BRUKER

Quickly analyse nutrients, additives, and contaminants in food, feed, supplements, and beverages with PXRF and TXRF

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Bruker Nano GmbH, Berlin, Germany
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Welcome

Speakers

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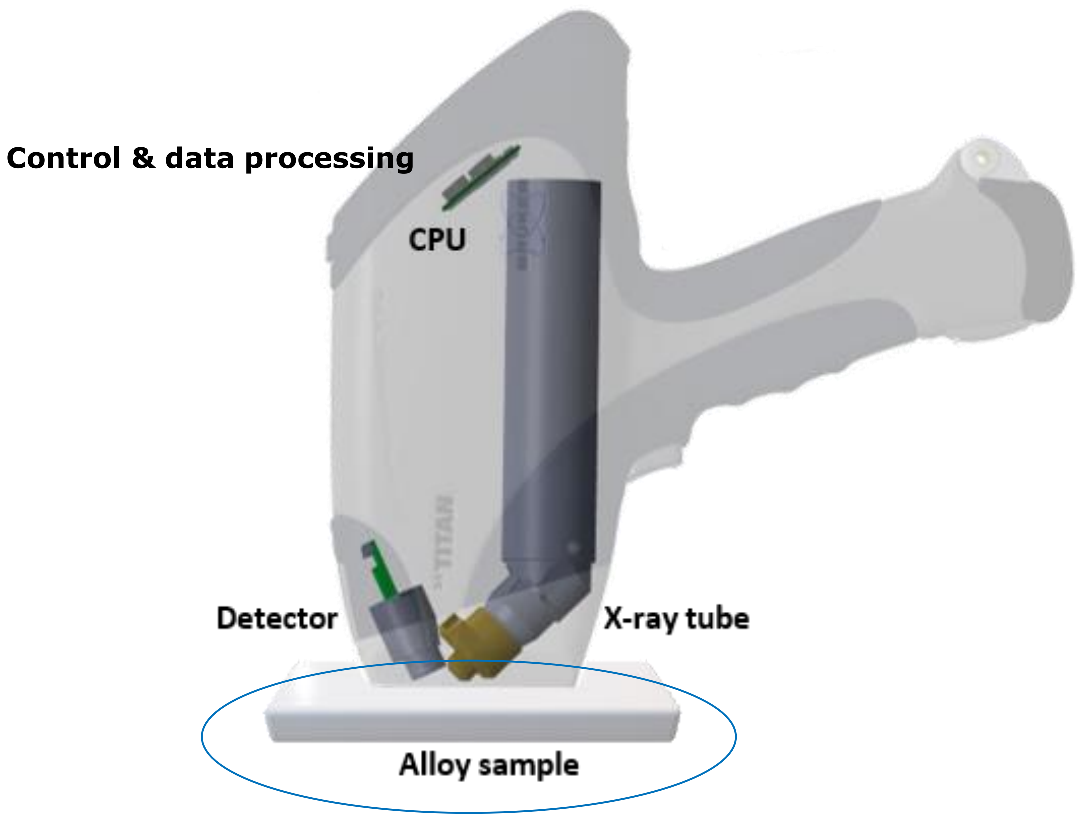
Itinerary

- Introduction
- PXRF and TXRF – How does it work?
- Measurements with portable XRF
  - Measurement of mineral nutrients in animal feed
  - Elements monitored in processing chocolate and edible oil
  - Physical contaminants in human and pet food
- Ultra-trace analysis with TXRF
  - micronutrients and toxic elements in solid food samples
  - dietary supplement pills
  - milk samples
- Q & A

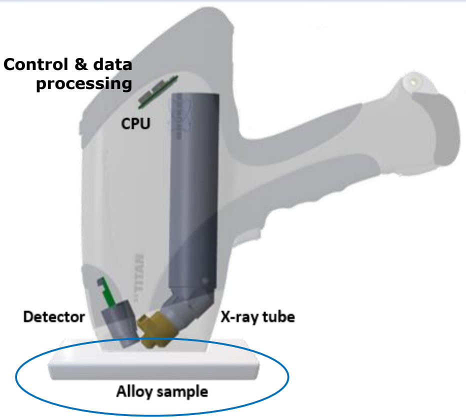
PXRF and TXRF

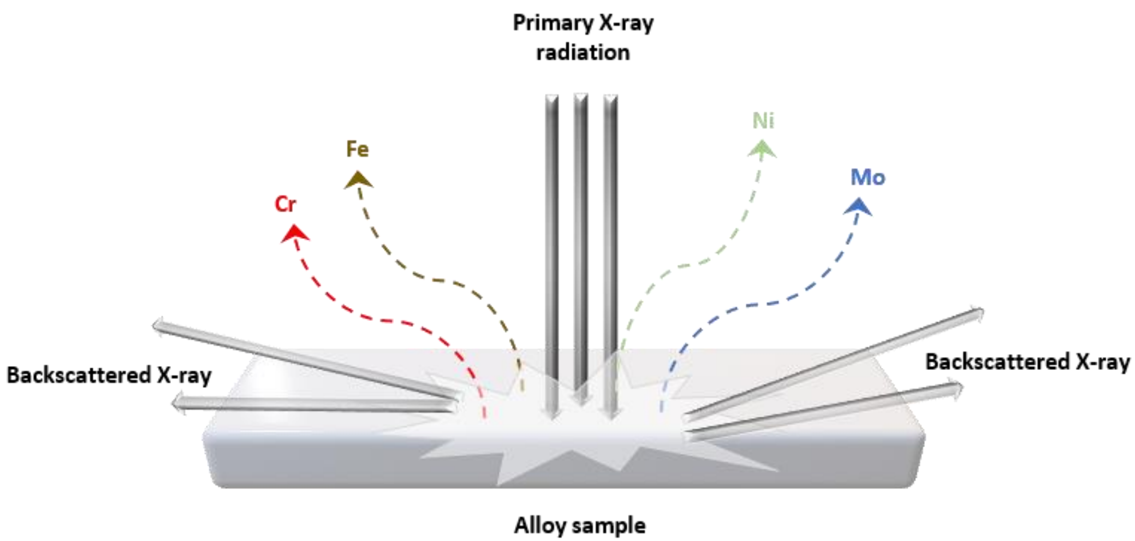
How does it work?

