Elemental Analysis of Food and Feed Products with XRF

Welcome!

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Today's Topics

- Some background
  - Why is monitoring of food & feed important?
  - Why is XRF the right tool to monitor food & feed quality?
- Features and benefits of the S2 PUMA Series 2 for food analysis
  - The importance of sample preparation and atmosphere mode
- Food & feed application examples
- Closing remarks

Why Monitoring Food and Feed is important?

Reasons for Food Analysis

- Legal regulations and recommendations
  - *Standards of Identity* specify type and amount of ingredients of certain foods
  - *Nutritional Labels* state e.g. contained Ca and Fe, and may inform about nutrient content claims ("low sodium")
  - *Food Inspection* ensures food stuffs meeting the appropriate laws and regulations

Nutrition Facts

Serving Size 1 cup (228g)
Servings per Container 2

Amount Per Serving

Calories 280	**Calories from Fat** 120
	% Daily Value*
Total Fat 13g	20%
Saturated Fat 5g	25%
Trans Fat 2g	
Cholesterol 2mg	10%
Sodium 660mg	28%
Total Carbohydrate 31g	10%
Dietary Fiber 3g	0%
Sugars 5g	
Protein 5g	

Vitamin A 4% • Vitamin C 2%
Calcium 15% • Iron 4%

*Percent Daily Values are based on a 2,000-calorie diet. Your daily values may be higher or lower depending on your calorie needs.

	Calories:	**2,000**	**2,500**
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Fiber		25g	30g

Calories per gram:
Fat 9 • Carbohydrate 4 • Protein 4

Reasons for Food Analysis

- **Food safety**
  - Avoid toxic chemicals (e.g. Ni, Pb), foreign material (e.g. metal, plastic particles)
- **Quality control**
  - Characterization of raw materials
  - Monitoring food during processing
  - Analysis of the final product
- **Research & development**
  - Constant need for optimization: healthier, cheaper, longer lasting etc.

Reasons for Food Analysis

Requirements determine the measurement method

- Mandatory regulatory control or routine quality control
- Need for certified method standards (USDA, ASTM, etc.)
- Quantitative determination or qualitative screening: results or pass / fail
- Laboratory QC analysis or on-line measurements in production
- Control of incoming raw materials or end products
- Element concentrations and limit values to be observed
- Urgency and (economic) relevance

Food Monitoring via EDXRF
What are we looking for?

Specific XRF application examples

- Milk powder: Fe fortification, Ca and Mg monitoring
- Pet food: Ash content (Na, Mg, K, and Ca oxides) as regulatory requirement, nutritional additives (e.g. Mn, Fe, Zn)
- Cl / Cl_2 compliance for salt labeling requirements for chips, processed meats, and cheese (NaCl, KCl or $CaCl_2$)
- Rice and grains: Fe fortification or trace process metal contamination?
- Bakeries: TiO_2 as product brightener

Why XRF is the right tool to monitor Food Quality?

Audience Poll

What are your main goals with XRF elemental analysis – What are you trying to achieve? (Check all that apply.)

- ❑ Check quality of incoming material
- ❑ Monitor the production process
- ❑ Verify/certify final product quality

- ❑ Optimize final product quality (R&D)
- ❑ Optimize production costs
- ❑ Increase throughput

- ❑ Other

Advantages of XRF

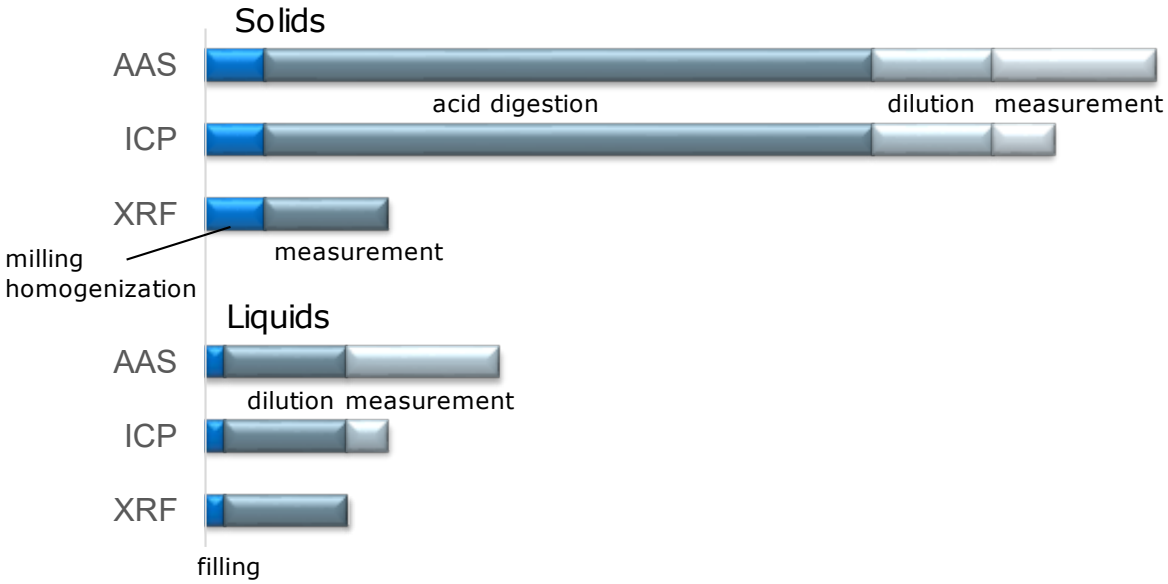
- Solid and liquid samples can be analyzed directly
- Little or no sample preparation required
- Most sample types can be measured easily without dilution / ashing, etc. (e.g. solid, loose, pressed and liquid samples)
- Short time from sampling to the result (e.g. compared to ICP and AAS)
- **Food & Feed:** Light matrix (biomass, liquids, etc.) prefers lower detection limits
- Non-destructive
- Quantitative and qualitative analysis
- Accuracy and long-term stability

Advantages of XRF
Time-to-Result: XRF vs. AAS and ICP

Effective quality and process control requires the shortest time-to-result possible. This is the time needed from sampling to the final quantitative result. Any advantage results in:

- Higher sample throughput
- Stable industrial processes due to immediate feedback
- Constantly high product quality

Time-to-result



Advantages of XRF: Its all about money!
Cost of Ownership: XRF vs. AAS and ICP

The investment for the analytical instrument is only one part of the total cost of ownership. Expenses for laboratory equipment and consumables add to that cost.

ICP/AAS

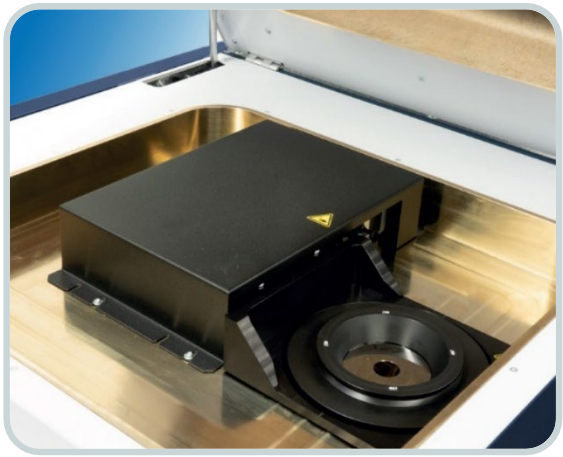
- **Use of expensive accessories** (AAS: graphite tubes)
- **Consumption of noble gases** (ICP: Argon)
- **Need for hazardous chemicals** (compliance with high-level safety regulations)
- **Complicated sample preparation equipment** (training and time)

EDXRF: No gas or very little He!

Features and Benefits of the S2 PUMA Series 2 for Food Analysis

S2 PUMA Series 2
Optimal Configuration for Your Application

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



S2 PUMA Series 2
XY Autochanger

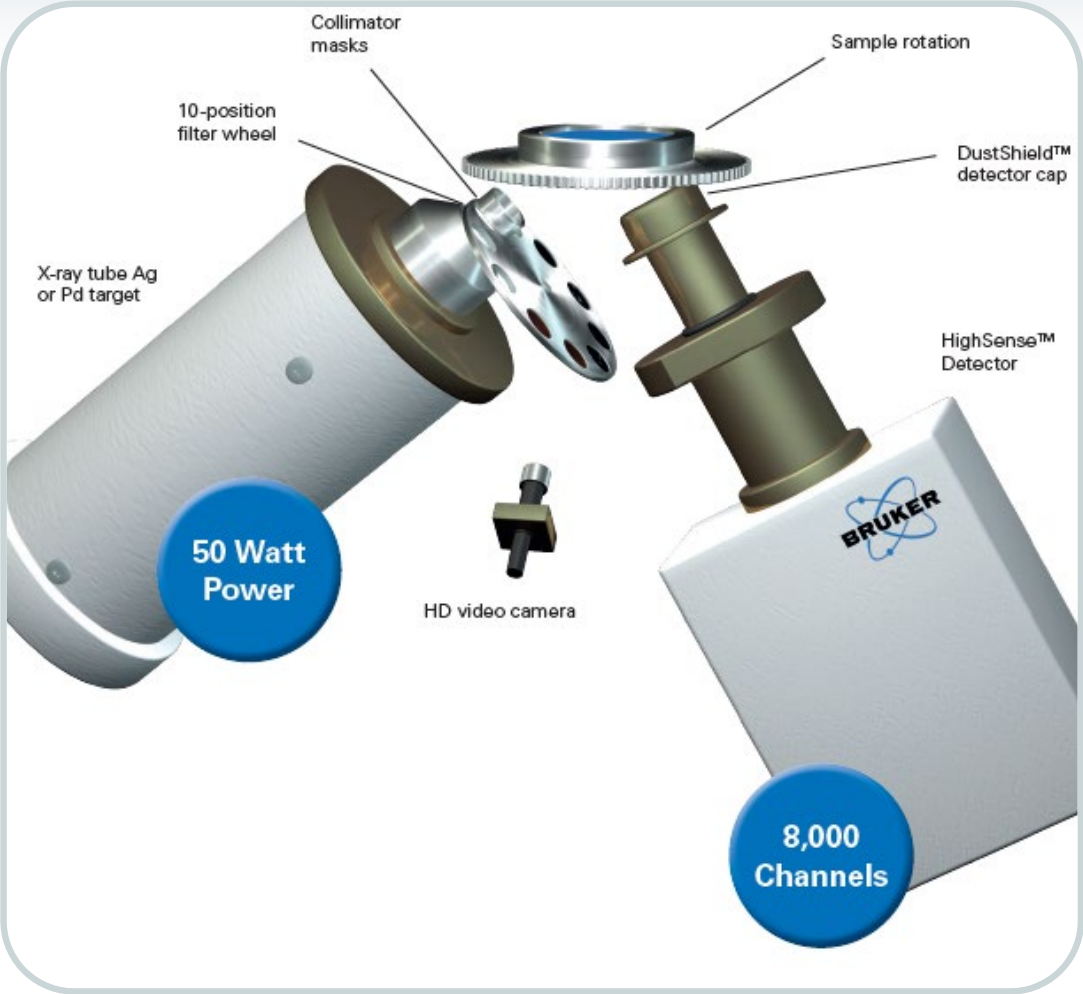
- 20-position EasyLoad™ XY sample tray
- Different sample types can be mixed in one sequence (liquids, powders, solids)
- New samples can be loaded at any time into the sample tray
- SampleCare™ guarantees highest instrument uptime

