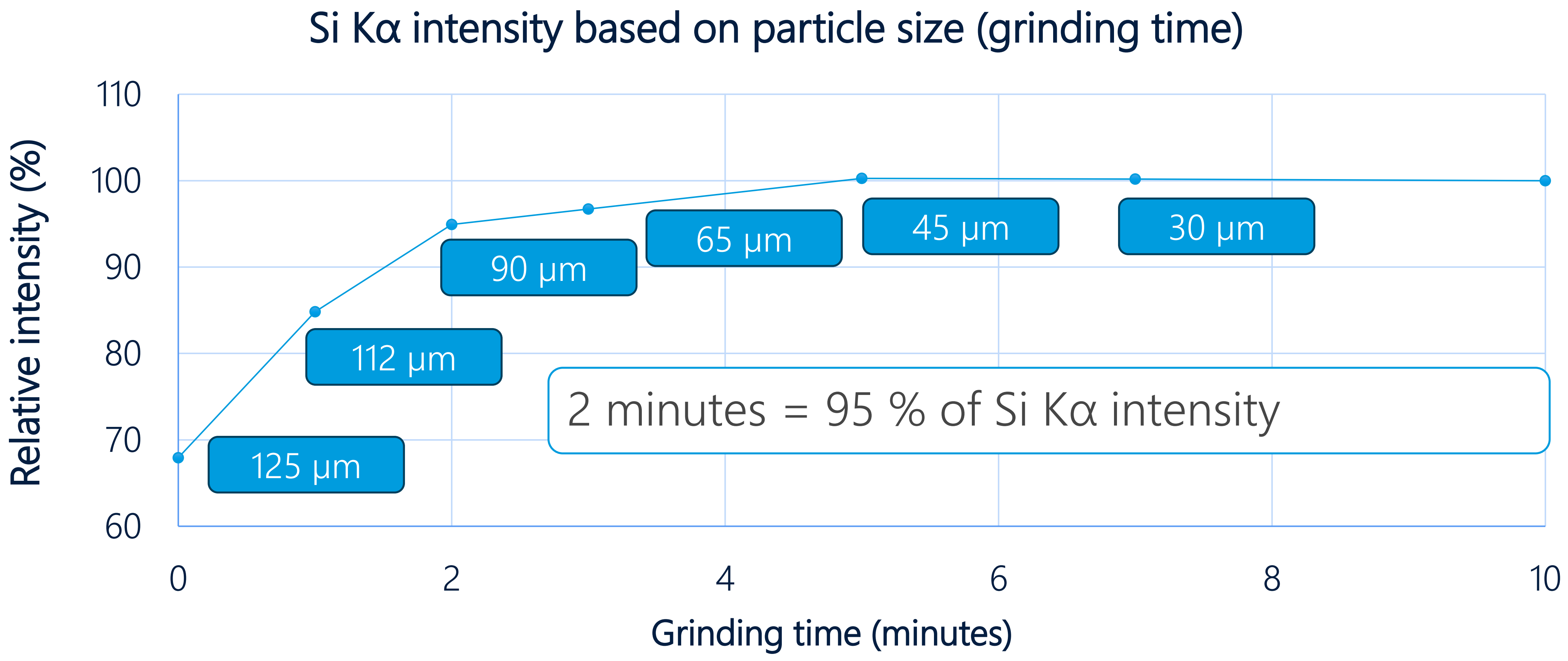
Influence of Sample preparation

Example – particle size effects



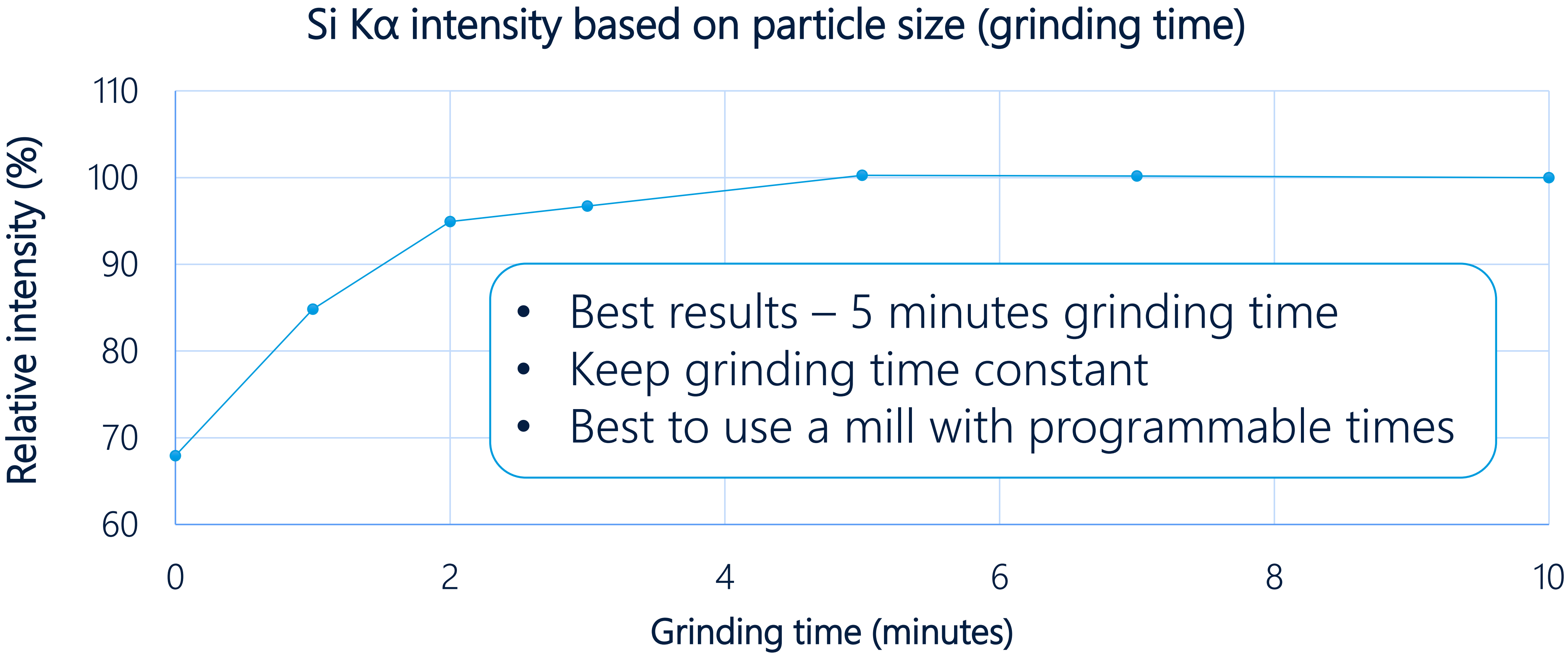
Influence of Sample preparation

Example – particle size effects



Influence of Sample preparation

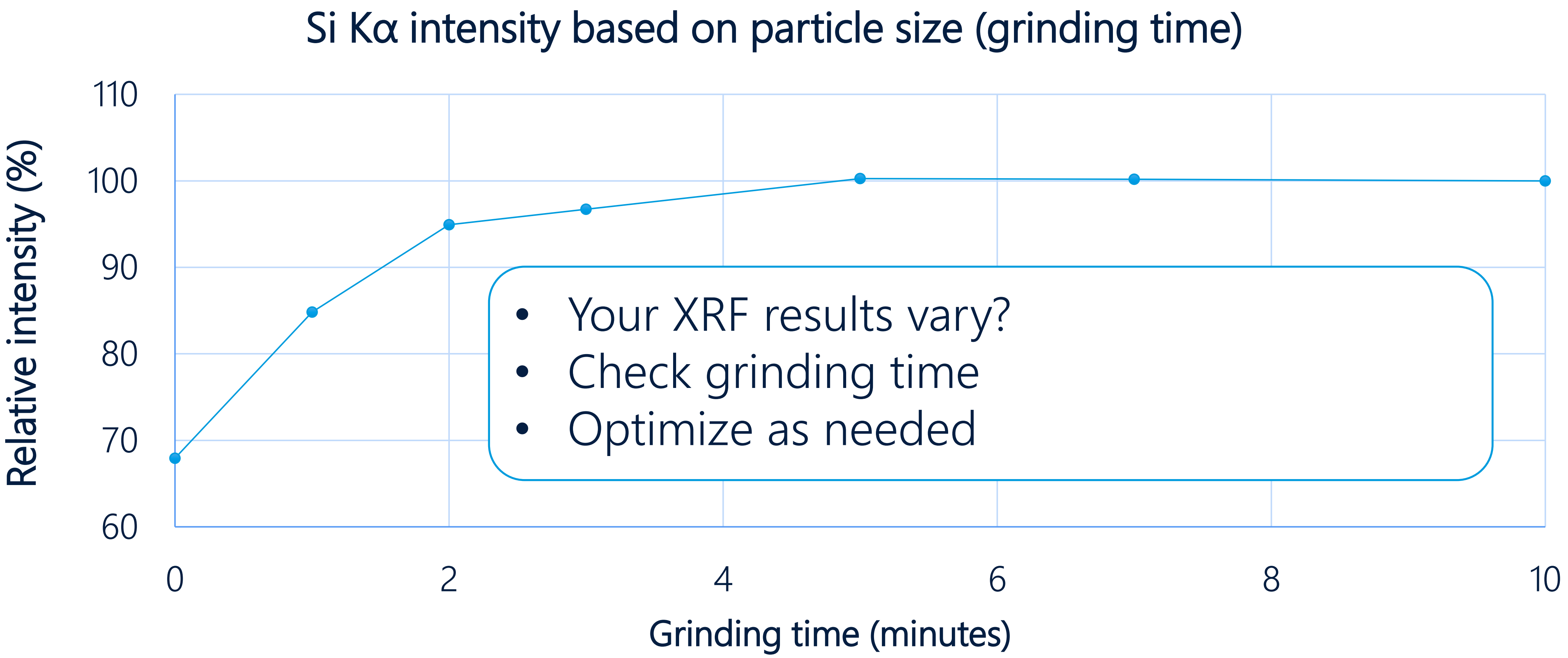
Example – particle size effects



- Best results – 5 minutes grinding time
- Keep grinding time constant
- Best to use a mill with programmable times