PXRF Technology

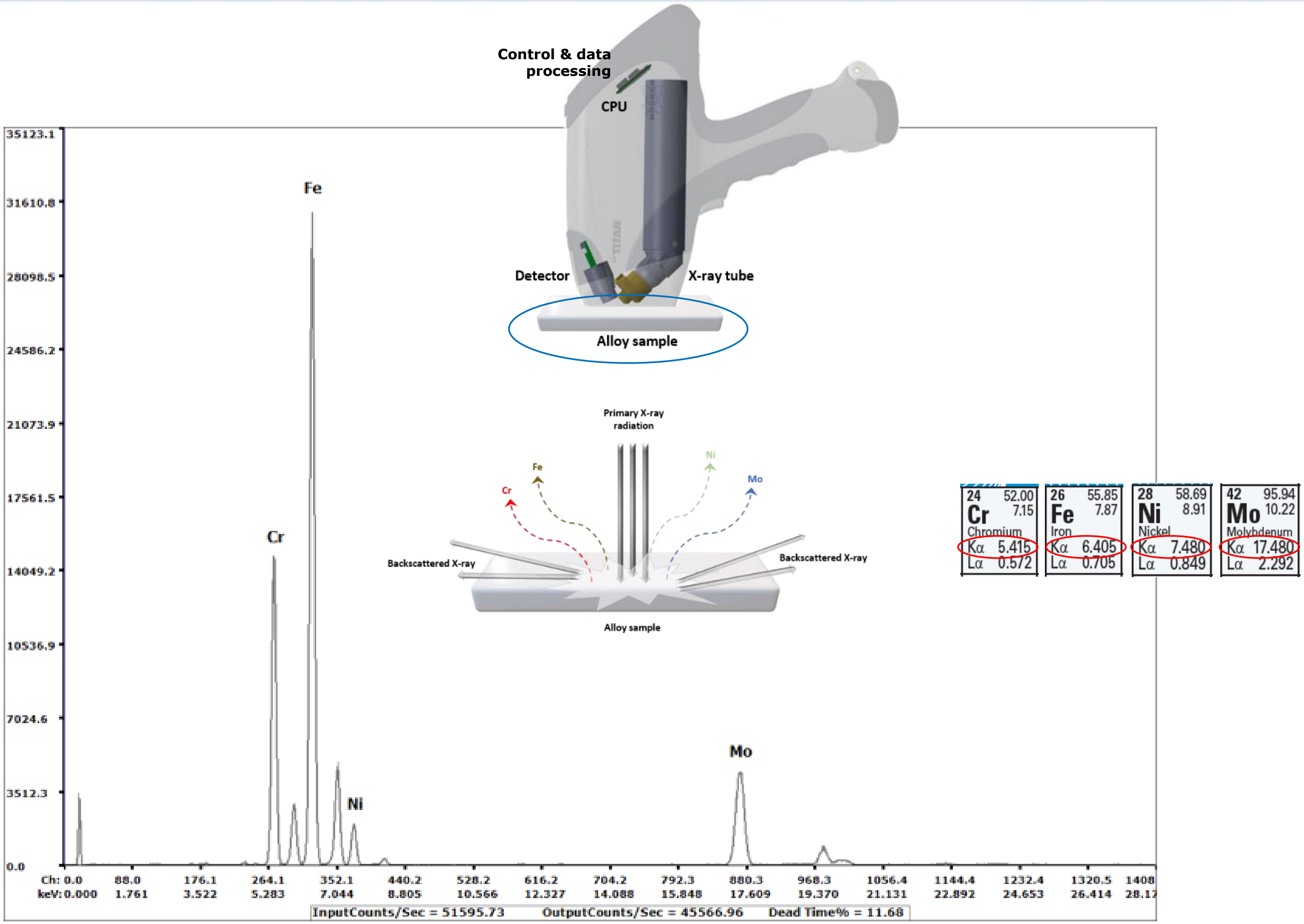


PXRF Technology

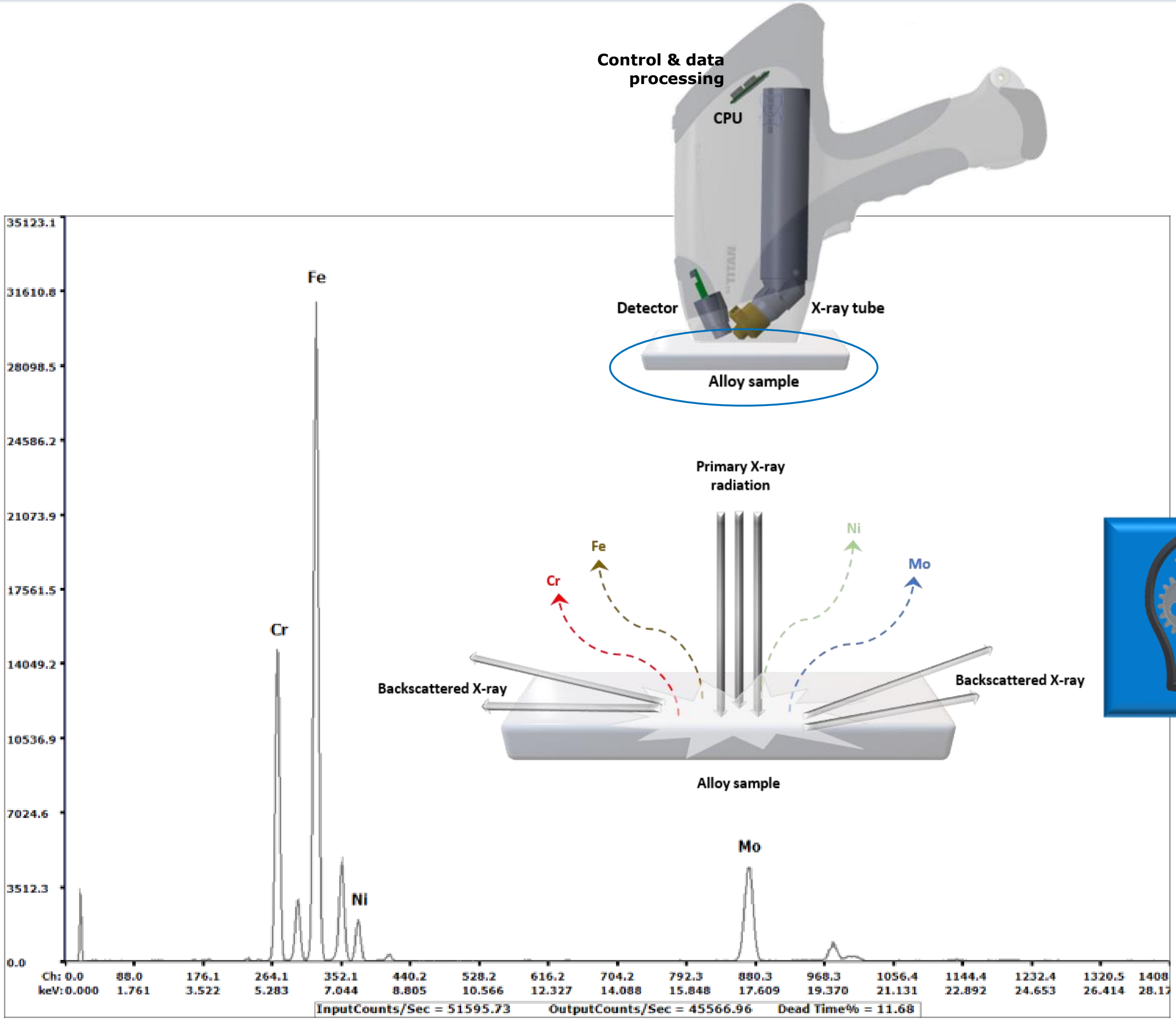


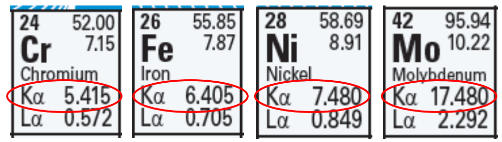


PXRF Technology



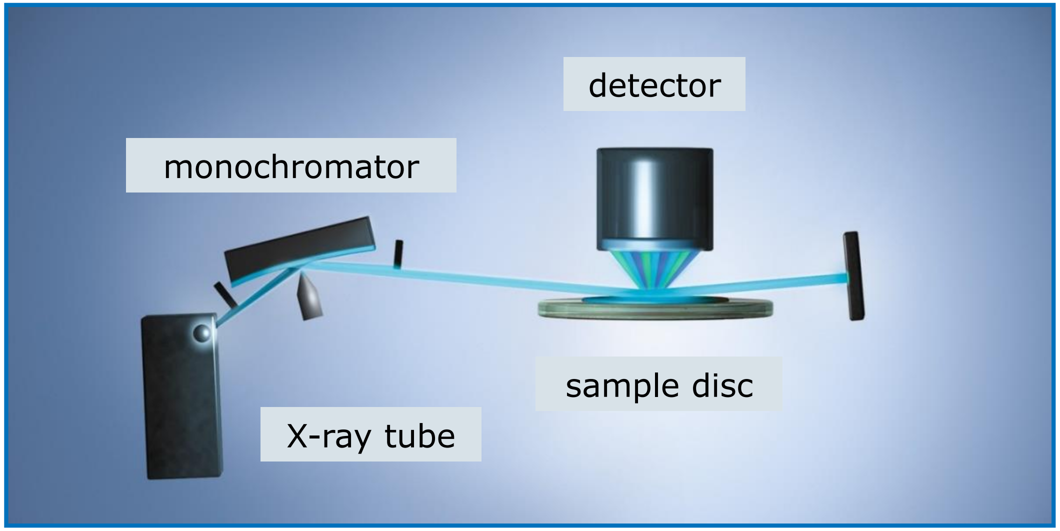
PXRF Technology





Principles of TXRF

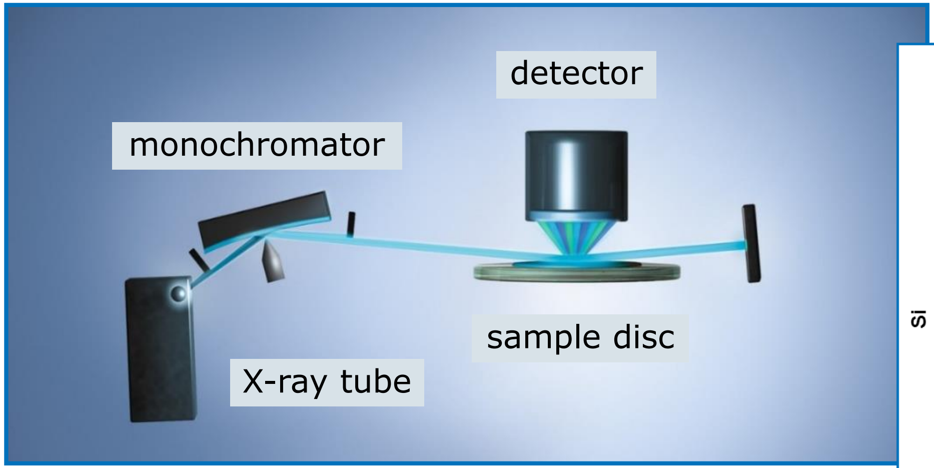
Total reflection X-ray fluorescence spectroscopy

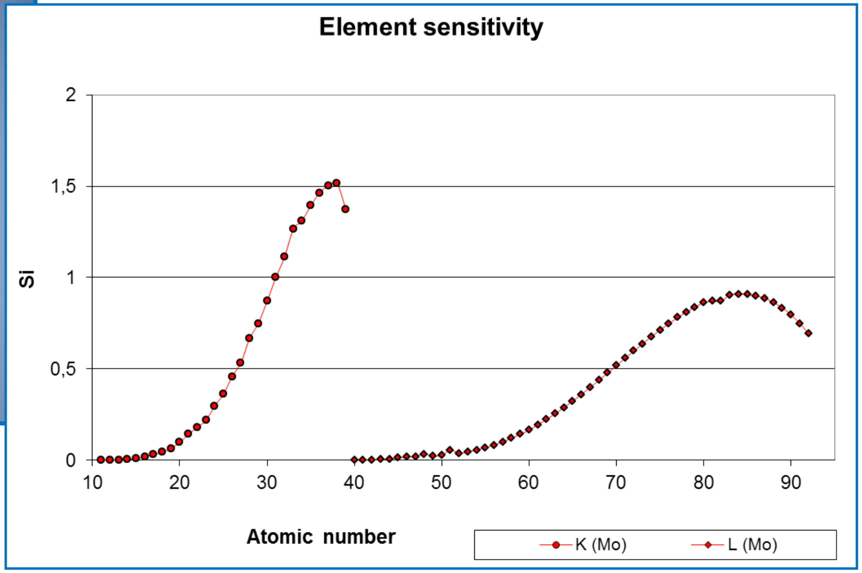


- Samples must be prepared on a reflective media
- Dried to a thin layer
- Matrix effects are negligible
- Quantification by internal standardization

Principles of TXRF

Total reflection X-ray fluorescence spectroscopy





- Samples must be prepared on a reflective media
- Dried to a thin layer
- Matrix effects are negligible
- Quantification by internal standardization

$$C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i}$$

Elements of interest in food analysis




Quickly analyze nutrients, additives, and contaminants in food, feed, supplements, and beverages with portable XRF and T-XRF

- Macro mineral nutrients: Ca, P, Mg, Na, K, Cl, S
- Trace mineral nutrients: Fe, Mn, Cu, I, Zn, Co, F, Se
- Toxic elements: As, Cd, Hg, Pb
- Processing elements: P, Fe, and others
- Physical contaminants: bits of metal, ceramic, glass and plastic

S4 T-STAR TXRF for ultra low detection limits of elements from sodium to uranium. High volume sample analysis is possible with stackable trays.

TRACER 5i battery operated, handheld XRF for analysis of elements from sodium to uranium wherever and whenever needed.

Measurement of mineral nutrients in animal feed with a portable XRF

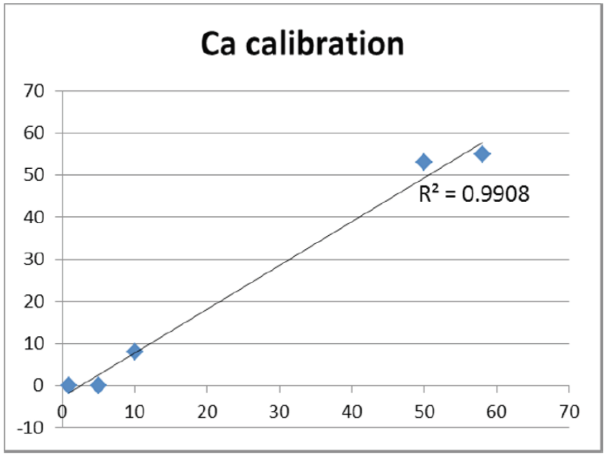
Application

- Macromineral nutrients, such as calcium (Ca) and phosphorus (P), are just as important in animal food as they are in human food.
- The optimum ratio of Ca to P (Ca:P) in feed is particularly critical for laying hens because it helps balance support for skeletal growth, eggshell formation, and immune responses.
- Portable XRF enables the measurement of these and other elements where feed materials are received, at feeding sites, or in the lab.

Methods and equipment

Simple steps to measure elements in feed with a portable XRF

1. Create or purchase an elemental calibration for feed to be installed on the PXRF using reference samples with a similar base matrix and concentrations covering the range of interest.



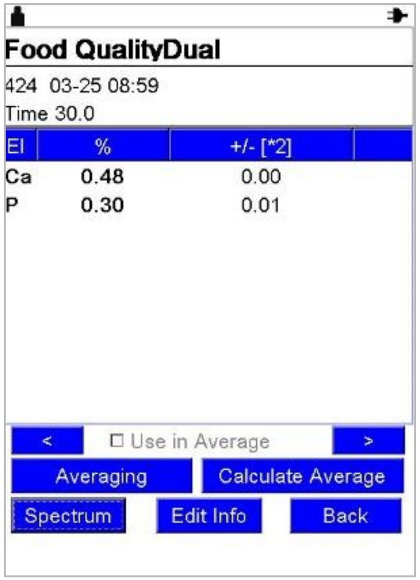
2. Put crushed feed in sample cup and cover with film.

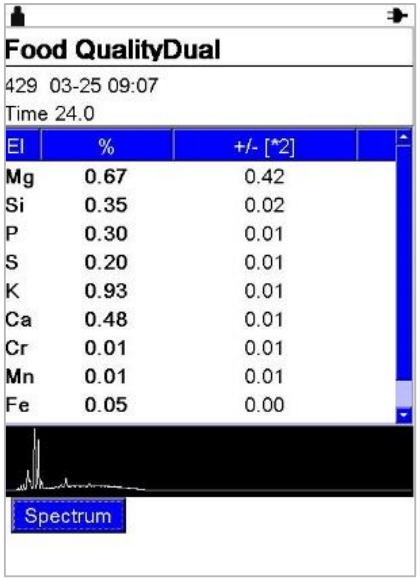
3. Place sample cup on XRF analysis window and close the cover.

4. Select the calibration and press start.

Results

View results on screen as elements of interest, full composition, P/F, or spectra. Results are stored in the instrument, but can be saved onto a USB stick or transferred to another data collection system.





Application

- Salt is a critical component of a nutritionally balanced diet for animals.
- Insufficient amounts of sodium can lead to serious health and behavioral issues as well as to a decrease in feed utilization.
- Recommended amounts of salt vary depending on the animal, its location, and its activity.
- Portable XRF enables the measurement of sodium and other elements where feed materials are received, at feeding sites, or in the lab.