S2 PUMA Series 2
Powered by HighSense™ Technology

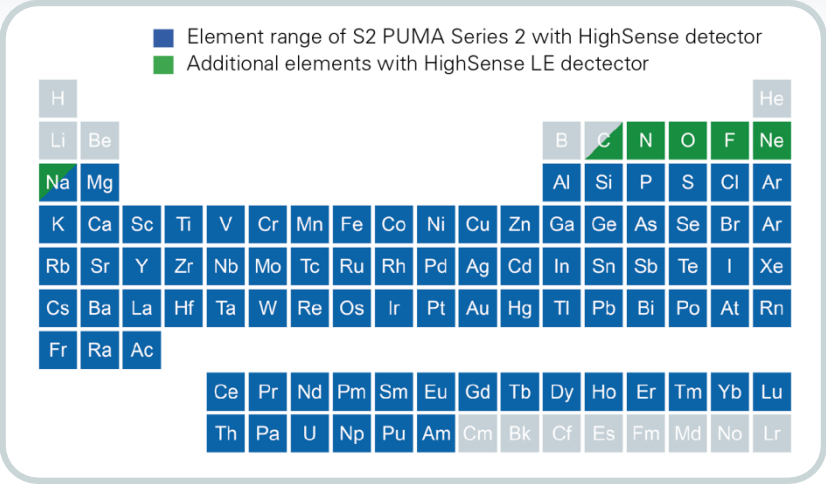
Optimal excitation of the sample is ensured by:

- 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



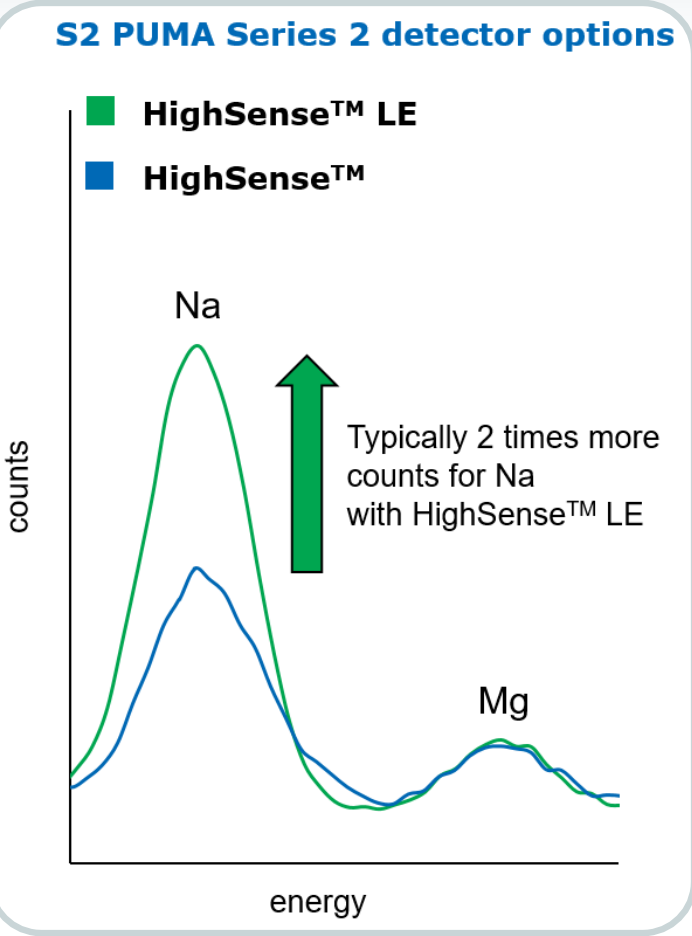
S2 PUMA Series 2
Food&Feed: Not always an LE Application!



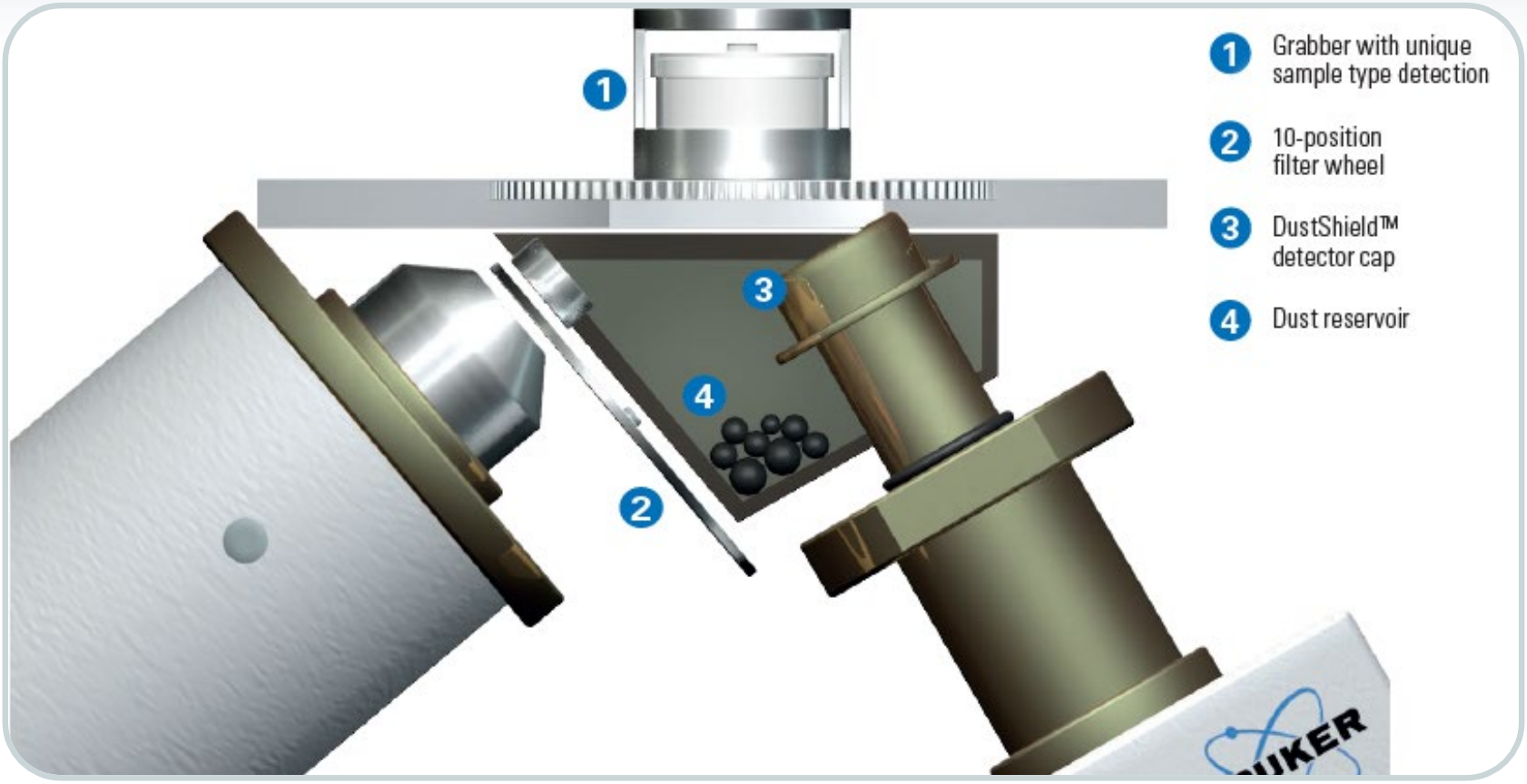
You have the choice!

- Select the standard HighSense™ detector and a X-ray tube with Pd target for Na – Am.
- Boost your performance for light elements with the HighSense™ LE detector and an Ag target.

Always with 50 Watt power!



SampleCare™ – A critical feature for liquids, powders and fragile pellets



SampleCare™: A unique, multi-layer system to protect vital system components

S2 PUMA™ Series 2 Atmosphere Modes

Helium free operation for best light element detection in solid samples

Lowest (0.08L/min) gas consumption for lowest running costs for volatile liquids

Optimal atmosphere

- Vacuum, helium, air, nitrogen

For all sample types and applications

- Solids, liquids, powders, pressed pellets, fused beads, bulk






Sample Preparation
Best Practice

Which preparation method is the best?

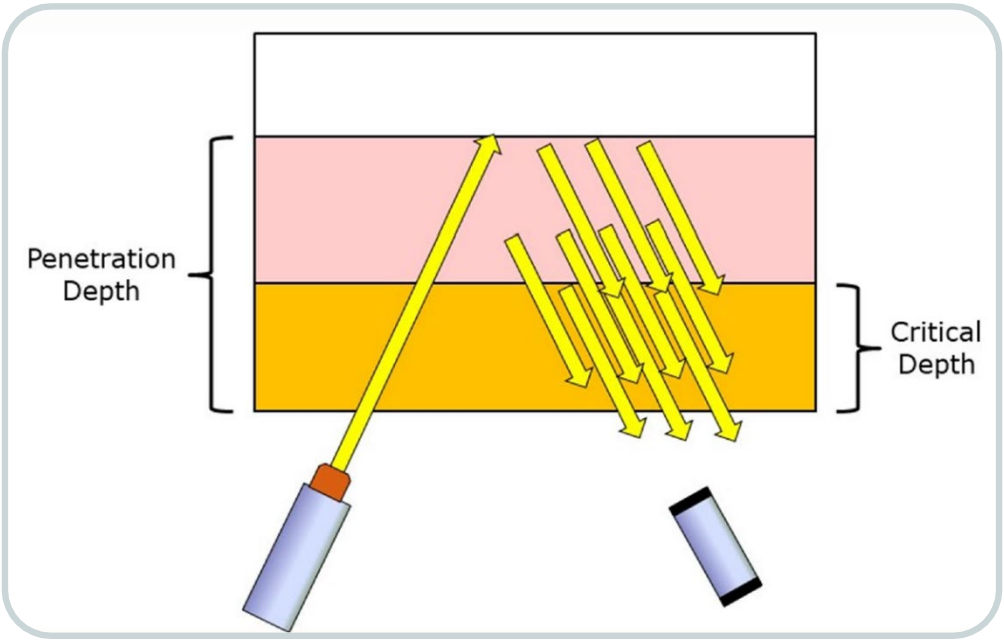
- XRF can analyze food and feed samples without (powder, grains, liquids) or after minimal sample preparation (ground powder, pressed pellets)
- Grain size and sample homogeneity can play an important role when it comes to precision and accuracy
- Lighter elements are more affected