Influence of Sample preparation

Example – particle size effects



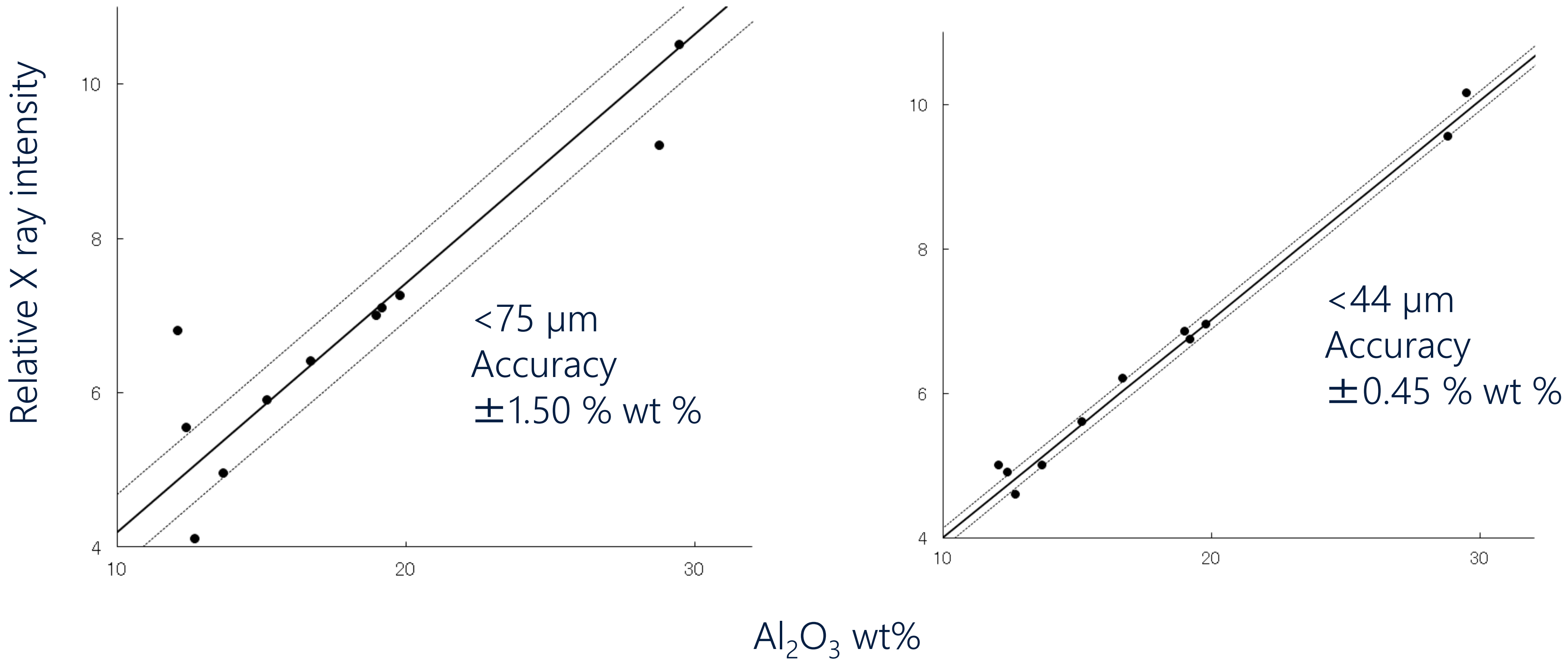
XRF

Example – Grain size effect on the accuracy of a calibration

- Sample - Clay
- Compound Al_2O_3
- Swing mill
- Standard Set A <75 µm
- Standard Set B <44 µm
- Constant pelletizing parameters
- Constant XRF parameters
- Calibration

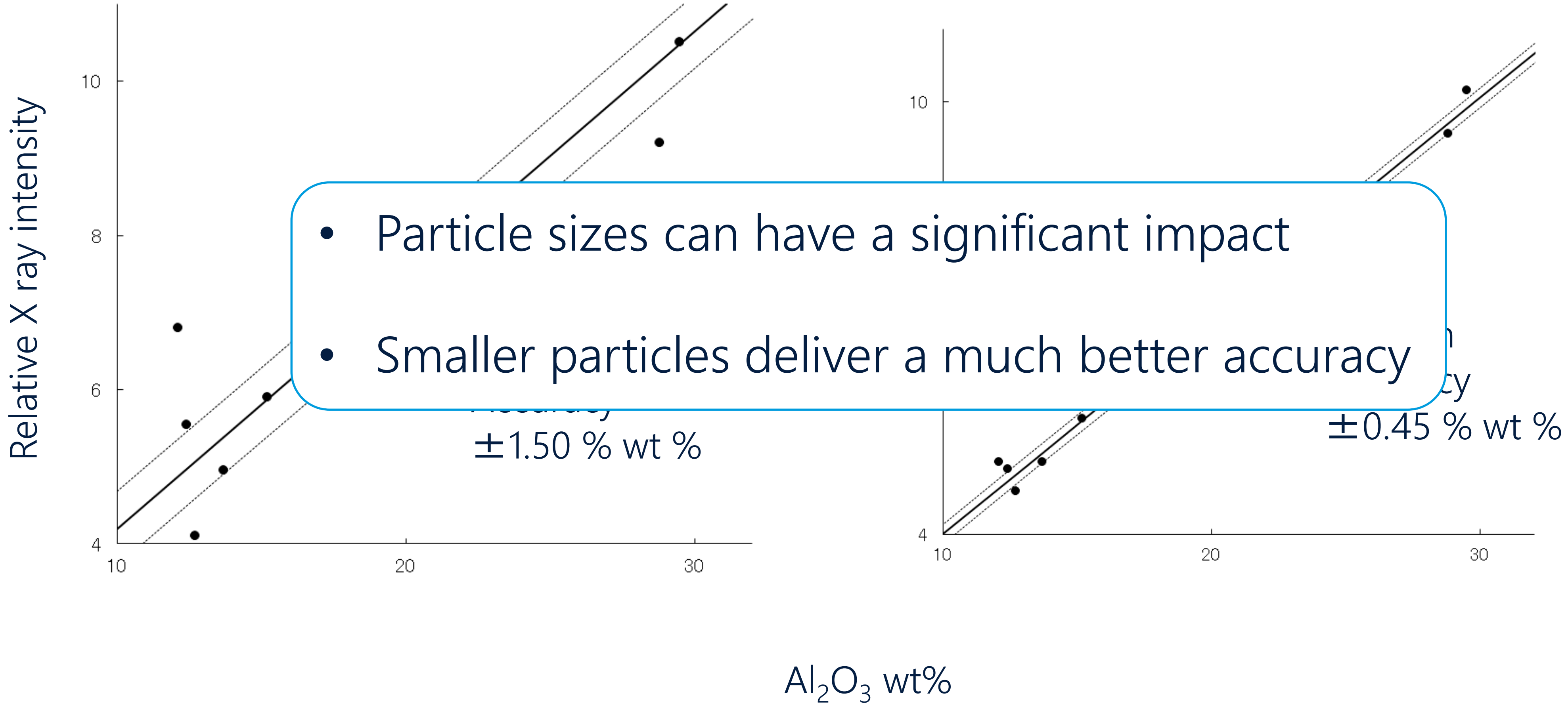
INFLUENCE OF SAMPLE PREPARATION

Example – Grain size effect on the accuracy of a calibration



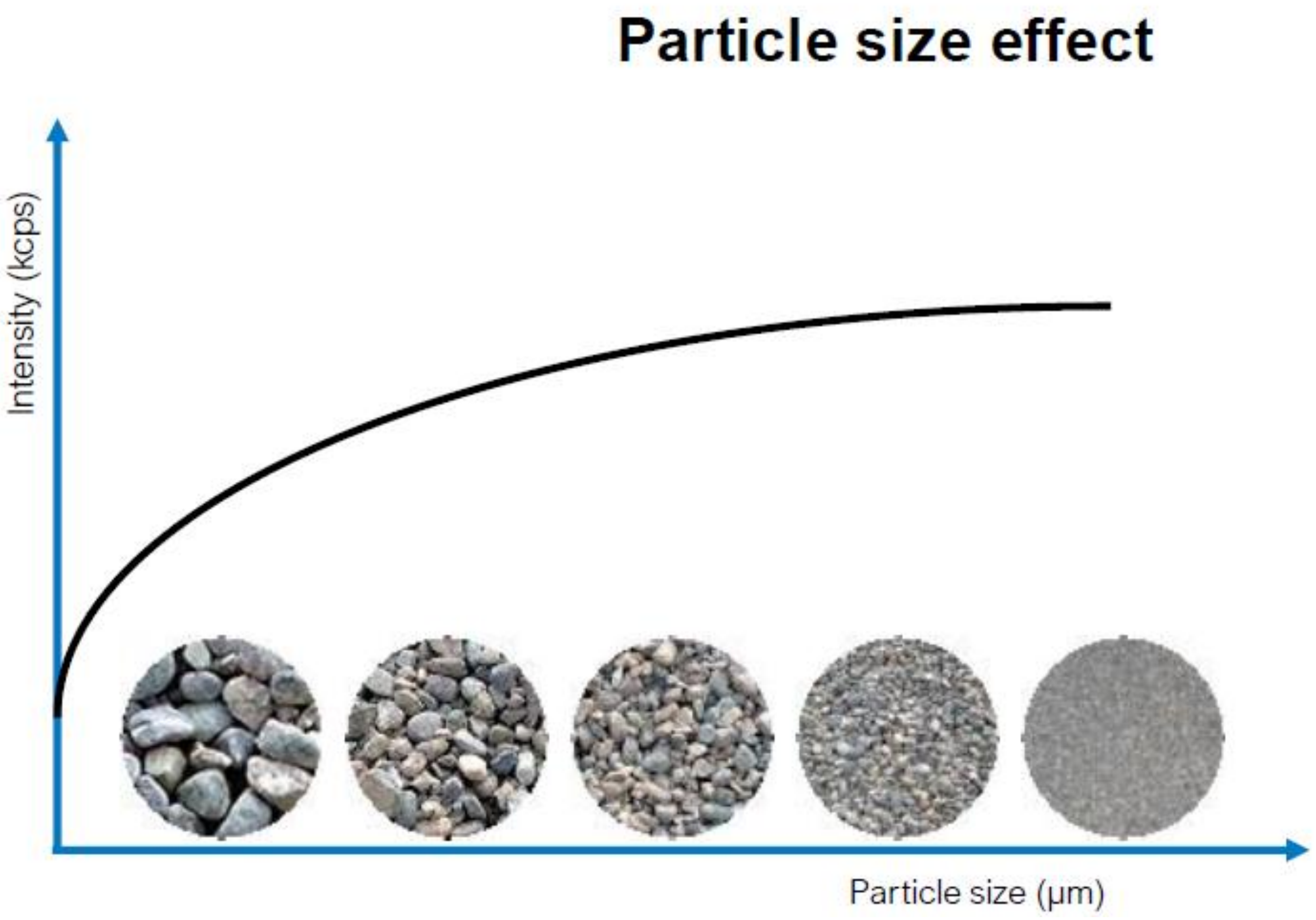
Influence of sample preparation

Example – Grain size effect on the accuracy of a calibration



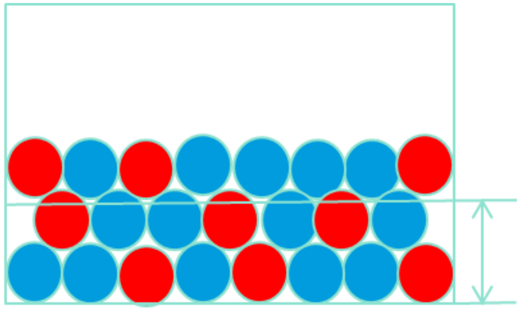
- Particle sizes can have a significant impact
- Smaller particles deliver a much better accuracy

Particle size effect on the intensity



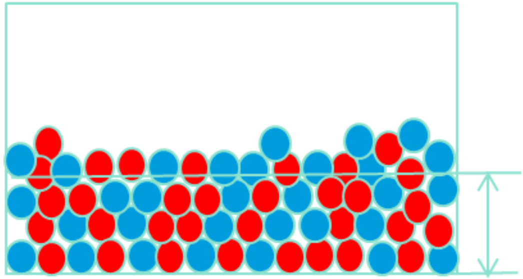
XRF

- Relative method
  - Calibration needed
- Focus on powder samples
- Intensities depend on particle sizes
- Intensities depend on pressure