Methods and equipment

- Sodium is a very light (low energy) element which presents a challenge for PXRF analysis.
- The TRACER 5 handheld XRF can perform Na measurements with the use of a helium path and the removal of windows and films between the analyzer and the sample.
- These steps increase the transmission of light element X-rays which in turn increases the sensitivity of the measurement enabling the analysis of elements as light as Na.

Methods and equipment

- The TRACER 5 platform provides the ability to control the excitation conditions.
- Users can adjust the current and voltage directly on the interactive touch screen display.
- Users can select filters from the integrated filter wheel or insert user-designed filters.
- Users can select one of three measurement paths – air, vacuum, or helium.
- TRACER 5 control and live spectra analysis via PC is also possible.

Methods and equipment

- Good working detection limits of light elements can be achieved with the TRACER 5g (1 µm graphene detector window) or the TRACER 5i (8 µm beryllium detector window).

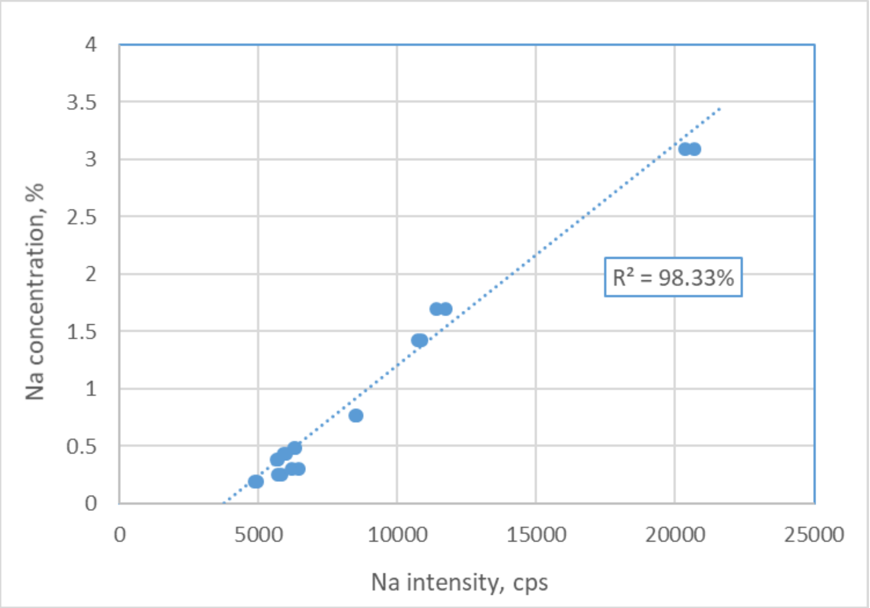
TRACER 5g		
Element	LOD (PPM)	Sensitivity (Counts/PPM)
Na	312	0.62
Mg	122	2.13
Al	134	4.41
Ca	24	14.04
Fe	50	25.87

TRACER 5i		
Element	LOD (PPM)	Sensitivity (Counts/PPM)
Na	828	0.20
Mg	185	1.17
Al	177	3.08
Ca	22	16.10
Fe	48	30.03

- Selection of a helium flow path and the removal of the instrument analysis window are required.
- Samples should be put in a cup without any film covering and placed under the tube (nose down) to prevent debris from falling inside.

Methods and equipment

- Users can create or purchase a custom calibration to be installed on the TRACER for Na analysis, using reference samples with a similar base matrix and with concentrations covering the range of interest.
- The measurement conditions must be the same for reference and unknown samples, including the use of helium and the preparation and presentation of the samples.
- Qualitative identification or screening tests for Na in feed are also possible without the need of an installed calibration curve.



Correlation for measuring Na using balloon He atmosphere with a handheld XRF

Elements monitored in processing chocolate and edible oil

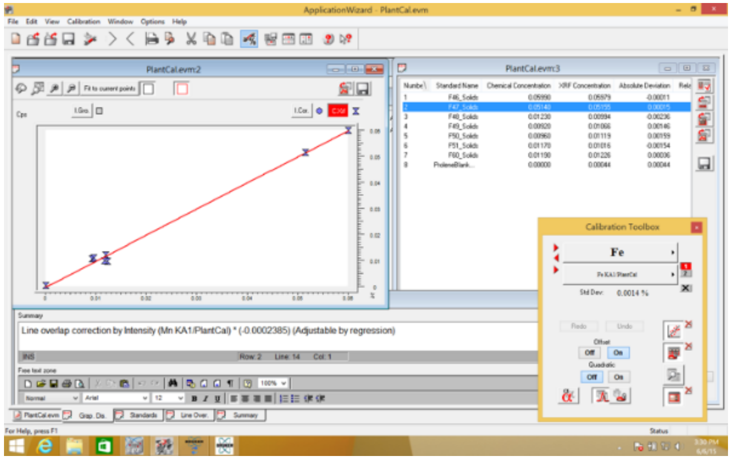
Application

- Iron (Fe) is an important mineral nutrient measured and reported in cocoa.
- It's also important to monitor Fe during production for taste consistency. In oxidative reactions, some iron compounds can result in off-flavors, colors, or odors.
- Iron is also monitored during production to prevent accidental Fe contamination from process equipment.
- Portable XRF enables the measurement of Fe and other elements where starting materials are received, on the production line, or in the lab.

Methods and equipment

Simple steps to measure Fe in cocoa with a portable XRF

1. Create or purchase a calibration for Fe in cocoa to be installed on the PXRF using reference samples with a similar base matrix and concentrations covering the range of interest.



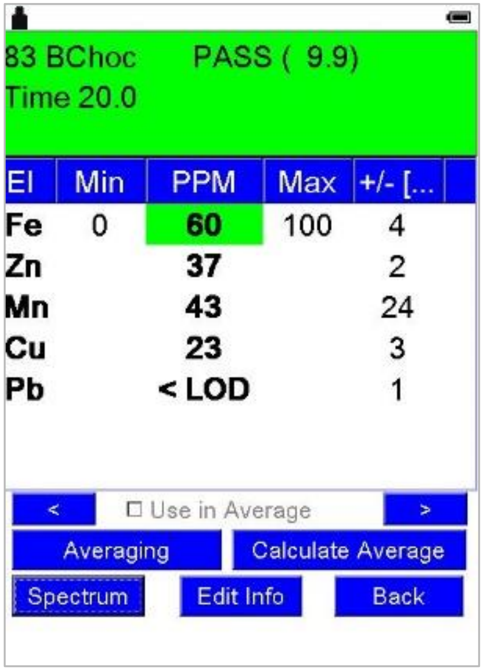
2. Put cocoa powder in sample cup and cover with film.

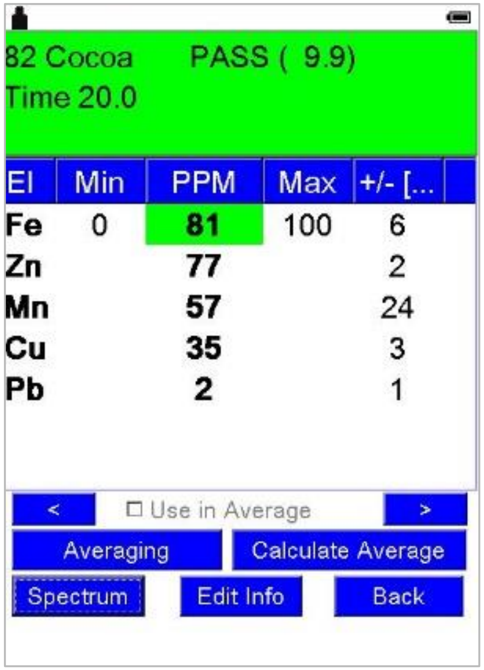
3. Place sample cup on XRF analysis window and close the cover.

4. Select the calibration and press start.

Results

View results on screen as elements of interest, full composition, P/F, or spectra. Results are stored in the instrument, but can be saved onto a USB stick or transferred to another data collection system.





Application

- Phosphorus is not an edible oil nutrient; however, its presence is important to monitor during processing.
- Measuring phosphorus helps monitor the refining of edible oils, especially important during the degumming process of seed oils, the settling of fruit oils, and the neutralization of all edible oils.
- Phosphorus measurements are indicative of phosphatide content which ultimately helps determine edible oil quality.
- Portable XRF enables the measurement of phosphorus and other elements where starting materials are received, on the production line, or in the lab.

Methods and equipment

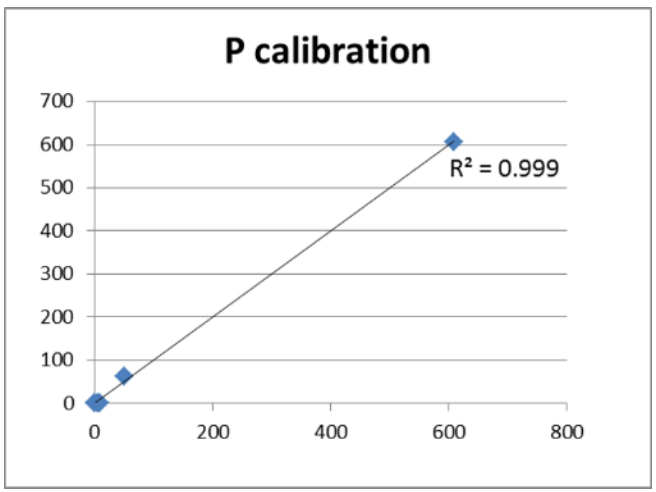
Simple steps to measure Phosphorus in edible oil with a portable XRF

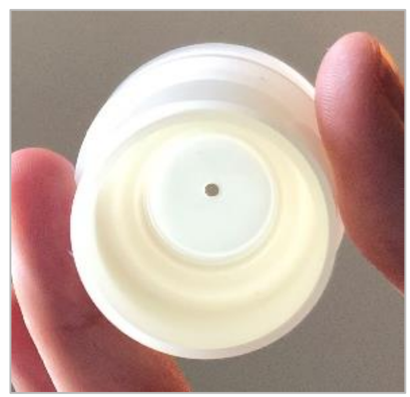
1. Create or purchase a calibration for Phosphorus in oil to be installed on the PXRF using reference samples with a similar base matrix and concentrations covering the range of interest.

2. Put oil in sample cup and cover with film.

3. Place sample cup on XRF analysis window and close the cover.

4. Select the calibration and press start.





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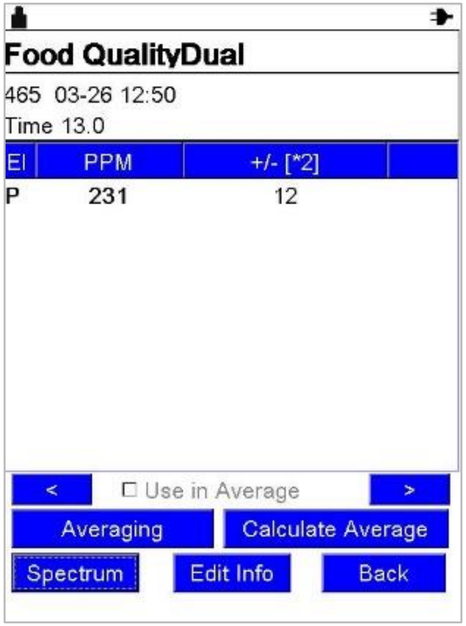
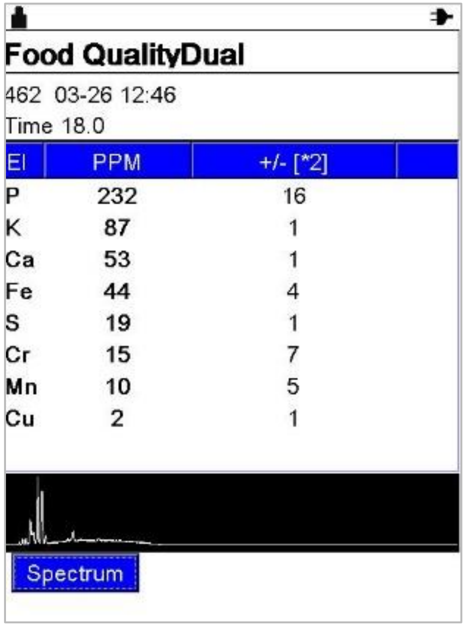
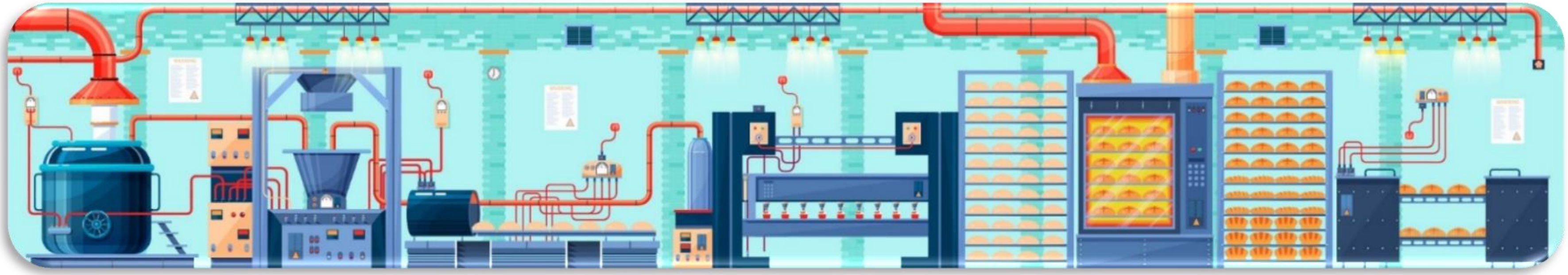




