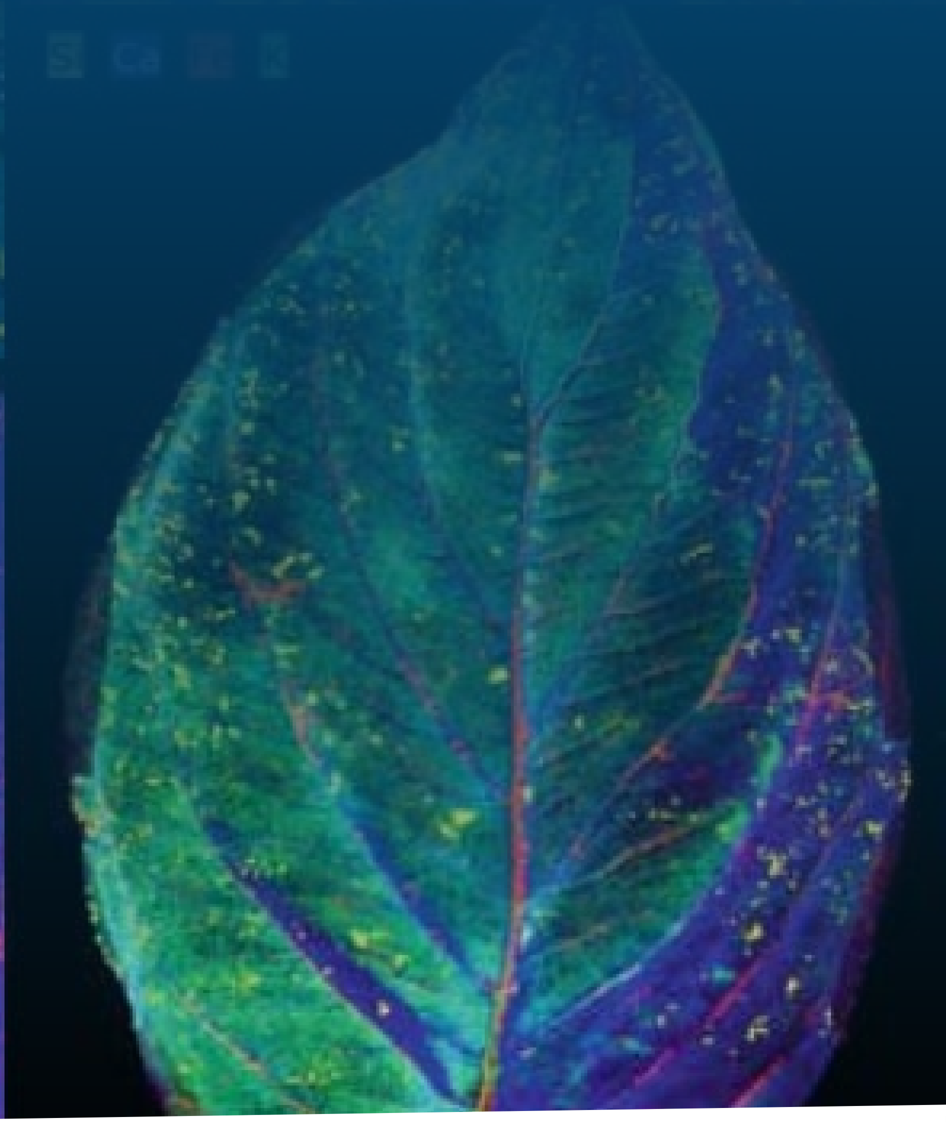
Micro-XRF
Back to the Roots – Part I

March 23, 2022

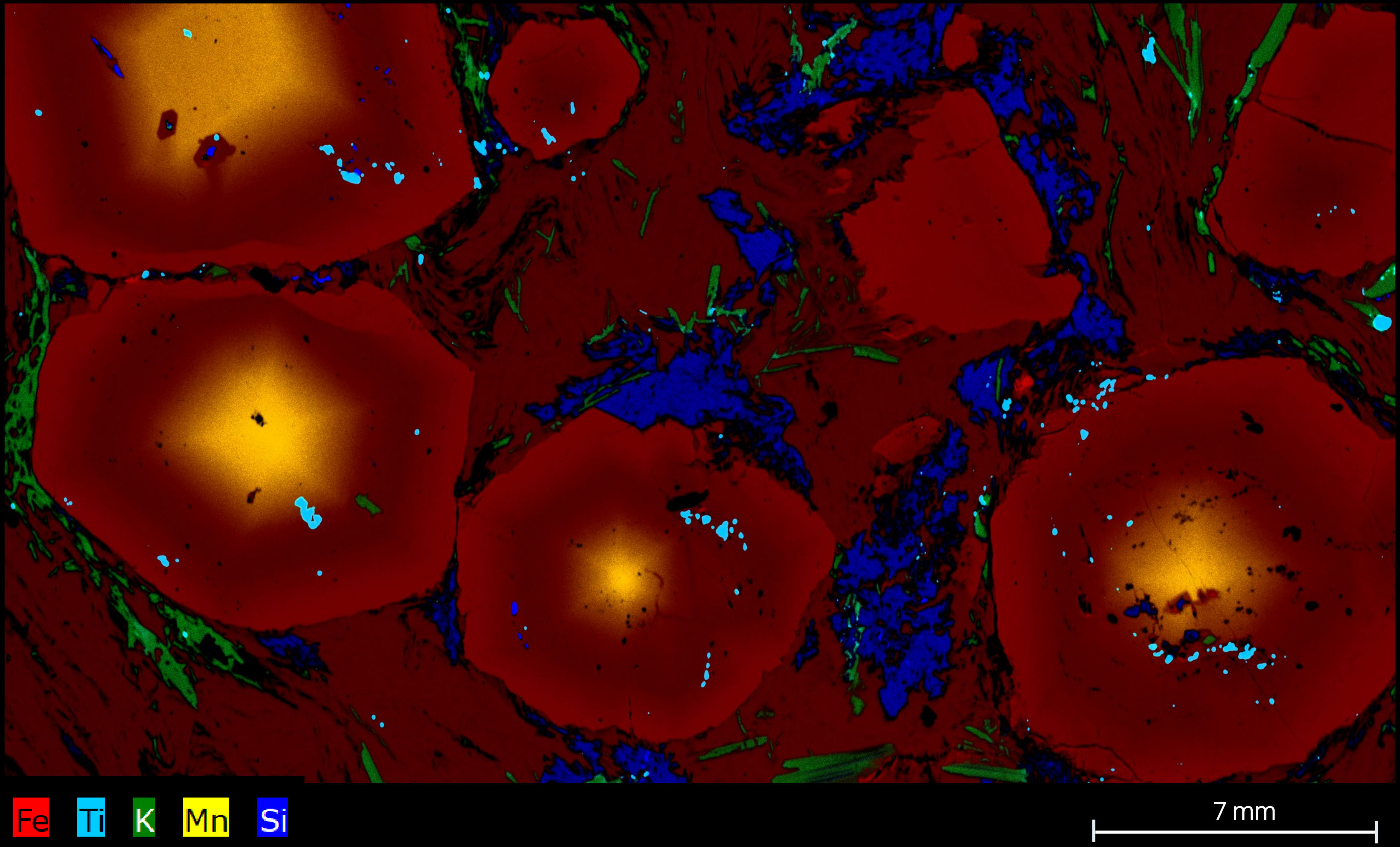


Leaves

Berlin, Germany

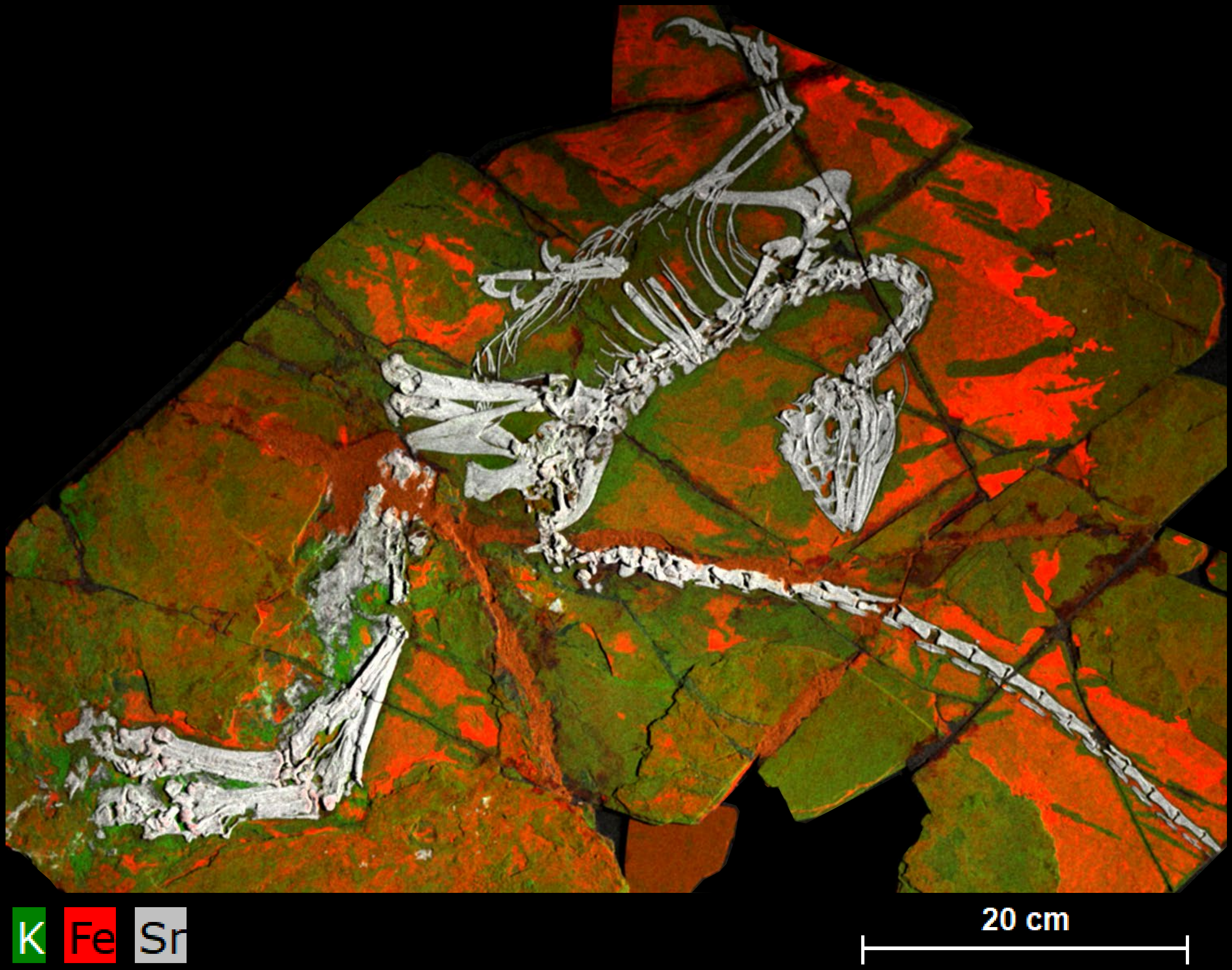
Garnets

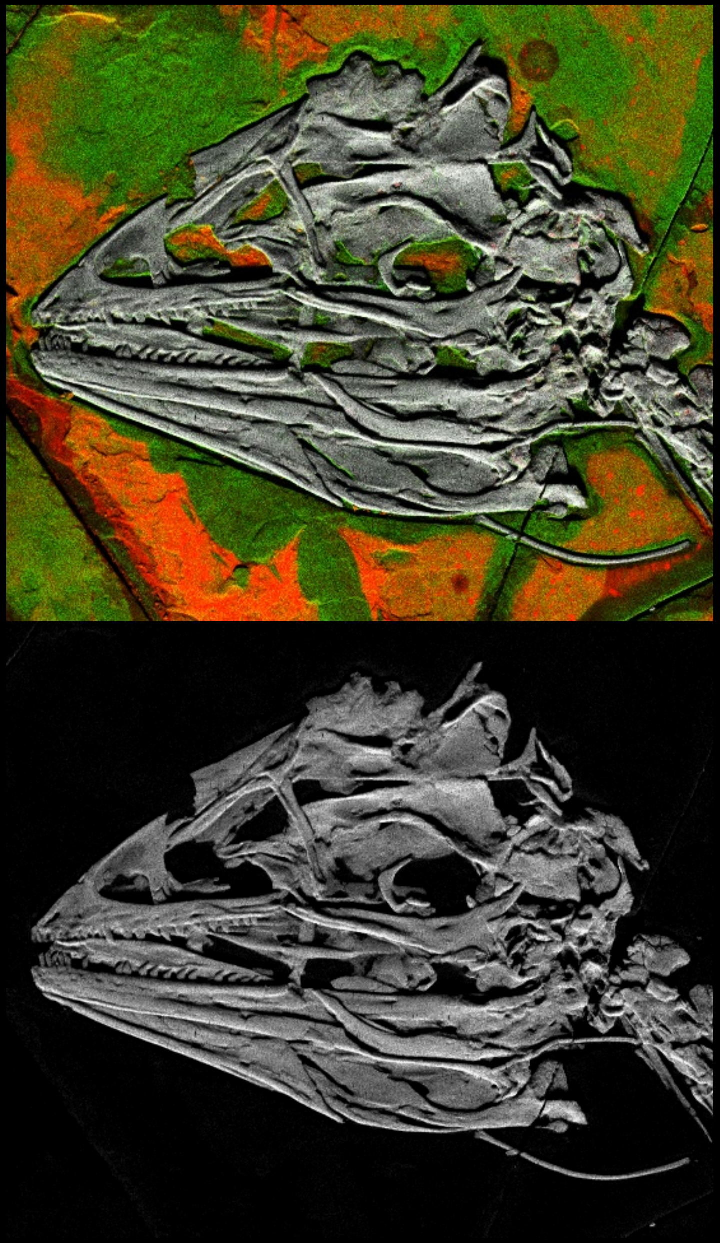
Zillertal, Austria