Larger grain sizes

Lower intensities



Smaller grain sizes

Higher intensities

Higher pressure

Higher intensities

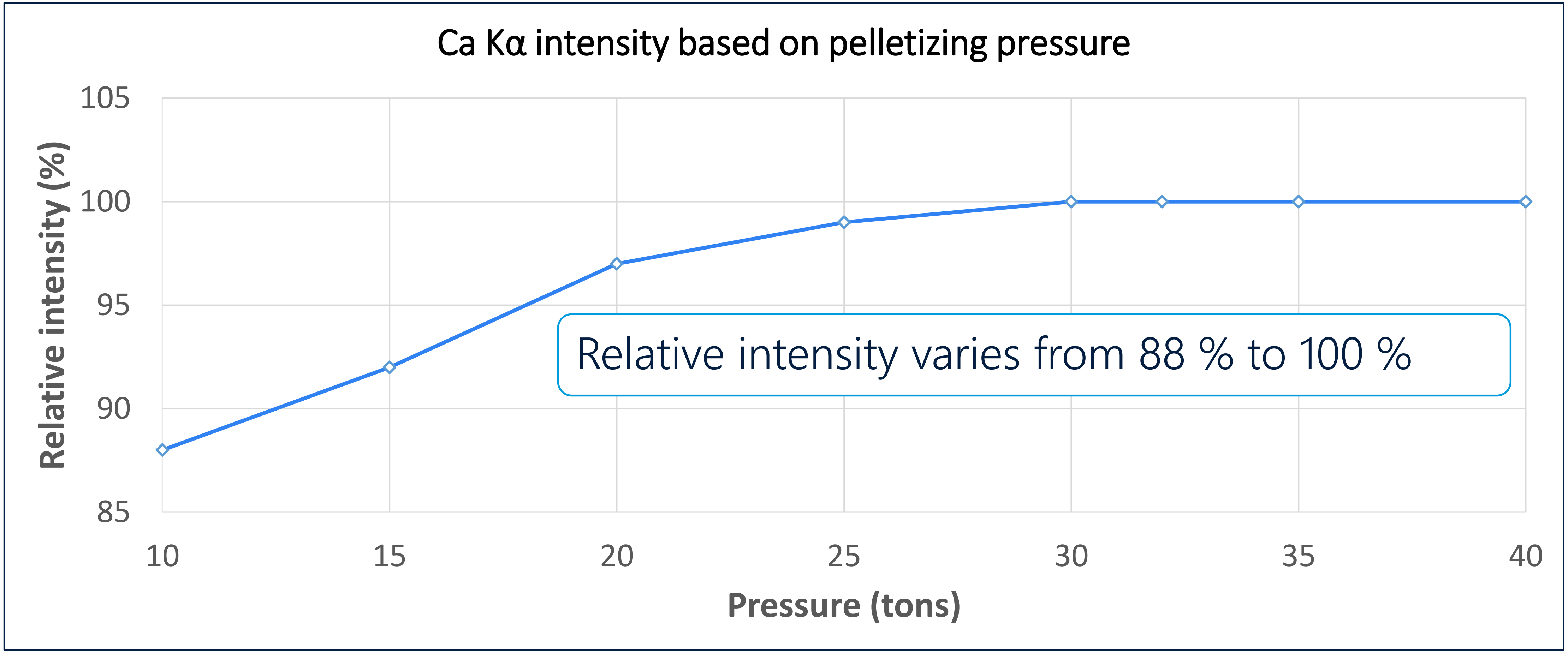
Influence of sample preparation

Example – pressure effects

- Sample Limestone
- Element Ca
- Constant milling parameters
- Automatic Press
- Force 10 to 40 tons
- Constant XRF parameters
- Relative intensities