Physical contaminants in human and pet food

Application

Illustration of baking production line equipment



Physical contaminants can enter food products from wear and tear of equipment

Metal

Stone and ceramic

Glass

Plastic and rubber

Application

Typical prevention

1. **Inspect** food material with X-ray or metal detector
2. **Detect** foreign body
3. **Remove** product containing foreign body

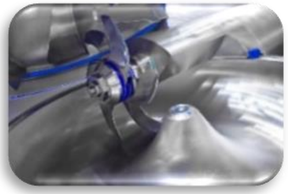
HHXRF for enhanced prevention

1. **Identify** found contaminant to determine its source
2. **Correct** issue based on source of the contaminant

Auger

Conveyor

Grinder/cutter



Mixer

Roller mill

Sorter/packager

Methods and equipment

- Small physical contaminants found in food products can be identified on the production floor or in the lab with handheld XRF
- A found metal object can be ID’d with handheld XRF by quickly determining its composition, the type of metal alloy, and the alloy grade name.

Methods, equipment results

Simple steps to ID small metal contaminants with Handheld XRF

1. Prepare found object	2. Select "Alloys" Cal	3. Position found object	4. Test & View Results

TXRF analysis of micronutrients and toxic elements in solid food samples

Introduction

Nutrition-relevant elements, also called "minerals"

- Minerals are inorganic substances required by the body in small amounts for a variety of different functions.
  - involved in the formation of bones and teeth
  - essential constituents of body fluids and tissues
  - components of enzyme systems
  - involved in normal nerve function
- The body requires different amounts of each mineral; requirements depend on age, sex, physiological state (e.g. pregnancy) and state of health
- Nutrition-relevant elements are calcium, phosphorus, magnesium, sodium, potassium, chlorine, iron, zinc, copper, selenium and iodine

  (Source: British Nutrition Foundation)

Introduction

Toxic elements

- Because of the high consumption of food the control of toxic metals is also of high importance
- Limit values for As, Cd, Pb and Hg are applied

Heavy metals	Stated limit (PTWI, weekly	Calculated daily limit (adult, 70 kg)
Arsenic	15 µg inorganic arsenic/kg bw	150 µg
Cadmium	7 µg cadmium/kg bw	70 µg
Lead	25 µg lead/kg bw	250 µg
Mercury	1,6 µg methylmercury/kg bw	16 µg

Source: JEFCA: The Joint FAO/WHO Expert Committee on Food Additives;
PTWI: provisional tolerable weekly intake

- The control of other toxic metals like Cr, Ni, Co and U would be beneficial

Introduction

Samples

- Round robin Cereal sample PTNATIAEA16 (http://www.pt-nsil.com/)
  - Nominal values from round robin test, applying different analytical techniques
  - Partly high number of outliers for the nominal values
- Certified reference standard NIST 1568a (rice flour)
  - Reference values based on measurements with high number of different analytical methods and laboratories

Methods and Equipment
Sample preparation

Sample preparation

Grinding (grain size < 20 µm)

Weighing of 100 mg in 15 ml vials

Suspension in 5 ml Triton X100 solution

Addition of internal standard solutions

Treatment in ultrasonic bath for 3 min

Pipetting 10 µl on siliconized quartz carrier, while samples are shaken at 900 r/min

Drying in vacuum

Methods and Equipment Measurements

S2 PICOFOX

- Mo tube, 50 kV/1000 µA
- 60 mm^2 XFlash SDD
- 25 position sample changer

Measurements

- Mo-K excitation, 1000 s

Methods and Equipment Measurements

S2 PICOFOX - Measurement program

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sb Antimony	51 Sn Tin	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astanine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium															
			L Lanthanides	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolynium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Th Thulium	70 Yb Ytterbium	71 Lu Luthetium
			Ac Actinides	90 Th Thorium	91 Pa Proactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Analysed using K-lines

Internal standard

Analysed using L-lines

Methods and Equipment Measurements

S4 T·STAR

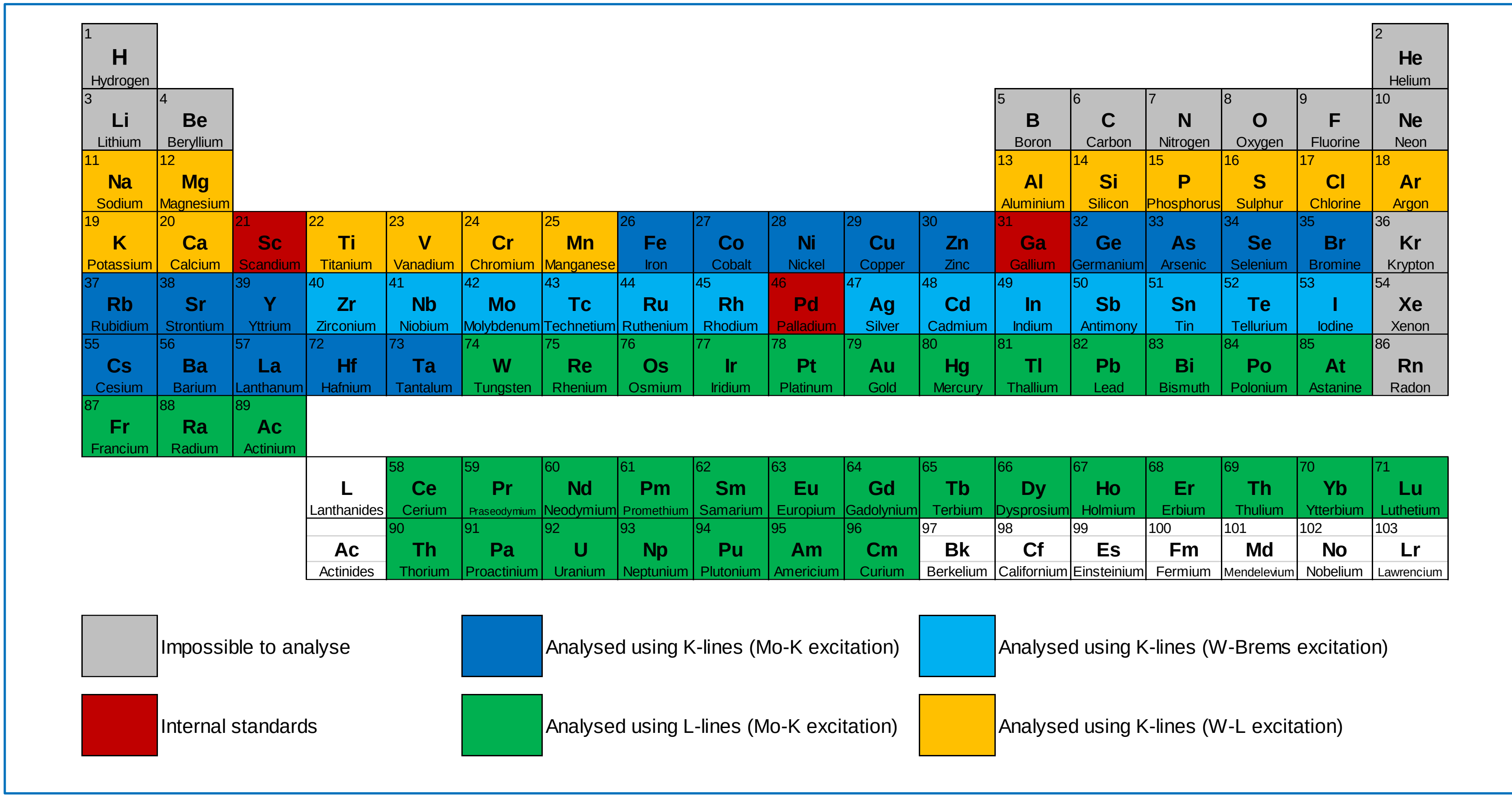
- Mo tube, 50 kV/1000 µA
- W-tube, 50 kV/1000 µA
- Monochromator system for Mo-K, W-L and W-Brems monochromatization
- 60 mm^2 XFlash SDD
- 90 position sample changer