Jianianhualong

Early Cretaceous theropod, China



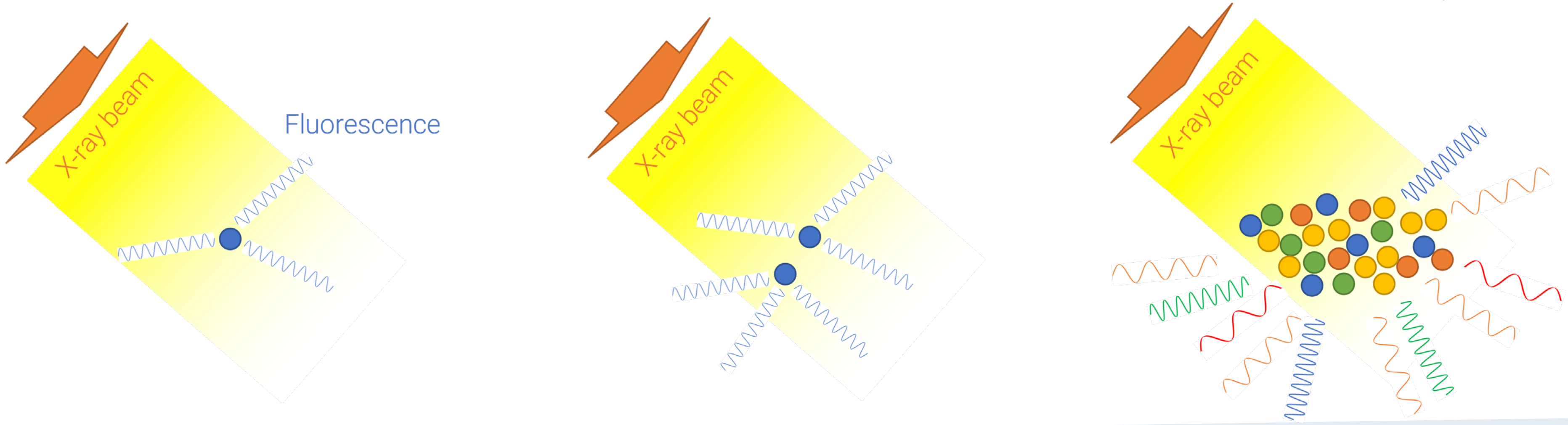


BACK TO THE ROOTS – PART I

What is micro-XRF?

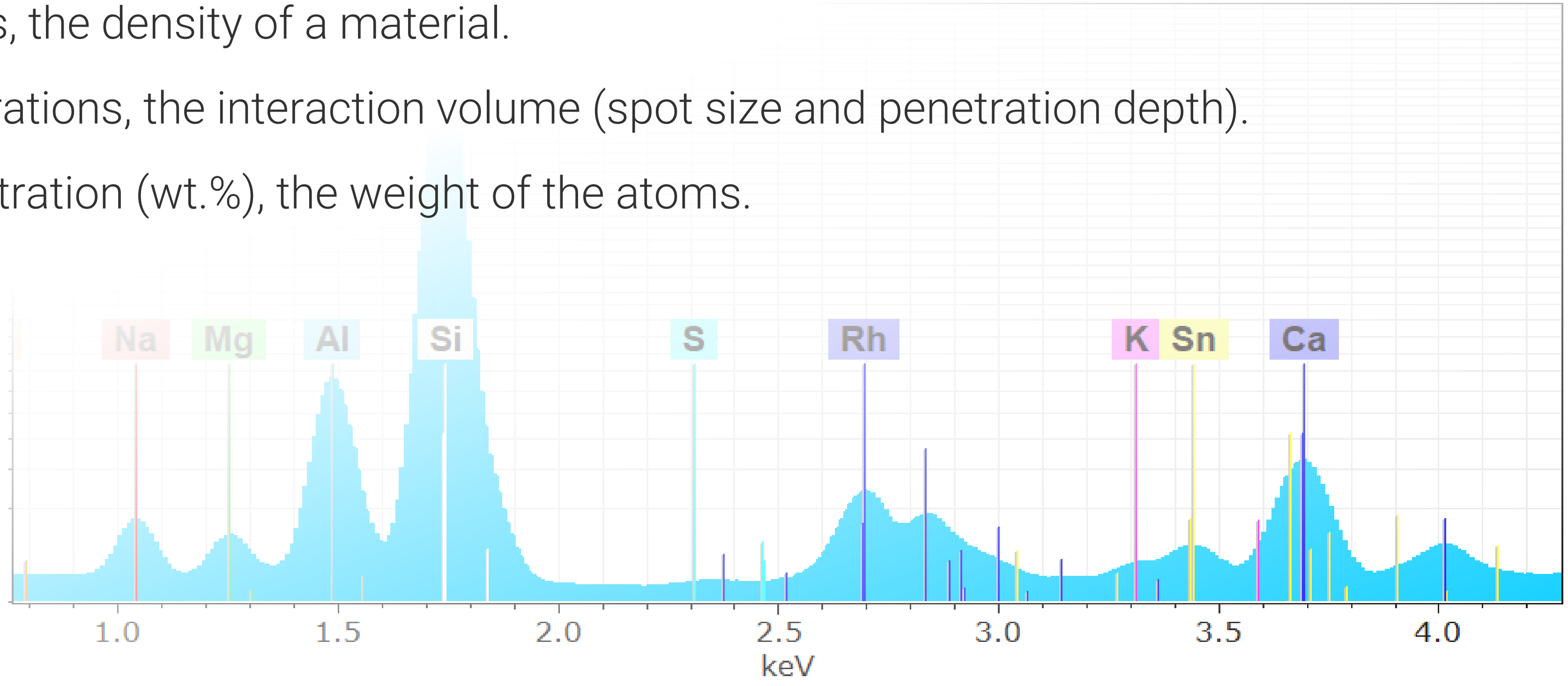
Qualitative and quantitative X-ray fluorescence analysis
Counting atoms