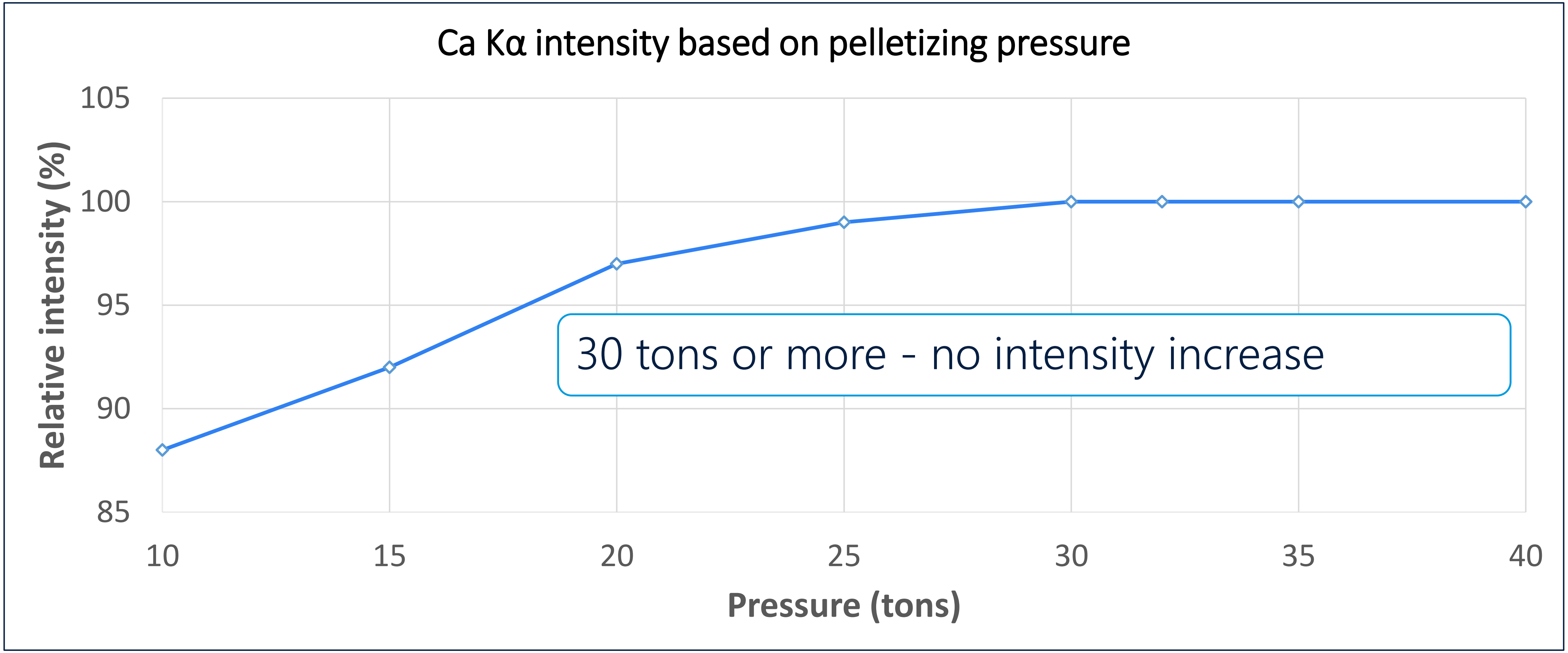
Influence of sample preparation

Example – pressure effects



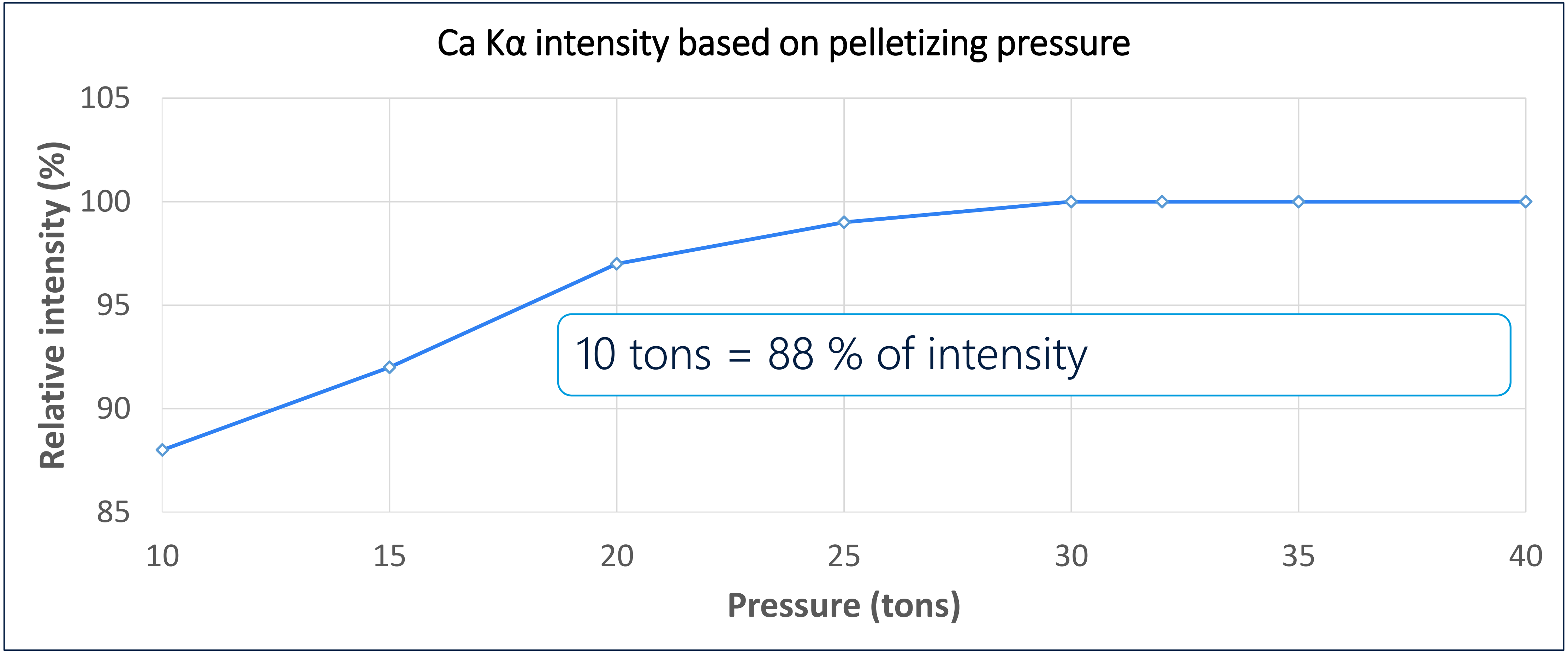
Influence of sample preparation

Example – pressure effects



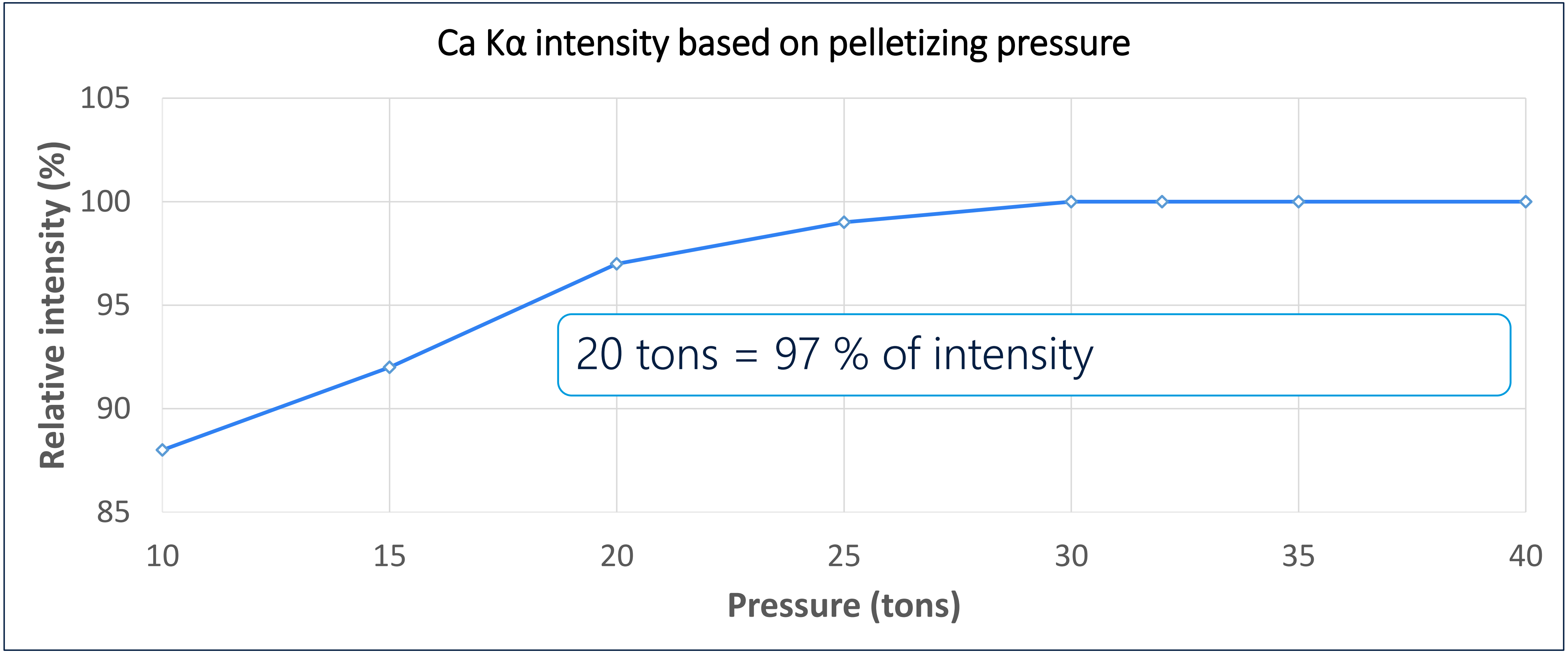
Influence of sample preparation

Example – pressure effects



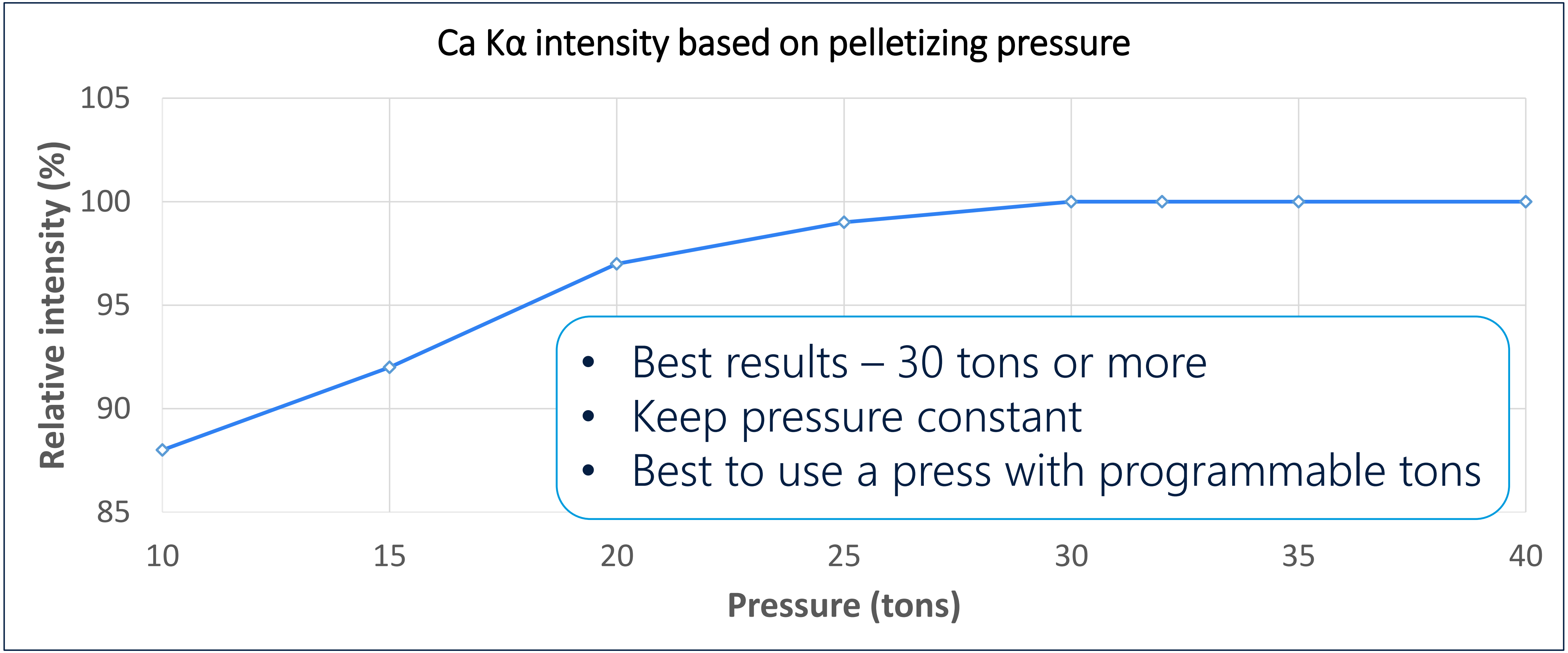
Influence of sample preparation

Example – pressure effects



Influence of sample preparation

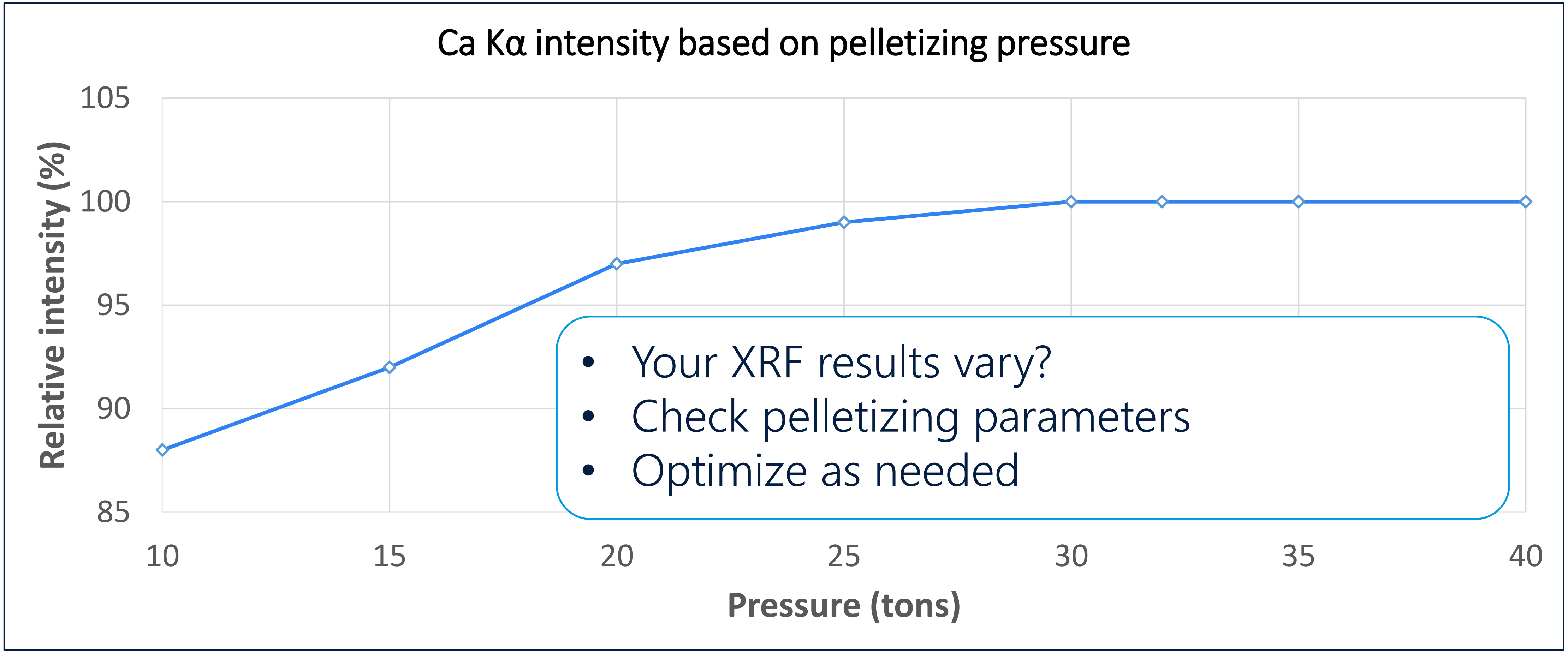
Example – pressure effects



- Best results – 30 tons or more
- Keep pressure constant
- Best to use a press with programmable tons

Influence of sample preparation

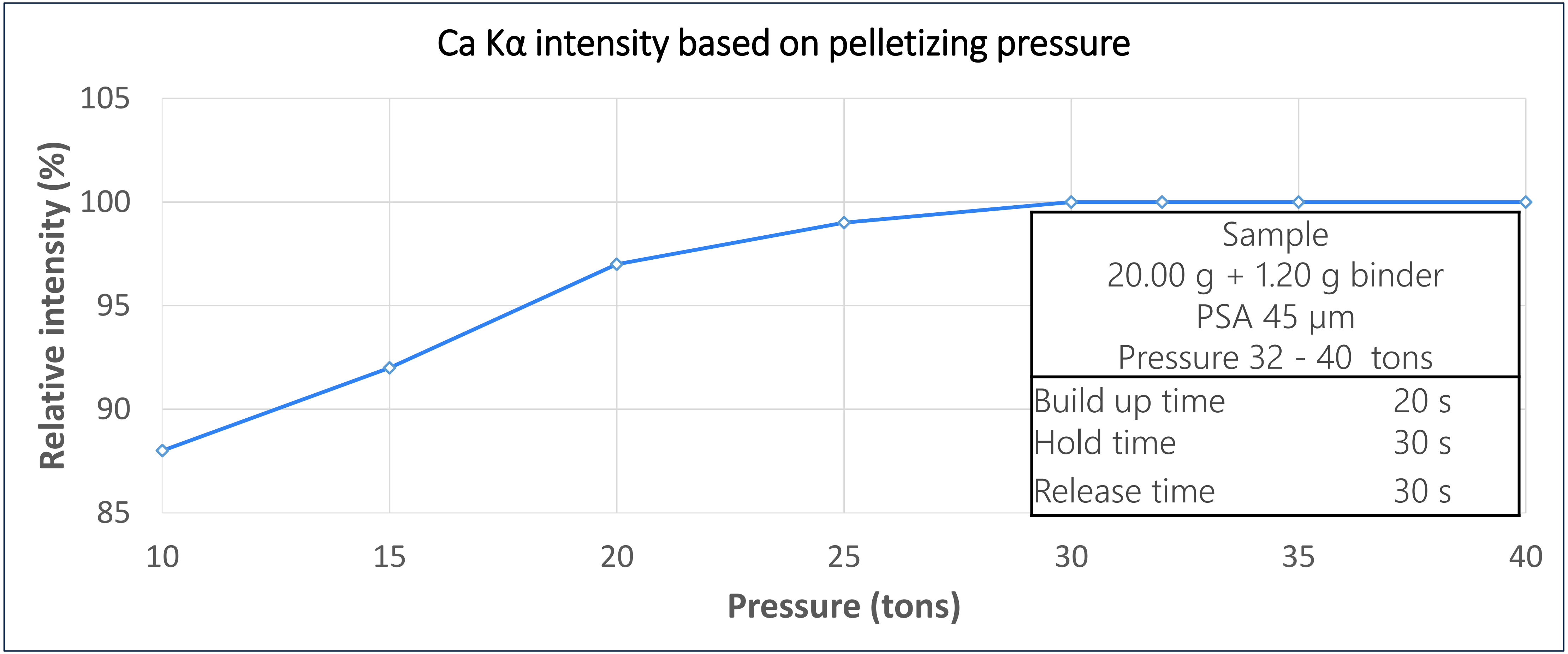
Example – pressure effects



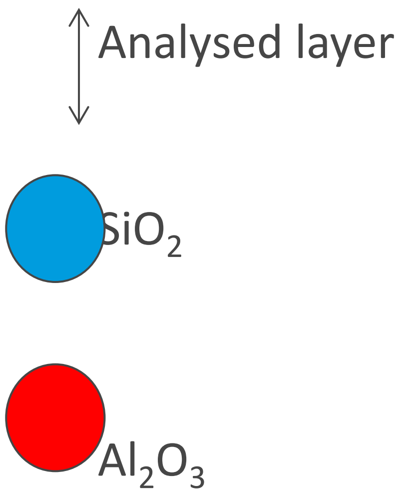
- Your XRF results vary?
- Check pelletizing parameters
- Optimize as needed