Measurements

- Mo-K excitation, 1000 s
- W-L excitation, 1000 s
- W-Brems excitation, 1000 s

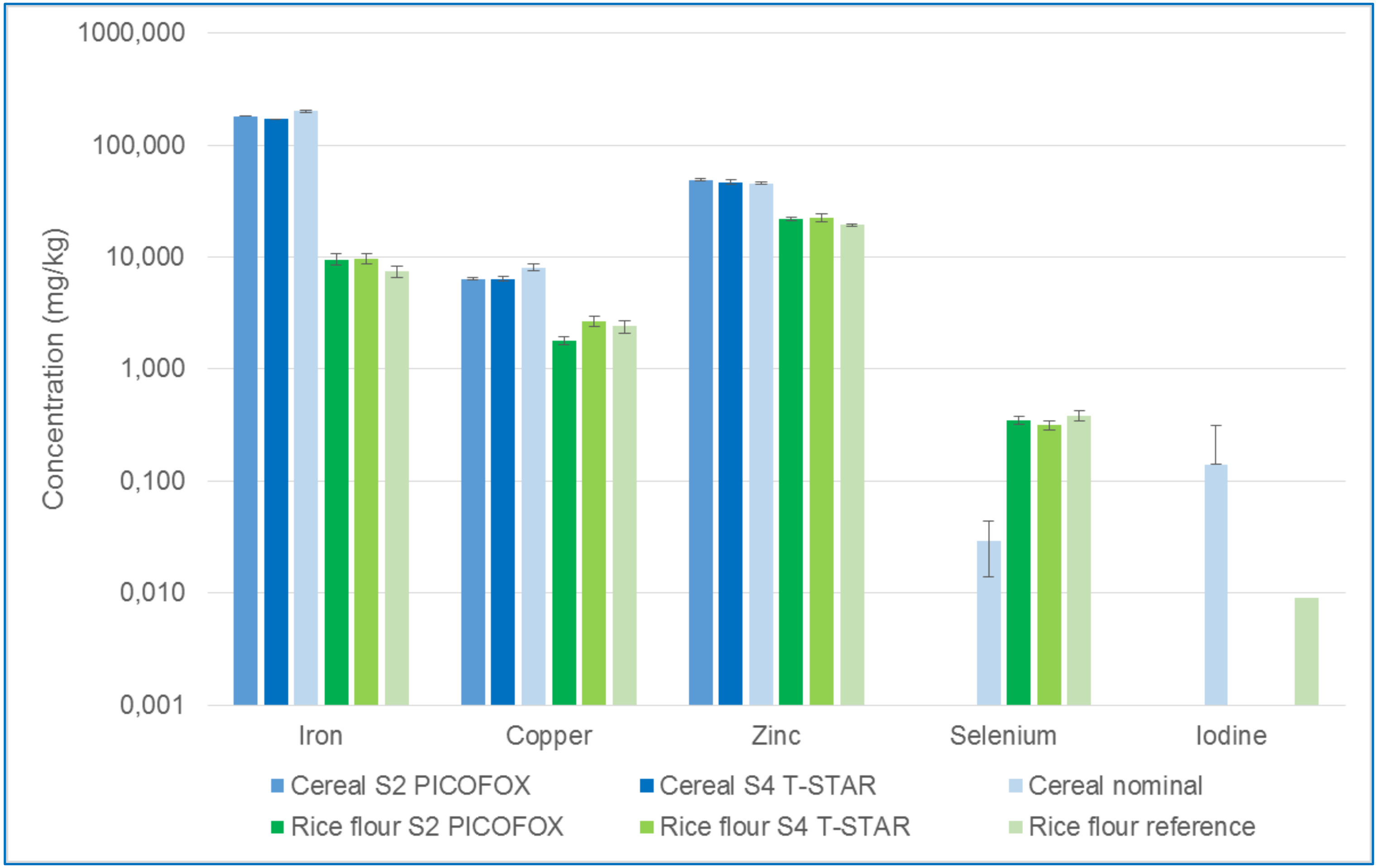
Methods and Equipment Measurements

S4 T·STAR – Measurement program



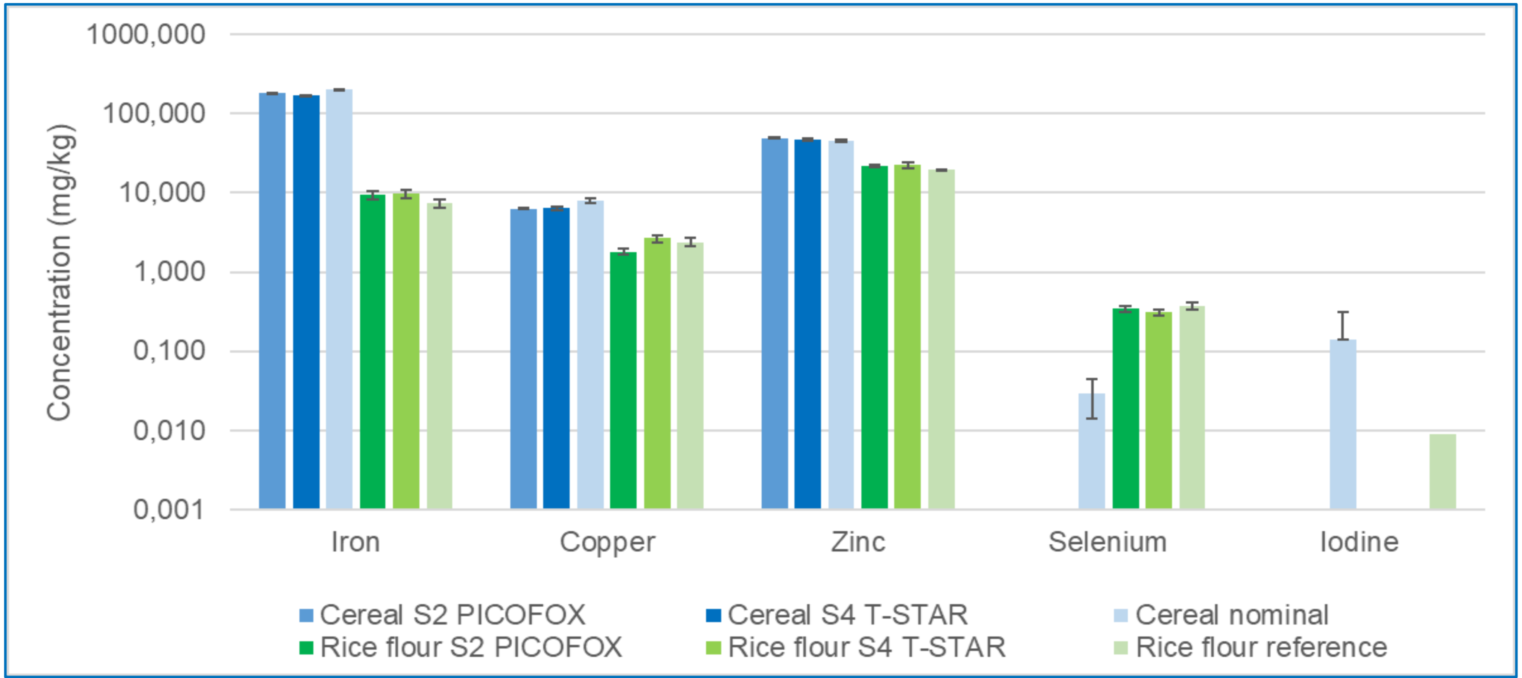
Results
Micronutrients

Micronutrients



Results
Micronutrients

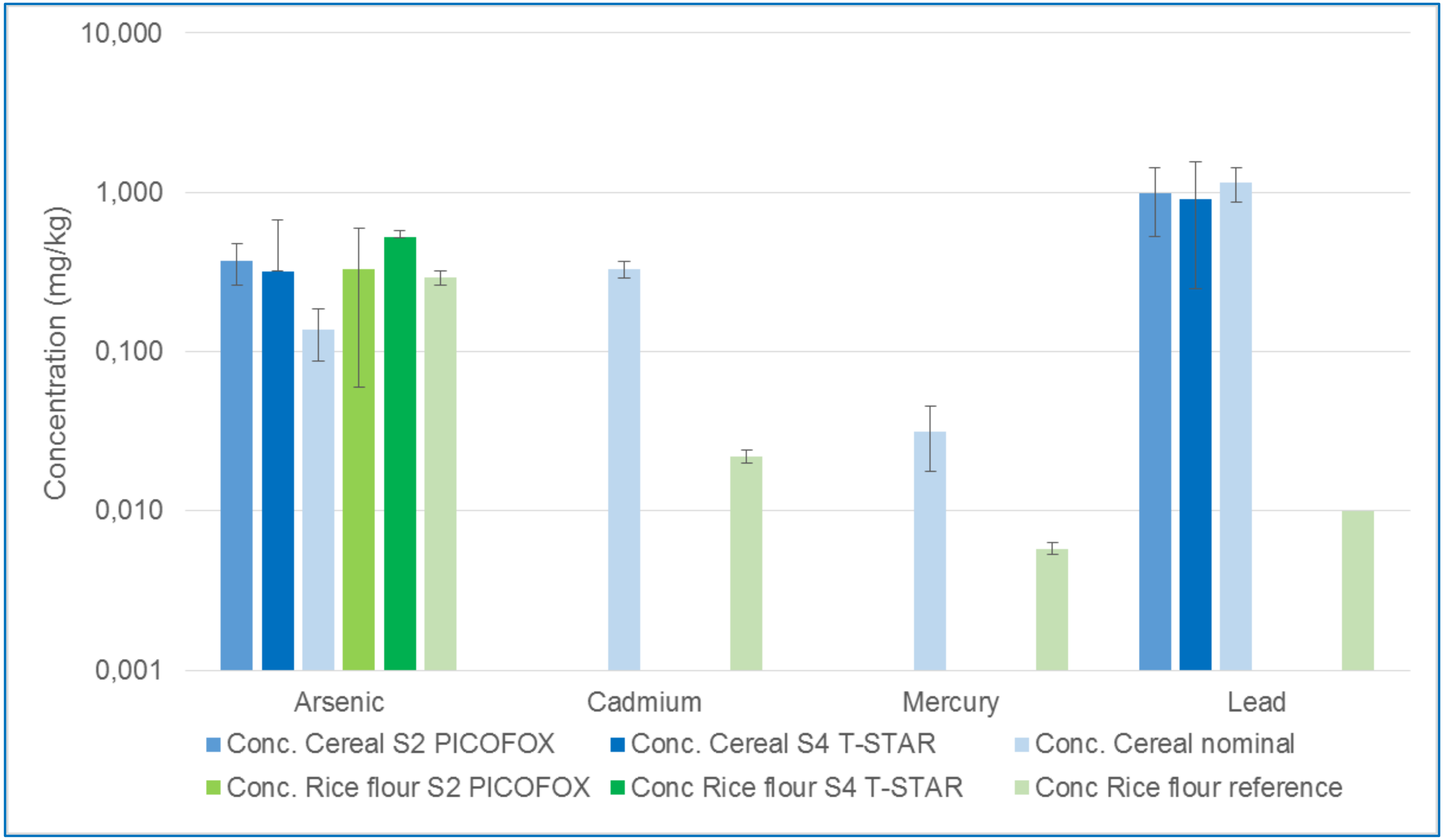
Micronutrients



- Fe, Cu and Zn could be analyzed with good accuracy
- Se could be quantified accurately in rice flour, but was below the detection limit in cereals (e.g. 110 µg/kg for the S4 T-STAR)
- Iodine was present in concentrations distinctly below the detection limit of 20 mg/kg

