Cement: Process-related analysis of all materials up to the finished product with XRF

Welcome

Cement: Process-related analysis of all materials up to the finished product with XRF

- What is XRF? A short tour
- XRF technologies! A comparison
- What is important to set up a quality control application?
- Device parameters and their influence on data quality
- Application examples for industrial quality control
- Summary

- Q&A

Dr. Adrian Fiege

Product Managment XRF

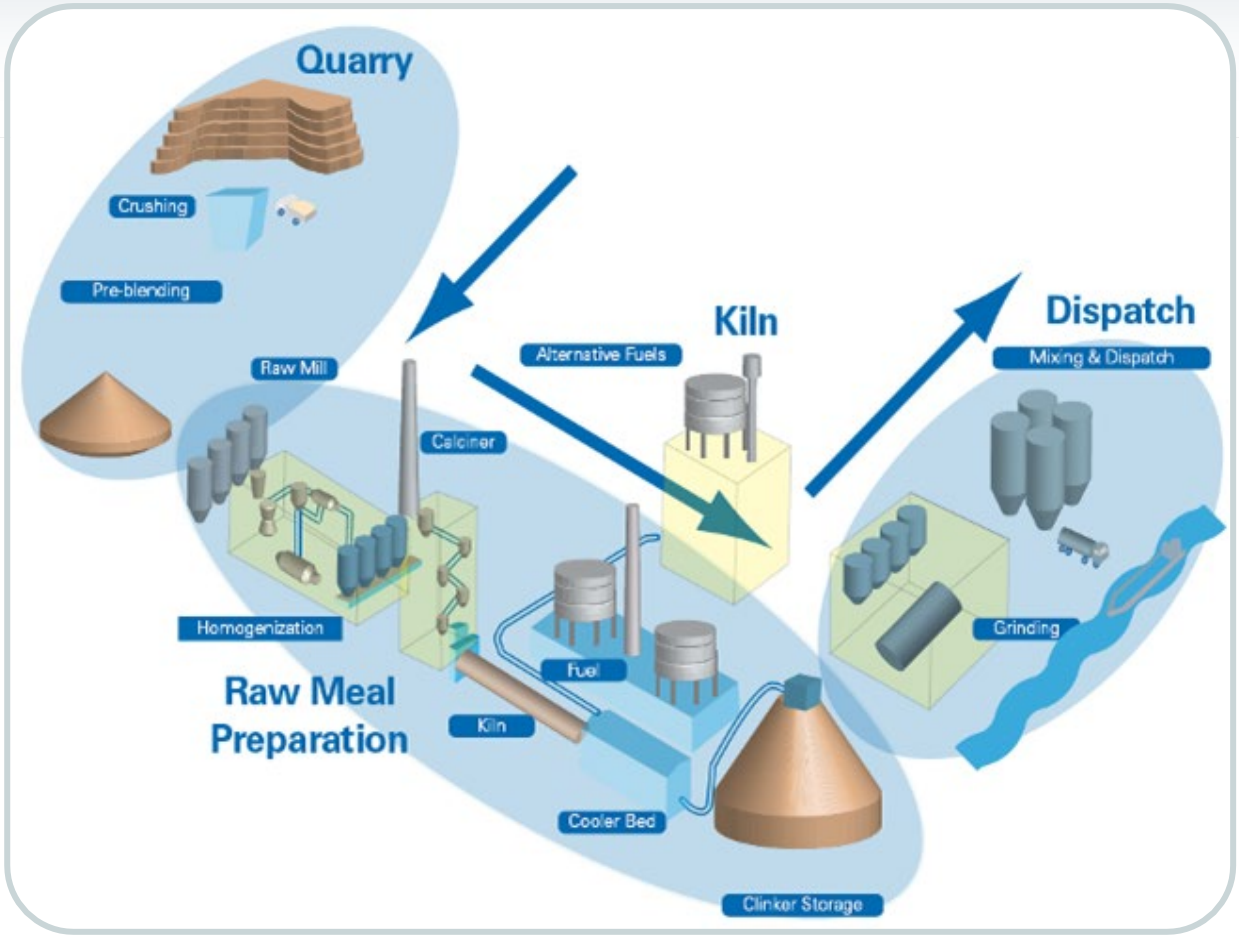
Karlsruhe, Germany

Dr. Kai Behrens

Head of XRF Product Management

Karlsruhe, Germany

Cement manufacture
Critical materials



Cement production:

- Raw materials (rocks, minerals)
- Raw meal (mix) (mixing, grinding)
- Fuels (fossil and secondary)
- Clinker (oven, burning)
- Cement (mixing, grinding)

Process and quality control in cement: element analysis

Cement as a binder in the construction industry has been known for centuries, but today it is more important than ever. Cement is literally the basis of our modern infrastructure:

Materials to be analyzed:

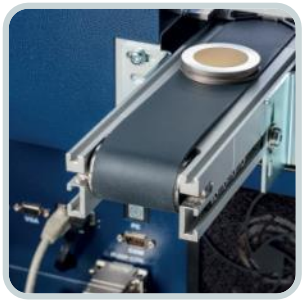
Cement, raw mix, clinker, limestone and more

Typical elements of interest:

F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Zn, Sr, Pb, Cd, Tl

Norms to be fulfilled:

ASTM C114 and ISO 29581-2 / DIN EN 196-2



Required throughput:

- The faster the better!
- New elements are always important!
- Fully automated sample preparation and analysis required.

All about cement
Which analytics should I choose?

The German cement industry has reduced energy consumption by more than 50%: through the use of alternative raw materials and fuels! This has an impact on the analysis

Production in 2019:
CN 2200 Mt
IN 320 Mt
VN 95 Mt
US 89 Mt
-> 4100 Mt ww

Multi-channel WDXRF spectrometer:

- Traditionally for high sample throughput, not flexible with trace elements and increasing numbers of elements

Sequential WDXRF spectrometers:

- Fast and flexible, also for AFRs (heavy metals), slag (F), hot meal (alkali chlorides)

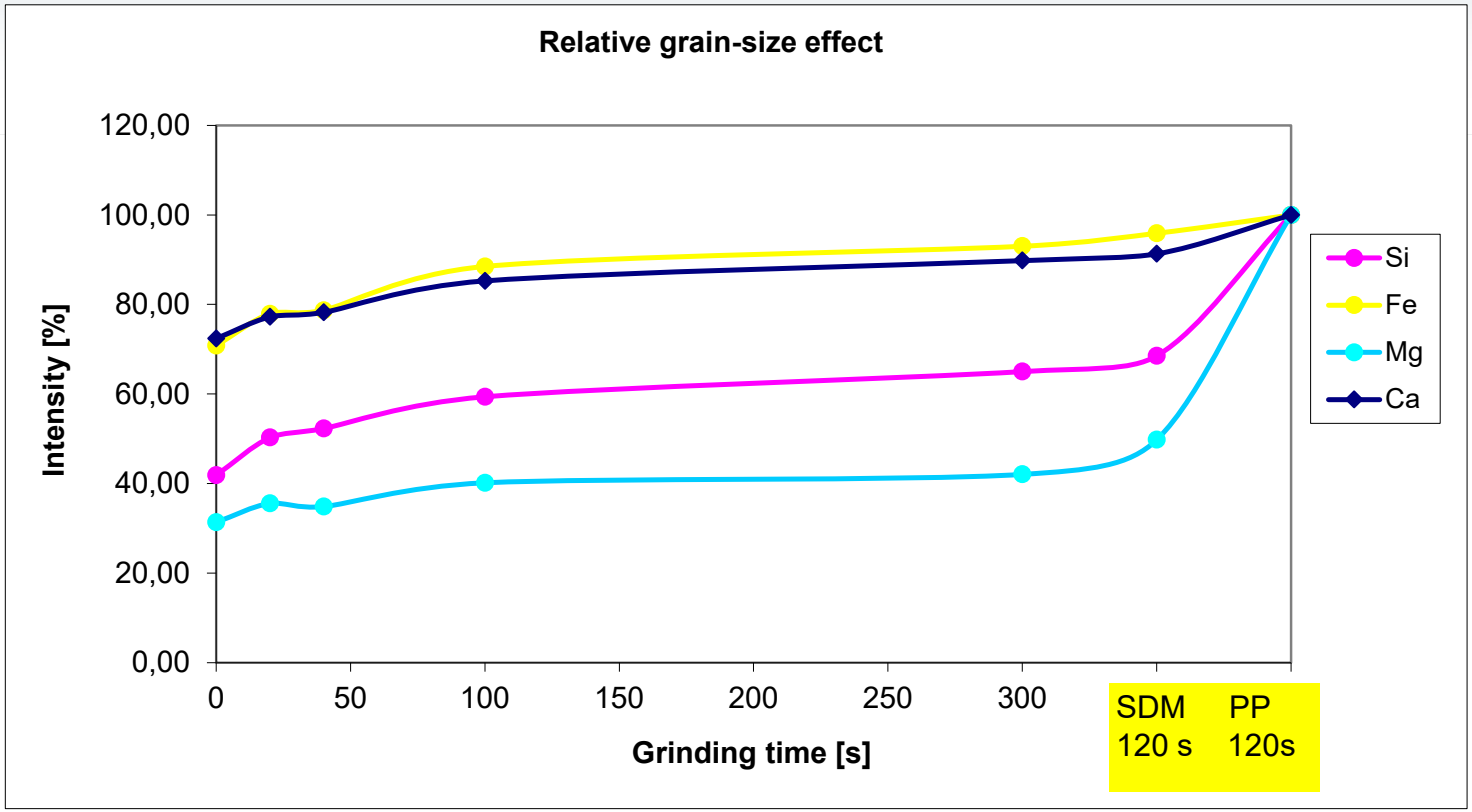
Which device do I choose for additional analysis and as a backup?

- EDXRF tabletop device for raw meal?
- Modern table WDXRF as a backup?