- XRF is widely known for quantitative analysis. Why? Because it works so straightforwardly.
- An atom in an X-ray beam will produce element specific fluorescence radiation.
- Two atoms of the same type will produce twice as much fluorescence radiation.
- Many different atoms in the X-ray beam will all produce their characteristic fluorescence radiation.
  - Detecting the radiation with wavelength- or energy-dispersive detectors enables qualitative analysis.
  - Counting the number of incoming photons allows to **count the atoms** → quantitative analysis.



Quantitative X-ray fluorescence analysis
From atoms to wt.%

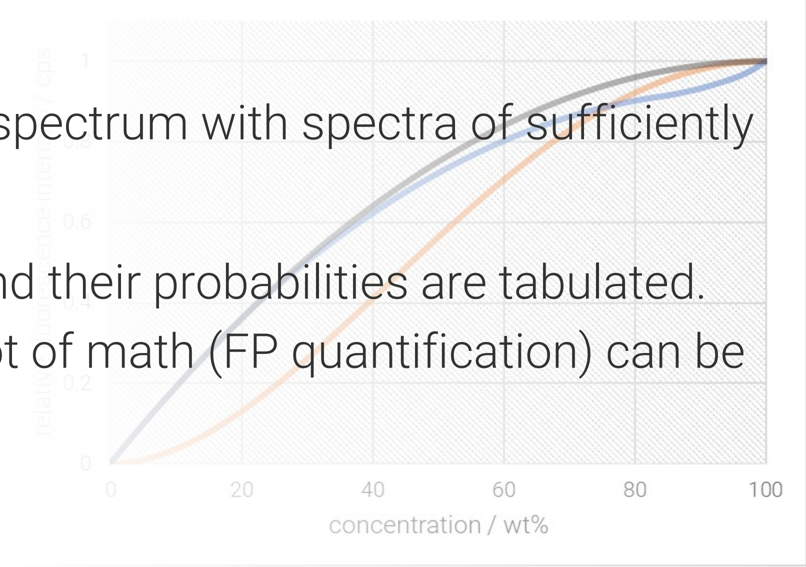
- With additional information, it is possible to convert this number of "atoms in an X-ray beam" to meaningful units:
  - To get the mass coverage, the size of the irradiated area.
  - To get a layer thickness, the density of a material.
  - To get atomic concentrations, the interaction volume (spot size and penetration depth).
  - To get to mass concentration (wt.%), the weight of the atoms.



Quantitative X-ray fluorescence analysis With standards or without

There are two distinct approaches to quantitative XRF:

- Element concentrations can be deduced by comparison of the sample spectrum with spectra of sufficiently similar standard samples with known compositions.
- All physical effects in XRF are reasonably well-understood nowadays and their probabilities are tabulated. Thus, a quantification based on these fundamental parameters and a lot of math (FP quantification) can be performed.



Mg	Al	Si	Mn	Fe	Ni	Cu	Zn	Ga	Rh	Pb	Bi
0.95	76.31	0.01	1.08	0.18	0.01	6.95	0.08	0.00	0.00	0.00	0.00
0.71	72.17	0.01	1.16	0.27	0.01	6.77	0.07	0.00	0.00	0.00	0.01
1.05	76.45	0.01	1.07	0.14	0.02	7.38	0.08	0.00	0.00	0.00	0.00
0.89	76.53	0.01	1.16	0.30	0.02	7.30	0.08	0.00	0.00	0.01	0.01
0.93	73.84	0.01	1.07	0.10	0.01	6.58	0.07	0.00	0.00	0.01	0.00
0.03	80.67	0.01	0.05	0.92	0.01	8.00	0.07	0.01	0.00	0.15	0.19
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0.01	80.14	0.01	0.07	0.80	0.05	7.48	0.07	0.00	0.00	0.16	0.25
0.07	79.28	0.01	0.05	0.94	0.03	8.35	0.07	0.01	0.00	0.11	0.19
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.14	0.24
0.08	79.88	0.01	0.22	0.87	0.01	7.83	0.07	0.00	0.00	0.11	0.22

There are numerous hybrid approaches with different contributions of either form of quantification:

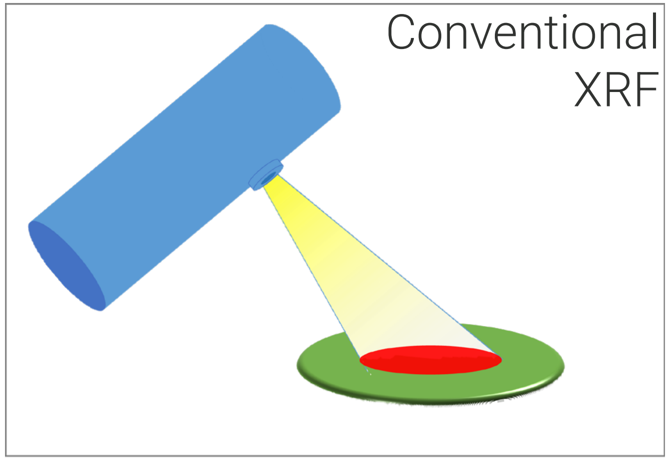
- FP-supported standard-based quantification
- Standard-supported FP quantification

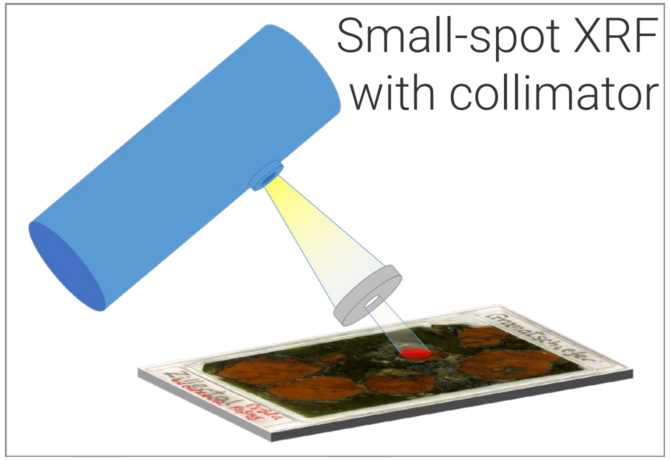
From XRF to micro-XRF
Why the need?

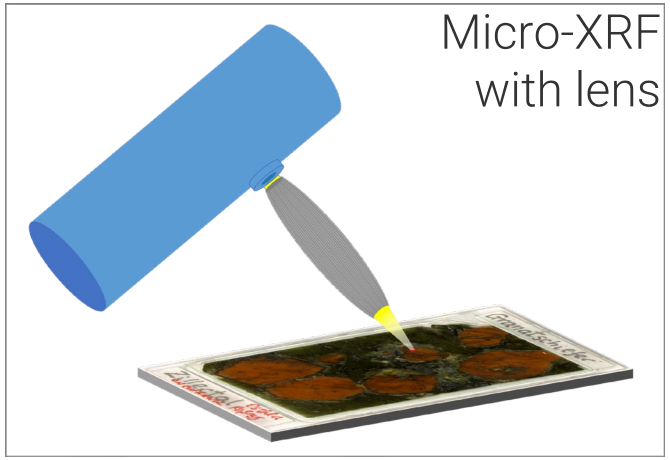
- Quantitative XRF is very sensitive, precise, and accurate.
- Large EDXRF and WDXRF instrument are part of ISO and ASTM workflows for routine QC analysis.
- These so-called bulk-XRF instruments work with samples prepared to ideal conditions (flat, homogenous, and infinitely thick) and often even diluted ($Li_2B_4O_7$ or wax) to reduce inter-element effects and optimize detection limits.