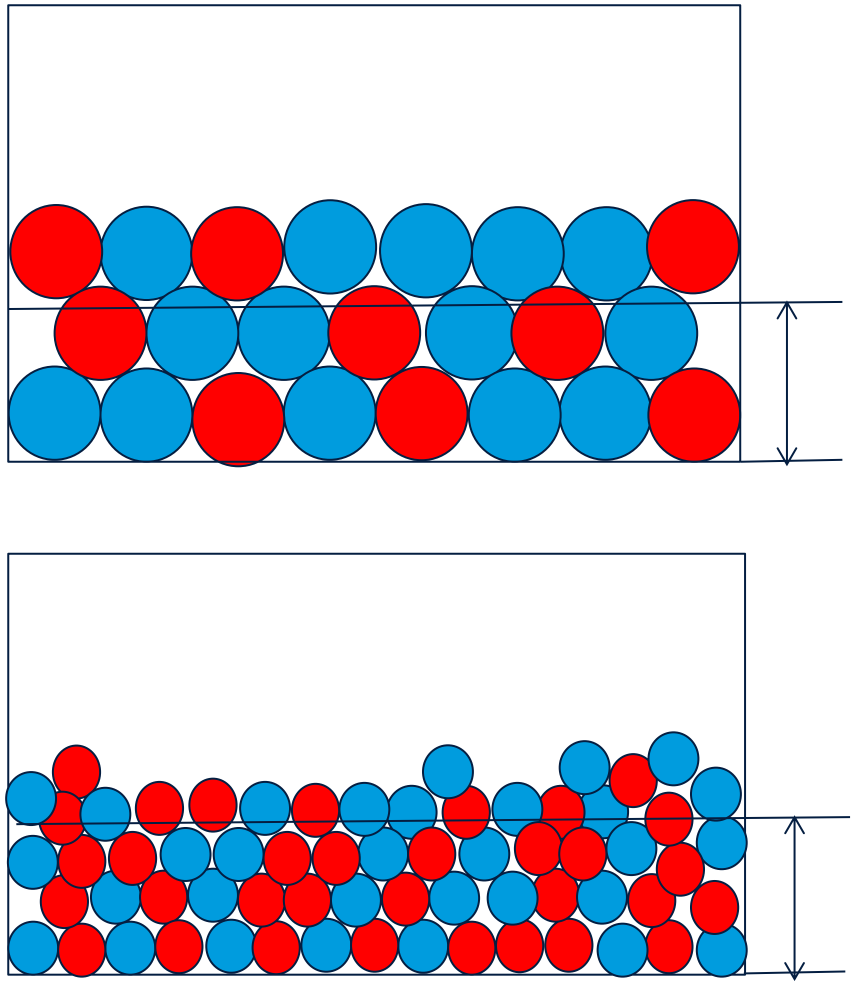
Influence of sample preparation

Example – pressure effects



Grain Size Effects - Principle

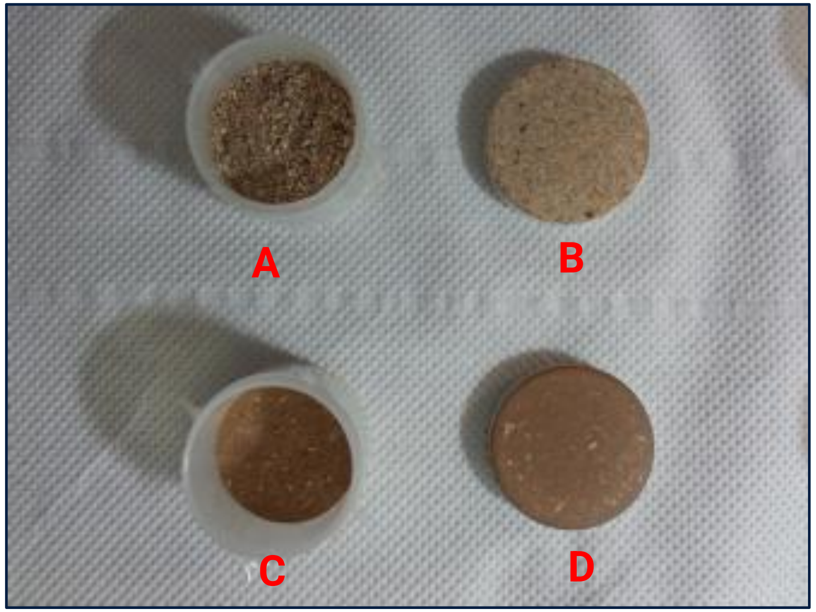




$I_{(SiO2)} = f(\#particles_{(SiO2),\ Analysed\ V})$

$I_{(Al2O3)} = f(\#particles_{(Al2O3),\ Analysed\ V})$

Grain Size Effects – Practical (1)



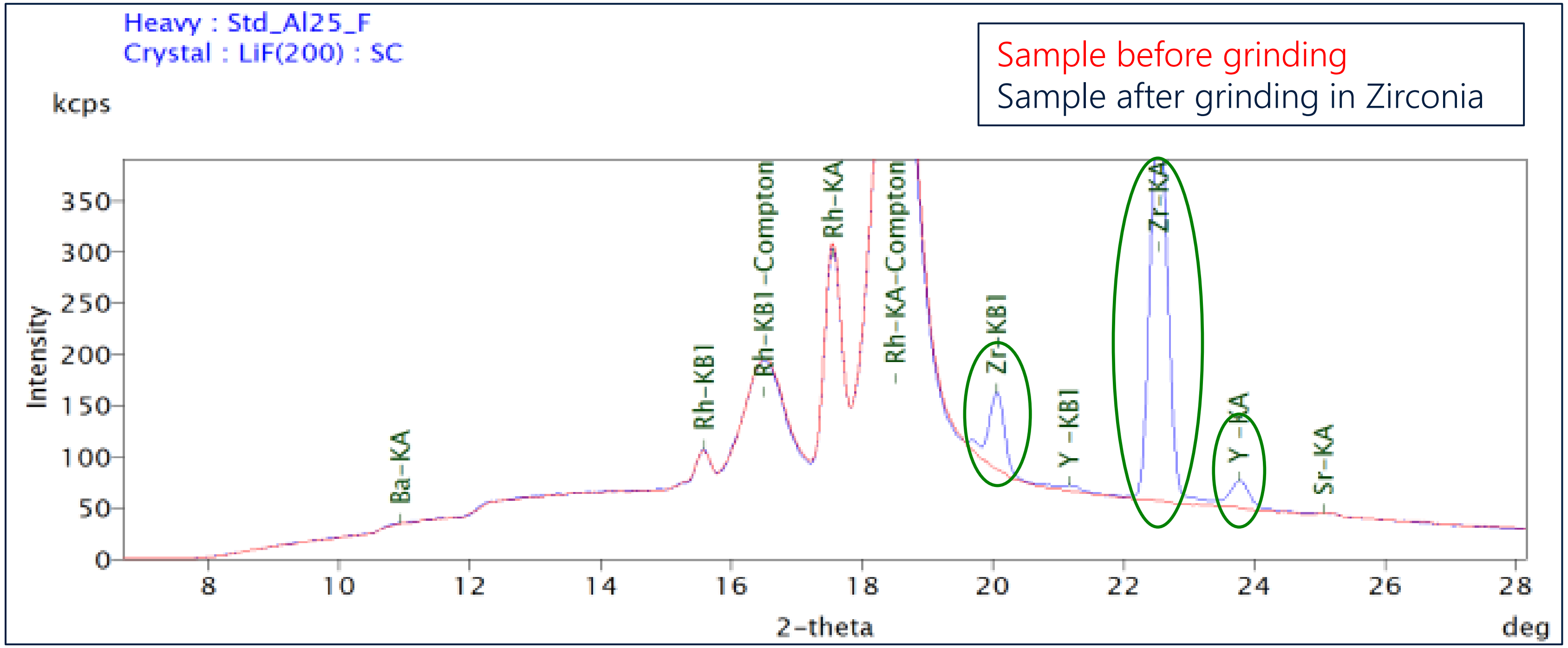
- The picture shows the same sample (wood biomass), prepared in four different ways:
  - *Original sample as loose powder (**A**)*
  - *Original sample as pressed pellet (**B**)*
  - *Ground sample as loose powder (**C**)*
  - *Ground sample as pressed pellet (**D**)*
- Interesting will be to have a look at the difference in intensities, for various elements (light, middle and heavy) and contamination from the grinding process

Contamination from grinding containers (1)