Sample preparation
Pressed pellets

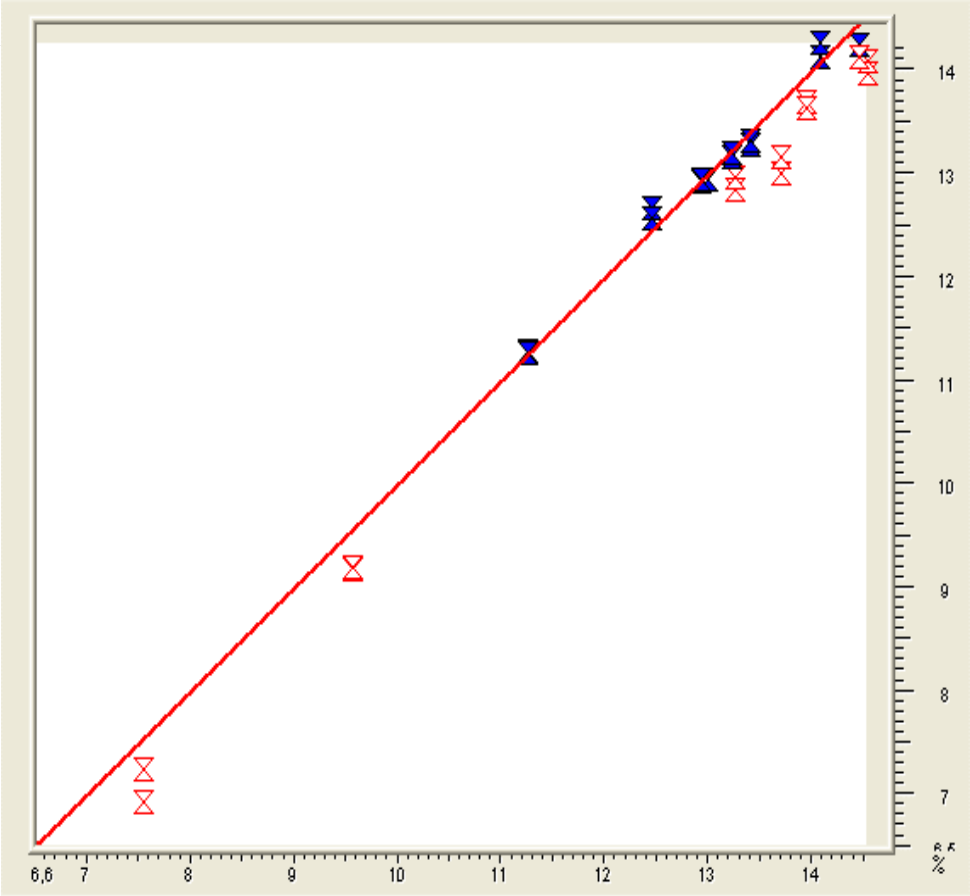
- Fast sample preparation method
- Easily automatable
- Grain size and matrix effects are not problematic for material-specific calibrations
- But sample contamination via the grinding vessel:
- **Agate: SiO_2 99.91%;**
  Al_2O_3 0.02%; Na_2O 0.02%; Fe_2O_3 0.01%; K_2O 0.01%; MnO 0.01%; CaO 0.01%; MgO 0.01%
  - **Corundum ceramic: Al_2O_3** with traces of K, Na, Si, Ca, Cu, Fe, Mg, Pb, B, Cr, Li, Mn and Ni
  - **Tungsten carbide: C 6%, Co 6% and W 88%**
  - **Chromium steel:** C 1.93%; **Cr 13.21%,** Cu 0.03%; Mn 0.46%; Mo 0.02%; Ni 0.08%; P 0.019%; Si 0.38%; S 0.005% and W 0.01%

Sample preparation
Pressed pellets



- Grinding was originally carried out with a mortar grinder (0-300 s). The grain size could only be reduced minimally.
- SDM = vibrating disc mill is used today to optimally reduce the grain size
- PP = A press pellet was produced from the SDM sample

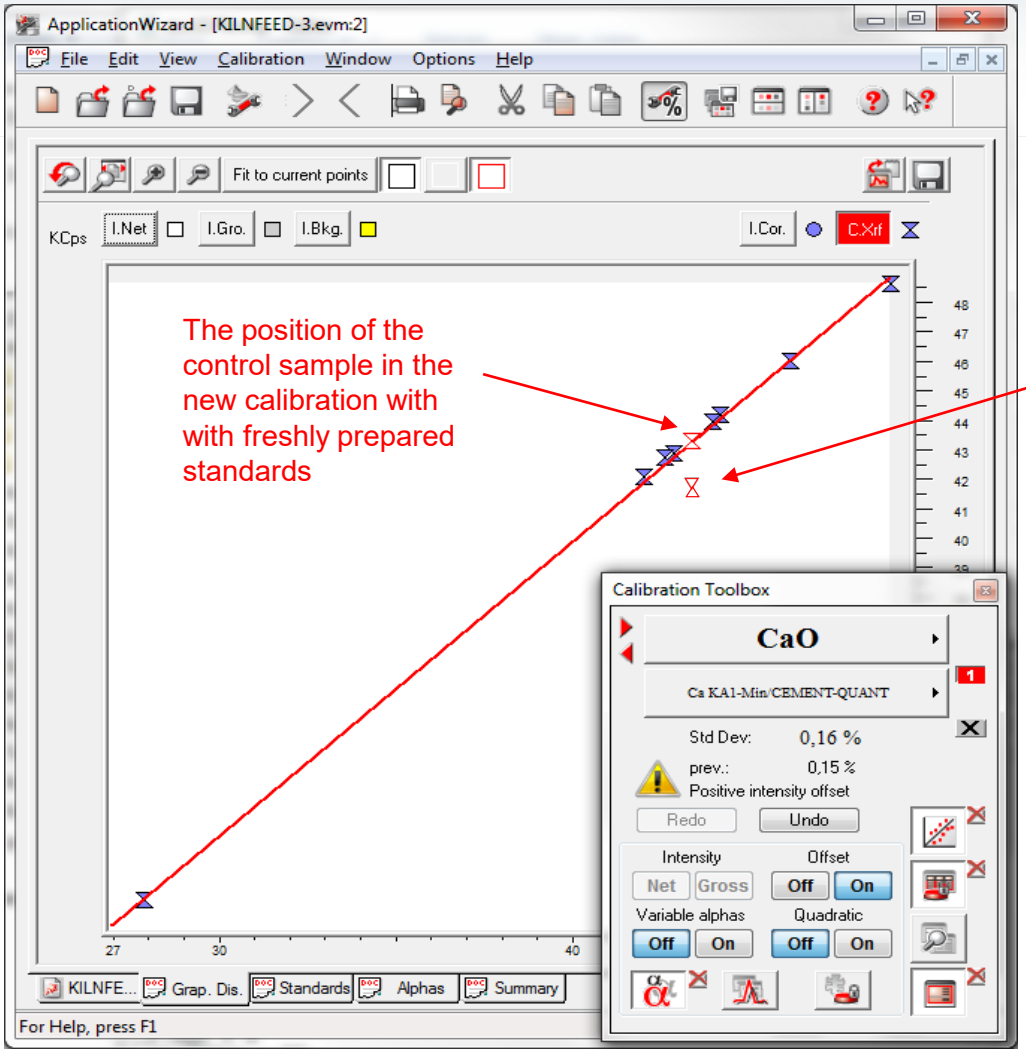
Sample preparation
Pressed pellets



Matrix and grain size effects not compensated
Raw meal and limestone

Solution:
Separation of methods

Sample preparation
Pressed pellets



Check control standards again and again with a fresh preparation

Secondary fuels
Practical example

An extreme example

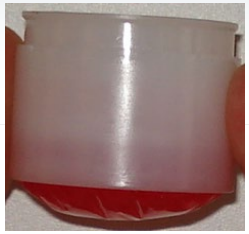
- Waste material
- Elements of interest: Cl and Br
- Usage: secondary fuel for cement kilns

- Take a sample from the waste bag
- Size reduction in a shredder to <200 µm
- Pressing the sample with 20 tons
- Prepare twice or even three times

Influence for loose powders and liquids

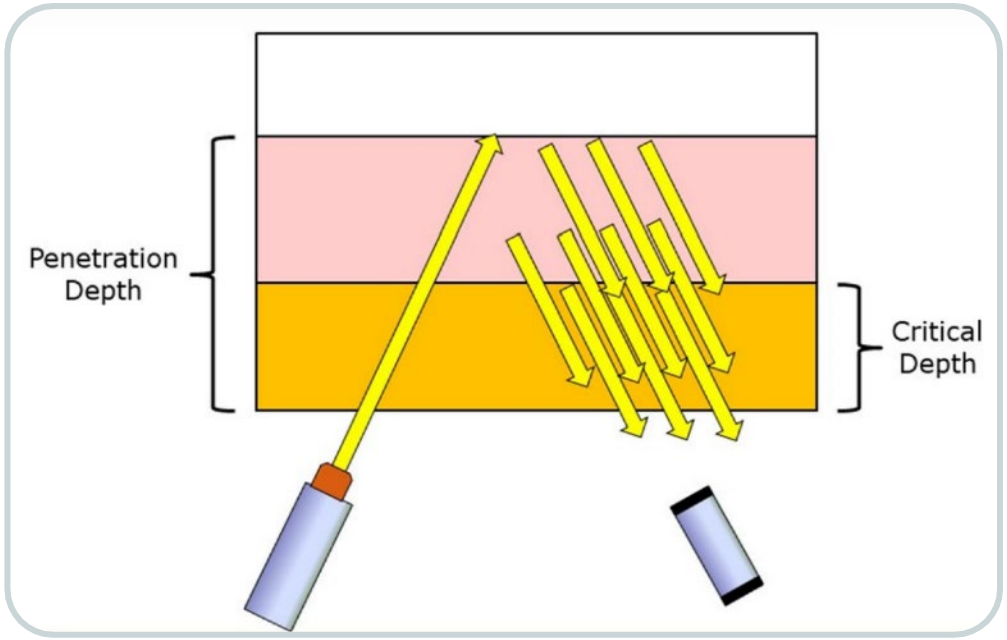
R(kcps) = f (1/d²)