- For inhomogeneous samples, bulk-XRF analysis is prone to fail (unless it has been calibrated with reference samples that have the exact same sort of inhomogeneity).
- For inhomogeneous samples, a method is needed that:
  - Can resolve the inhomogeneity in the first place.
  - Can quantify small parts of the sample, where it can be considered “locally homogeneous”.

From XRF to micro-XRF







Composition

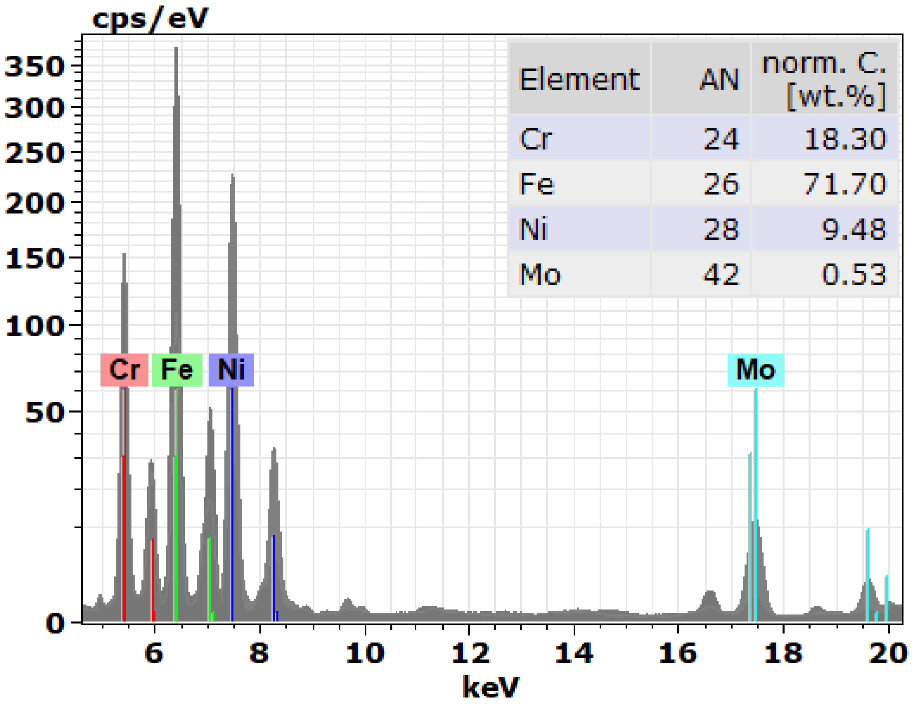
Compositional variations

From XRF to micro-XRF

- **Conventional X-ray fluorescence analysis** (XRF) is an analytical tool for qualitative and quantitative material analysis. It performs ideally in a **standardized workflow**.
- XRF tells you **which** elements are in the sample and **how much** of each one.
- Usually a sample needs "**preparation**", including **homogenization** and/or **dilution** for matrix reduction.

Information is lost!

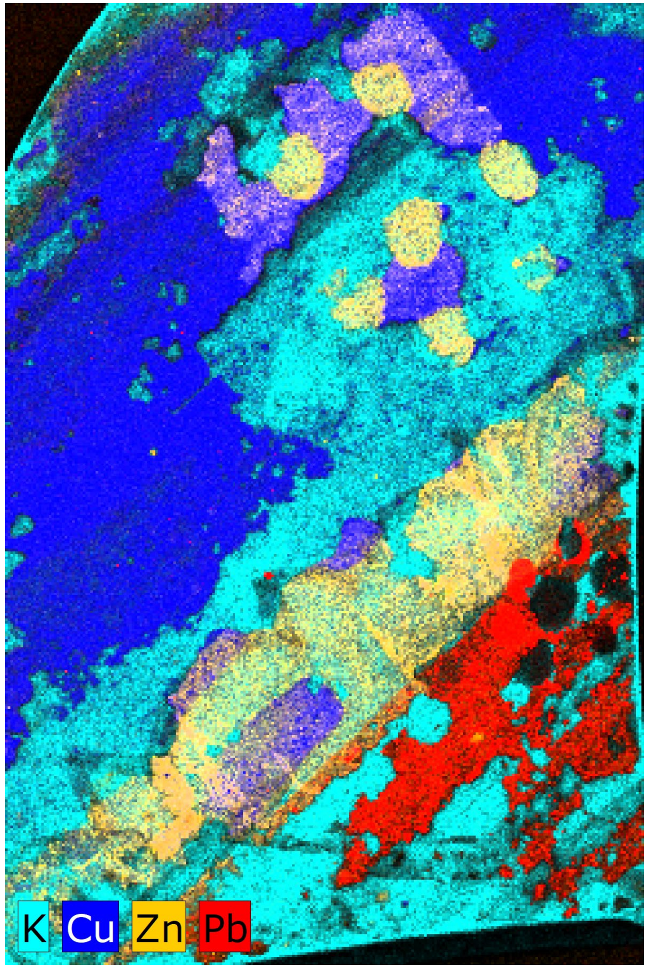
The compositional variations in a sample may be a crucial property of the material



Element	AN	norm. C. [wt.%]
Cr	24	18.30
Fe	26	71.70
Ni	28	9.48
Mo	42	0.53

Micro-XRF

- Micro-XRF is XRF with a small spot (nowadays typically < 20 µm).
  - → Micro-XRF reveals where elements are.
  - → Micro-XRF is ideal for non-homogeneous samples.
- It usually requires minimal or no sample preparation.
- Quantitative micro-XRF is feasible for sufficiently homogeneous areas of the sample, which can be even below 100 µm in diameter.
- The measurement conditions are very flexible in order to address different analytical tasks or requirements posed by the sample.

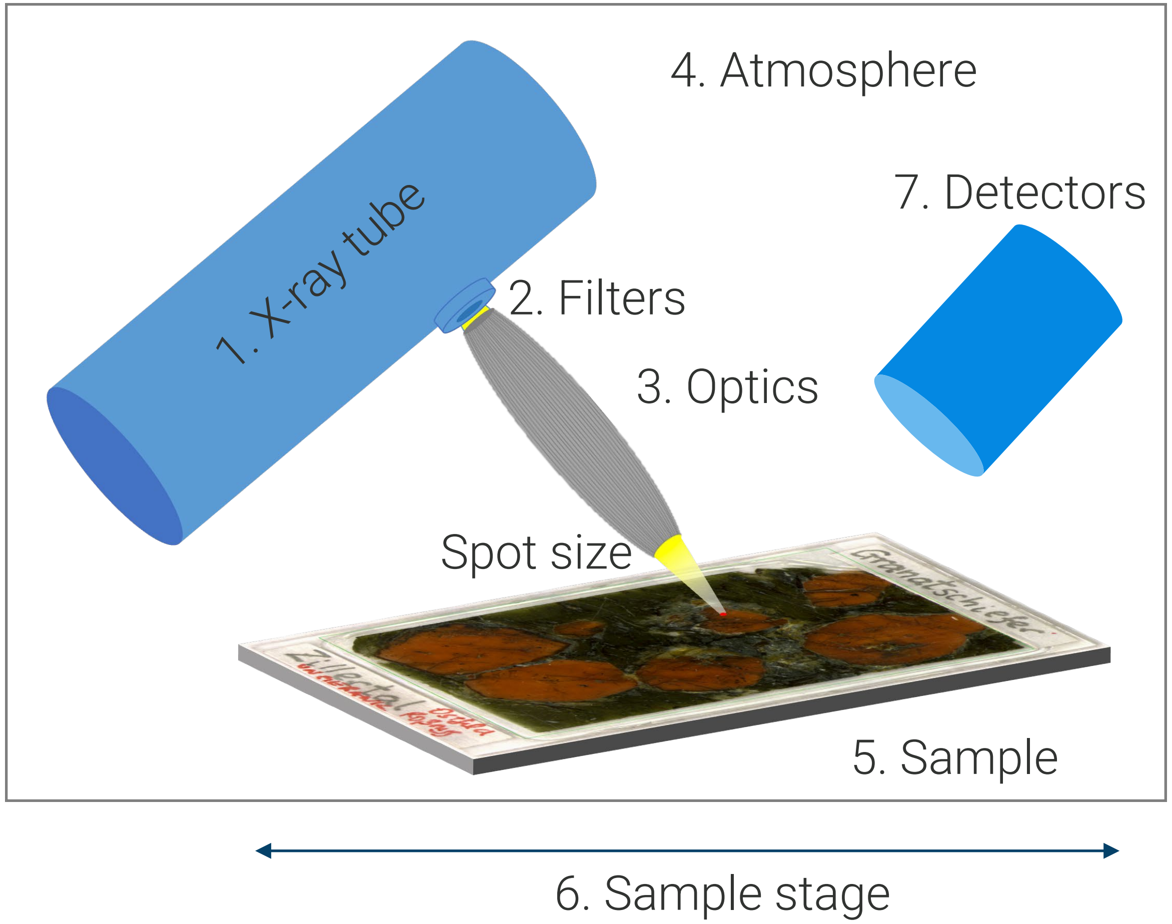


Micro-XRF
A comparison to similar methods

Parameter	EDS: E-beam (SEM-EDS)	WDS: E-beam (SEM-WDS)	Micro-XRF (XRF-EDS)
Analyzed Volume	Ø: few microns Information depth: microns (depending primarily on electron energy)	Ø: few microns Information depth: microns (depending primarily on electron energy)	Ø: 15-30 microns Information depth: microns to millimeters (depending on analyzed element and matrix)
Detectable Elements	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 6 (carbon)
Energy range	up to 20 keV (K – L – M – lines)	70 eV – 3.6 keV (L – M – lines)	up to 40 keV (K – L –M – lines)
Concentration Range	Down to 1000 ppm	Down to 100 ppm	Down to 1 ppm
Quantification	Standardless and standard-based	Standard-based	Standardless and standard-based
Data collection	Simultaneous	Sequential	Simultaneous
Sample Preparation	Sample needs to be electrically conductive (commonly carbon-coated); polishing required	Sample needs to be electrically conductive (commonly carbon-coated); polishing required	Electrical conductivity not required; samples don't need to be polished
Sample Stress	Heating due to absorbed electrons	Heating due to absorbed electrons	Minimal