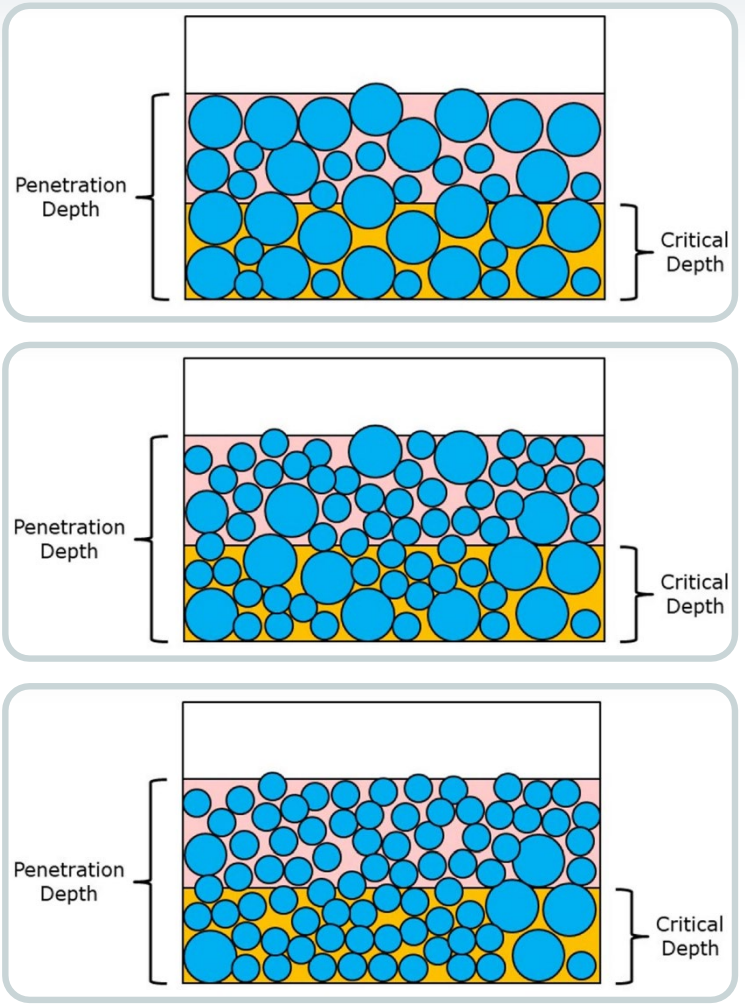
→ **The optimal preparation methods depends on the sample type and the analytical requirements**
(e.g. precision, accuracy, throughput)

→ *Heads-up:* We will show an example for milk powder

Sample Preparation
Best Practice

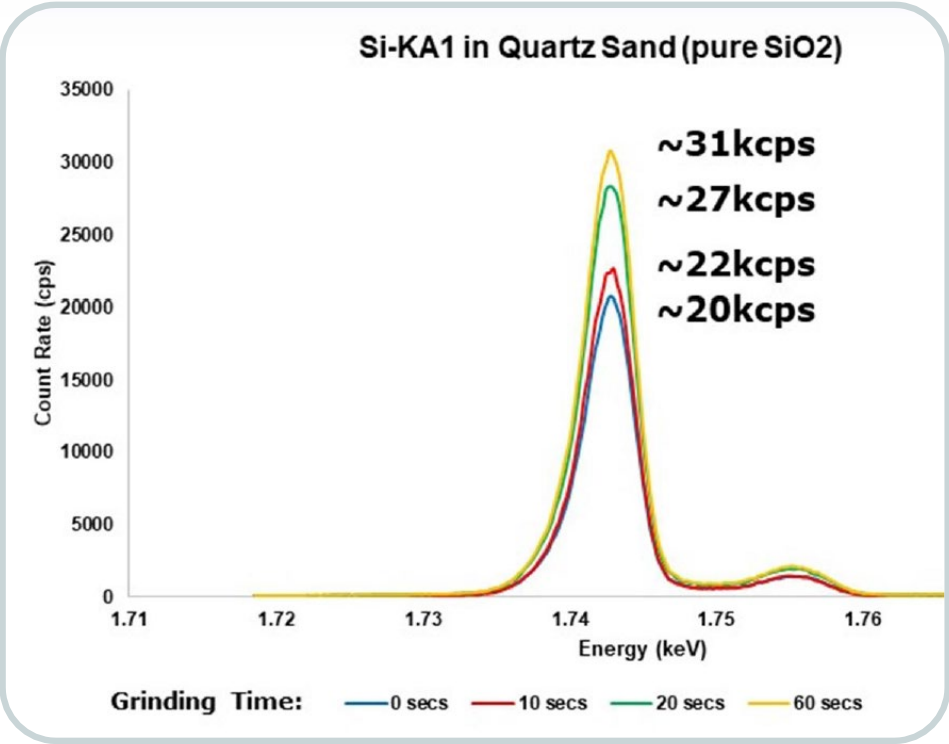
Example: The effect of grain size

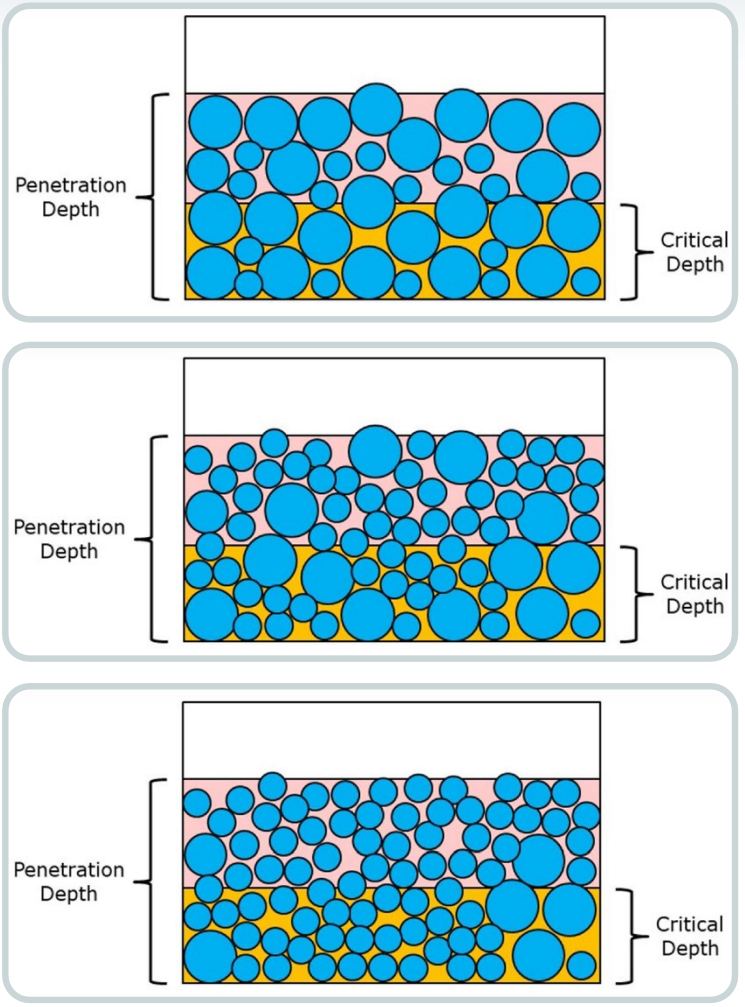




Sample Preparation
Best Practice

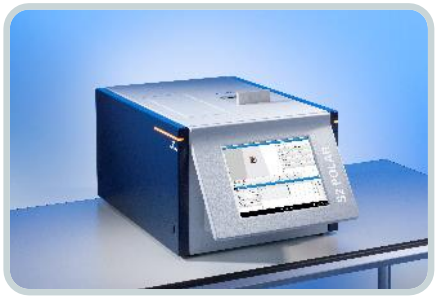
Example: The effect of grain size





Food & Feed Example Applications

S2 PUMA vs. S2 POLAR vs. S6 JAGUAR



Most Food & Feed Applications are EDXRF tasks.

- Typically the **S2 PUMA Series 2** with XY Autochanger is the ideal configuration
  - Since Na is often the lightest element a Pd System with Standard HighSense can be sufficient
- Select the **S2 POLAR** when dealing with trace elements in liquids (such as P in edible oil)
- Typical reasons to switch a **S6 JAGUAR**
  - Measure traces of F (or Na)
  - Higher throughput required (but smaller number of elements)
  - Very low LLD for medium and heavy elements (< 10 ppm)
  - Cases where peak-overlap becomes problematic (rather rare)
  - Prerequisite: Samples must be relatively stable (higher power!)

S2 PUMA Series 2
Ideal for Food and Feed

Requirements for food and feed analysis

Many elements:

- Na, Mg, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Se, Mo, …

Wide range of concentrations:

- Low ppm to several wt%

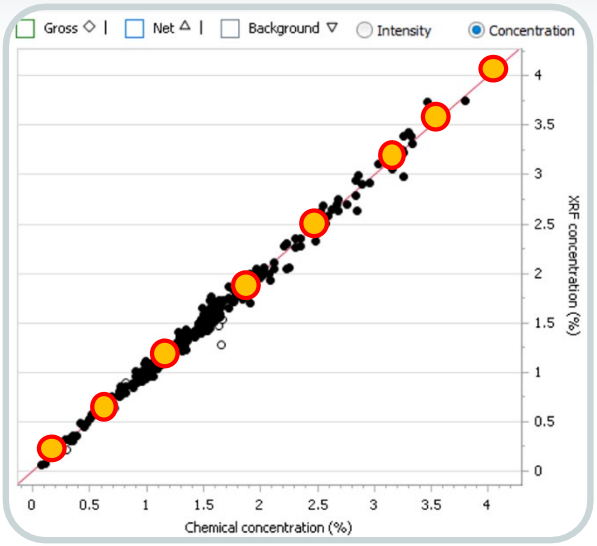
Minimal sample preparation:

- Loose powder, 7 g of material placed in liquid cup with prolene thin film 4 µm

Several calibrations for different matrices

- Typically using large sets of reference materials and secondary standards which may be not very stable

S2 PUMA Series 2
Ideal for Food and Feed



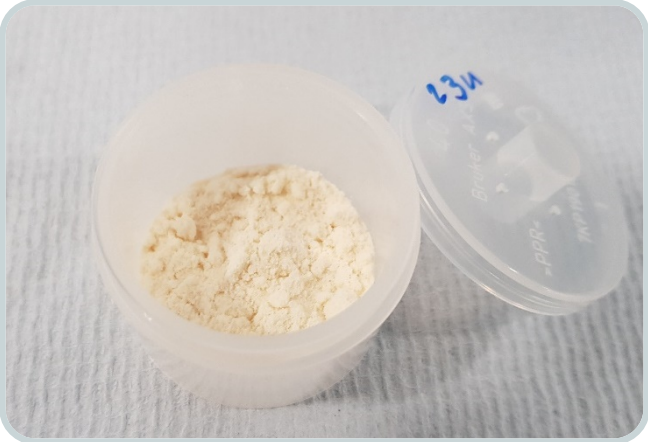
Calibration curve K Kα1

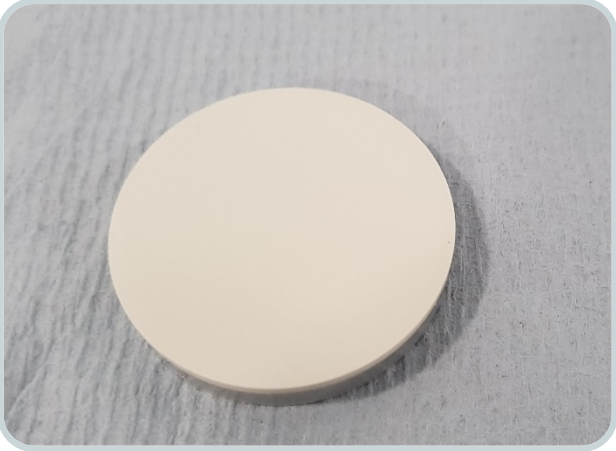
- **Excellent performance for loose powders**
- We developed a **transfer-kit** in close collaboration with Cumberland Valley Analytical Services
- Allows the method transfer from one unit to another via analysis of few stable glass beads

	Compositional Ranges Master System [wt%]
Na	0 – 1.06
Mg	0.07 – 0.75
Si	0.16 – 4.75
P	0.06 – 0.74
S	0.06 – 0.56
Cl	0.04 – 2.67
K	0.11 – 6.07
Ca	0.01 – 2.65
Mn	3.9 – 288.6 ppm
Fe	20.9 – 2853.1 ppm
Cu	1.2 – 38.7 ppm
Zn	6.5 – 150.4 ppm
Se	0 – 586.5 ppm
Mo	0 – 27.7 ppm