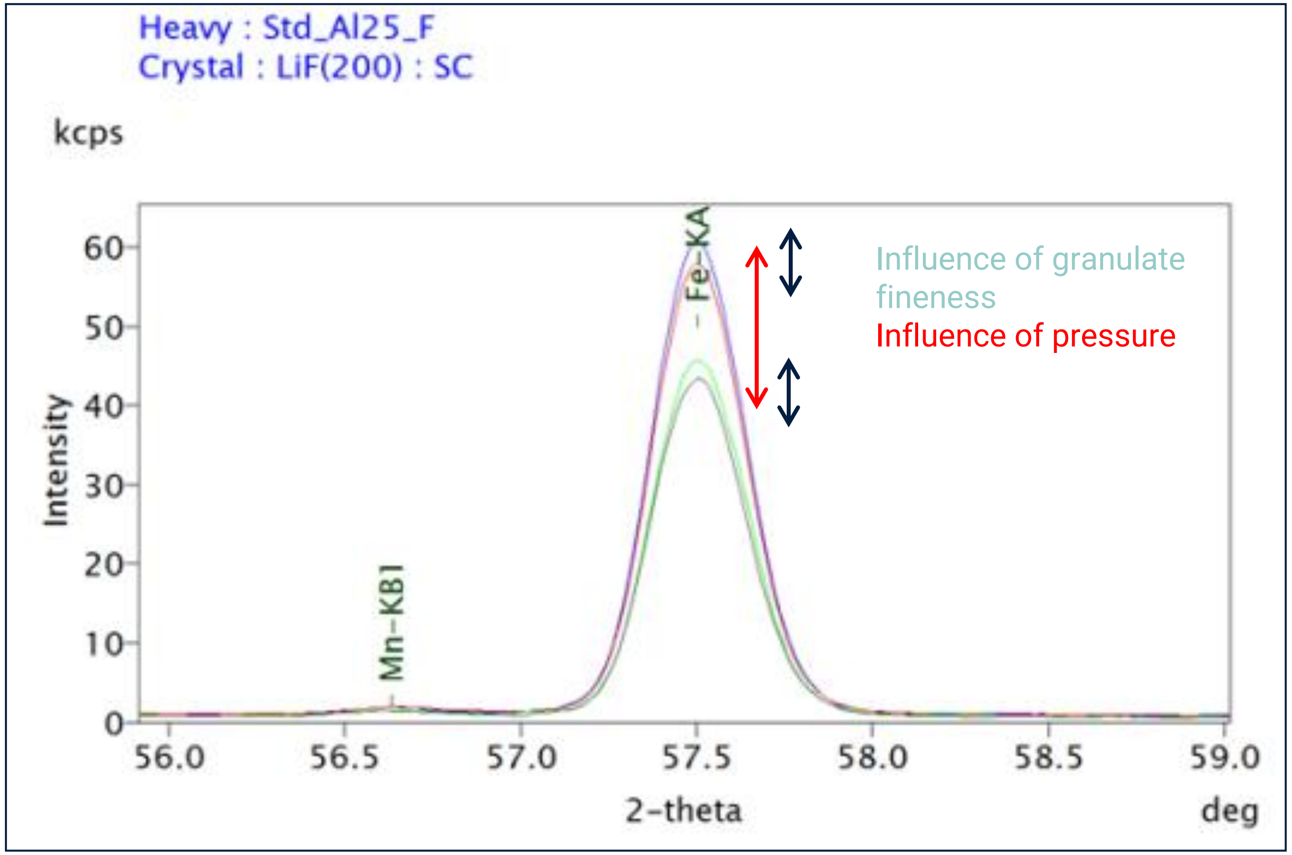
Vessel Type	Contaminants
Tungsten Carbide	W, Co and C
Special (C or Cr) Steel	Fe, Cr, C
Agate	Si
Zirconia	Zr, (Y)

Contamination from grinding containers (2)

- **Contamination** through the grinding process can take place
- In this example, a ZrO_2 grinding vessel was used to reduce the grain size
- A clear signal for Zr (and Y) can be observed



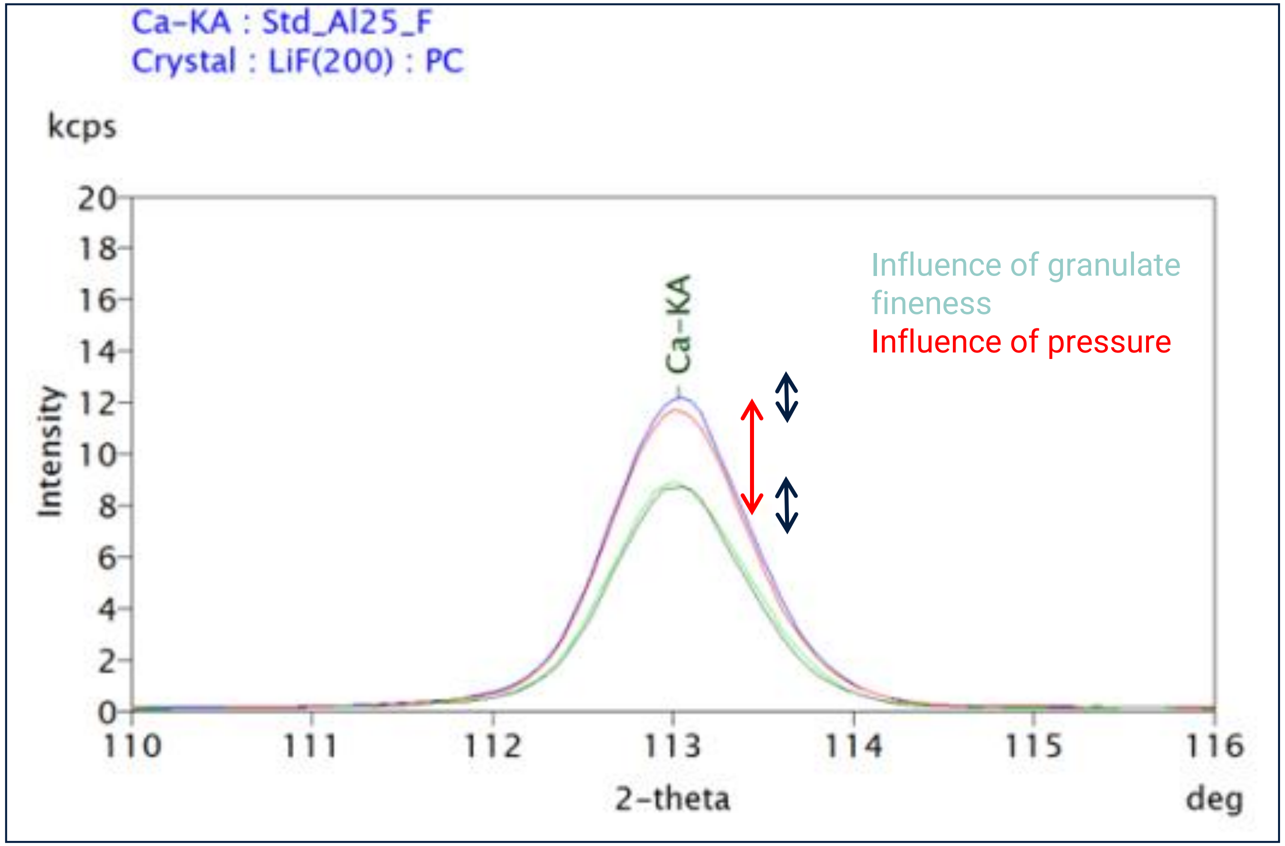
Grain Size Effects – Practical (3)



Heavy element (Fe)

- Ground pressed powder (D)
- Original pressed powder (B)
- Ground loose powder (C)
- Original loose powder (A)

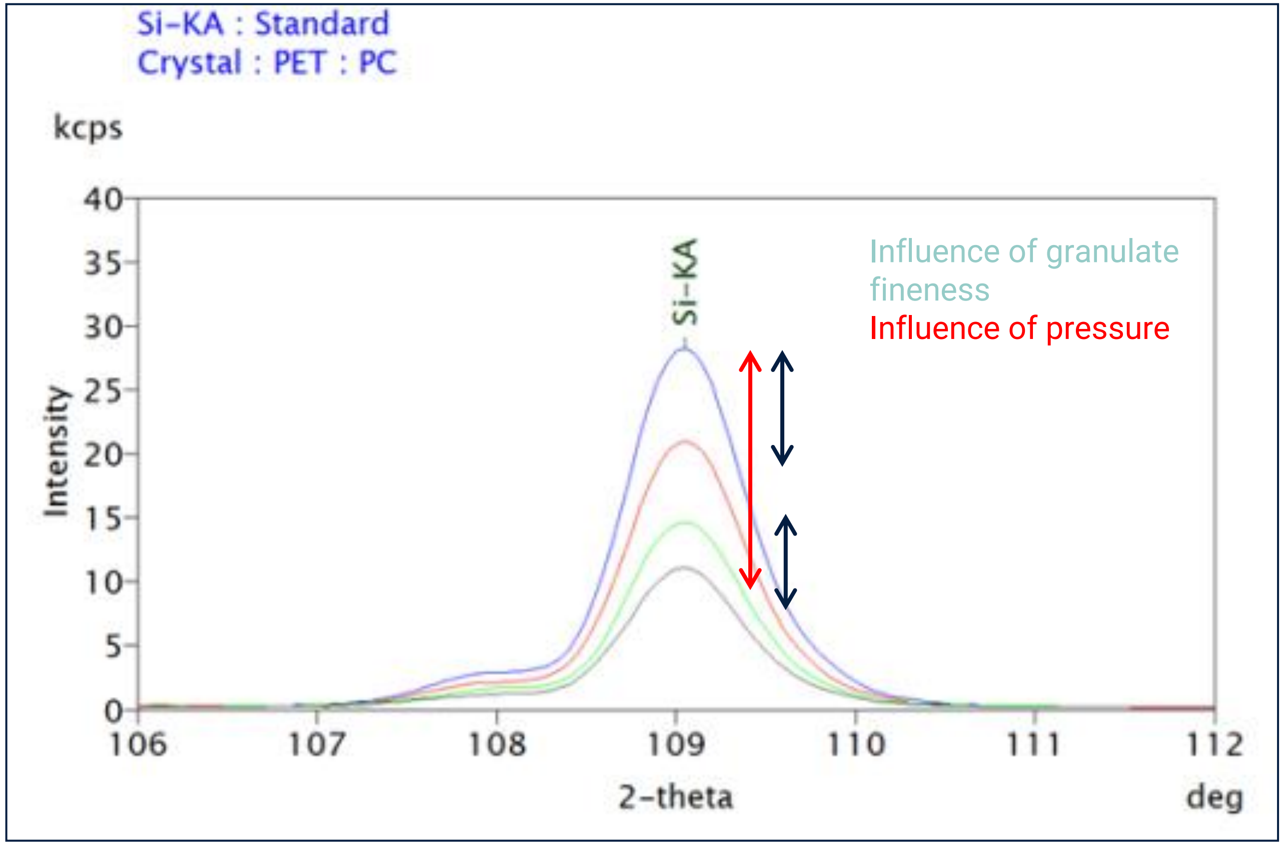
Grain Size Effects – Practical (4)



Medium element (Ca)

- Ground pressed powder (D)
- Original pressed powder (B)
- Ground loose powder (C)
- Original loose powder (A)

Grain Size Effects – Practical (5)