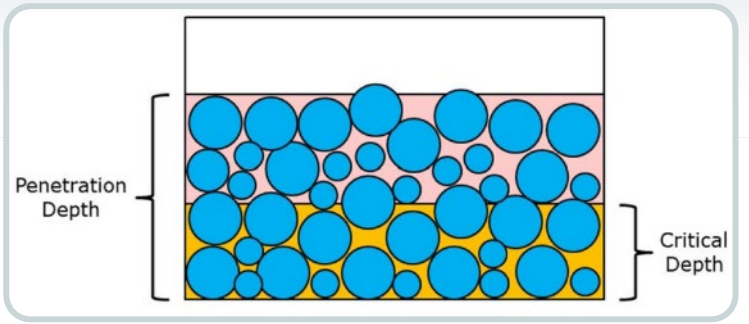
Δd Anode to sample

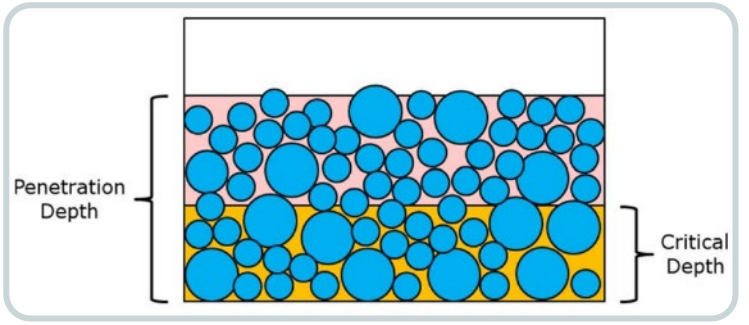


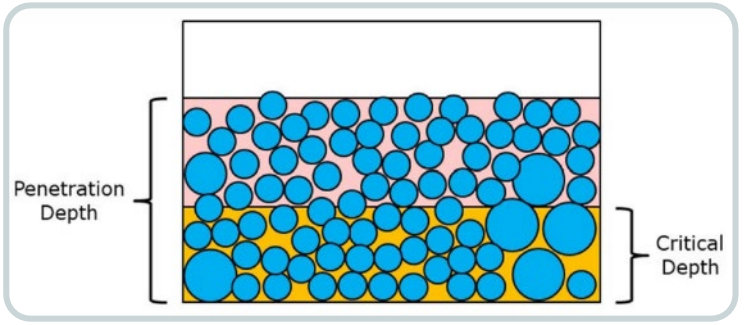
Sample not flat:

→ Distance- and shadow-effect



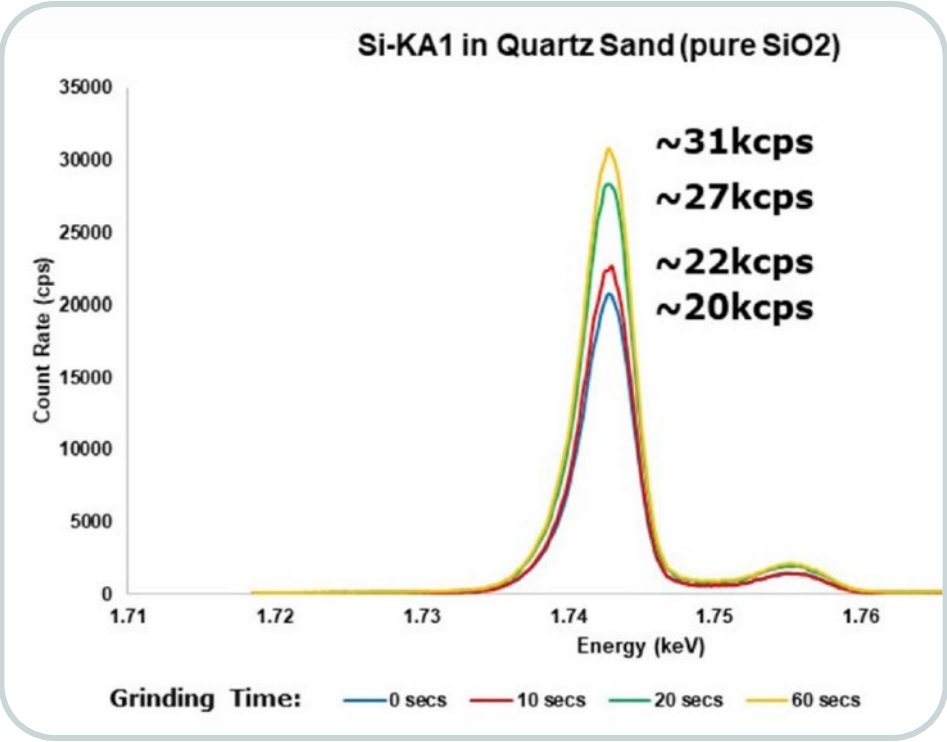


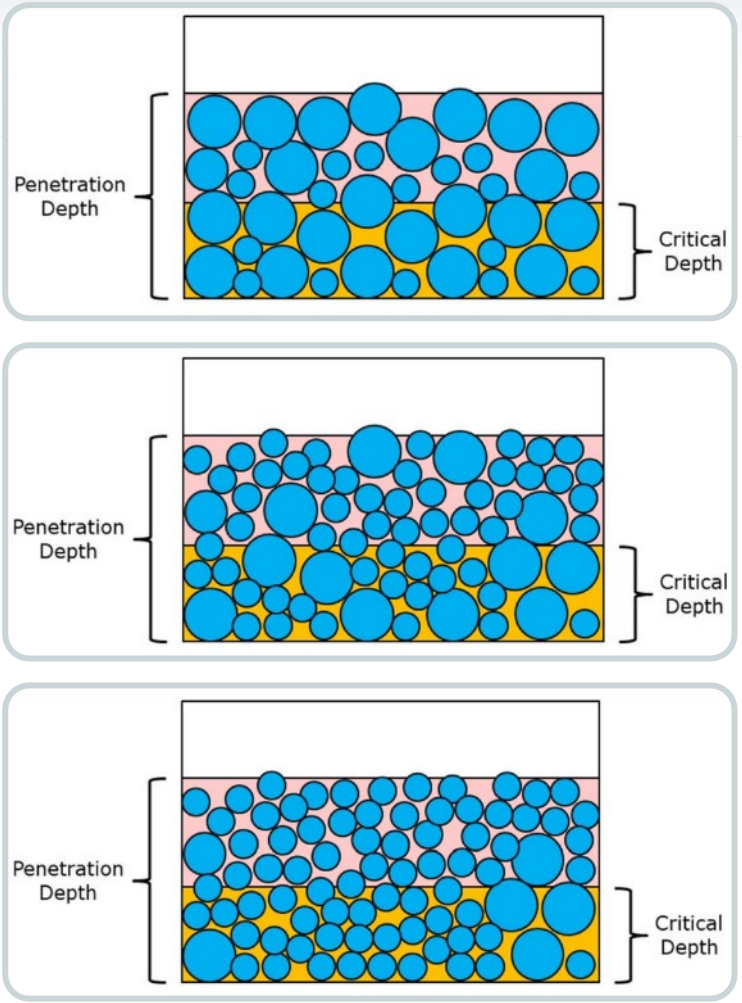




Sample preparation

Example: Influence of the grain size





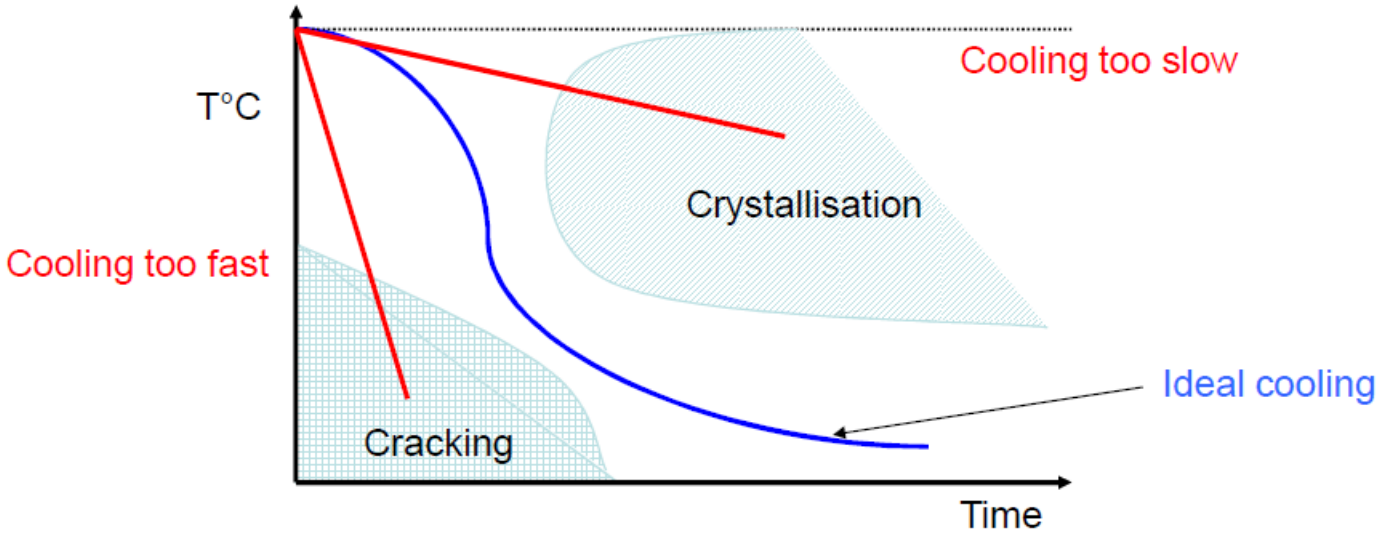
Sample preparation
Fused beads

- Sample amount e.g .: 1g
- Melting in electrical, induction or gas devices can be (semi-) automated
- Platinum vessels required
- Pre-melted flux
  - Lithium tetraborate $Li_2B_4O_7$ (920° C)
  - Lithium metaborate $LiBO_2$ (850 ° C)
  - Mixtures of $Li_2B_4O_7$ and $LiBO_2$