S2 PUMA Series 2
Ash content in milk components

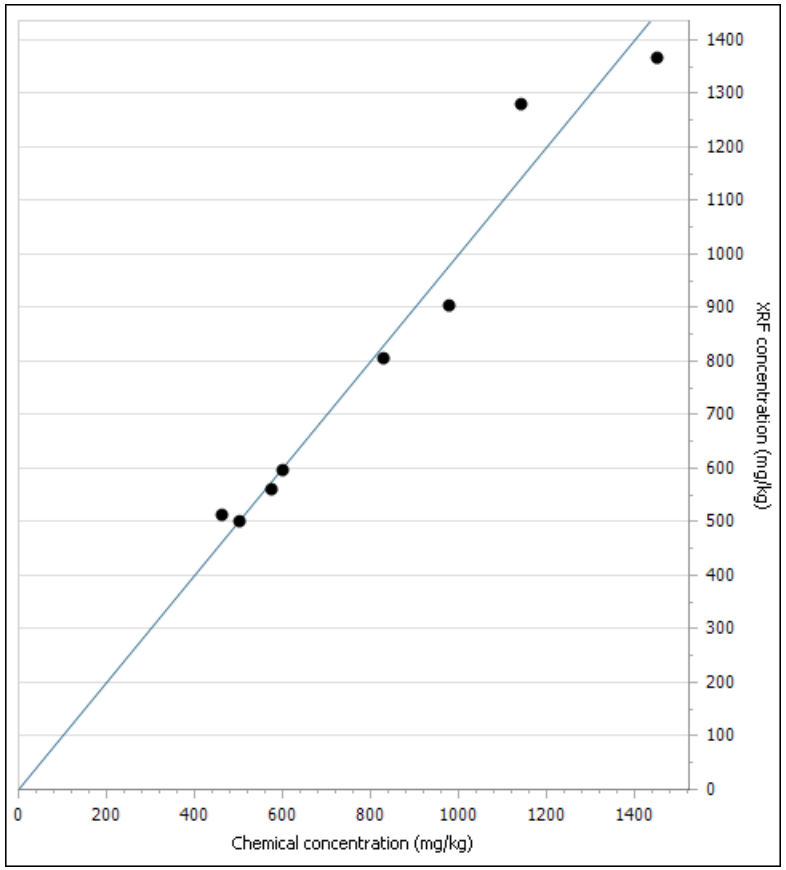
- **Calibration with 8 secondary reference materials** (ICP, titration, gravimetric)
- Lactose, milk protein, whey protein, milk-calcium
- Covering up to 9 elements with concentrations ranging from few ppm (e.g., Fe, Zn) up to couple wt% (e.g. Ca, P) (Na, Mg, P, Cl, K, Ca, Mg, Fe, Zn)
- Pressed pellets (no wax) and loose powder

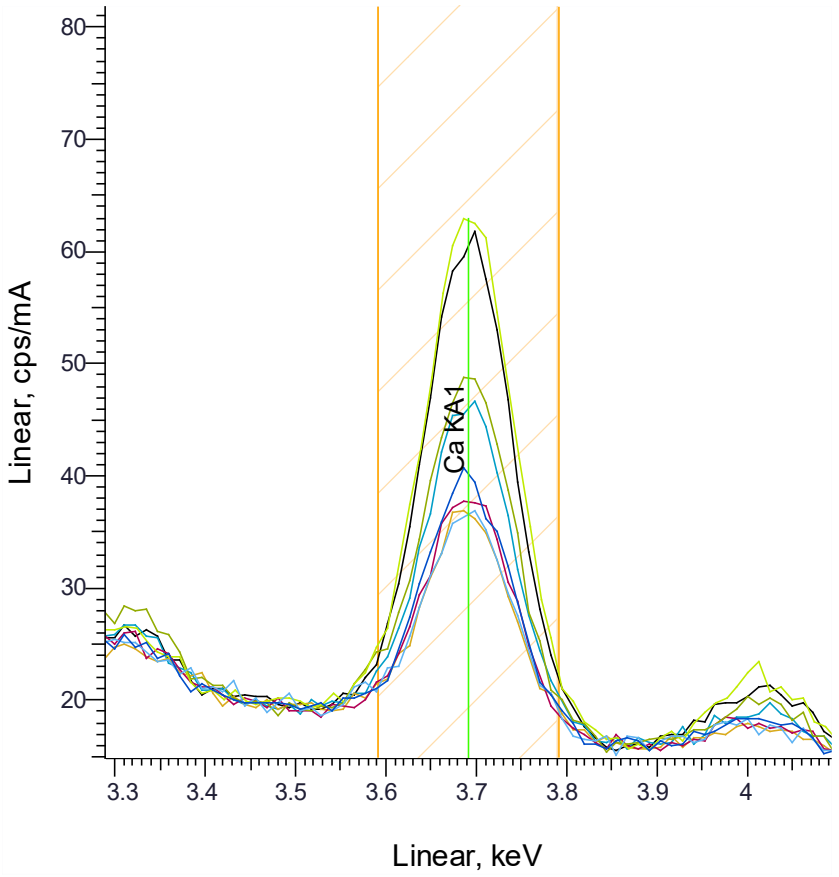




S2 PUMA Series 2
Ash content in milk components

- **Lactose calibration – Ca KA1**





S2 PUMA Series 2
Ash content in milk components

- **Milk calcium results**

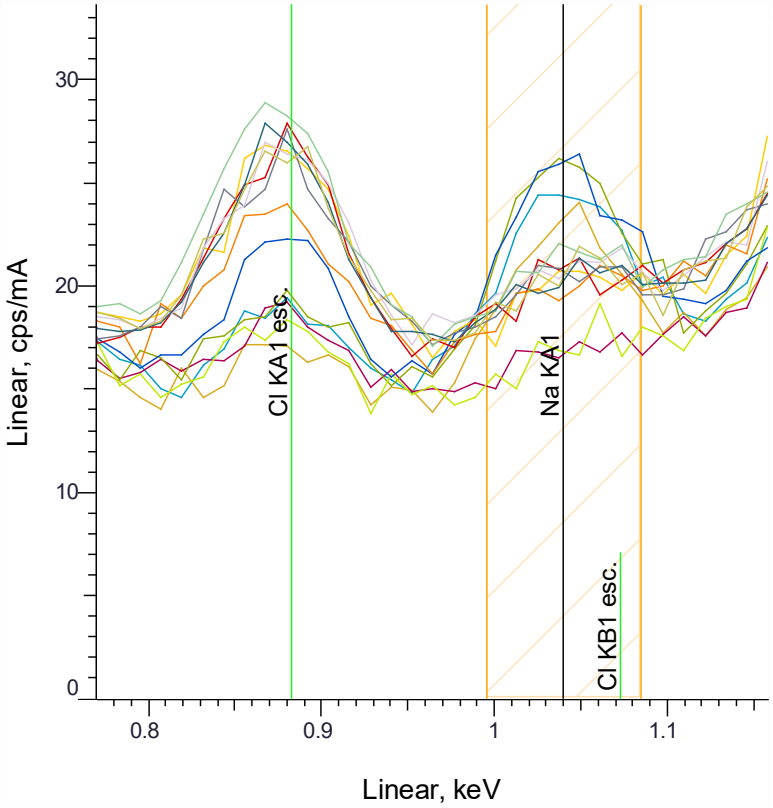
Element	Concentration range
Ca	23.6 – 27.8 %
P	13.5 – 17 %
Mg	9640 - 12400 mg/kg
K	6800 – 9100 mg/kg
Na	4040 – 5330 mg/kg
Zn	35 – 60 mg/kg
Cl	1350 – 2780 mg/kg
Ash	72.7 – 77.7 %

Ash (%) gravimetric	Ash (%) XRF calc.	Diff. Abs.	Diff. Rel. (%)
72.67	71.45	1.2	**1.7**
75.94	71.20	4.7	**6.2**
75.41	67.61	7.8	**10.3**
75.10	74.86	0.2	**0.3**
75.10	75.08	0.02	**0.03**
77.71	72.85	4.9	**6.3**
74.56	81.84	7.3	**9.8**
74.58	70.71	3.9	**5.2**

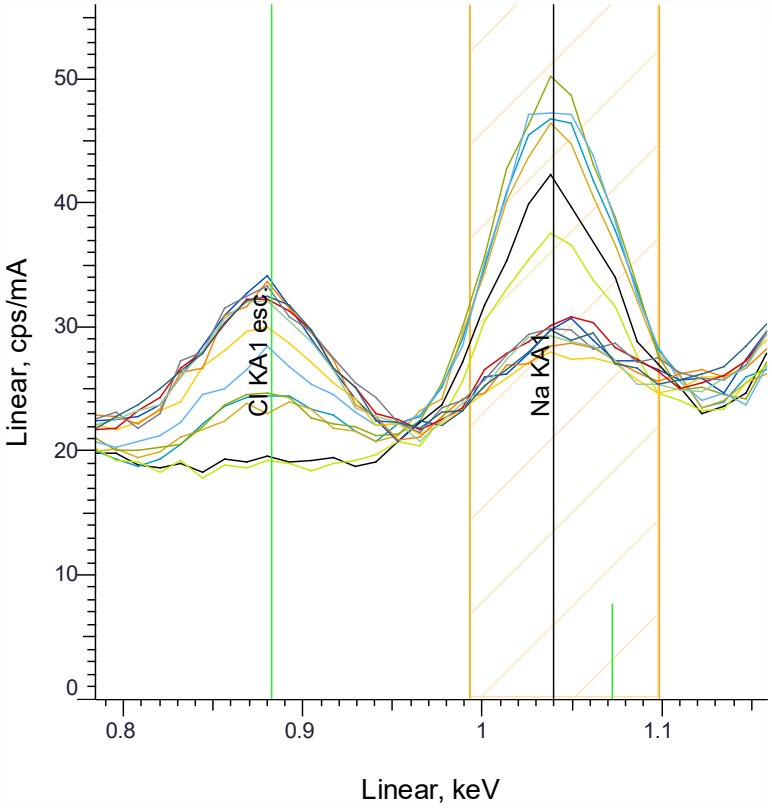
- Gravimetric ash determination is very time consuming (ashing at 550°C), while the measurement on a S2 PUMA Series 2 takes only a few minutes

S2 PUMA Series 2
Ash content in milk components

- **Milk protein – Na KA1**



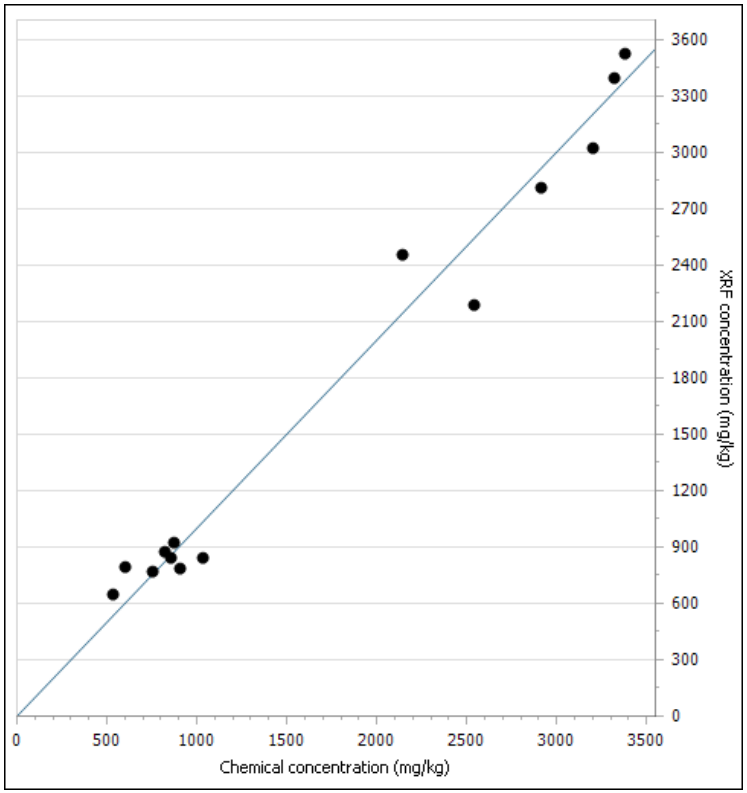
- Loose power
- He, 4 µm prolene® foil
- ~27 cps/mA