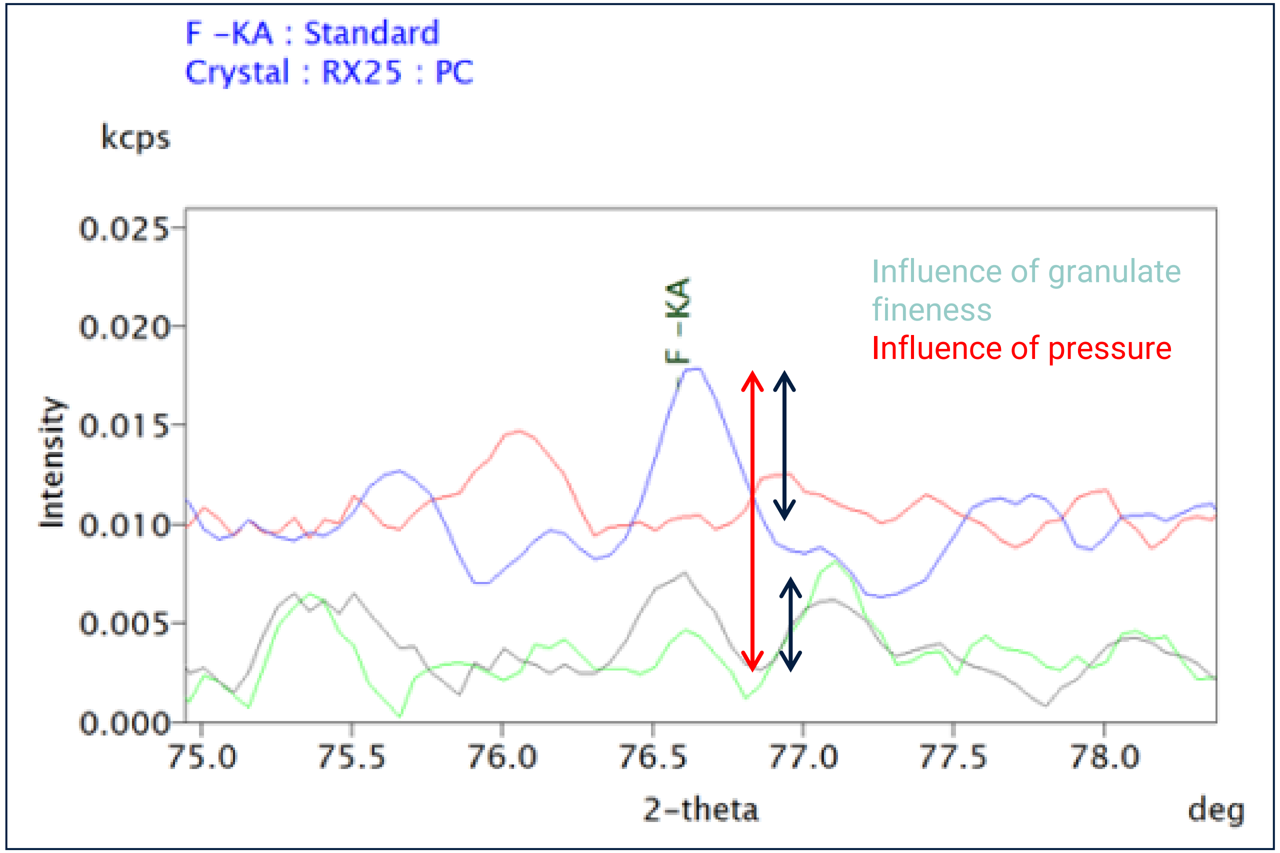


Light element (Si)

- Ground pressed powder (D)
- Original pressed powder (B)
- Ground loose powder (C)
- Original loose powder (A)

Rigaku

Grain Size Effects – Practical (5)



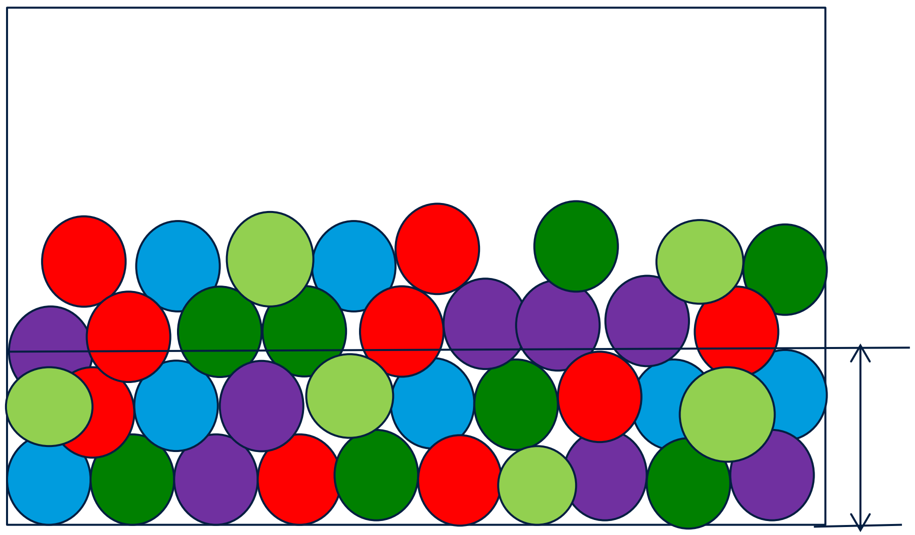
Extreme Light element (F)

- Ground pressed powder (D)
- Original pressed powder (B)
- Ground loose powder (C)
- Original loose powder (A)

Mineralogical effects - Principle

3CaO.SiO2	C3S	
2CaO.SiO2	C2S	
3CaO.Al2O3		C3A
2CaO(Al2O3,Fe2O3)		C2AF
CaO		Free Lime

Analysed layer



The elements are not present as pure oxides, as mostly presumed during XRF analysis, but as „phases“. The phase distribution does have an influence on the measured intensities

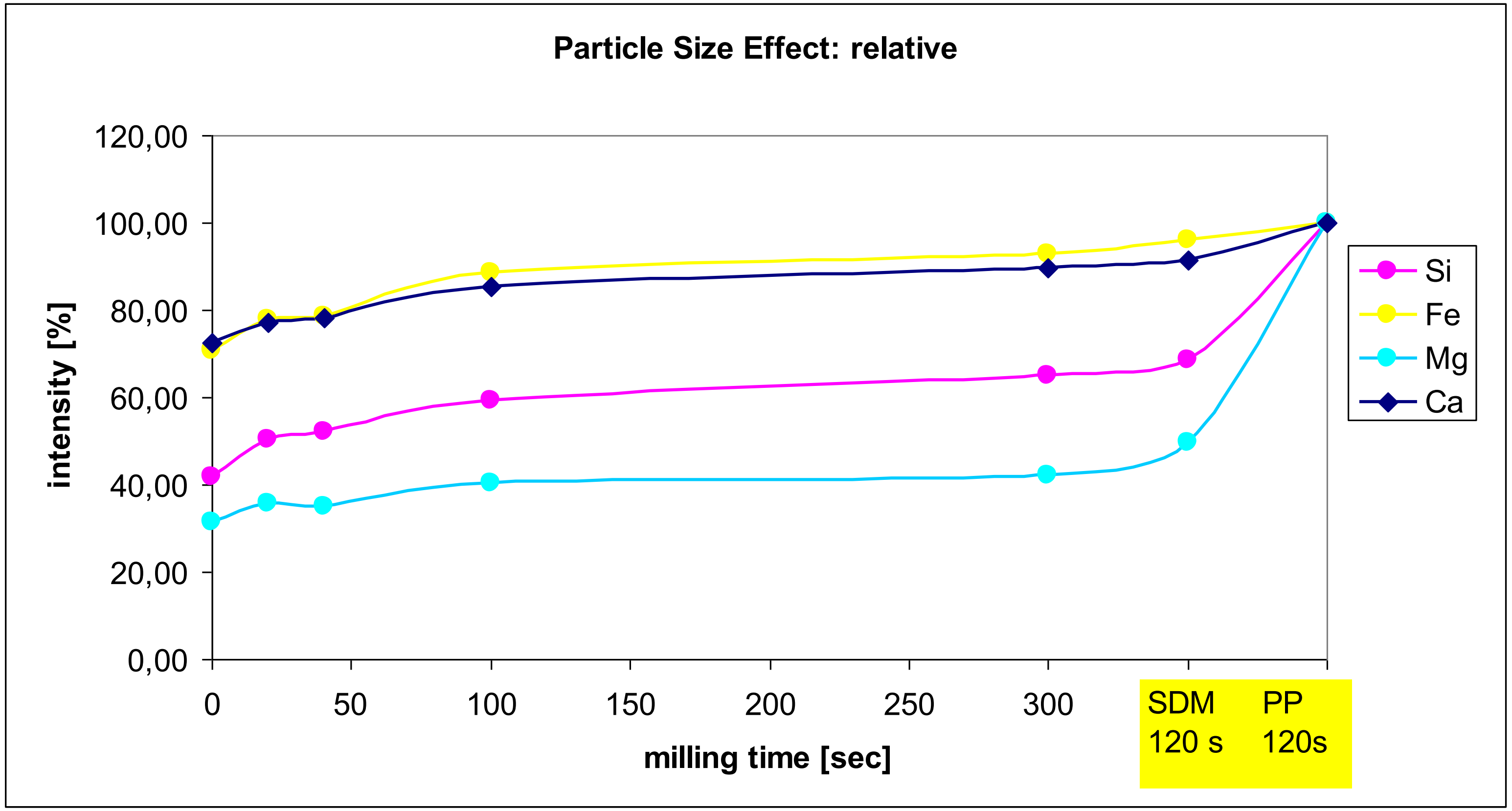
I_{Ca} = f(C3S,C2S,C3A,C2AF)

I_{Si} = f(C3S,C2S)

I_{Al} = f(C3A,C2AF)

I_{Fe} = f(C2AF)