Micro-XRF
Back to the roots – part I

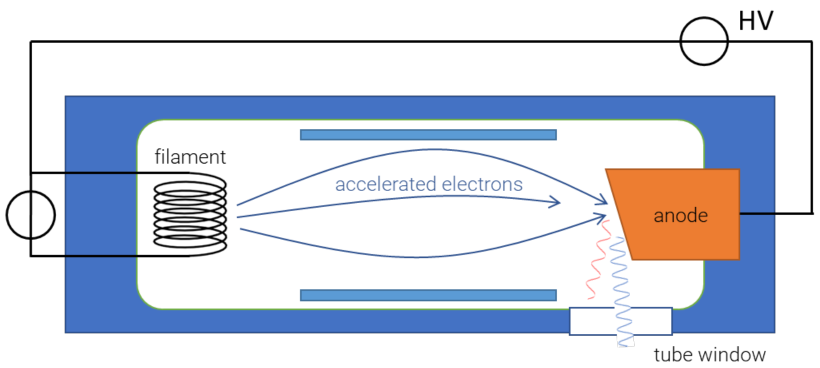
1. X-ray tube
2. Filters
3. Optics
   - Spot size
4. Atmosphere
5. Sample
6. Sample stage
7. Detectors
8. Data mining



BACK TO THE ROOTS – PART I

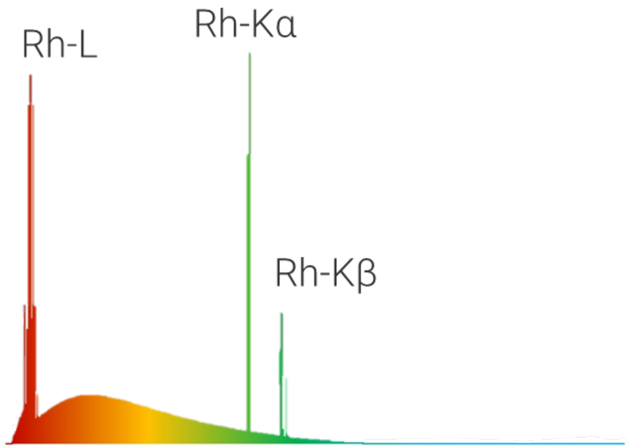
1. X-ray tubes

X-ray tubes
Working principle



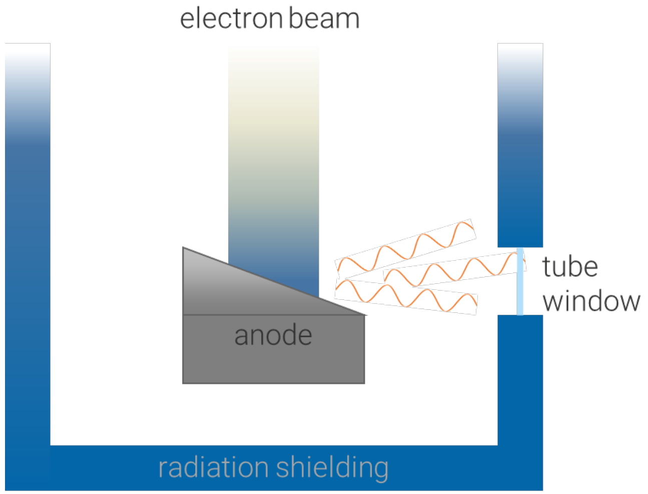
- The filament is heated by electrical current, emitting electrons.
- The HV between filament and anode accelerates the electrons.
- When hitting the anode, the electrons are strongly decelerated.
- Their kinetic energy is thereby transformed into the continuous **bremsstrahlung** (in addition to **characteristic X-ray fluorescence**).

- Only 1 ‰ of the tube power is transformed to X-rays, the rest is heat.
- The local heat load in the area where the electrons hit the anode is the limiting factor for the X-ray tube's power.
- The high voltage times the electron current (10 kV · 100 µA = 1 W) and the area into which the electrons are focused are the crucial parameters.

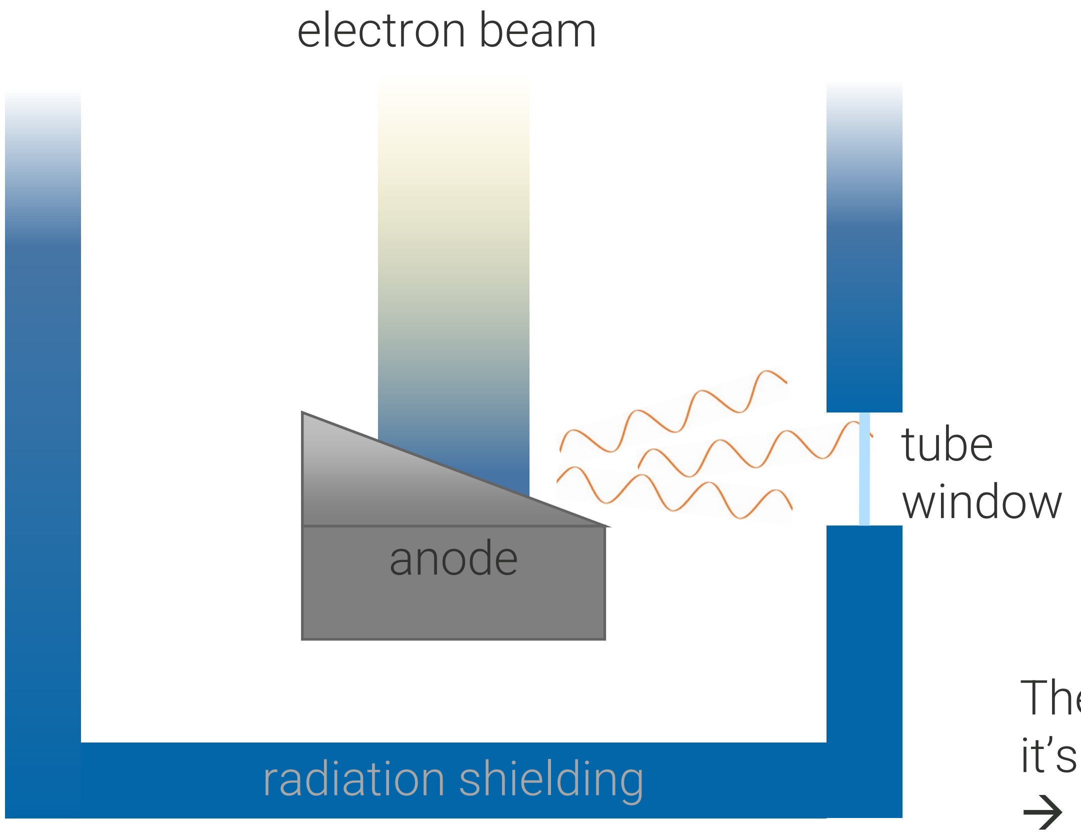


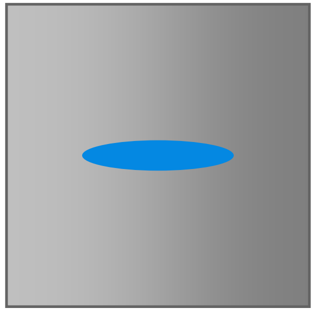
X-ray tubes
Different types

- There are different types of X-ray tubes for small-spot and micro-XRF:
  - **Fine focus tubes** are used for collimator systems. The accelerated electrons are focused into an area of ≳ 100 µm diameter. This relatively large area allows to operate an X-ray tube at moderate power (~ 50 W).
  - A polycapillary lens is a beam guide, much more than a real lens. All X-rays that do not come from the focus area are just not transmitted. So, when a polycapillary lens is used, the anode X-ray spot needs to be small. Therefore, **micro-focus tubes** are used, where the electrons are focused into an area ≲ 50 µm and the maximum power is lower, i.e. around 30 W.
- Another design parameter is the **anode angle**:
  - When the angle is small, the spot appears to be small from the perspective of the tube window.
  - When the angle is steep, more of the low-energy radiation gets out of the anode (and tube window).