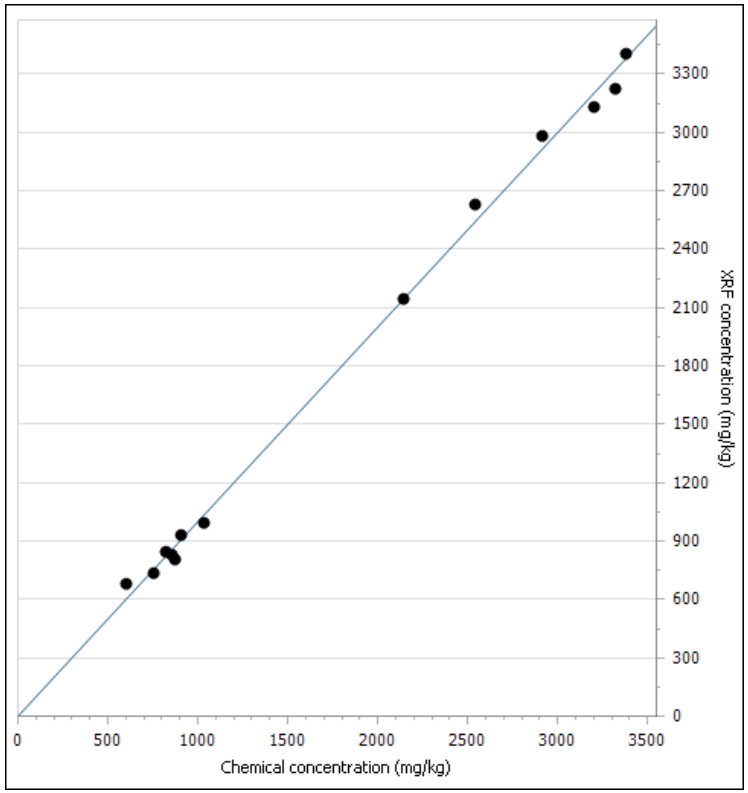
- Pressed pellet
- Vacuum
- ~50 cps/mA

S2 PUMA Series 2
Ash content in milk components

- **Milk protein – Na KA1**

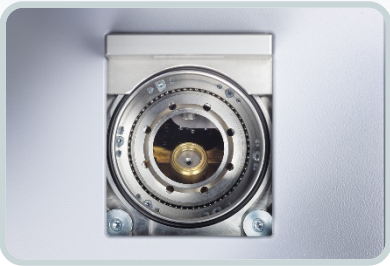


- Loose power



- Pressed pellet

S2 PUMA Series 2
Optimal Configuration for Food & Feed



Throughput

- Single Low (<50 sample per day)
- **XY Autochanger** (50-100 samples per day)
- XY Automation (>100 samples per day)

- QC / Production control and control of incoming raw material typically requires an XY Autochanger

- **LE Configuration?**
  Required for low Na contents (<0.5 wt%)

- **Sample Rotation?**
  Yes for loose powders, recommendable for pressed pellets

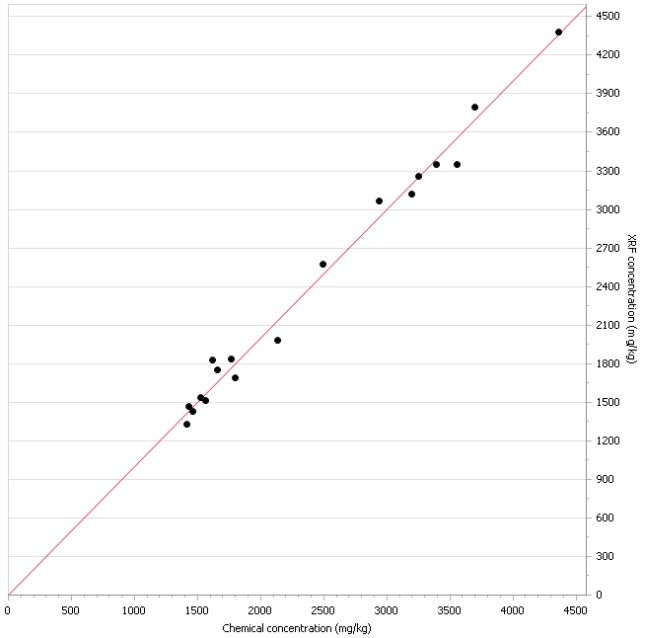
- **Preparation? Atmosphere?**
  Vacuum + Pressed pellet for best performance
  He + Loose powder for fastest preparation

S2 PUMA Series 2
Maize kernel

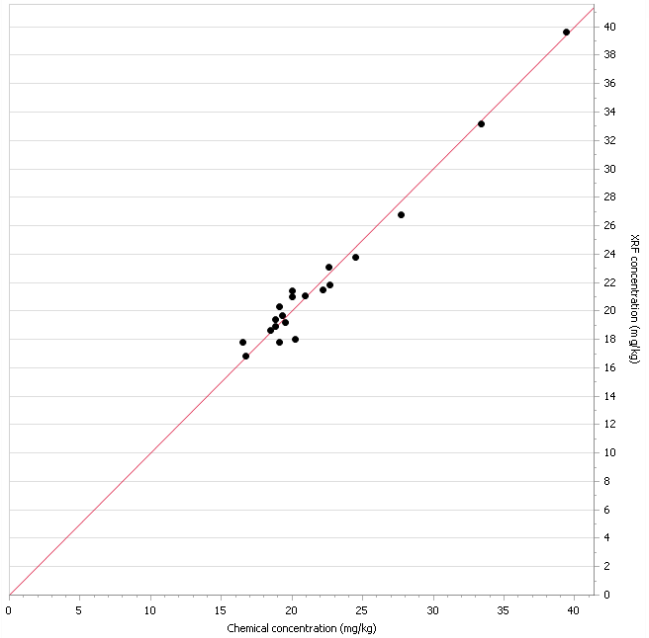
- **Calibration with 23 secondary reference materials** (measured by ICP)
- Covering 9 elements with concentrations ranging from few ppm up to ~ 1 wt% (Mg, P, S, Cl, K, Ca, Mg, Fe, Zn)
- Pressed pellets with wax

S2 PUMA Series 2
Maize kernel

- Examplary line P KA1 and Zn KA1



Line	P KA1
Conditions	20 kV, auto. current, no filter
Concentration range	1412 – 4363 mg/kg
Std. dev.	105 mg/kg
R^2	0.9881



Line	Zn KA1
Conditions	40 kV, auto current, 500 µm Al-Filter
Concentration range	15 – 40 mg/kg
Std. dev.	1.9 mg/kg
R^2	0.9731

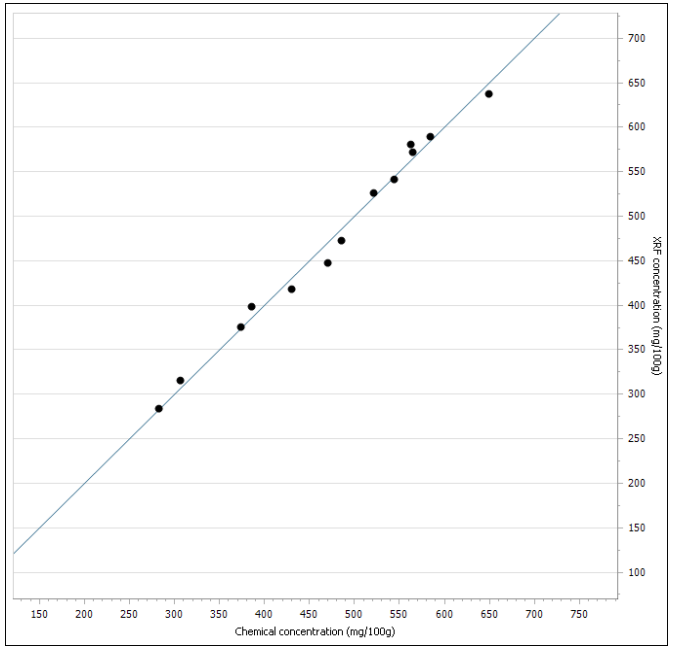
S2 PUMA Series 2
Maize kernel

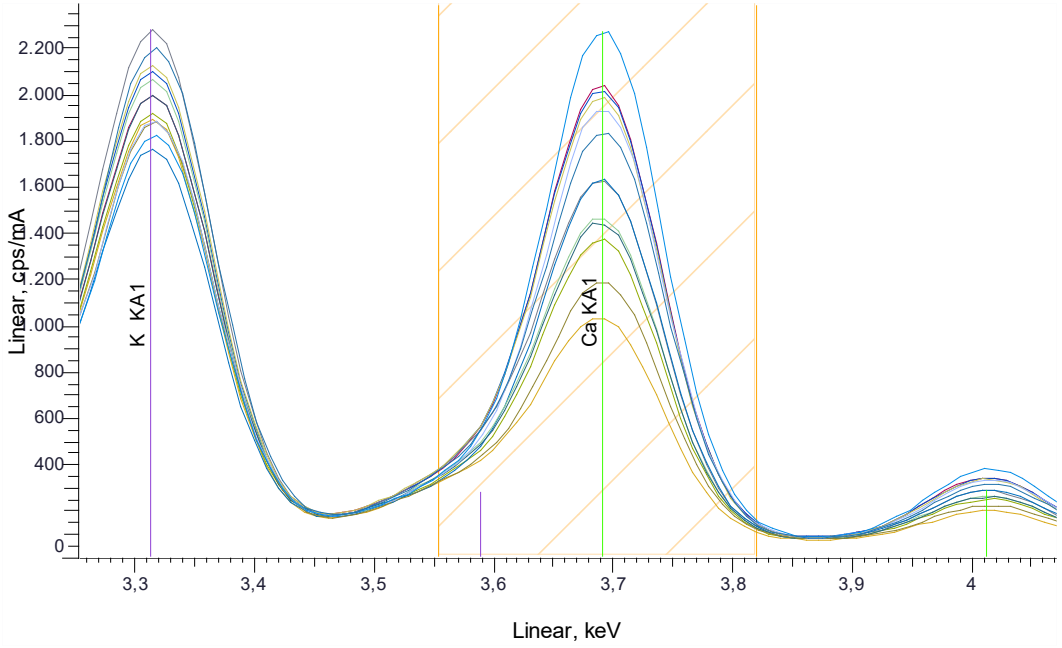
- **Excellent precision and accuracy even for concentrations below 10 ppm**