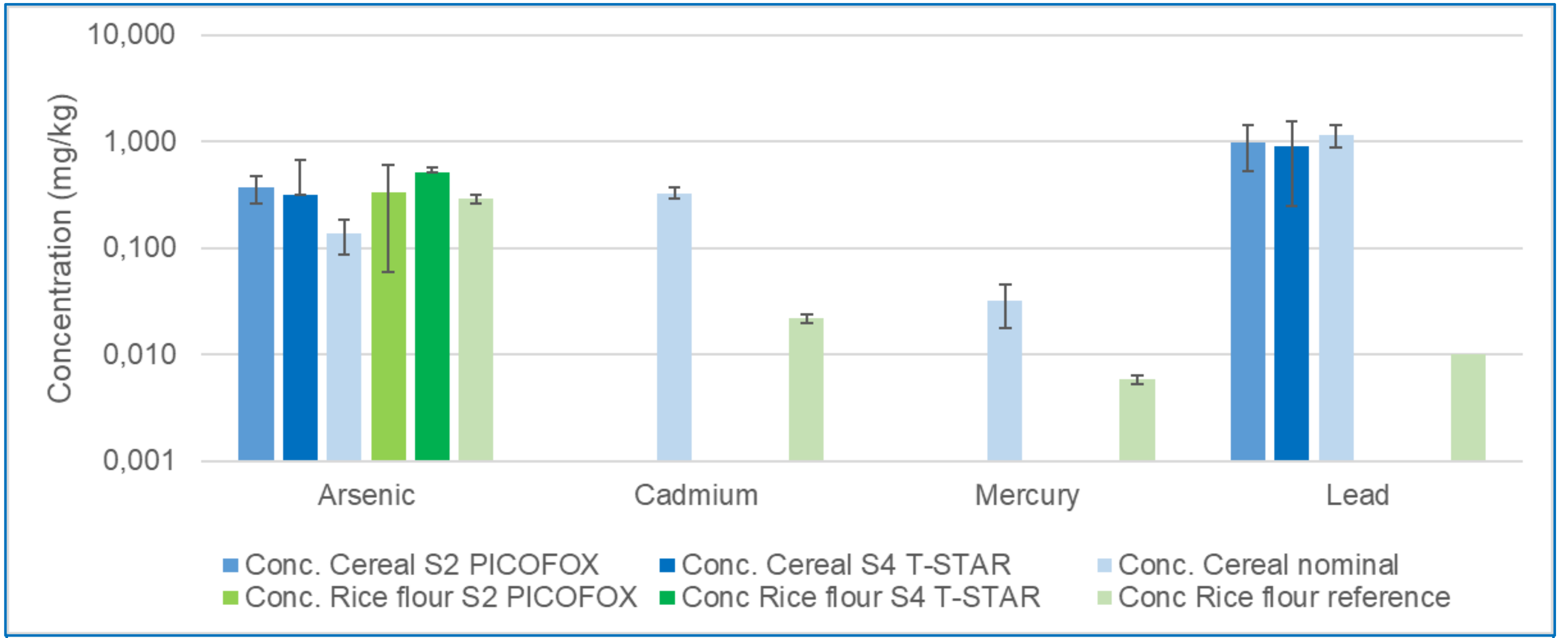
Results
Toxic metals

Toxic heavy metals



Results
Toxic metals

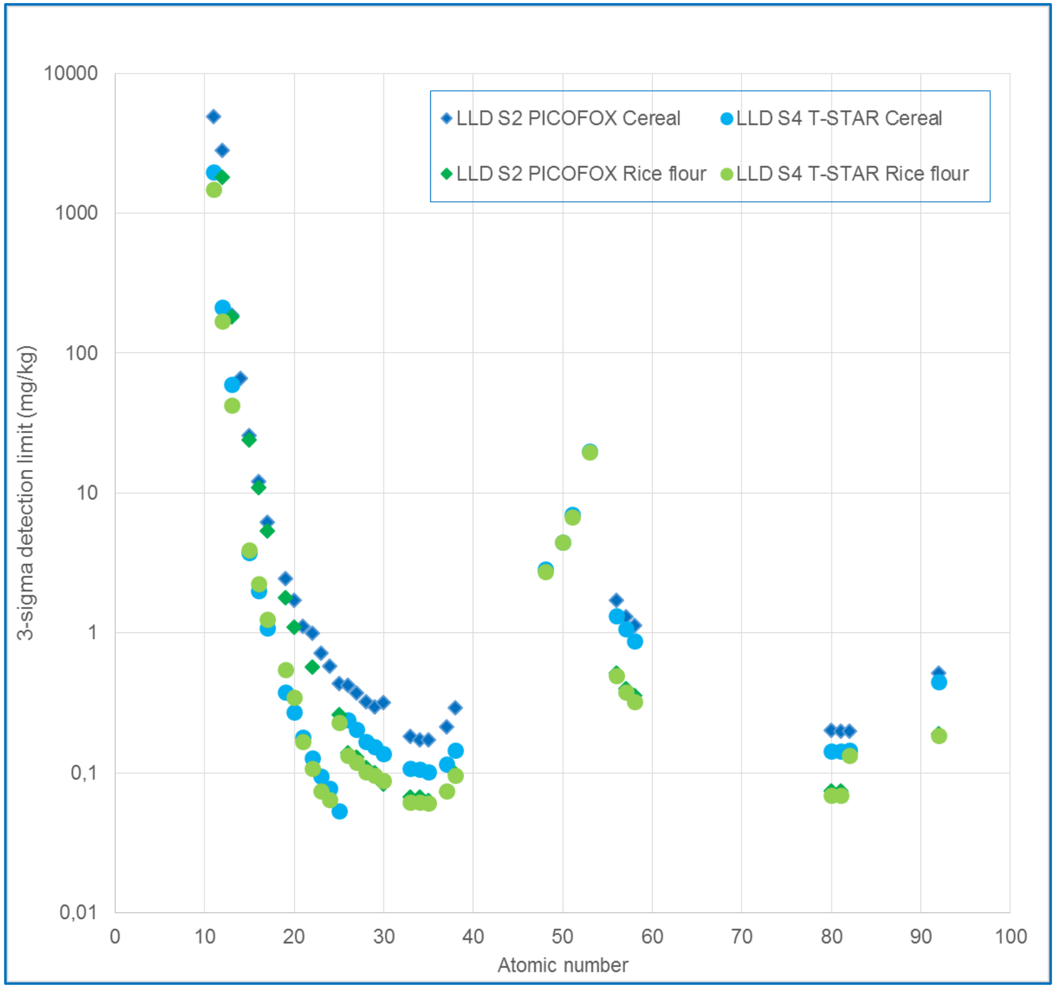
Toxic heavy metals



- As could be analyzed in both samples
- Cadmium was distinctly below the detection limit of 2,8 mg/kg
- Hg was slightly below the detection limits (70 – 200 µg/kg)
- Pb could be analyzed in the cereal sample, but was below the detection limit in rice flour samples (~ 130 µg/kg)

Results
Detection limits

3-sigma detection limits



Summary

- All food sample types, which can be dried and ground to a fine powder, can be analyzed with TXRF applying the described easy suspension preparation
- The quantification is done by means of internal standardization; no external calibrations are necessary
- Elements are detected simultaneously and independent from the concentration ranges
- It was demonstrated that macro nutrients Mg, P, Cl, K and Ca as well as micronutrients Fe, Cu, Zn and Se could be analyzed
- The control for the toxic heavy metals As, Pb and with restrictions Hg is possible
- The S4 T-STAR offers best detection limits and a high analytical flexibility
- The S2 PICOFOX is optimally suited for rapid onsite screening

TXRF analysis of dietary supplement pills

Objective

- The purpose of food supplements is to supplement the normal diet
- This supplements are concentrated sources of nutrients or other substances with a nutritional or physiological effect
- Relevant regulations are the European Directive 2002/46/EC and the US-FDA Dietary Supplement Health and Education Act of 1994

Methods and Equipment
Samples and sample preparation

Samples

2 multivitamin/mineral pills

Analytical task

Analysis of Mg, P, Ca, Cr, Zn, Se, Mo and I

Sample preparation

- Grinding in agate mortar
- Weighing of 100 ± 5 mg sample into vials
- Suspension in 5 ml aqueous Triton X 100 solution (1 vol.-%)
- Addition of 10 µl Ni (1 g/l) and 10 µl Pd (1 g/l)
- Homogenization
- Pipetting of 10 µl sample onto quartz glass carriers
- Drying in vacuum