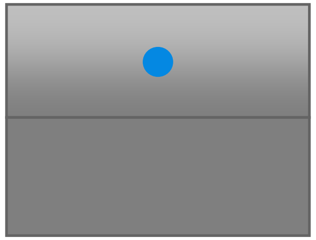


X-ray tubes
The anode angle





Top view
The direction from where the electrons come

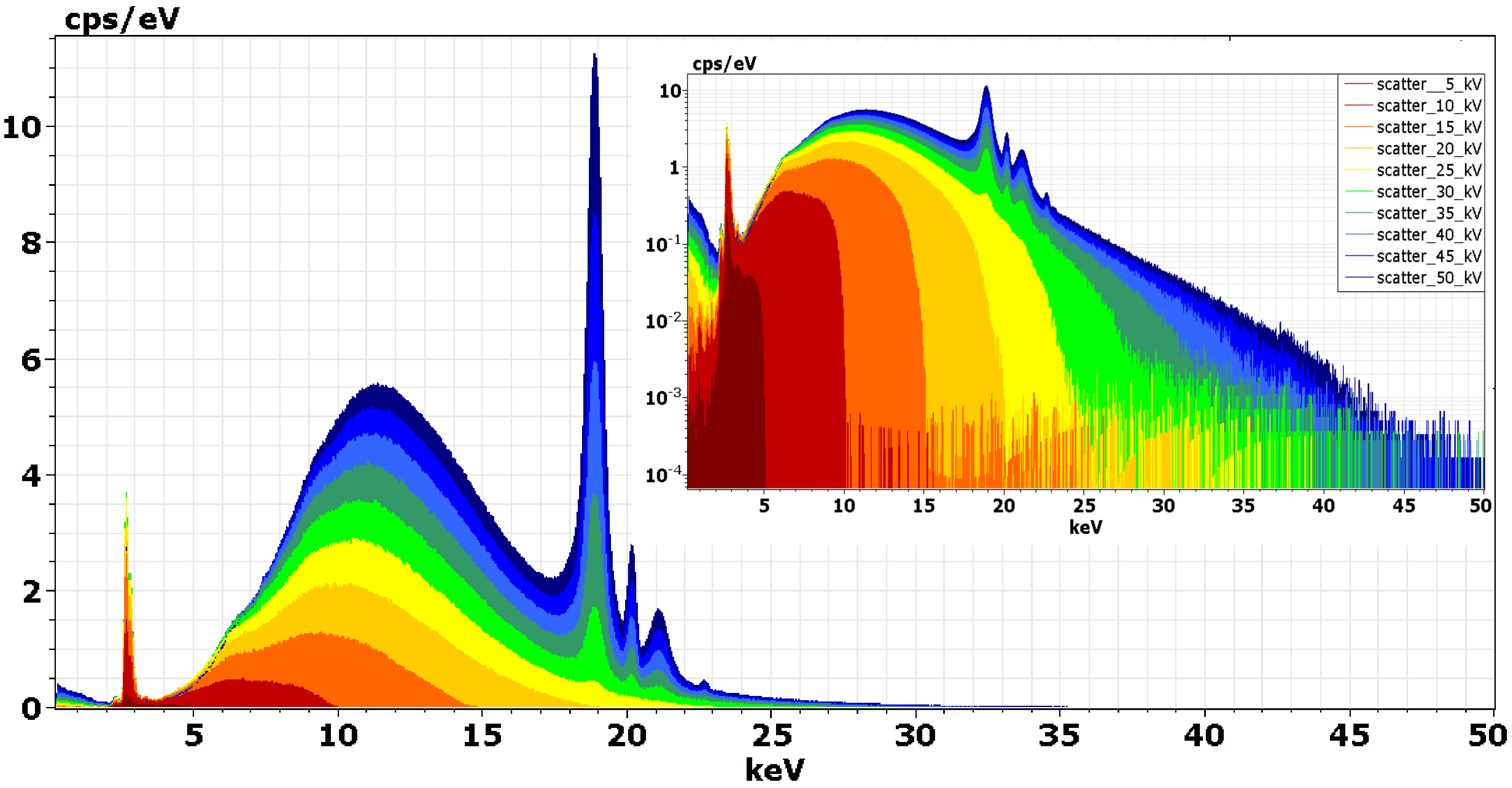


Side view
(from the window)
The direction to where the photons go

The lens “sees” a small spot even though it’s true area is large in one direction
→ larger areas allow for higher tube power

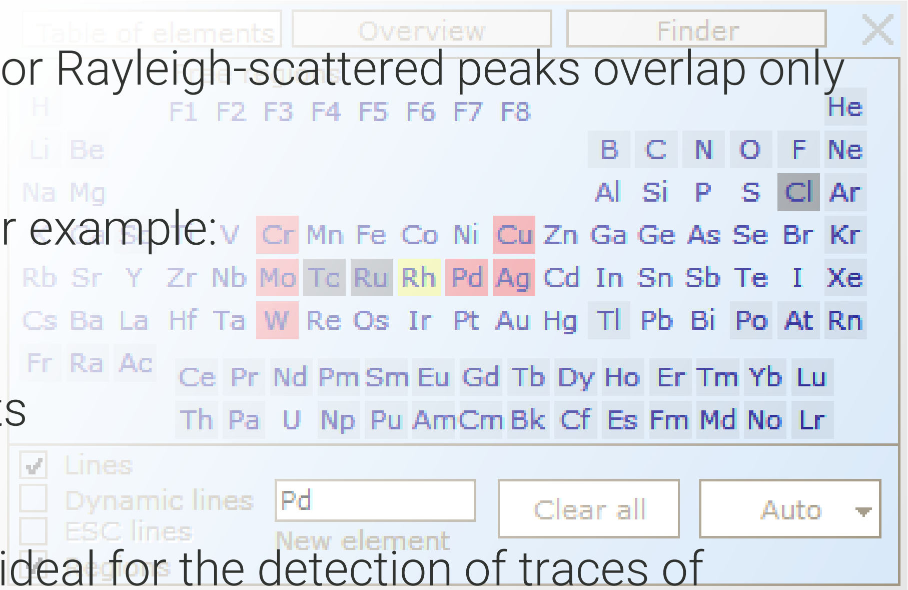
X-ray tubes
Effect of the acceleration high voltage

- The HV defines the high-energy cut-off.
- Higher HV creates higher X-ray intensity in the whole spectral range.
- The low-energy X-rays are attenuated by the tube window.
- The low-energy background (< 2 keV) is caused by Compton scattering of high-energy photons in the detector.

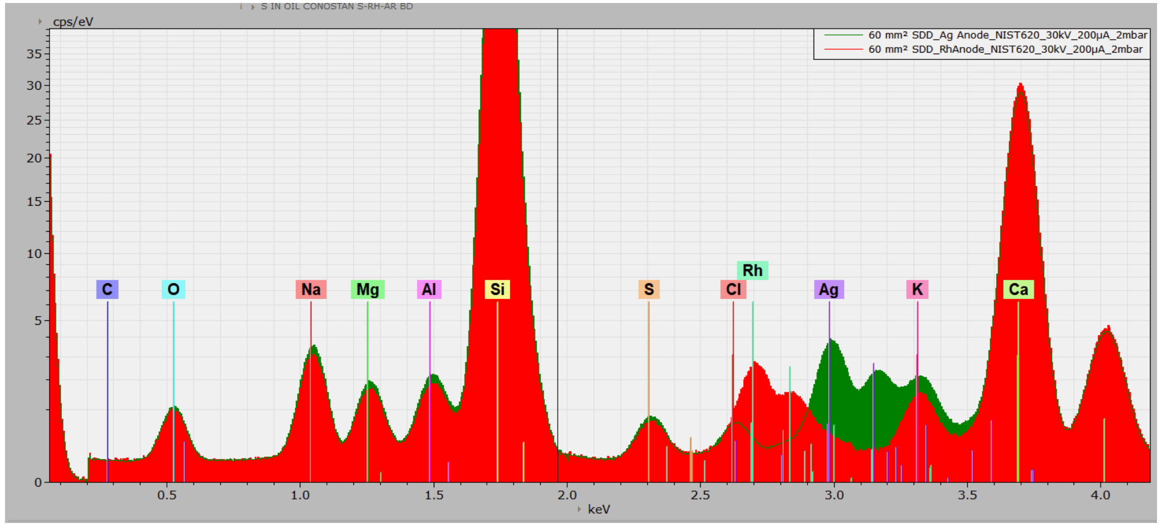


X-ray tubes
Anode materials

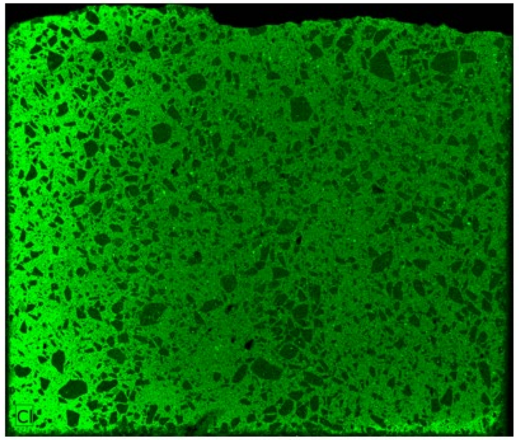
- The anode material used in the X-ray tube to generate the X-rays may vary from instrument to instrument.
- Basically, the elements in the tube can be divided into K-line tubes (Cr, Cu, Mo, Rh, Pd, or Ag) or L-line tubes, for which W is a well-known example.
- Among all materials Rh is the most universal one, as its Compton- or Rayleigh-scattered peaks overlap only with Cl (the L lines) and Tc and Ru (the K lines).
- The other anode materials are much more application-specific. For example:
  - Cr is fantastic for elements between Ti and K.
  - Ag is fantastic to visualize traces of Cl in samples like fingerprints or sea water interactions with concrete.
  - W with its high bremsstrahlung and “clean” high energy range is ideal for the detection of traces of elements between Rh and Eu.