	Mg (mg/kg)	P (mg/kg)	S (mg/kg)	Cl (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Zn (mg/kg)
ICP	1140	3254	1152	380	3232	43	6	15.4	20.9
S2 PUMA	**1207**	**3279**	**1149**	**384**	**3295**	**58**	**5.6**	**16.3**	**21.0**
SD	13	13	8	4	17	3	0.7	0.7	0.1
rel. SD (%)	1.07	0.40	0.74	1.02	0.52	5.00	12.42	4.00	0.39
Abs. diff.	**67**	**25**	**3**	**4**	**63**	**15**	**0.4**	**0.9**	**0.1**

S2 PUMA Series 2
Milk Powder

- Milk powder measured as pressed pellets
- **Elements covered:** Na, Mg, P, Cl, K, Ca, Fe
- ~ 5 min per sample





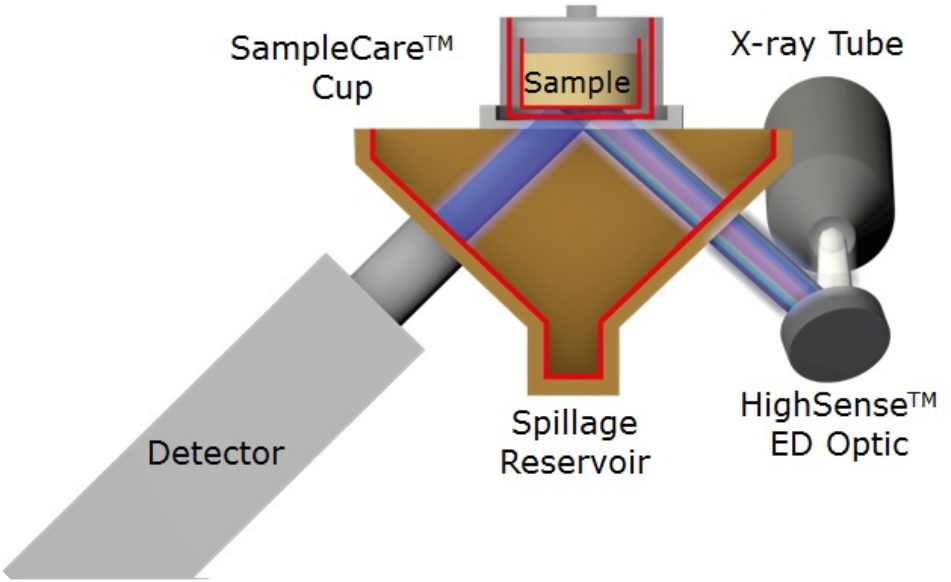
S2 PUMA Series 2
Milk Powder

- **Excellent precision!**
- Low detection limits, even for light elements (~75 ppm Na, ~30 ppm Mg)

Table 3: Analytical precision of milk powder measurements.

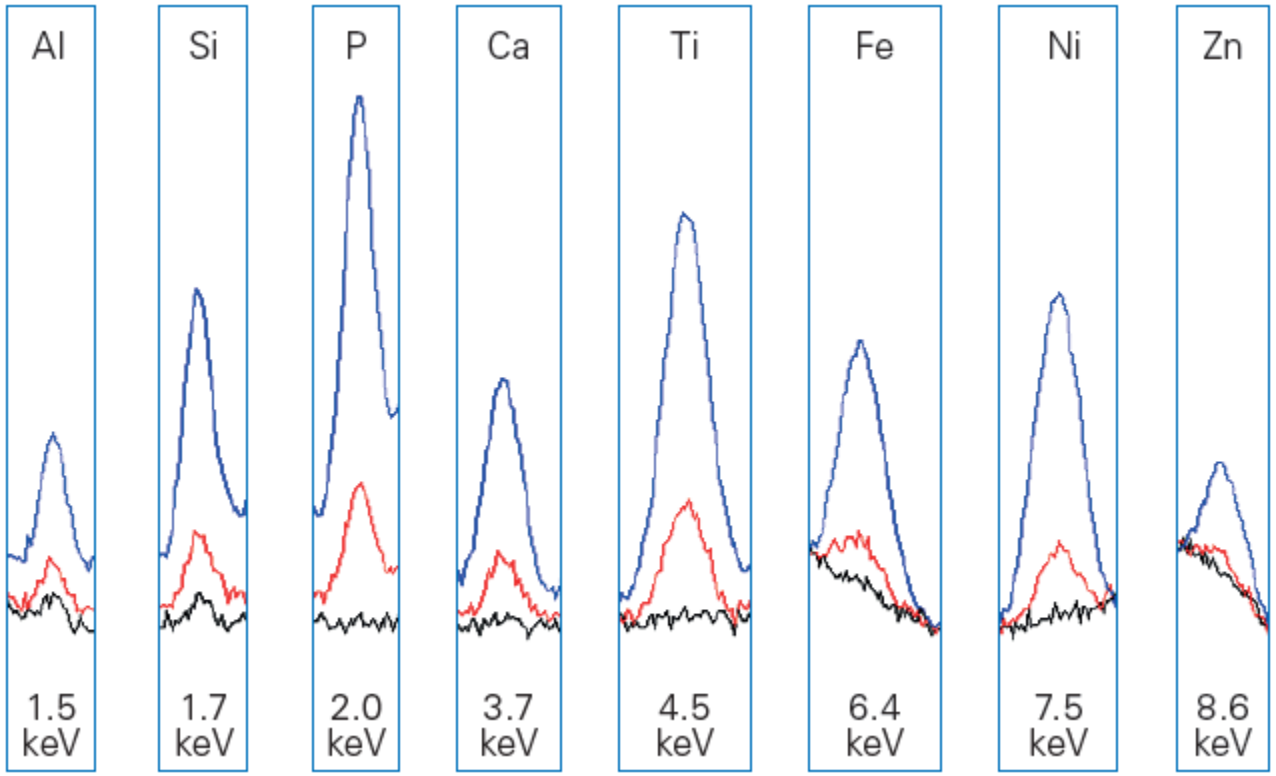
Element	Mean [mg/100 g]	Standard Deviation [mg/100 g]	Relative Standard Deviation [%]
Na	240	2.5	1.04
Mg	61	1.4	2.34
P	257	0.8	0.33
Cl	418	0.8	0.20
K	597	4.5	0.75
Ca	381	2.1	0.55
Fe	4.86	0.05	1.06

S2 POLAR
Perfect fit for Light Matrices



- Polarizing HighSense™ beam path
- Perfect excitation conditions for light matrices such as edible oils or polymers
- Reduced background due to polarization
- SampleCare™ cup prevents leakages of liquid samples and protects important system components
- S2 POLAR SampleCare™ Technology guarantees highest instrument uptime

S2 POLAR
Excellent Multi-element Capability



Selected elements of overlaid multi-element oil standards
(Black: blank sample, red: 10 ppm, blue: 100 ppm)

S2 POLAR
Edible Oil

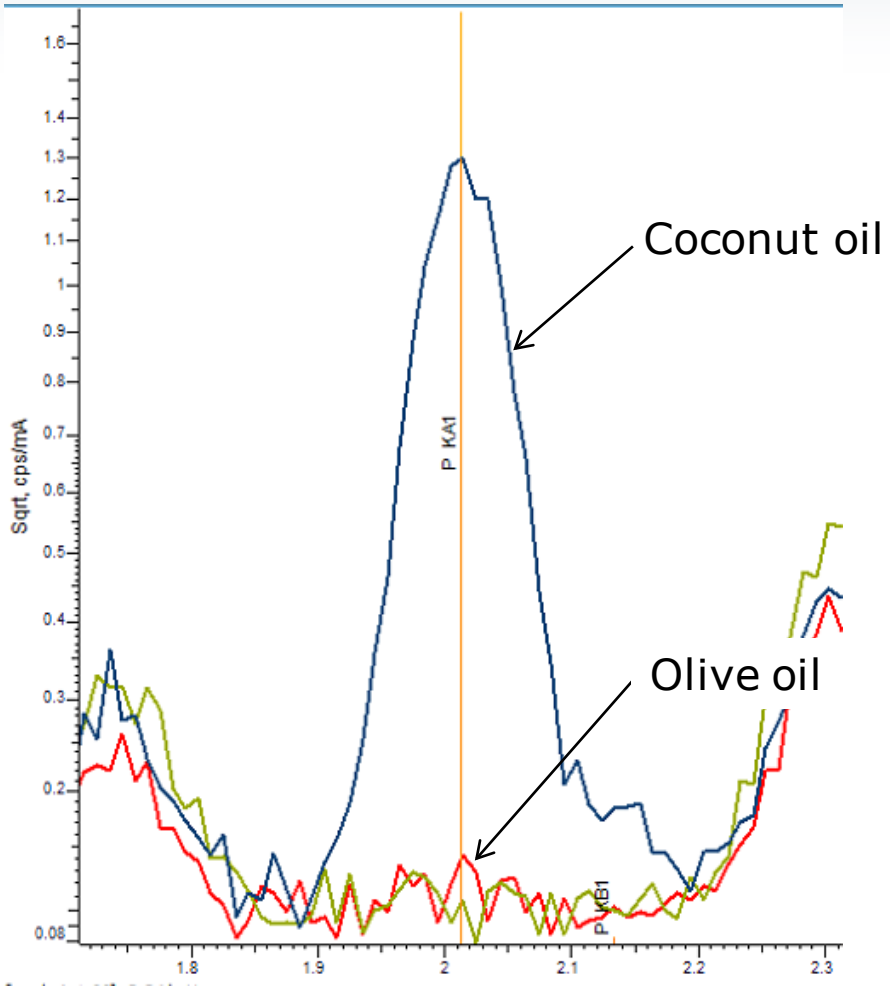
P in edible oil:

- Total phosphorus content is used to optimize the oil refining process
- Available phospholipids can have a negative impact at various process steps
- Hence total P is measured to monitor the phospholipids removal

P in cooking oil:

- Used cooking oil (UCO) from fast-food chains and restaurants is usually recycled
- UCO is often used for later biodiesel production
- In biodiesel, P, as well as S and Cl, must not exceed certain limits and needs to be monitored