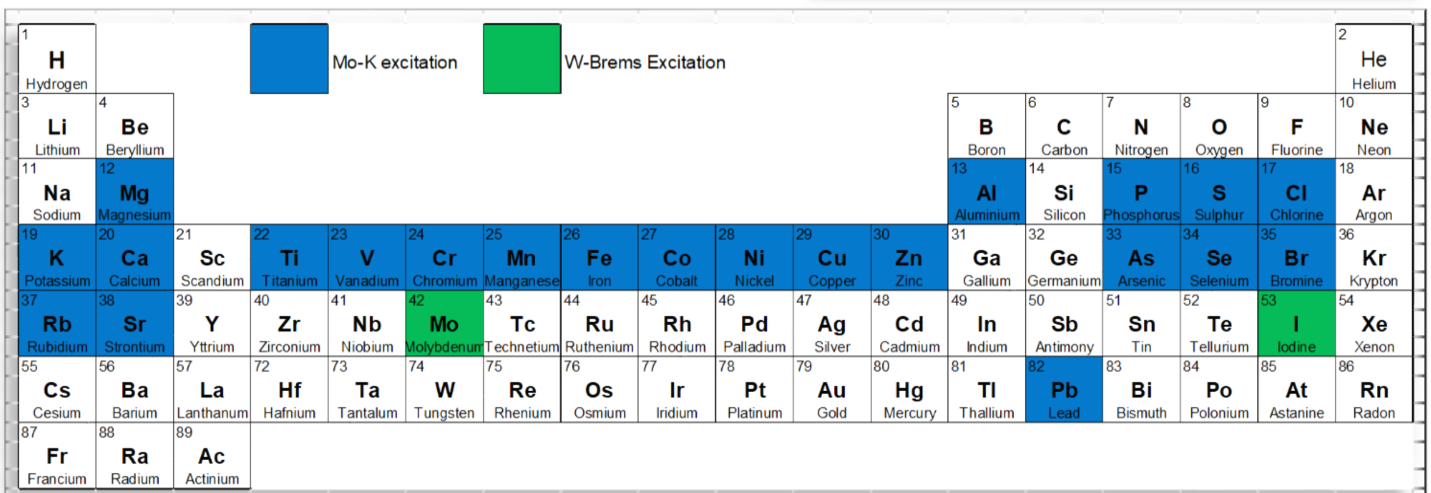
Methods and Equipment Measurements

S4 T·STAR

- Mo tube, 50 kV/1000 µA
- W-tube, 50 kV/1000 µA
- 100 mm² XFlash SDD

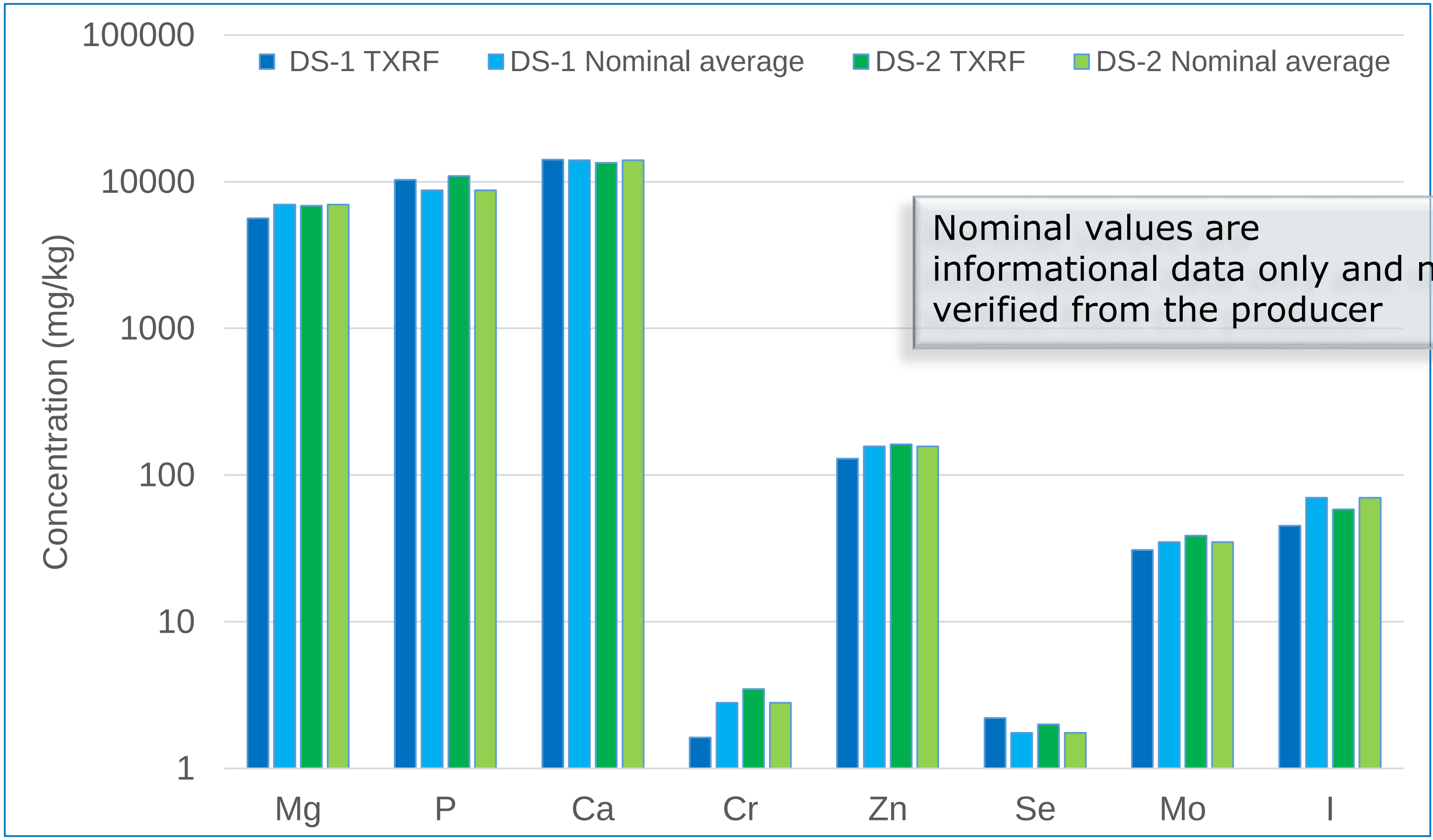
Measurements

- Mo-K excitation, 1000 s
- W-Brems excitation, 1000 s



Results
Element concentrations

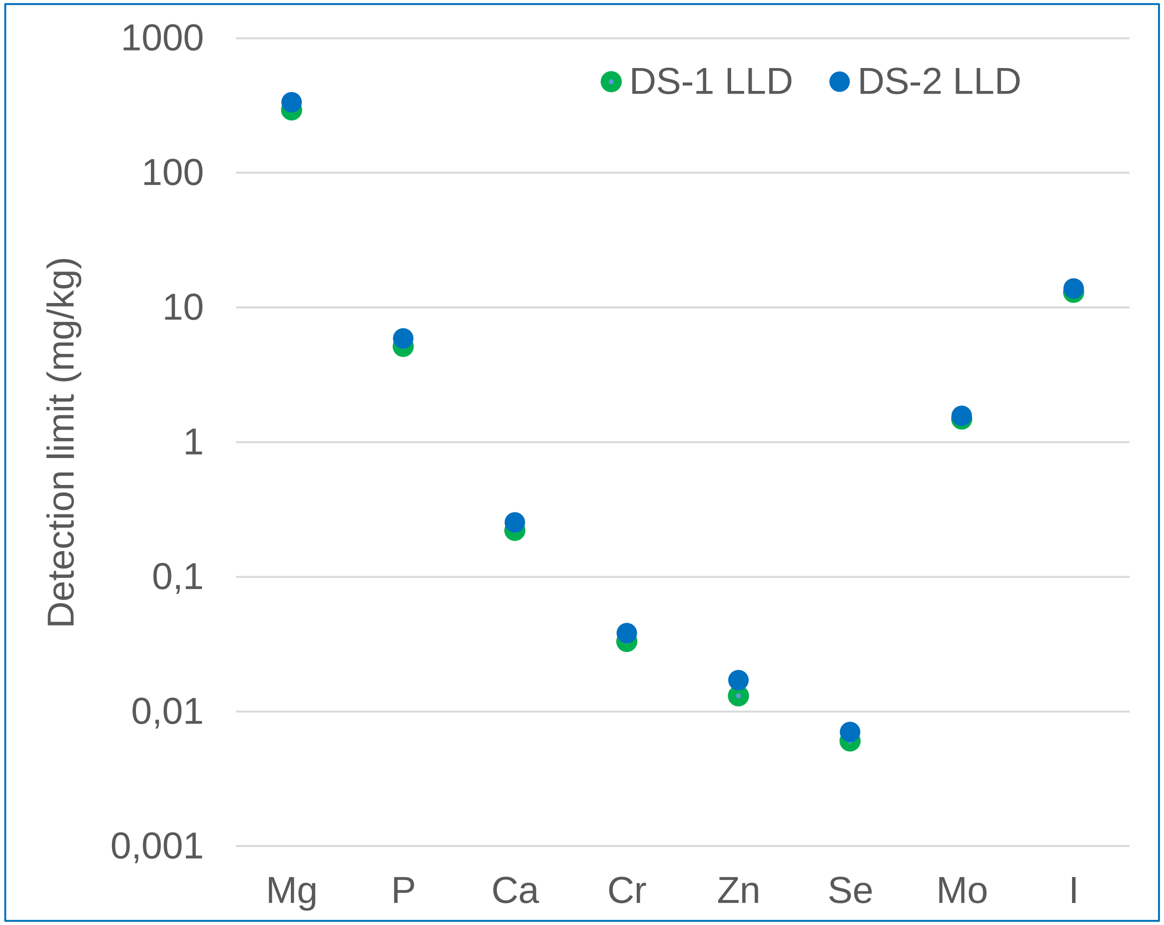
Element concentrations



Nominal values are informational data only and not verified from the producer

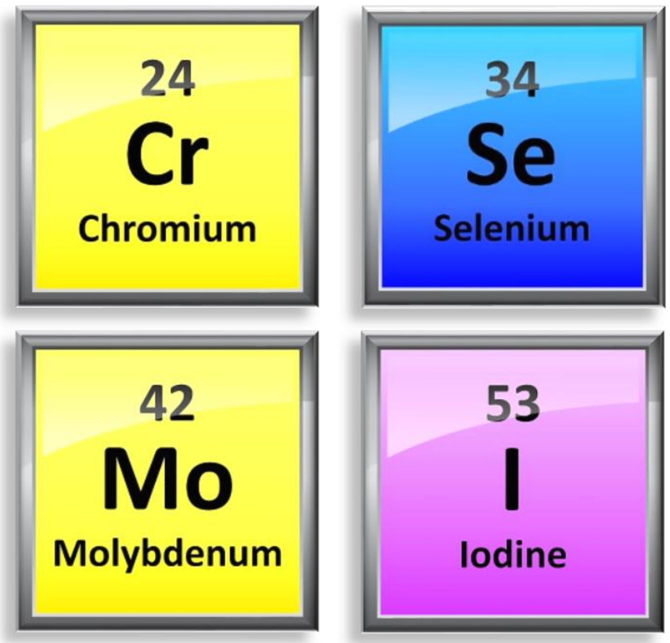
Results
Detection limits

Detection limits



Summary

- All elements of interest can easily be analyzed with the S4 T·STAR
- The detection limits are sufficient for the accurate analysis of major and trace nutrients
- The analysis of Cr, Se and Mo according to several AOAC and EN norms is possible (AOAC 2011.19, AOAC 986.15, AOAC 996.17, AOAC 2006.03, EN14627, EN 14082, EN 14083)
- In addition, iodine can be monitored in dietary supplements without laborious sample treatment



TXRF analysis of milk samples

Objective
Samples and sample preparation

Samples

- 8 milk samples

Analytical task

- Analysis of Na, Mg, I and transition metals

Sample preparation

- Weighing of 1 ml milk into reaction vials
- Dilution with 1,5 ml ultrapure water
- Addition of 10 µl V (1 g/l), 10 µl Ga (100 mg/l) and 5 µl Pd (1 g/l)
- Homogenization
- Pipetting of 10 µl sample onto quartz glass carriers
- Drying in vacuum

Measurements

S4 T·STAR

- Mo tube, 50 kV/1000 µA
- W-tube, 50 kV/1000 µA
- 60 mm^2 XFlash SDD

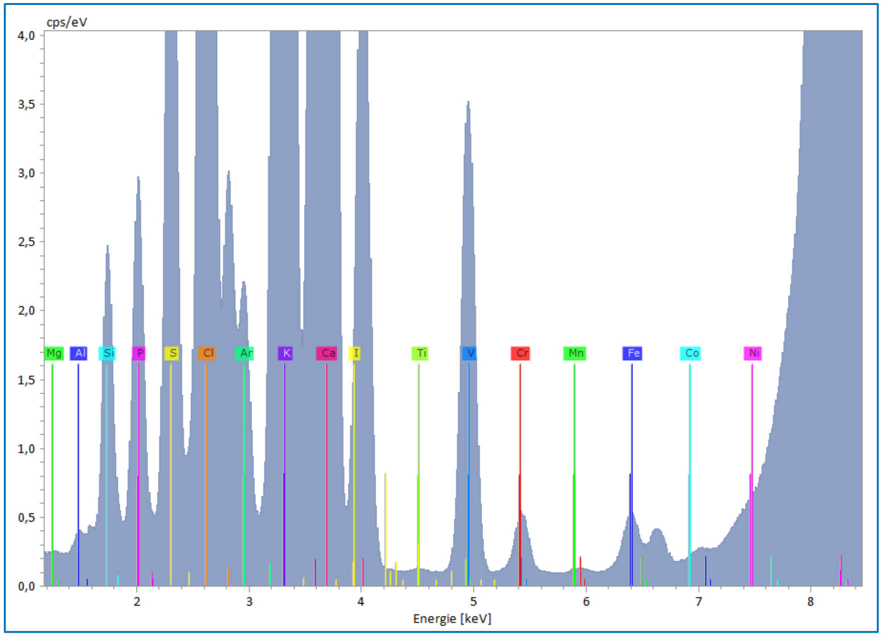
Measurement conditions

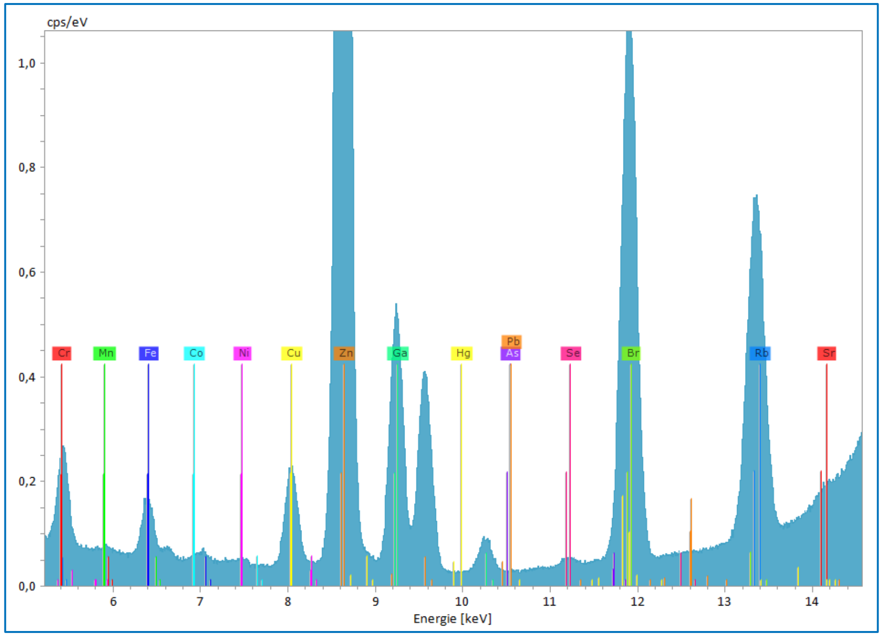
- Mo-K excitation, 1000 s
- W-L excitation, 1000 s
- W-Brems excitation, 1000 s