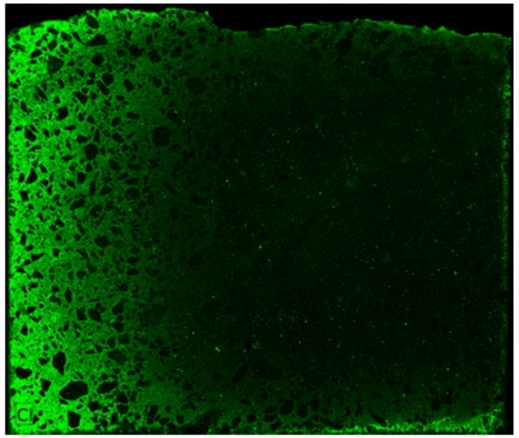
X-ray tubes
Anode materials



Cl-ROI with Rh tube



... and with Ag tube

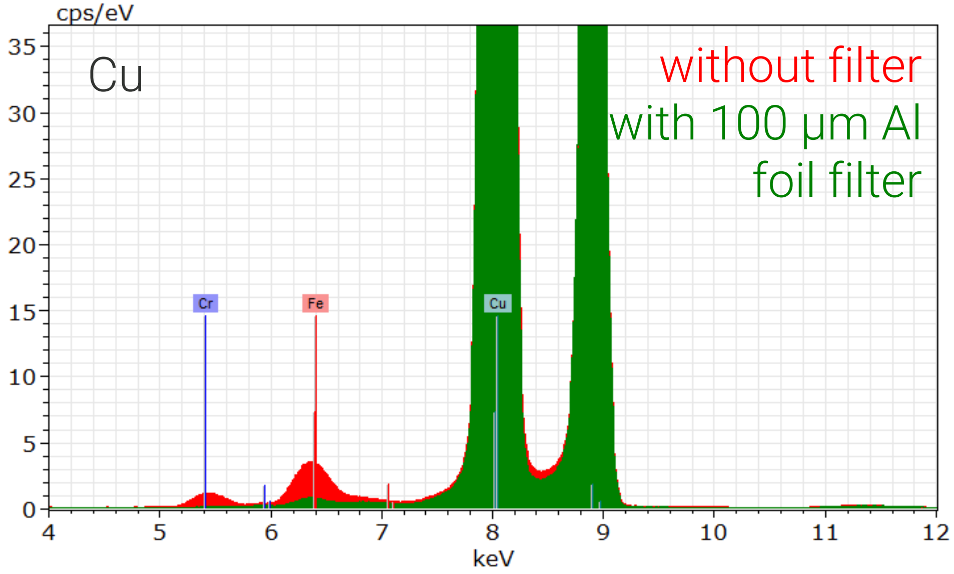


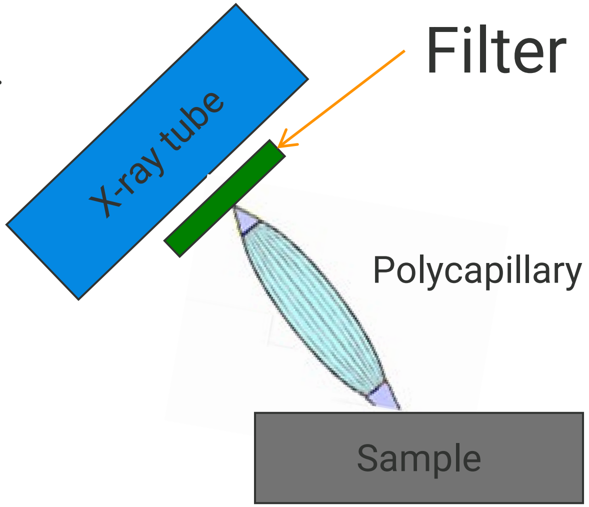
BACK TO THE ROOTS – PART I

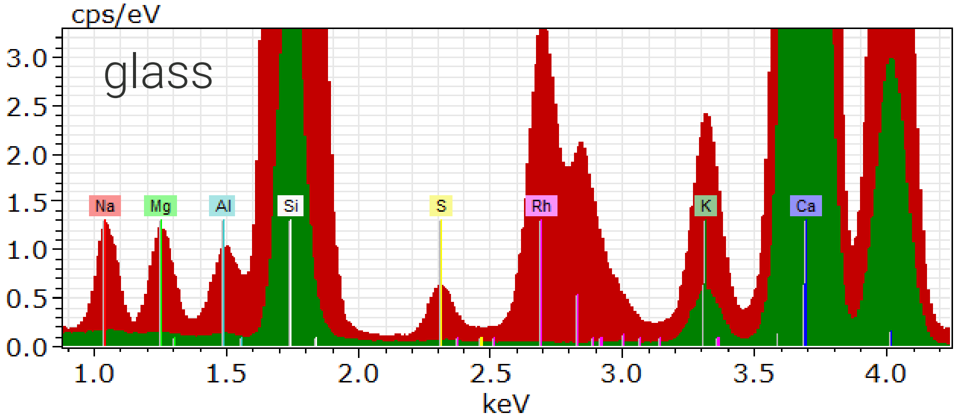
2. Filters

Filters
Where and why?

- (Primary) filters are located right at the exit of the tube.
- They affect the low-energy onset of the spectrum.
- They can be used to:
  - Avoid diffraction.
  - Optimize signal-to-noise ratio for selected elements.



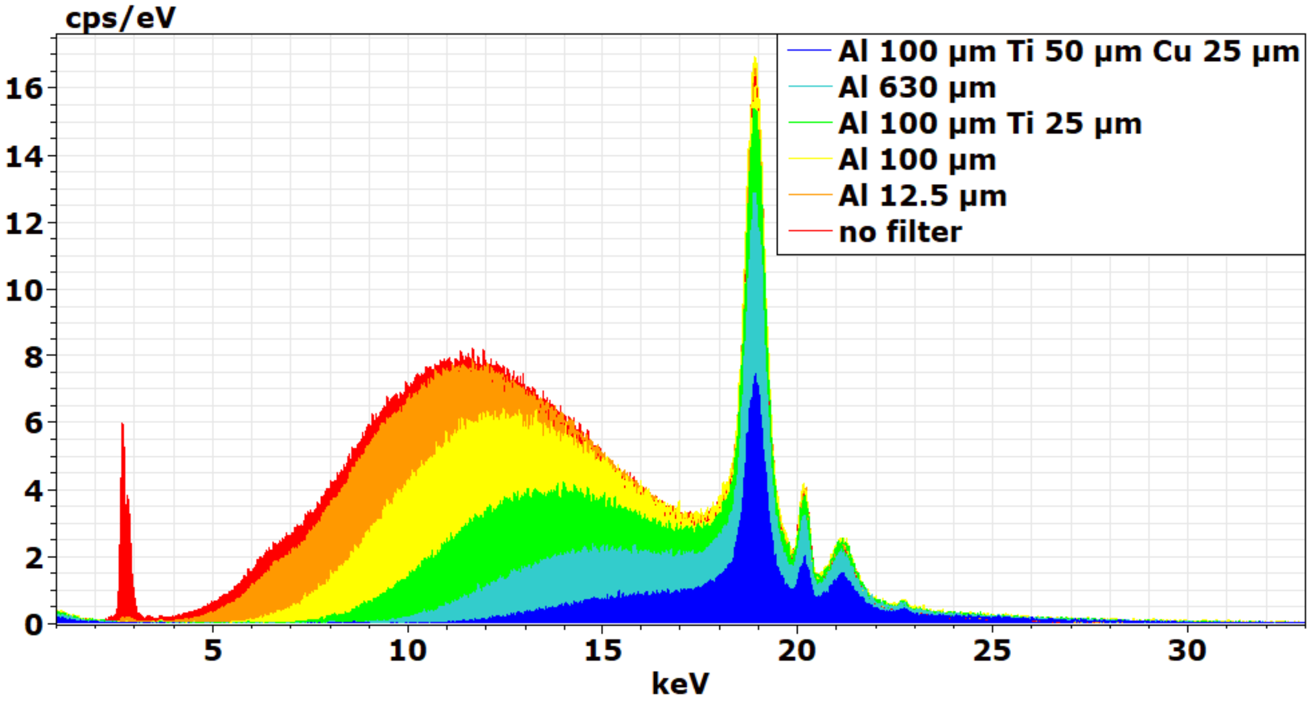




Filters
Why so many?

- Filters cut the low energies from the excitation spectrum.
- The instrument's sensitivity for light elements is thereby impeded.
- Ideally the filter to optimize for a few elements does not cut away more excitation radiation than needed.
- Therefore, some flexibility is needed.
  → Many filters to reflect the versatility of the method.

- Stacked foils are used to:
  - Avoid visible absorption edges of the filter elements in the scattered spectra.
  - Avoid fluorescence signal of the filter elements as blind values.