- Oxidizing agents: for ferro alloys, sulphides
- Nitrates of NH4, Li, Na, K, Sr
- Efficiency of melting and pouring; Lowering the melting temperature
  - LiF, B_2O_3, Na2 / Li_2CO_3
- Non-wetting agents for better watering
  - Iodides, bromides, periodides of Li or NH4 as a salt or solution
- Heavy absorbers - reduction of matrix effects
  - La, Ce, Ba oxides are no longer used frequently these days because good matrix corrections are available
- Internal standard

Sample preparation
Fused beads

- Not only the melting process is critical, but also the cooling phase

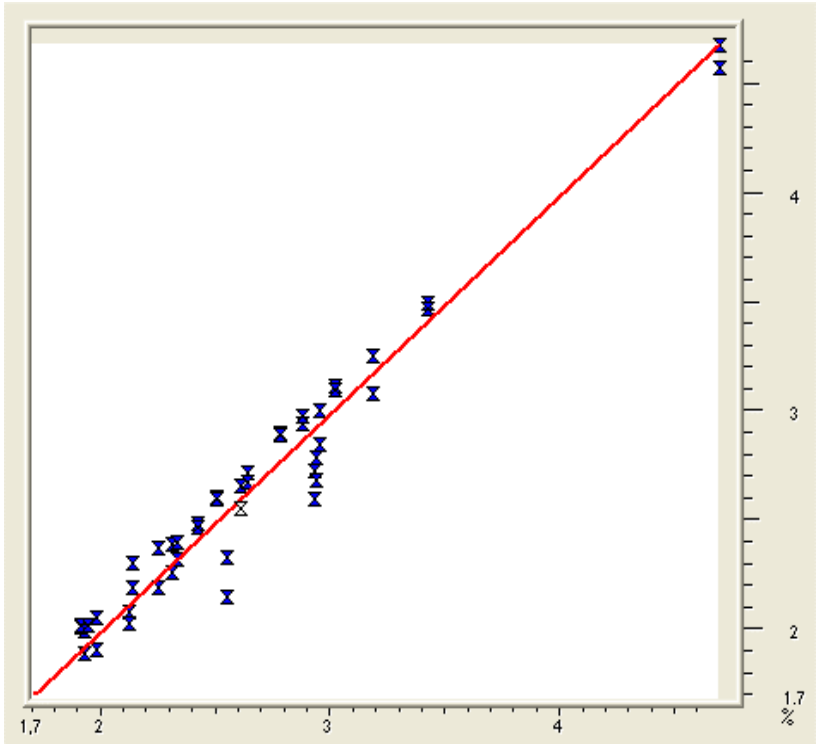


Quelle: XRFScientific

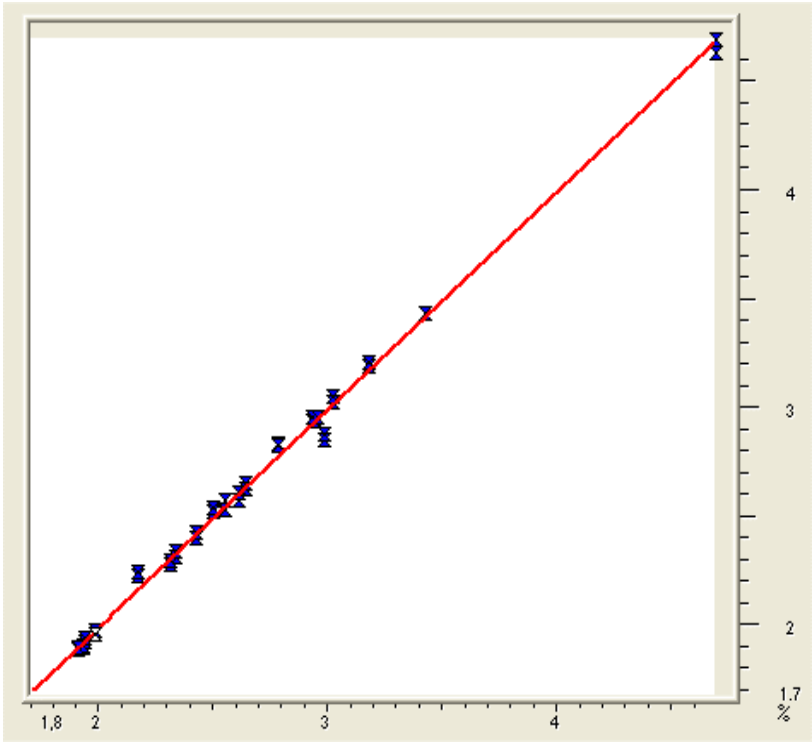
Sample preparation
Fused beads - Test

Preparation:
Same standards
Same fusion device
Same recipe and flux

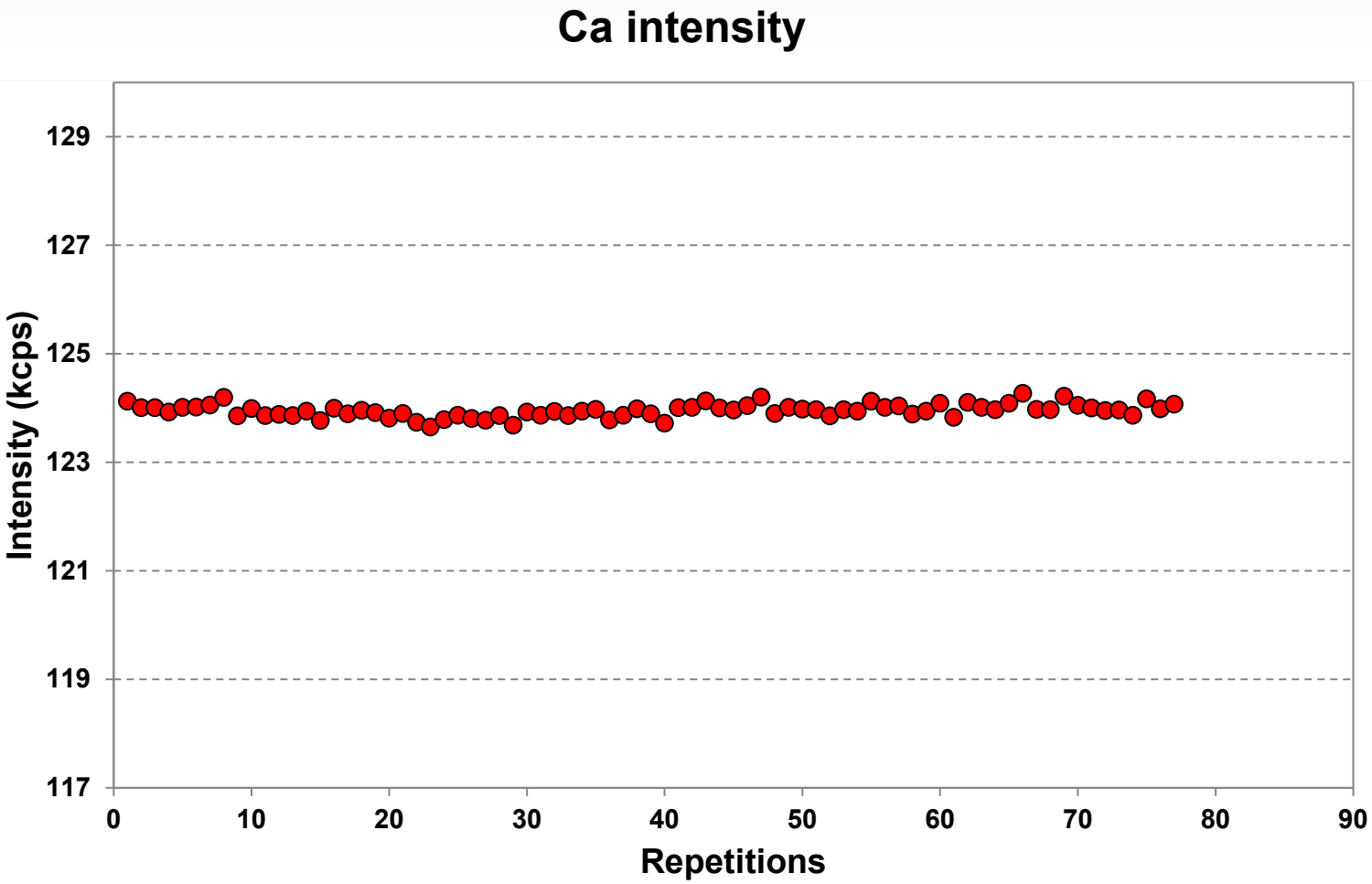
SD: 1.3%



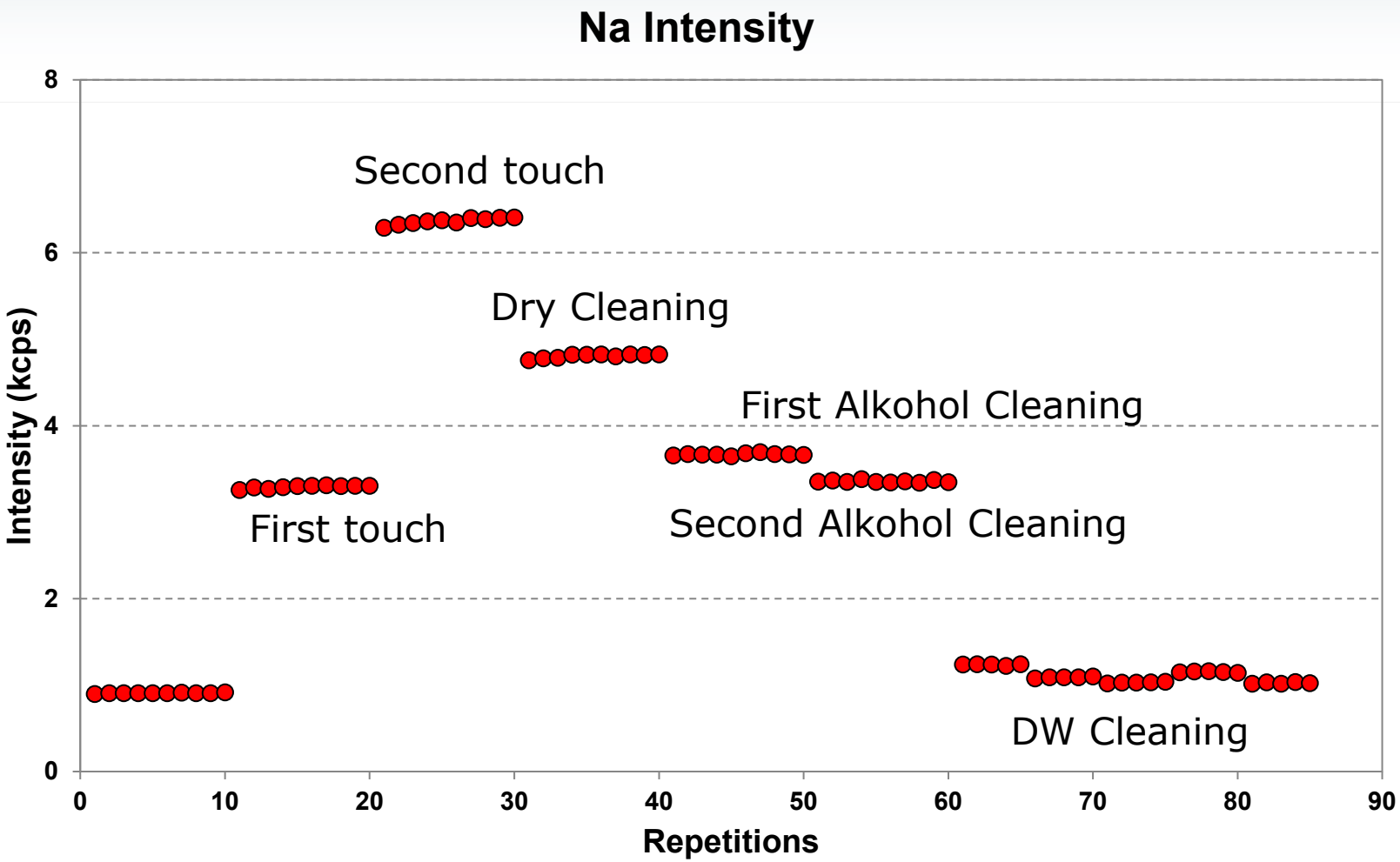
SD: 0.036%



Sample preparation
Fused beads – Test → Ca all good



Sample preparation
Fused beads – Test → Na – Oh God!



Quiz-Show Facts

Which cement / concrete structures are world record holders?

- ☐ Trump Tower (USA, Illinois)
- ☐ Lakhta Center Multifunctional Complex (Russia)
- ☐ Hoover Damm (USA, Arizona)
- ☐ Seikan-Tunnel (Japan)
- ☐ Pantheon (Rome)
- ☐ Viaduc de Millau (France)

S2 PUMA & S6 JAGUAR
Modern EDXRF & WDXRF

Compact X-ray fluorescence devices are now very powerful due to new detector technologies