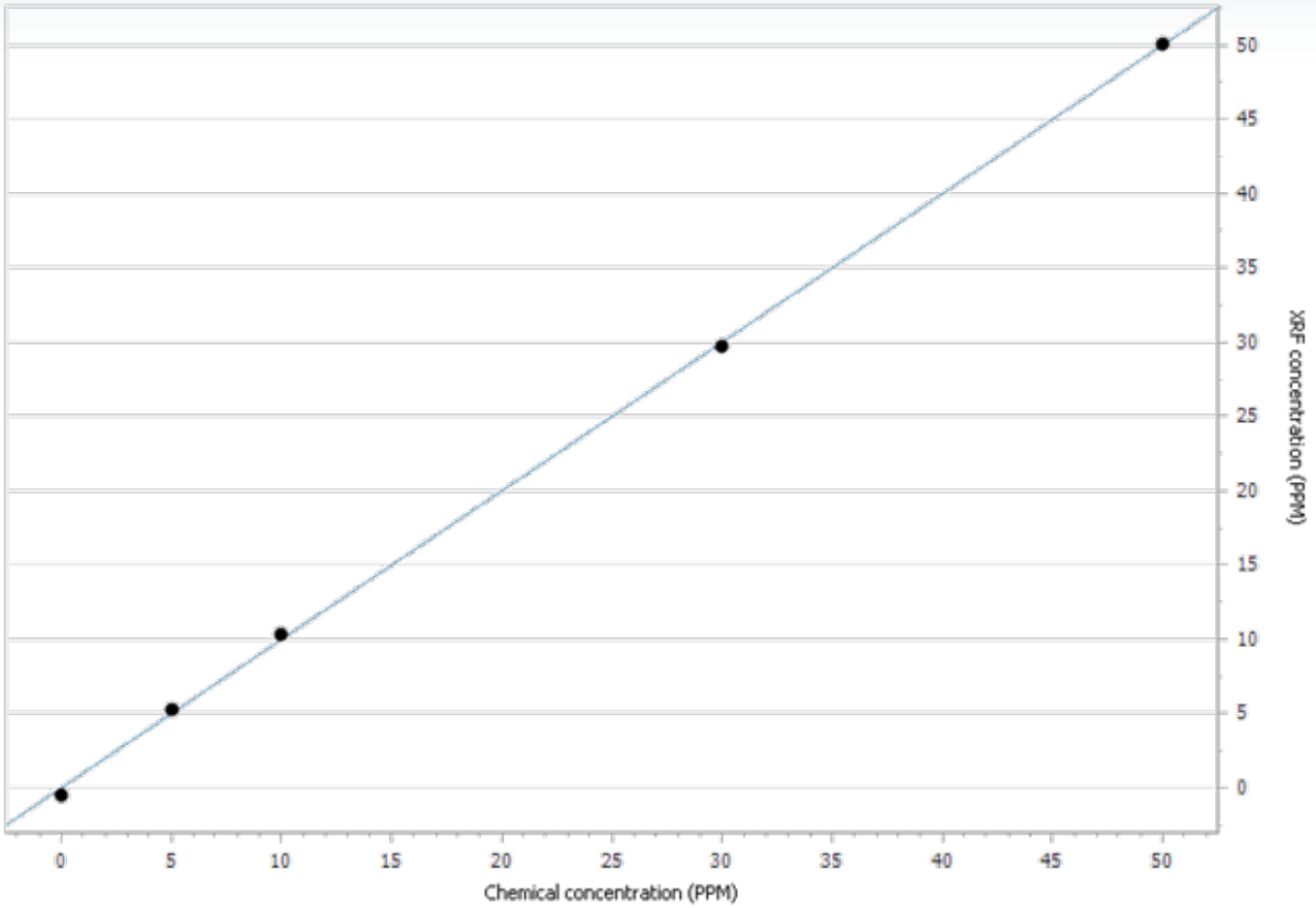
S2 POLAR
Cooking Oil



P in cooking oil:

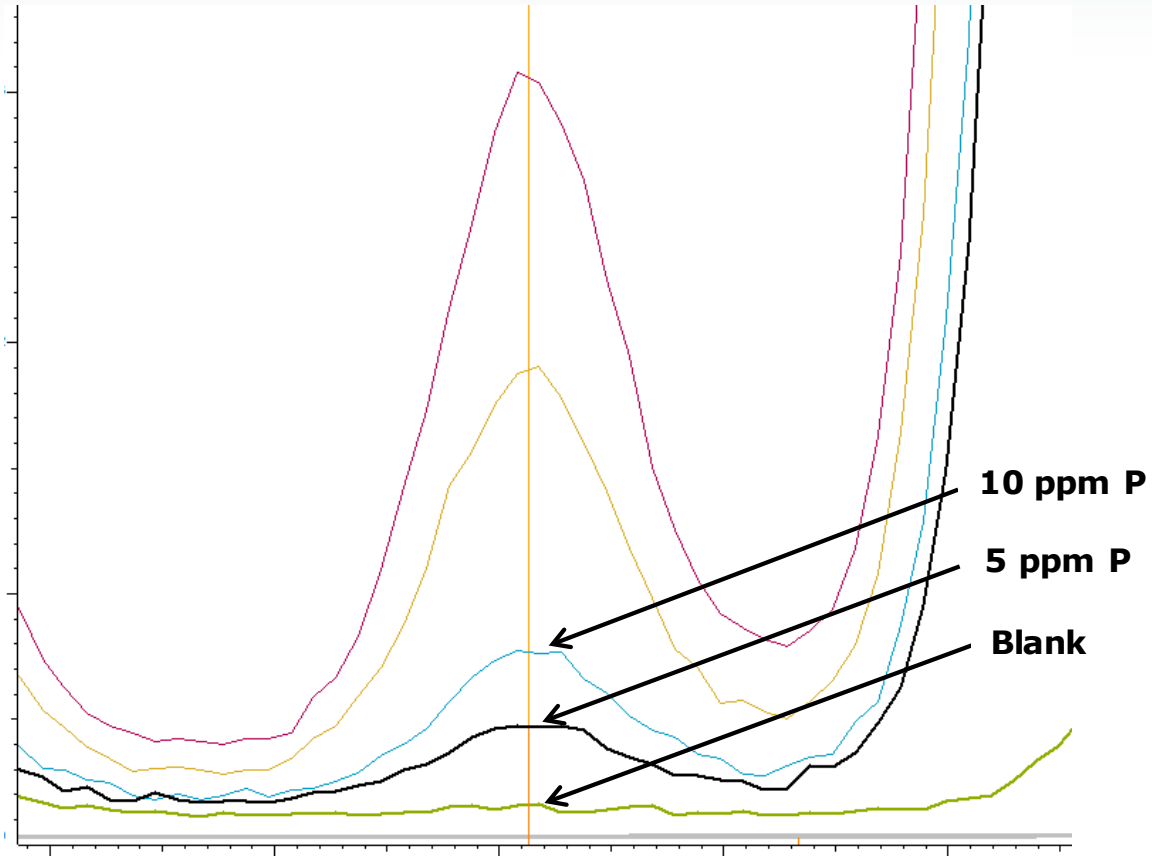
- Virgin coconut oil: 23 ppm (blue signal)
- Cooking olive oil: < 1.8 ppm (red signal)
- Blank oil (paraffin) (green signal)

S2 POLAR
P in Oil



- Example of P calibration curve in the range of 0 to 50 ppm P

S2 POLAR
P in Oil



- Clear separation of low P concentrations

S2 POLAR
P in Oil

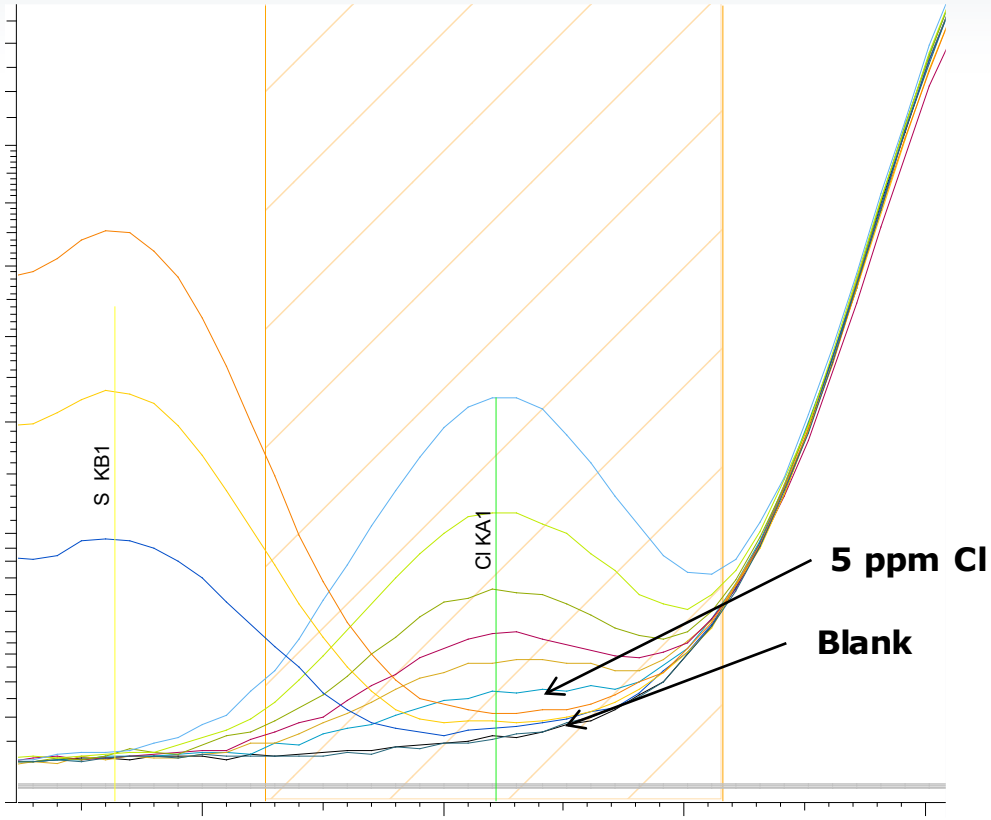
# Measurement	P [ppm]
1	10.4
2	10.4
3	10.2
4	10.2
5	10.2
6	10.4
7	10.2
8	10.2
9	10.1
10	10.3
Mean value	10.22
Min. value	10.1
Max. value	10.4
Abs. std. dev.	0.11
Rel. std. dev. [%]	1.10

- 10 ppm P oil standard
- Very good repeatability for low P concentrations
- LLD: 0.4 ppm (300 s, with SampleCare™ cup)

S2 POLAR
Repeatability of P and Cl in Oil

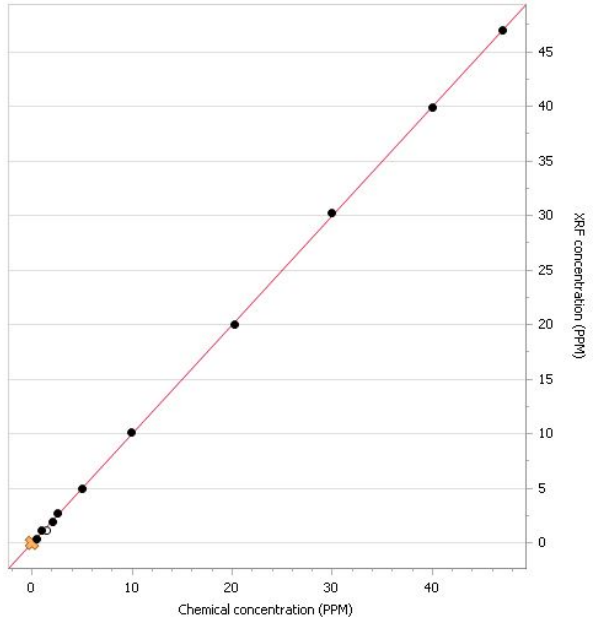
	Mg [%]	P [%]	S [%]	Cl [%]	Ca [%]	Zn[%]	Mo [%]
Rep 01	0.099	0.111	0.511	0.027	0.204	0.119	0.010
Rep 02	0.097	0.112	0.514	0.026	0.201	0.120	0.010
Rep 03	0.102	0.111	0.509	0.026	0.202	0.118	0.010
Rep 04	0.101	0.112	0.514	0.026	0.203	0.121	0.010
Rep 05 - 16	…	…	…	…	…	…	…
Rep 17	0.104	0.111	0.512	0.026	0.202	0.118	0.010
Rep 18	0.098	0.111	0.513	0.027	0.202	0.121	0.009
Rep 19	0.101	0.112	0.513	0.026	0.203	0.119	0.009
Rep 20	0.094	0.111	0.511	0.026	0.203	0.119	0.009
Mean value	**0.100**	**0.111**	**0.512**	**0.026**	**0.202**	**0.119**	**0.009**
Abs. Std. Dev.	**0.0025**	**0.0004**	**0.0016**	**0.0001**	**0.0010**	**0.0009**	**0.0002**
Rel. Std. Dev.[%]	**2.49**	**0.36**	**0.31**	**0.40**	**0.51**	**0.78**	**1.98**
Min. [%]	**0.094**	**0.111**	**0.509**	**0.026**	**0.200**	**0.118**	**0.009**
Max. [%]	**0.104**	**0.112**	**0.515**	**0.027**	**0.204**	**0.121**	**0.010**
Certified value	**0.100**	**0.110**	**0.500**	**0.025**	**0.200**	**0.120**	**0.0100**