Measurements

Spectra

- Typical spectra of milk measured with W-L (left) and Mo (right) excitation

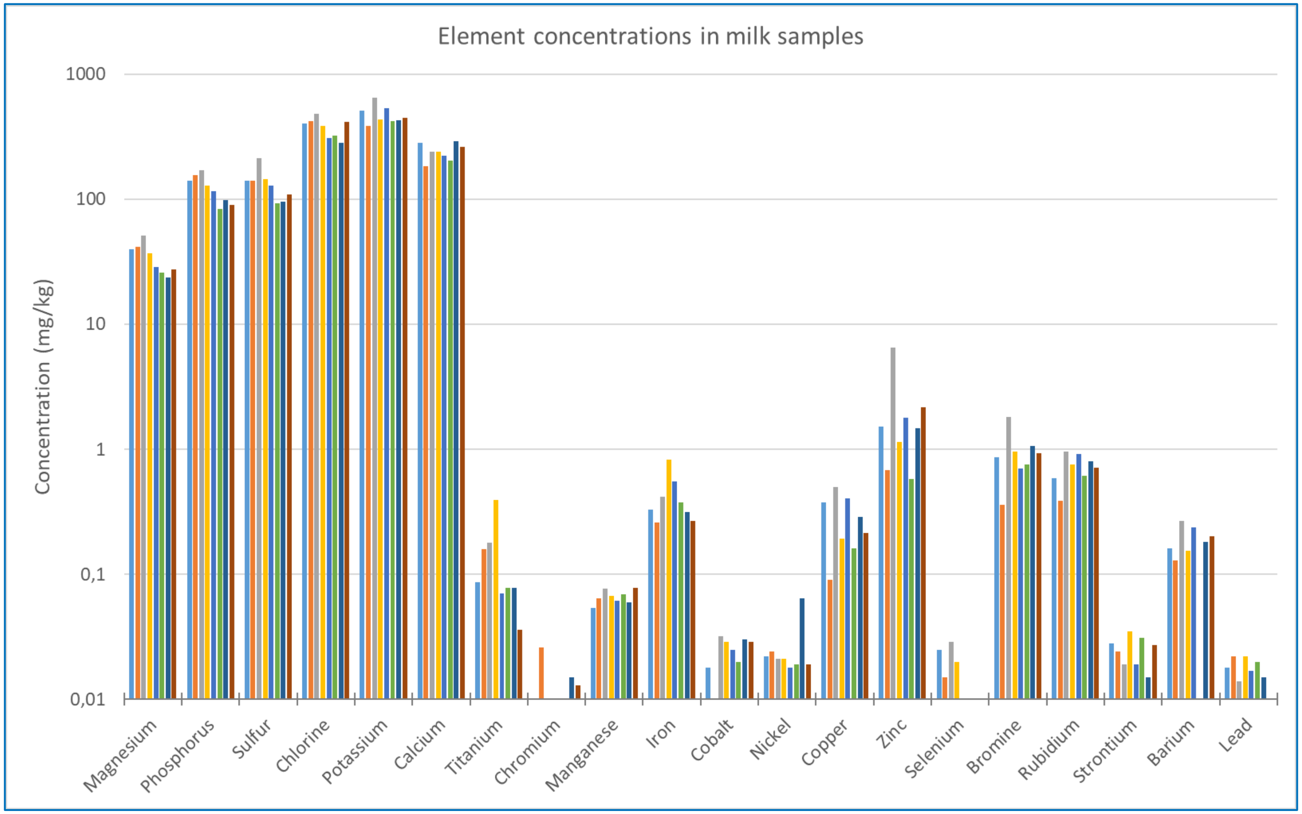




Results

Element concentrations

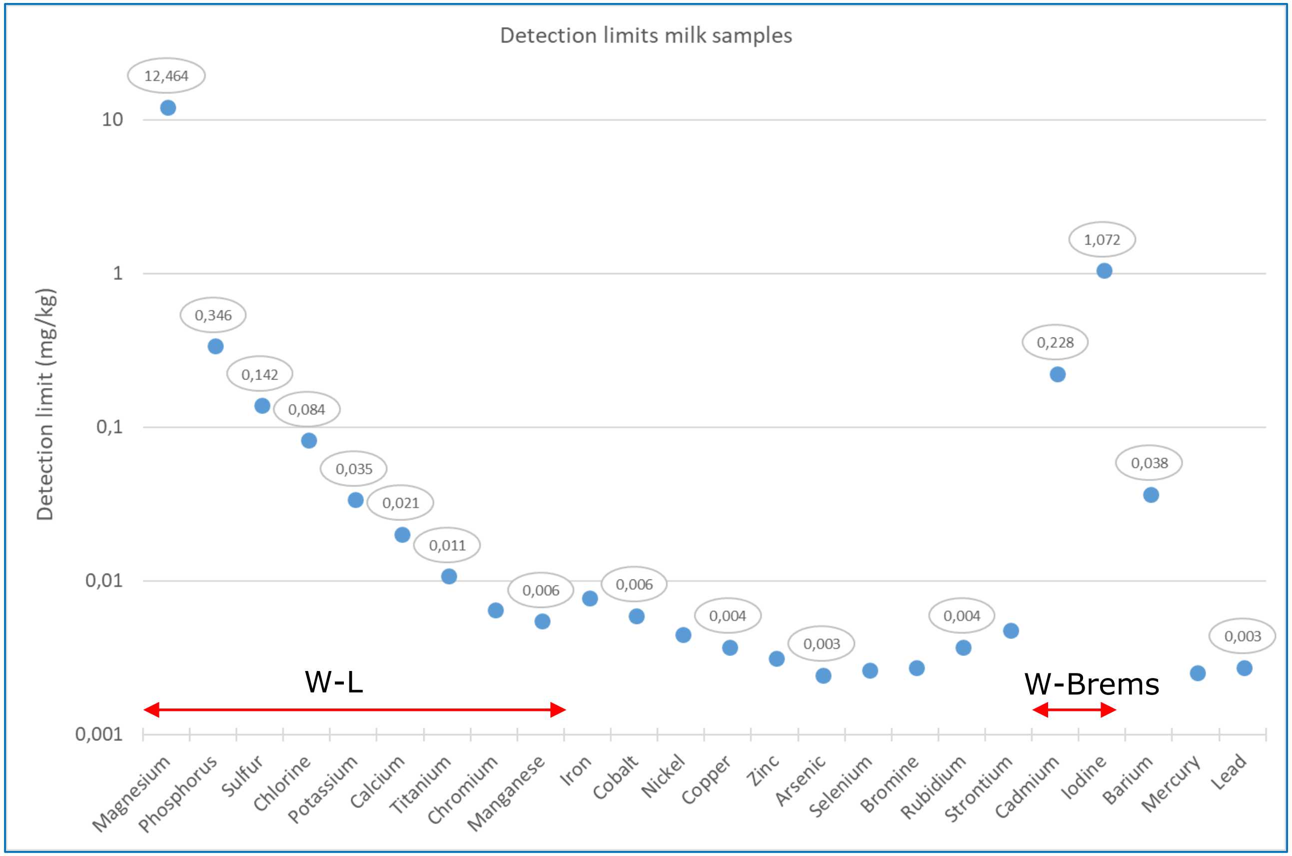
- Different colored bars represent 8 milk samples
- Nutrient element concentration range from 50 ppm to 0,1%
- Trace elements can be detected below 10 ppb



Results & Discussion

Detection limits

- Untagged elements were measured with Mo excitation
- W-L provides 3 to 10 times better LLD for elements lighter than Cr
- Identification of toxic elements As, Pb, Cd, Hg at low levels is possible

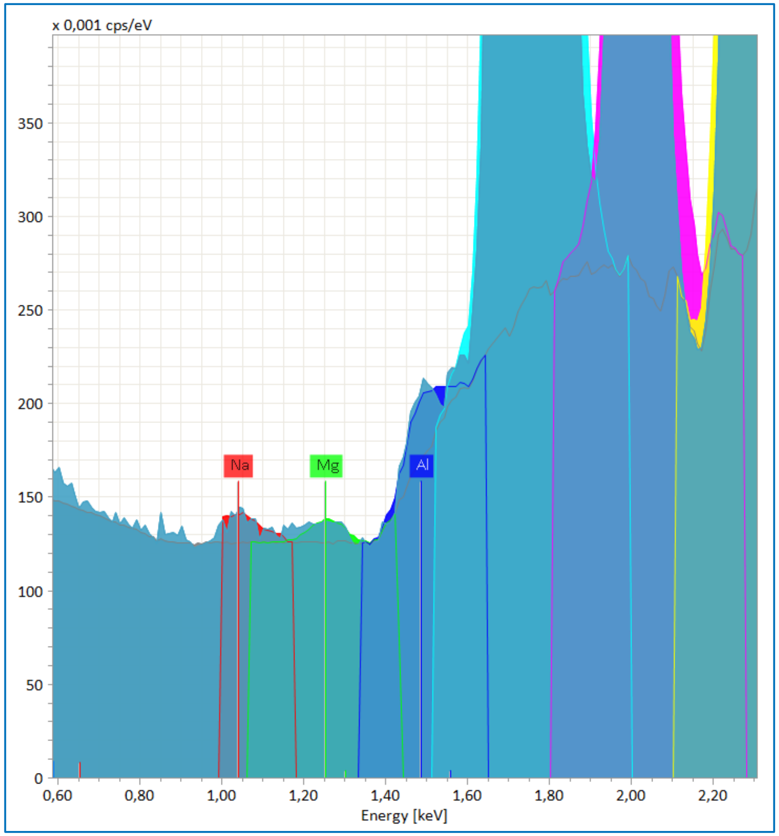


Results & Discussion

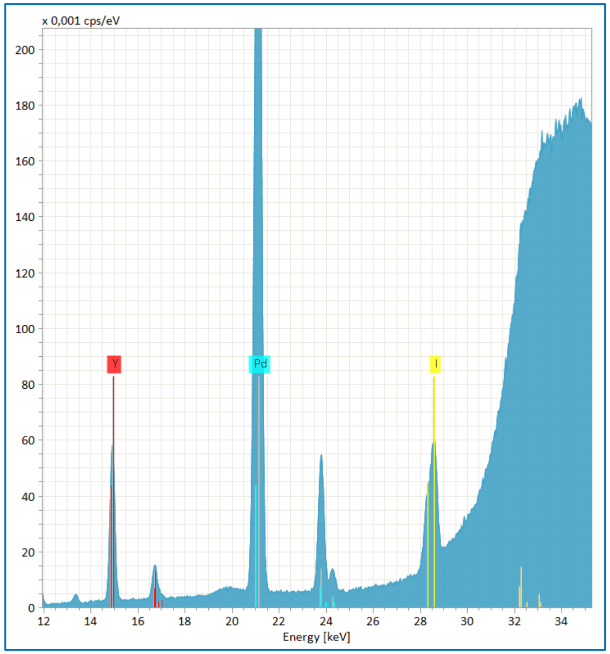
Challenging elements

- Na: detectable with W-L excitation
  - Detection limit about 50 mg/kg
- I: improved detection limit of 0,7 mg/kg without sample dilution

W-L spectrum with 200 ppm sodium

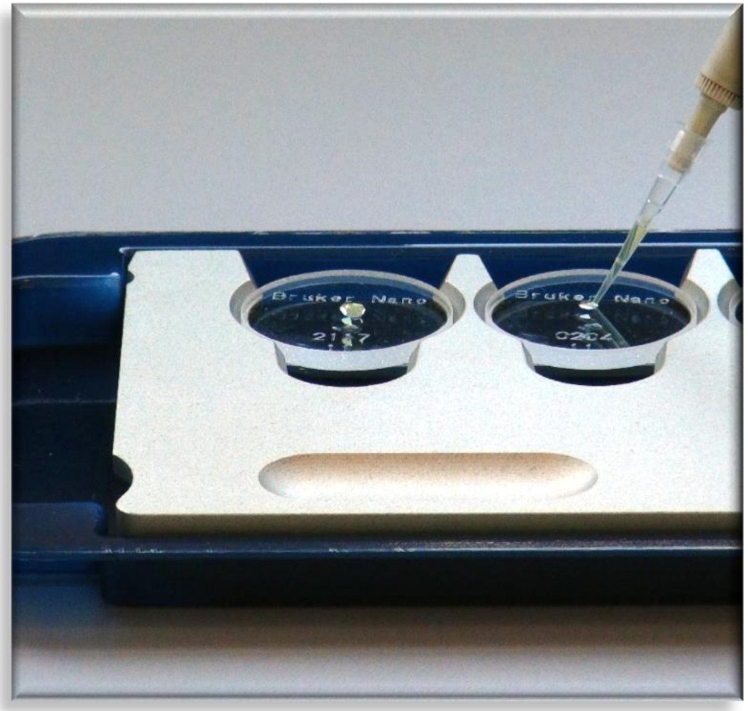


W-Brems spectrum with 42 ppm iodine



Summary

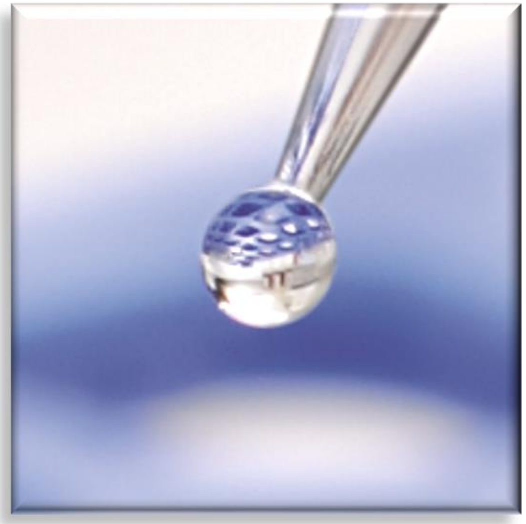
- Applying the S4 T-STAR the entire element range from Na to U can be detected in milk samples
- Detection limits are in the ppb range for almost all elements



Q & A

Any Questions?

Please **type in** the questions you may have for our speakers in the **Questions Box** and click **Submit**



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