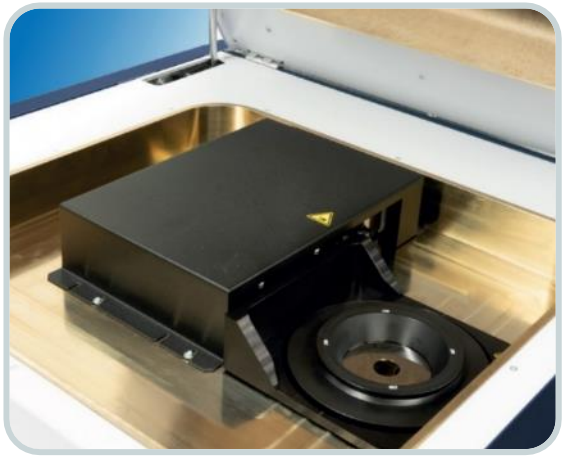
- Improved spectral resolution
- High analytical precision thanks to higher counting rates
- Simple operation and therefore quick integration into quality control

Decision about the technology (ED or WD) by:

- Element range, number of elements
- Required precision
- Detection limits
- Required sample flexibility

S2 PUMA Series 2
Ideal Back-up System, fully automated

- Single
- XY Autochanger
- XY Automation
- Carousel
- Mapping-Stage



S2 PUMA Series 2
XY Autochanger

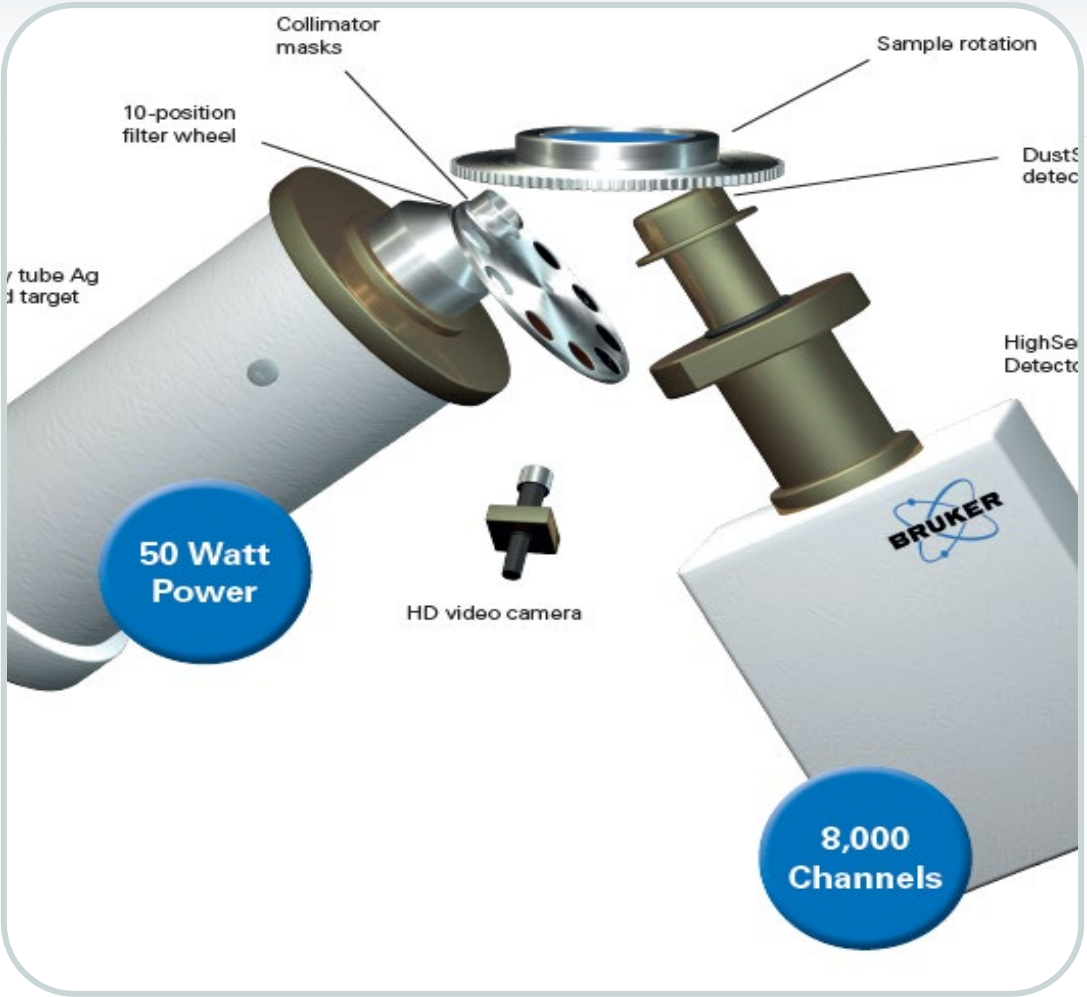
- 20-position EasyLoad™ XY sample tray (plus 2 fixed positions)
- Different sample types can be mixed in one sequence (liquids, powders, solids)
- New samples can be loaded at any time into the sample tray
- SampleCare™ guarantees highest instrument uptime
- Soft shut-down feature – important for liquid samples!

S2 PUMA Series 2
Mit HighSense™ Technologie

Optimal excitation of the sample is ensured by:

- High power 50 Watt X-ray tube
- Up to 2 mA and 50 kV
- Optional 30 kV version
- Closely coupled optics
- 10-position primary beam filter
- The Next generation silicon drift detectors (SDD) with super high count rate and excellent energy resolution

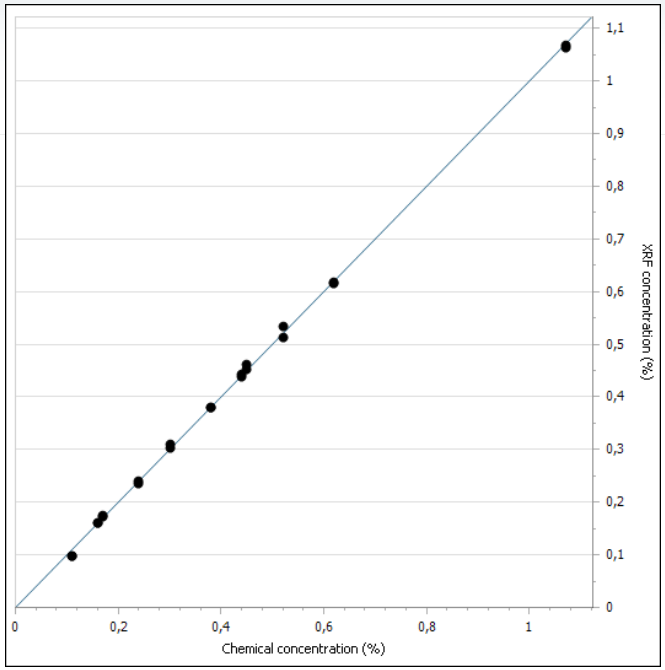
HighSense™ is the key to the unrivaled analytical performance of the S2 PUMA Series 2