Reducing the particle size effect

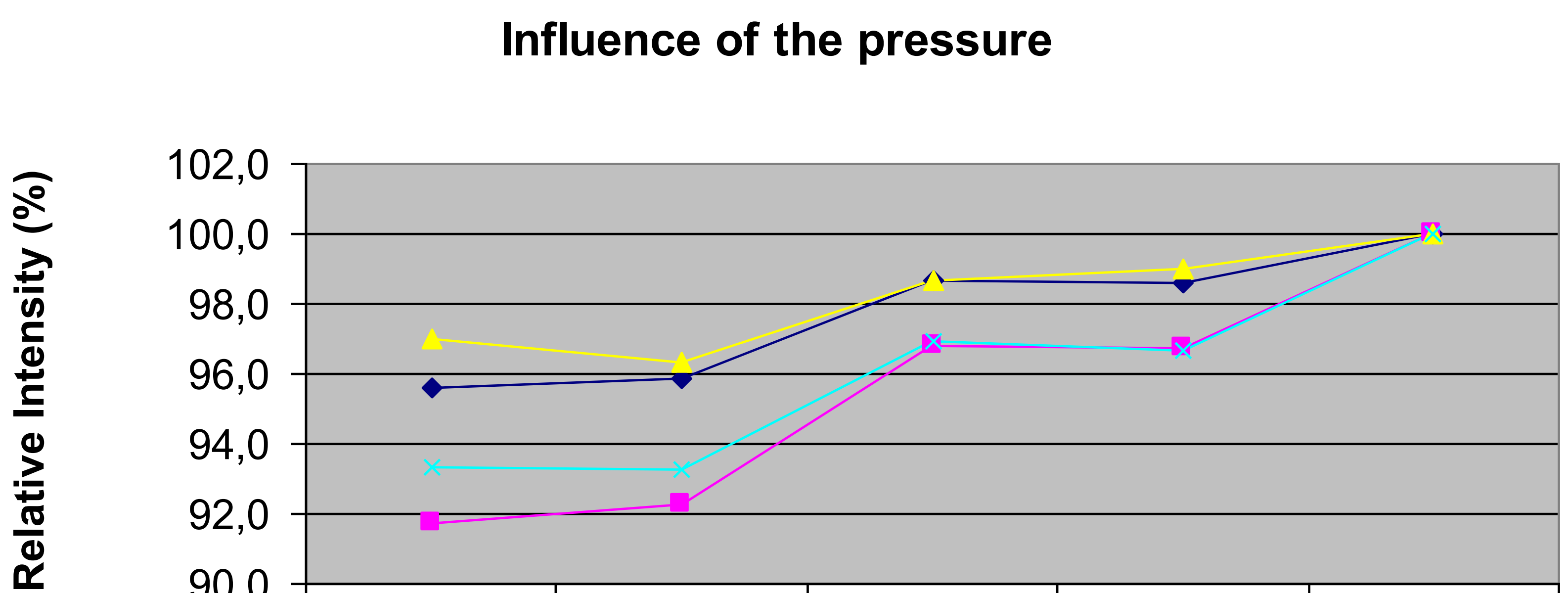


A. Milling was initially done in a mortar mill (0 – 300 s)→ grain size can only minimally be reduced

B. RS200 = Vibratory Disk Mill was used for optimally reducing the grain size

C. PP = A Pressed Pellet was made from the RS200 sample

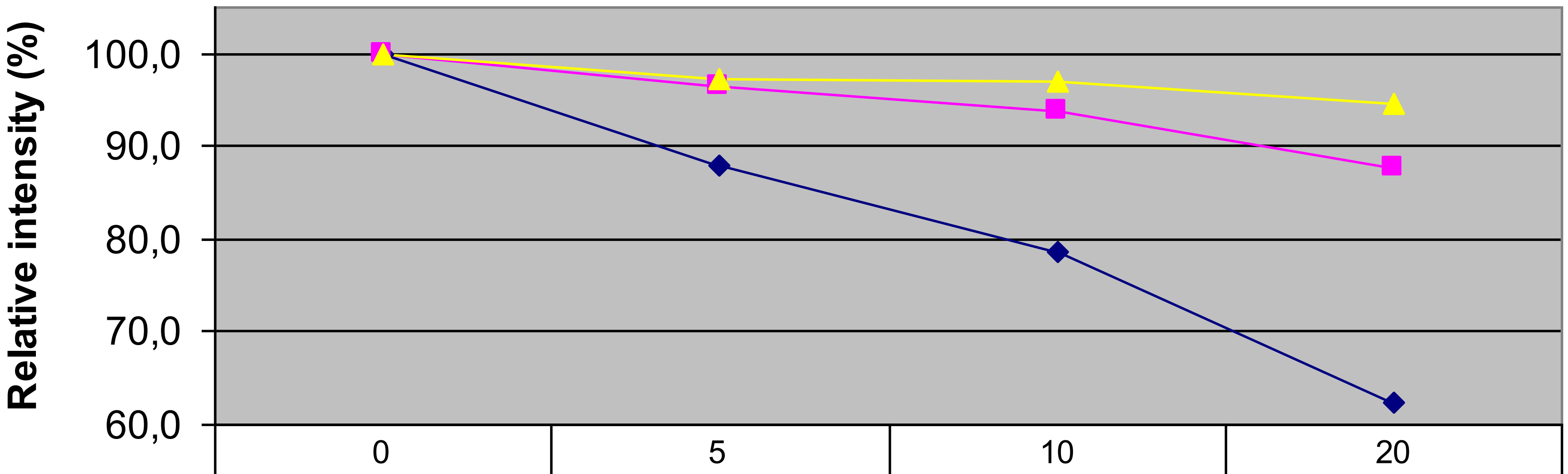
Influence of the applied pressure



	5 ton	10 ton	20 ton	30 ton	40 ton
Ca (kcps)	95,6	95,9	98,7	98,6	100,0
Si (kcps)	91,7	92,2	96,8	96,7	100,0
Fe (kcps)	97,0	96,3	98,6	99,0	100,0
Al (kcps)	93,3	93,2	96,9	96,6	100,0

Effect of applied binder

Effect of Binder



	0	5	10	20
Al	100,0	87,9	78,7	62,4
Ca	100,0	96,6	93,9	87,8
Fe	100,0	97,4	97,1	94,5

Percentage of wax

XRF

Accurate XRF results require

- Homogenous samples
- Reproducible sample preparation

Retsch®

MILLING SIEVING ASSISTING

Maintaining a calibration

Maintaining a Calibration

- Keep calibration working / valid
  - Define and run QC samples
    - Review SPC chart
    - Out of limits -> run drift correction samples
    - Review SPC chart
  - Run verification samples

- Round Robins

Maintenance – Repeatability Testing

- Methodology
  - Same sample: Limestone
  - Prepare 10 times
    - pressed pellet
  - Analyse each pellet

Maintenance – Repeatability Testing

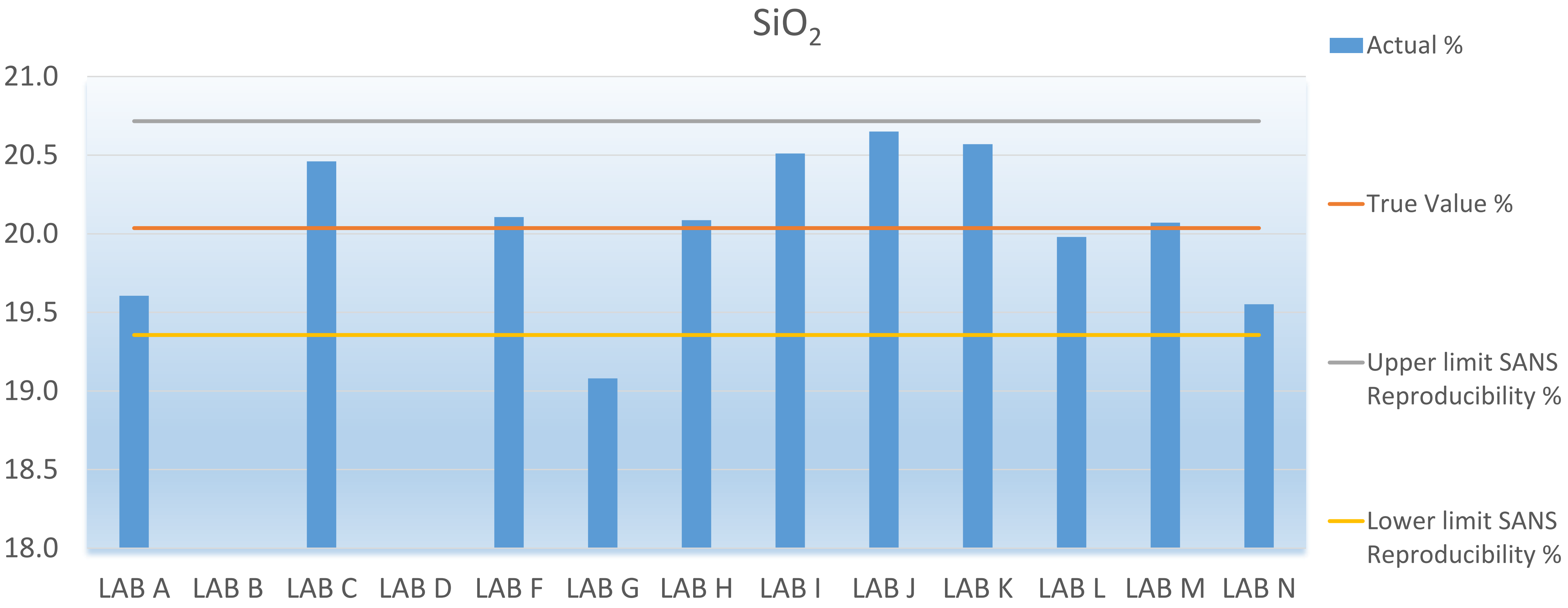
Component	CaO	SiO_2
Unit	mass%	mass%
Measurements	10	10
Average	60.6	0.69
Maximum	60.6	0.70
Minimum	60.5	0.69
Range	0.09	0.02
Std dev	0.04	0.005
EN DIN 196-2 Std Dev	0.565	0.08

Maintenance – Internal round robin

- Methodology
  - 13 different laboratories
  - 13 analysts
  - Same sample
  - Prepare as pressed pellet
  - Analyse on different spectrometers
    - Same calibration standards
    - Calibrations done locally

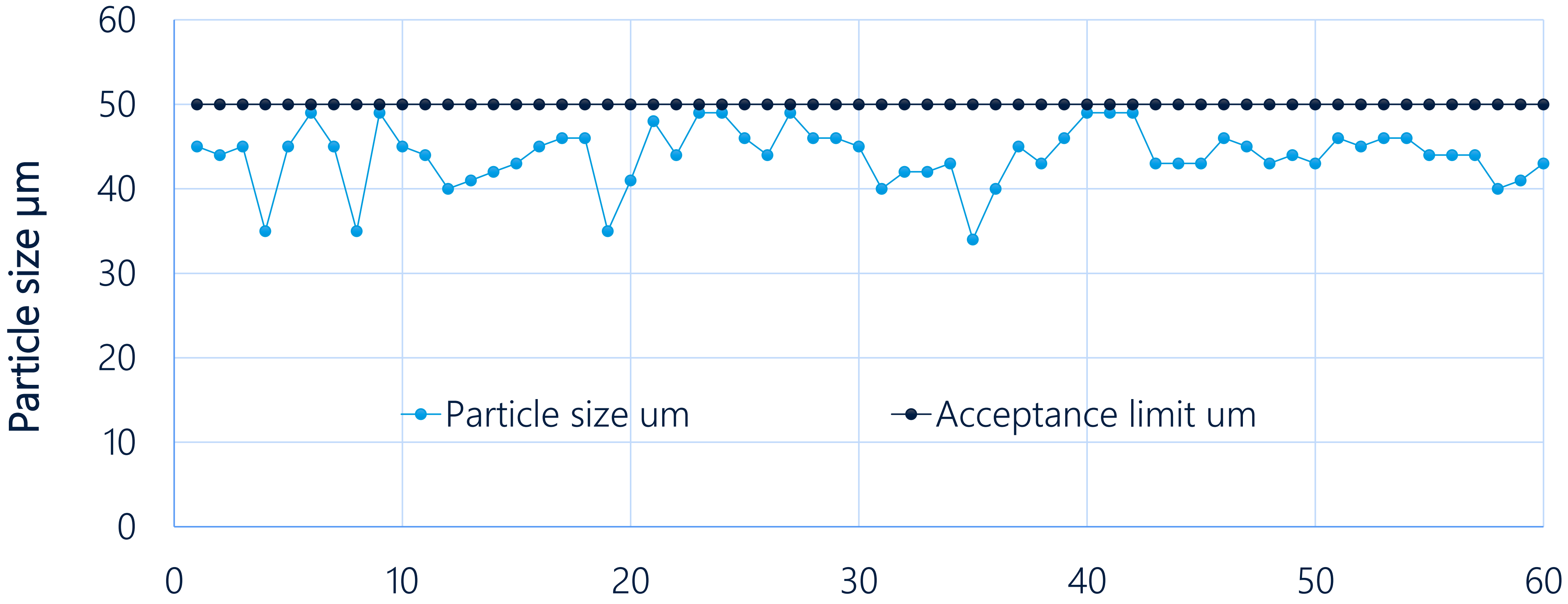
Maintenance – Internal round robin

Sample – Cement (CEM I)



Maintenance – Sample grinding

Ensuring consistent particle sizes – Retsch vibratory disc mill RS200



Maintenance – Instrument

- Scheduling preventative maintenance
  - Sample preparation equipment
  - XRF Spectrometer
  - Chiller
- Valid Data Backups

Take-home messages to keep in mind

Take-home messages to keep in mind

Sample preparation

- Key to achieve accurate XRF results
- Consistent grinding and pressing a MUST

Calibrating a XRF system

- Valid calibration range
- Sufficient number of standards

Verification

- Continuous quality control checks
- Assessment of a valid calibration range

Maintaining of a calibration

- Drift correction using long term stable standard
- Continuous assessment of precision and accuracy

Contact us

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