S2 POLAR
Cl in Oil or similar Matrices

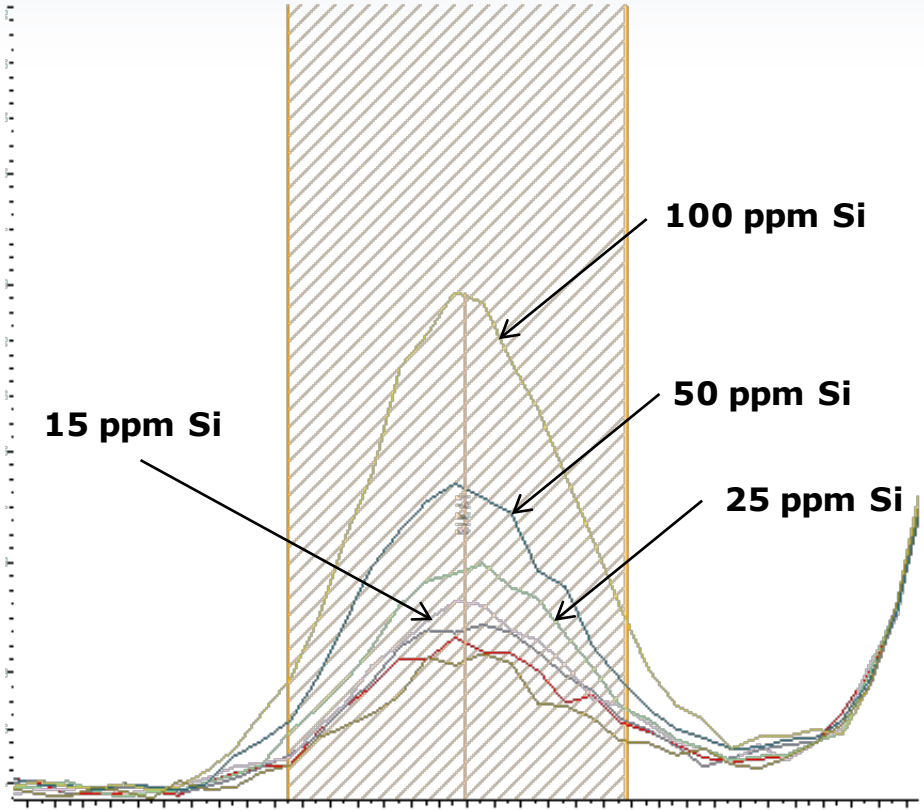


- Signal at Cl KA1

- Analysis of low levels of chlorine
- 1 to 50 ppm Cl

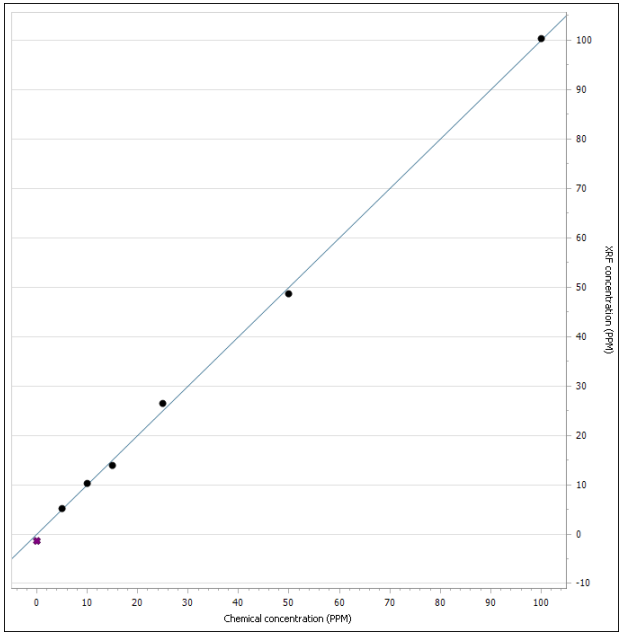


S2 POLAR
Si in Oil or similar Matrices

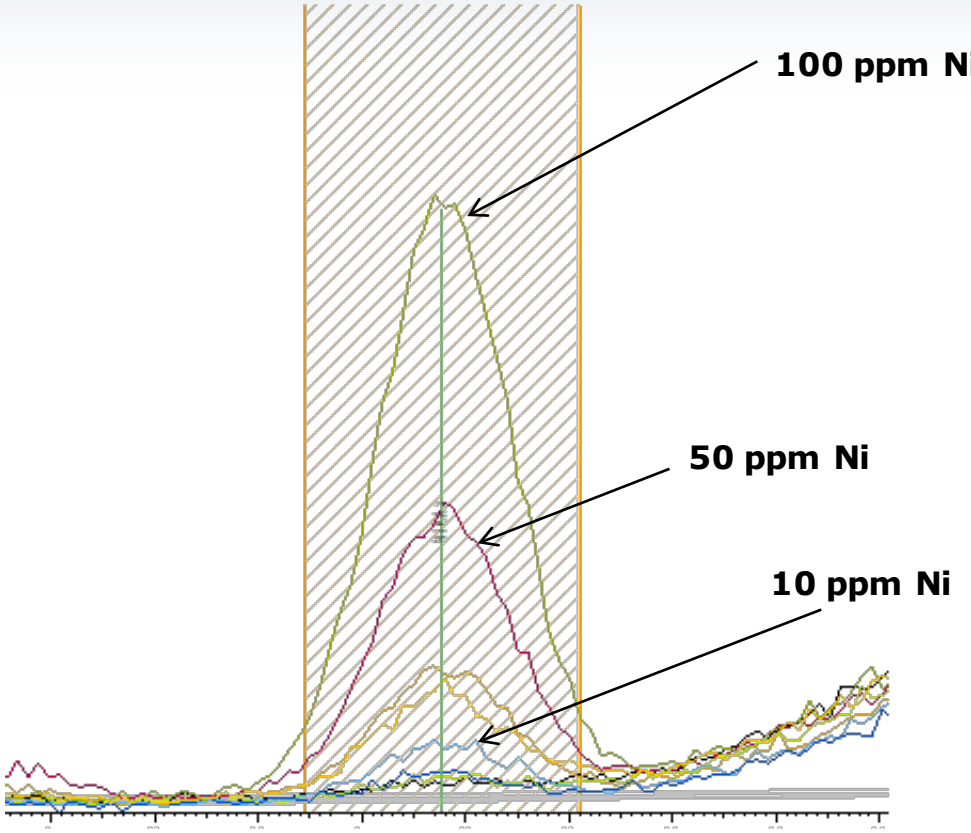


- Signal at Si KA1

- Calibration line for Si
- Conc. 5 to 100 ppm
- R^2 = 0.99924
- **LLD ~ 1 ppm**
- Blank correction enabled

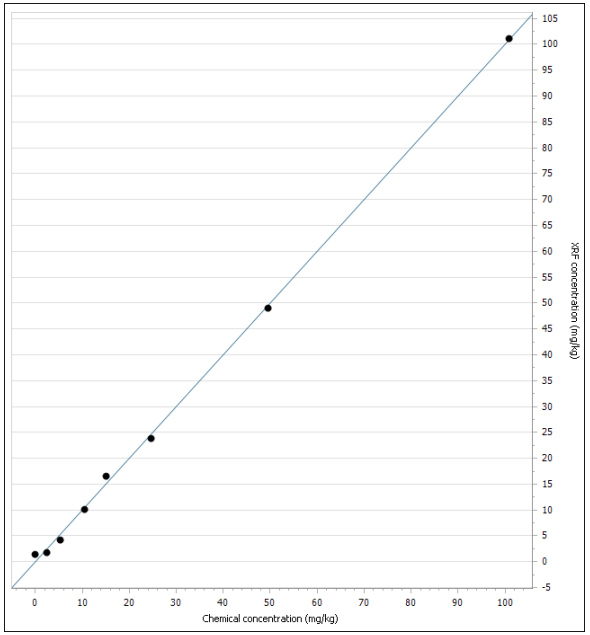


S2 POLAR
Ni in Oil or similar Matrices



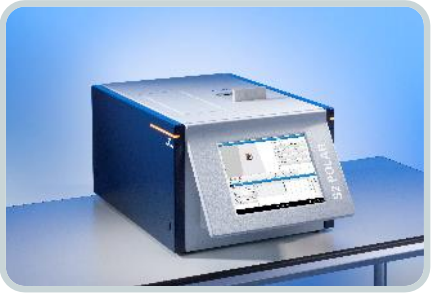
- Signal at Ni KA1

- Calibration line for Ni
- Conc. 0 to 100 ppm
- R^2 = 0.99914
- **LLD ~ 0.7 ppm**



Summary

XRF for Food & Feed Summary

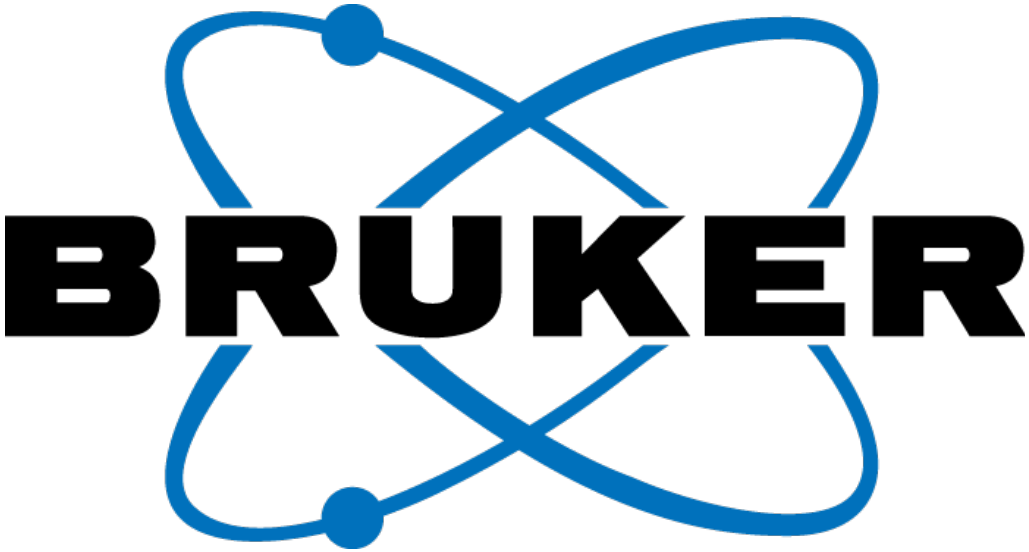


- XRF is the optimal technique for a wide range of applications in the food and feed industry
- **Key benefits of XRF**: Wide range of elements and concentrations, simple sample preparation, ease-of-use, low operation costs, high accuracy & precision, high throughput.
- Bruker offers a full portfolio of laboratory equipment for food and feed applications:
  - **S2 PUMA Series 2** is the ideal choice for many food and feed applications – including milk powder, forage/feed premix, etc.
  - **S6 JAGUAR** is used for very low trace element contents (<10 ppm) and for (low) F
  - **S2 POLAR** is used for traces in liquids (e.g. P, Ni)

Q&A

Thank you!

Any questions?



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