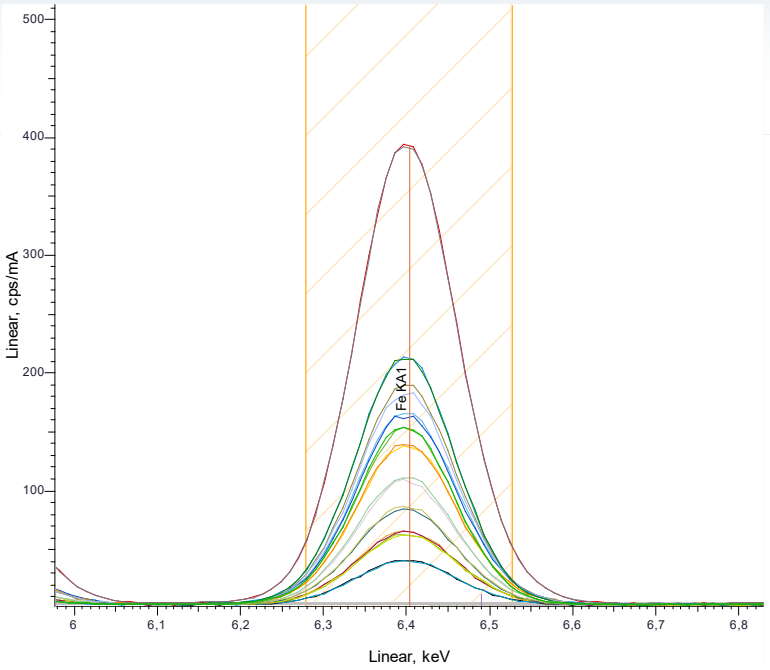


S2 PUMA EDXRF
Elemental analysis of raw materials

- The quality of the raw materials (limestone, quartz sand, ...) plays an essential role in cement production,
- The elemental composition of the individual raw materials influences the properties of the end product and also its value,
- For a cost-efficient and reliable cement production, the quality of the raw materials must be monitored.

S2 PUMA EDXRF
Elemental analysis of raw materials





- Calibration: Fe (KA1) in limestone measured with the S2 PUMA Series 2
- Conditions: **Vacuum**, Al-Filter, 40 kV, auto current
- Concentration range: 0.1 – 1.1 % Fe_2O_3
- Statistics: $R^2 = 0.99939$

S2 PUMA EDXRF
Elemental analysis of raw materials

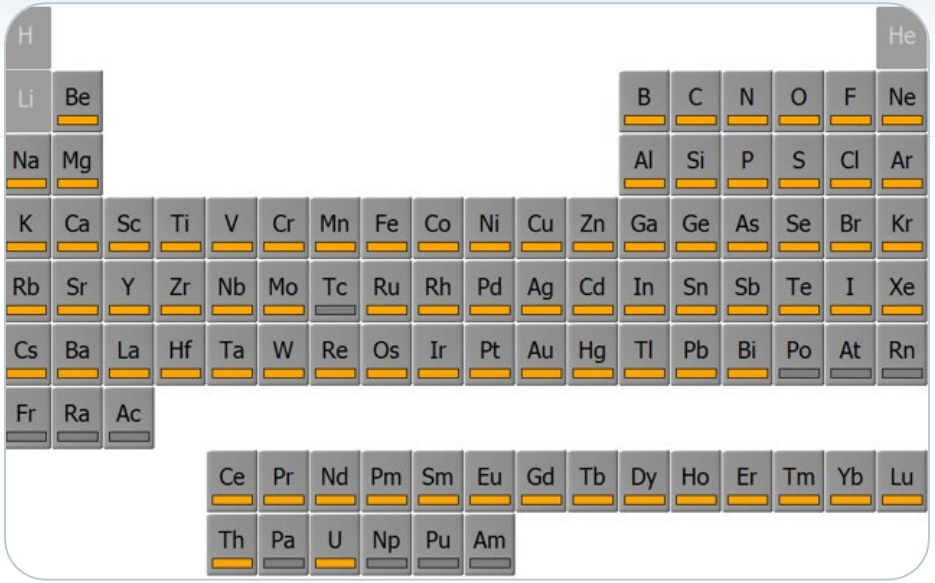
Rep-#	CaO (%)	MgO (%)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	Mn3O4 (%)	SO3 (%)	Sum (%)
1	97,058	1,117	1,137	0,452	0,302	0,048	0,066	100,18
2	97,034	1,075	1,147	0,435	0,300	0,047	0,067	100,11
3	97,092	1,139	1,135	0,447	0,303	0,047	0,067	100,23
4	97,012	1,079	1,145	0,443	0,300	0,046	0,067	100,09
5	97,005	1,078	1,152	0,442	0,301	0,048	0,067	100,09
6	97,046	1,075	1,146	0,437	0,301	0,047	0,067	100,12
7	97,052	1,120	1,142	0,441	0,301	0,047	0,066	100,17
8	97,027	1,083	1,139	0,439	0,302	0,048	0,066	100,10
9	97,055	1,122	1,137	0,447	0,302	0,047	0,069	100,18
10	96,800	1,079	1,173	0,437	0,301	0,046	0,067	99,90
11	96,627	1,098	1,200	0,432	0,300	0,047	0,068	99,77
Min	96,627	1,075	1,135	0,432	0,300	0,046	0,066	99,77
Max	97,092	1,139	1,200	0,452	0,303	0,048	0,069	100,23
Mittelwert	**96,983**	**1,097**	**1,150**	**0,441**	**0,301**	**0,047**	**0,067**	**100,09**
SD	0,134	0,022	0,019	0,006	0,001	0,001	0,001	0,13
RSD(%)	**0,14**	**2,04**	**1,62**	**1,28**	**0,31**	**1,42**	**1,27**	**0,13**

- Excellent data quality for the 7 most important major and minor elements in limestone (total at 100.1%)
- Very good precision even at low concentrations (RSD: 0.1-2%)

X-ray Fluorescence (XRF) spectrometry
Element range

X-ray Fluorescence (XRF) analysis is qualitative and quantitative method for the determination of element concentrations via excitation of atoms in the sample and detection of the characteristic X-rays.

- High-power WDXRF (4–1 kW):
  Be (B) – Am
- Medium WDXRF (400 W):
  O (F) – Am
- Modern EDXRF:
  C (F) – Am
- Low-power EDXRF:
  Na (Mg) – Am



- Element range XRF:
  (Be) B to Am
- Concentration range:
  Sub-ppm to 100 %

S6 JAGUAR
High Performance Benchtop WDXRF

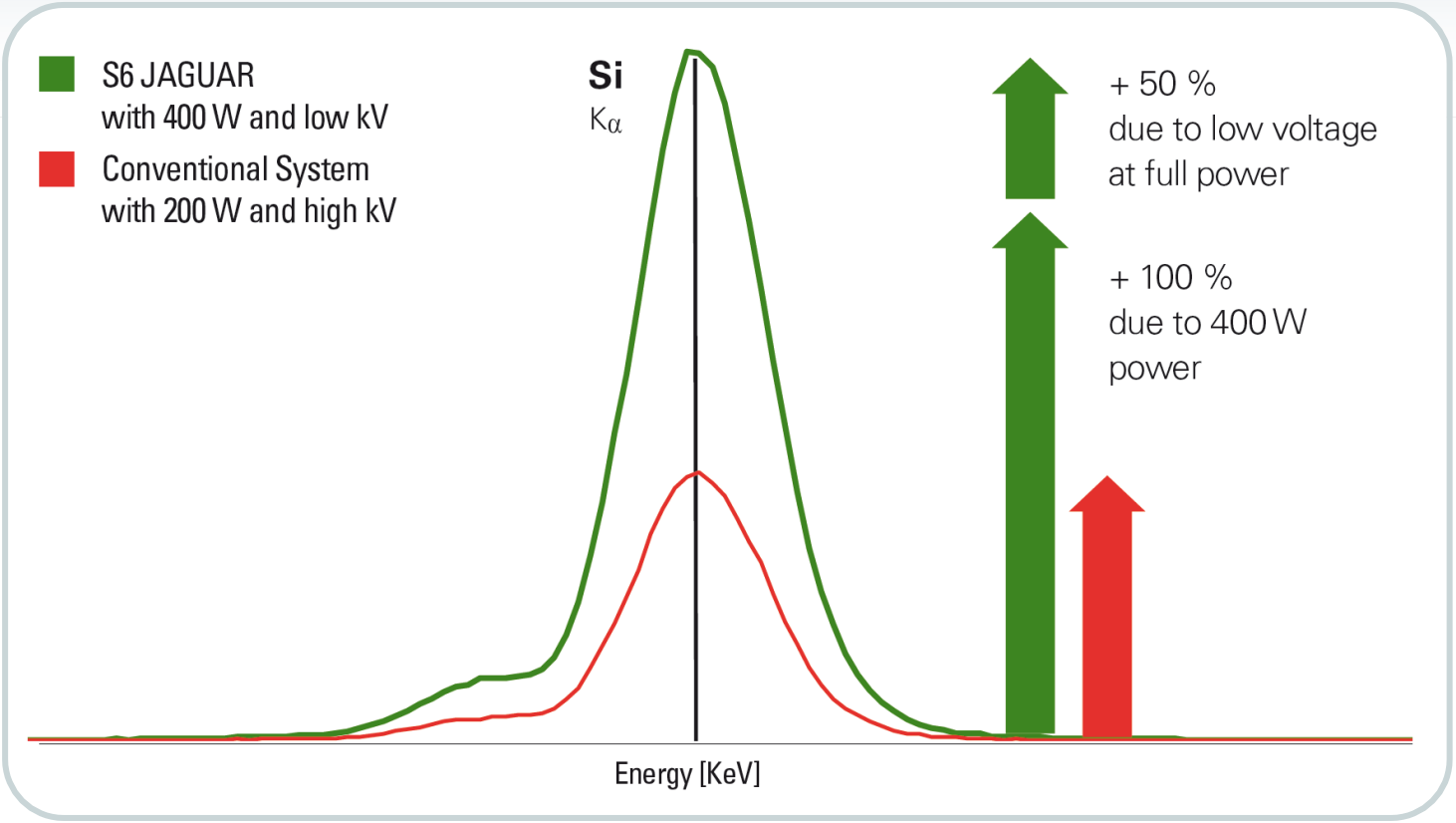
Maintain WDXRF resolution:

- Compact goniometer with high precision gears and closely coupled X-ray beam path
- Optimized analyzer crystals for the entire element range and special applications

Maintain analytical precision and sensitivity:

- Higher power X-ray tube compared to EDXRF (there is no saturation due to single element detection)
- HighSense detection with 2 Mcps count rate
- HighSense XE detector for medium and heavy elements

S6 JAGUAR
HighSense™: Light Elements



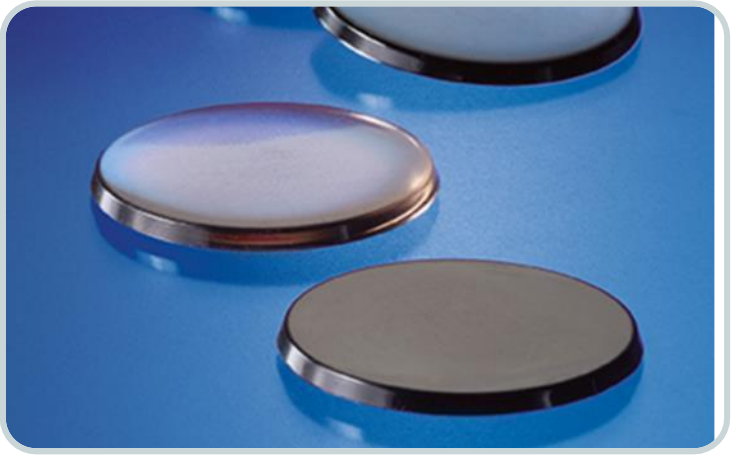
Not only the overall performance is important! Also the excitation parameters: The S6 JAGUAR analyzes light elements with optimal low voltage and full 400 W power settings!

Example: S6 JAGUAR White Portland Cement

Quality control of cements according to ASTM C114 and ISO 29581-2 / DIN EN 196-2

- Determination of the elemental composition
- Analysis of major elements:
  - Ca, Al, Si, S, Fe as oxides
- Evaluation of minors
  - Na, Mg, P, K, Ti, Cr, Mn, Zn, Sr

- Fused bead preparation for optimal accuracy eliminating mineralogical effects



XRF - X-ray Fluorescence Analysis
Precision and Counting Statistics

Precision limited by counting statistical error

$$\Delta c / c = \text{SQRT}(N) / N = 1 / \text{SQRT}(N)$$

N =	100	SQRT (N) =	10	3*SQRT(N) / N =	30 %
N =	1000	SQRT (N) =	30	3*SQRT(N) / N =	10 %
N =	10 000	SQRT (N) =	100	3*SQRT(N) / N =	3 %
N =	100 000	SQRT (N) =	300	3*SQRT(N) / N =	1 %
N =	1000 000	SQRT (N) =	1000	3*SQRT(N) / N =	0.3 %
N =	10 000 000	SQRT (N) =	3000	3*SQRT(N) / N =	0.1 %

The S6 JAGUAR delivers more precise results:

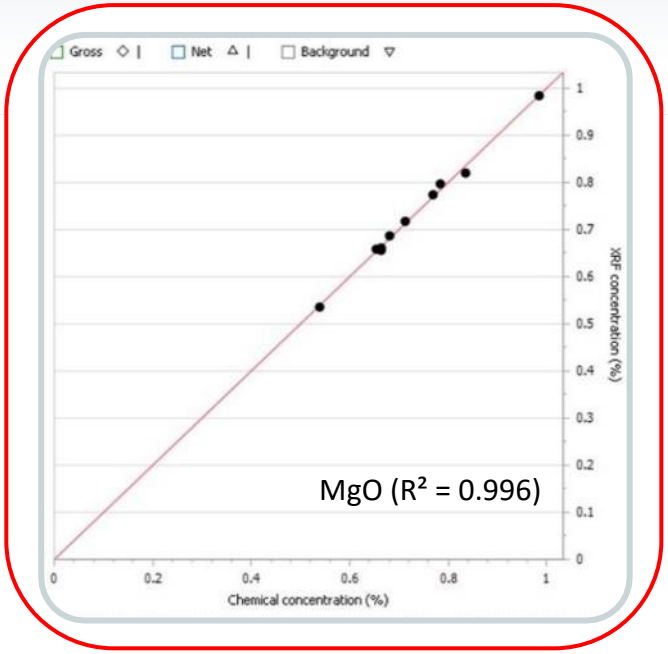
- 400 W power, closely coupled optics
- Optimal excitation
- Enhanced sensitivity with optimal analyzer crystals
- HighSense detectors and counting electronics with up to 2 Mcps

Example: S6 JAGUAR White Portland Cement

Color-relevant secondary components (e.g. Fe, Mn) must be kept below a certain threshold value.

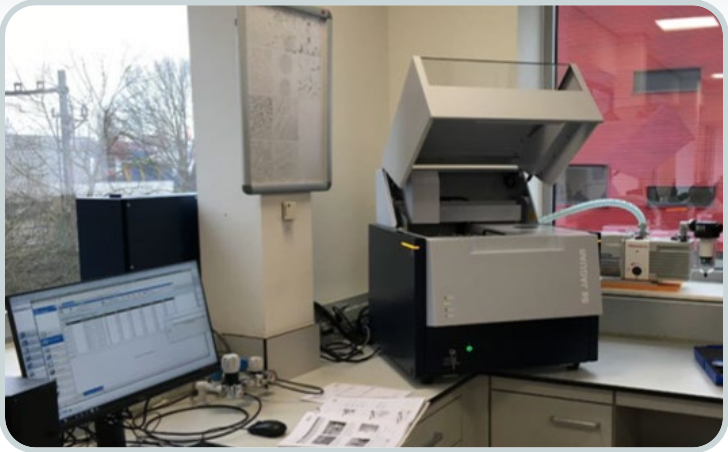
Simple sample preparation with pressed pellets

Very low standard deviations for traces of Fe (0.162 ± 0.001 wt% Fe2O3) and Mn (72 ± 1 ppm MnO)



	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Average	0.156	0.665	2.496	15.83	0.018	0.041	429	0.331	44.09	0.091	72	0.162
Abs. Std. Dev.	0.003	0.005	0.005	0.02	0.000	0.000	6	0.001	0.02	0.001	1	<0.001
Known composition	0.138	0.663	2.51	15.9	0.019	0.048	423	0.334	44.21	0.092	74	0.164
Abs. diff.	0.018	0.002	0.014	0.07	0.001	0.007	6	0.003	0.12	0.001	2	0.002

S6 JAGUAR
Customer feedback

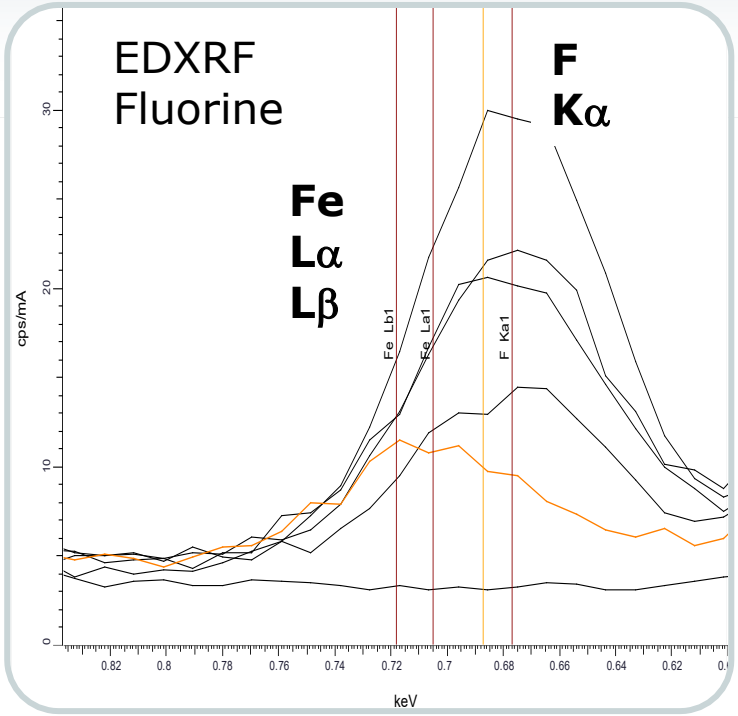


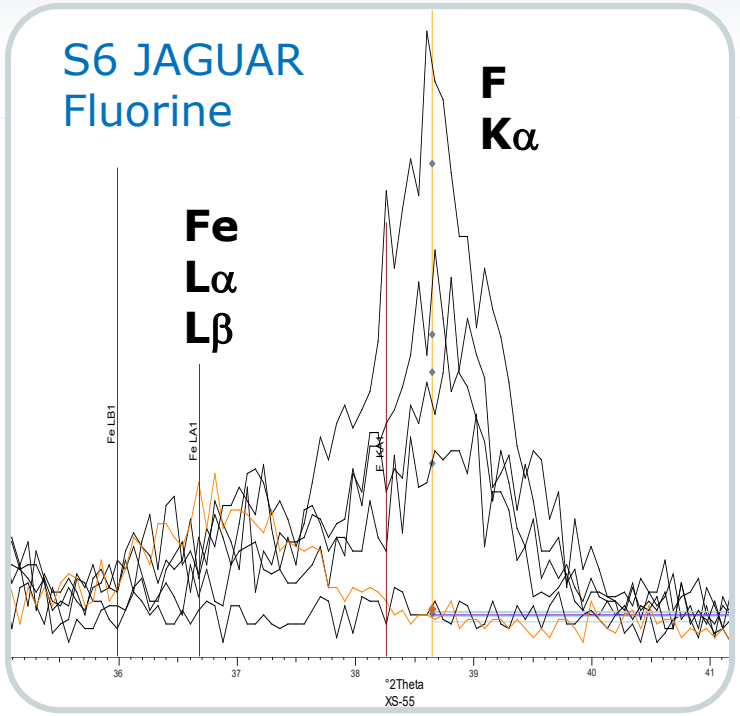
A world-famous manufacturer of refractory and foundry products was looking for a spectrometer for the analysis of main elements in magnesites, etc.,….

- In addition to traces, the analysis of fluorine was also important:
  - Is a large WDXRF spectrometer required, although only a few samples have to be analyzed per day?

The S6 JAGUAR showed excellent performance for light and important elements with optimal accuracy, surpassing the EDXRF due to the better dissolution of fluorine in the presence of high iron (Fe La overlay)
→ preference for WDXRF

S6 JAGUAR versus EDXRF
F in Foundry Products





Strong overlap of F Ka and Fe La with **EDXRF** leads to medium accuracy and precision: **Min 3.59 % –> 3.78 % <- Max 4.07 %**

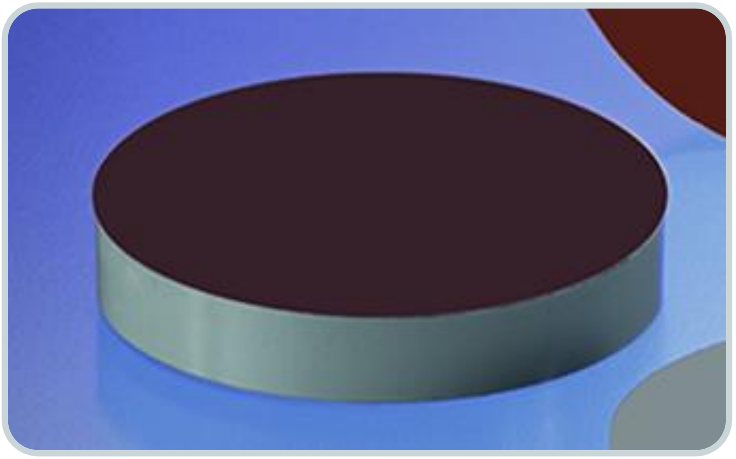
S6 JAGUAR: Optimal resolution, clear separation of both lines, high sensitivity with 400 W power: **Min 3.97 % -> 4.03 % <- Max 4.07 %**

Benchtop WDXRF for fuel analysis
Coal, coke, carbon

Coal is widely used in metal making (aluminum, steel) and power generation (electricity)

Analysis of coal, coke and carbon products is vital:

- Prevent contamination of metal products
- Inhibit (steel) corrosion (monitoring of Cl)
- Reduce environmental impact (reducing S content)



Benchtop WDXRF for fuel analysis
Coal, coke, carbon

Element	XRF conc.	Cert. Conc.	Abs Std Dev.	Rel Std Dev.
S [%]	3.40	3.30	0.02	0.72
Ni [ppm]	128.00	124.00	4.48	3.50
Si [ppm]	24.00	28.00	1.15	4.80
Fe [ppm]	276.00	266.00	2.65	0.96
Na [ppm]	623.00	645.00	43.61	7.00
Al [ppm]	153.00	150.00	5.66	3.70
Ca [ppm]	112.00	107.00	2.35	2.10
K [ppm]	17.00	17.00	1.84	10.80
Cl [ppm]	100.00	n.a.		
Ti [ppm]	5.00	4.00	0.31	6.10
Zn [ppm]	40.00	41.00	0.10	0.25
V [ppm]	302.00	300.00	2.33	0.77

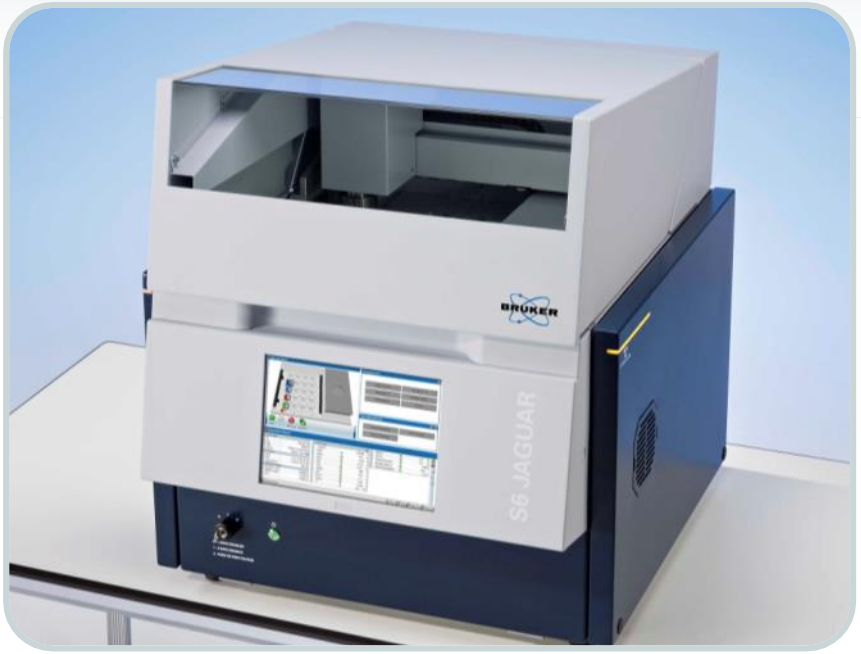
Optimal accuracy for:
- Minor elements, such as S
- Traces, e.g. Si, Cl, Fe

S6 JAGUAR & S2 PUMA
Manual: Quick Sample Change

- Easy access to large sample chamber
- For all kinds of samples:
  - Solids
  - Pressed powders
  - Fused beads
  - Liquids with helium mode
  - Loose powders in cups with helium
- Economical option for lower sample throughput

S6 JAGUAR & S2 PUMA
EasyLoad™: High Productivity

- Automatic measurement of sample batches for high throughput
- Load and prioritize new samples at any time
- Loading of entire batches by swapping trays
- Automatic liquid cup detection
- Soft shut-down in case of power outage
- Automation ready for robot and belt interfaces



EasyLoad: 20 Positions on a tray

EasyLoad ONLINE: 20 positions on a tray (51.5-mm rings); 2 fixed positions for QC samples

Elemental analysis: Cement
Would you like a little more?

- Ready for automation: professional integration in fully automated environments
- The samples are fed directly from the automatic sample preparation system
- AXSCOM communication interface for connection to the control software
- EasyLoad™ tray with 20 positions for external samples: add, replace, remove and prioritize samples at any time.

- **CEMENT-QUANT**: Out-of-the-box-solution for the analysis process materials in the cement industry:
- Fully compliant with ASTM C114 and ISO 29581-2 / DIN EN 196-2
- 20 certified reference materials (CRM)
- 2 drift correction samples
- 1 quality check sample
- Covers 14 elements

All about cement
Which analytics should I choose?

In modern XRF laboratories in the cement industry with the need to measure traces of elements and heavy metals, the following strategies are successful:

Multi-channel WDXRF spectrometer S8 LION:

- For very high number of process samples

Sequentielle WDXRF spectrometer:

- S8 TIGER: Fast and flexible, also for AFRs (heavy metals), slags (F), hot meal (Alkali-Chloride), S speciation
- S6 JAGUAR -> Backup, additional WDXRF capacity, also for F in slags

Benchtop EDXRF S2 PUMA:

- Fast analysis of raw meal at the mill, excellent backup, also in automated environments

Ground Granulated Blast Furnace Slag Cement (GGBS) is the contribution to reduce global warming, but needs activating with portland cement (mixtures between 20 – 80%)

Quiz-Show Facts

Which cement / concrete structures are world record holders?

- ☐ Trump Tower (USA, Illinois)
- ☐ Lakhta Center Multifunctional Complex (Russia)
- ☐ Hoover Damm (USA, Arizona)
- ☐ Seikan-Tunnel (Japan)
- ☐ Pantheon (Rome)
- ☐ Viaduc de Millau (France)

Bruker AXS
Total Cement Solutions

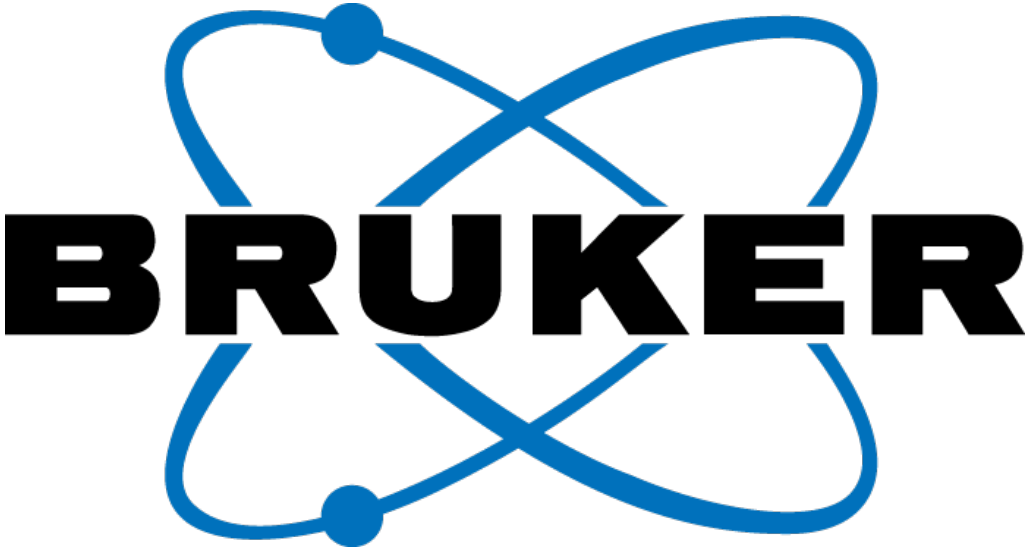
- **S2 PUMA**
  - Backup
  - Rohmehl
- **S6 JAGUAR**
  - Mahlwerke
  - Backup
  - Zentral. Lab
- **S8 TIGER**
  - Prozess/Qualitätskontrolle
  - Flexibilität, AFR
  - Process & Central Lab.
- **S8 LION**
  - Prozess/Qualitätskontrolle
  - Durchsatz

- **D2 PHASER**
  - Backup
  - spot test
- **D8 ENDEAVOR**
  - Prozess/Qualitätskontrolle
- **D8 ADVANCE**
  - Zentral. Lab

Q&A

Any questions?

Thanks for your time and interest!



Innovation with Integrity