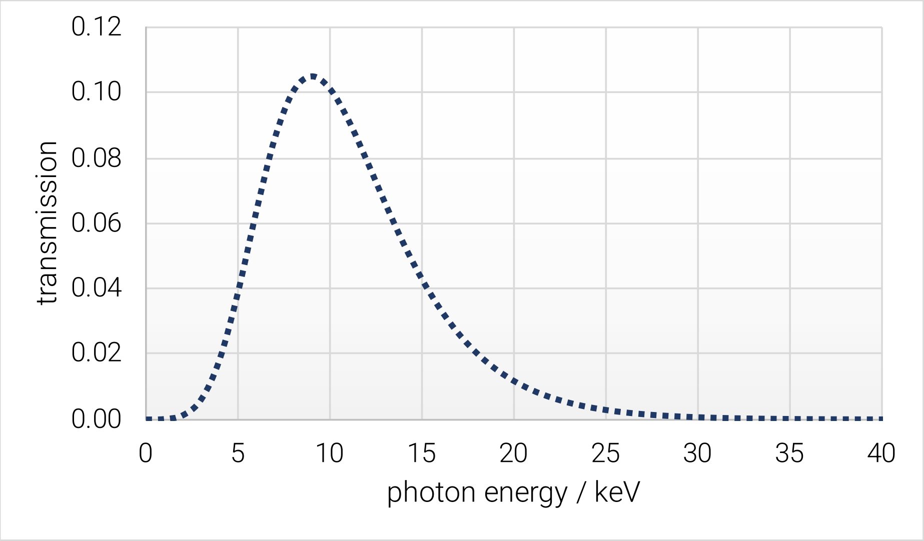
BACK TO THE ROOTS – PART I

3. X-ray optics and attainable spatial resolution

X-ray optics
Collimators and polycapillary lenses

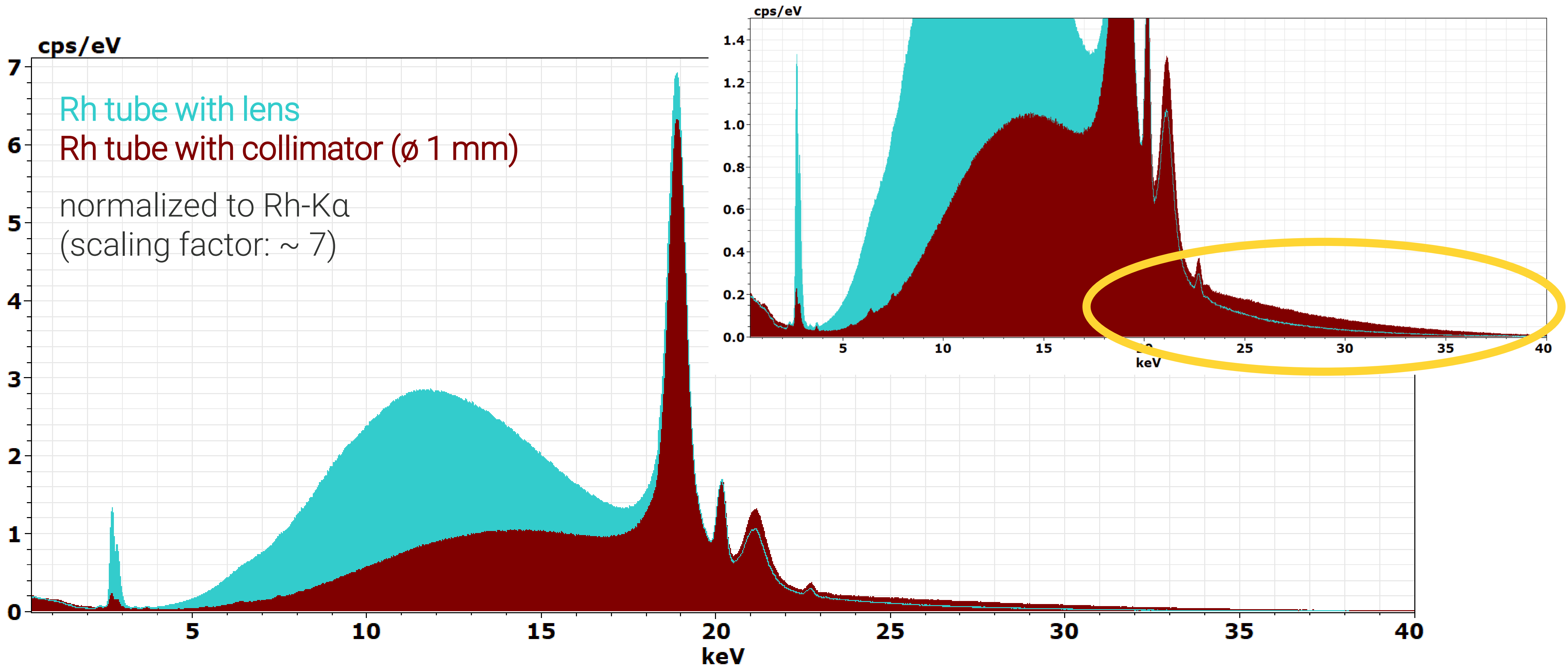
- Apart from the very different spot size, there is one major difference between a polycapillary and a collimator:

  Their transmission properties!
- A collimator is just a hole. It limits the area (and the intensity), but it does not change the spectrum.
- The polycapillary is made of many bundles of hollow glass tubes, where the X-rays are guided using external total reflection.
  - Low-energy X-rays are easily absorbed by the glass.
  - High-energy X-rays need a very shallow angle* to be reflected.
  - Overall, only the mid-energy X-rays are transmitted effectively.
- The overall intensity with a ø 20 µm spot is similar to that of a ø 3 mm collimator.
- High-energy excitation works much better with a collimator.



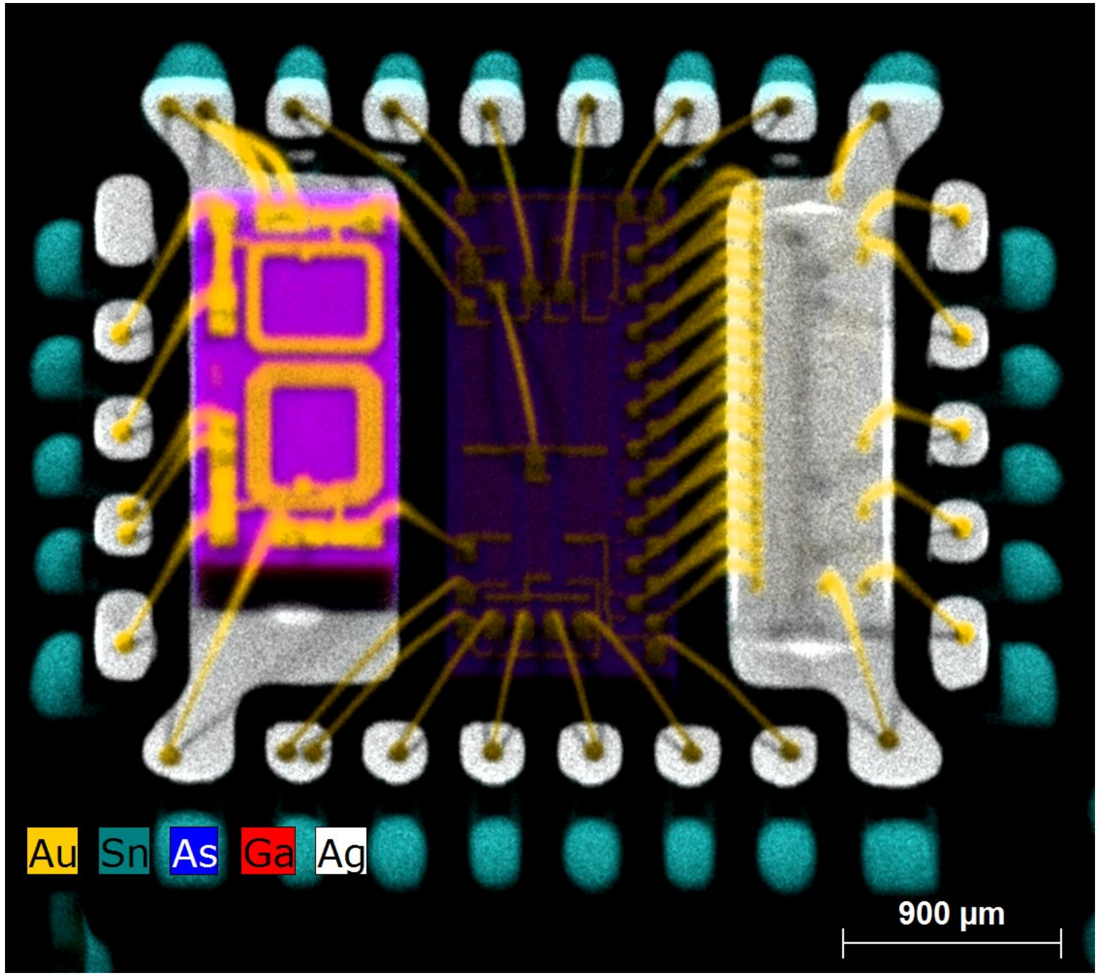
* it's < 0.1° for 20 keV photons

X-ray optics
High-energy excitation



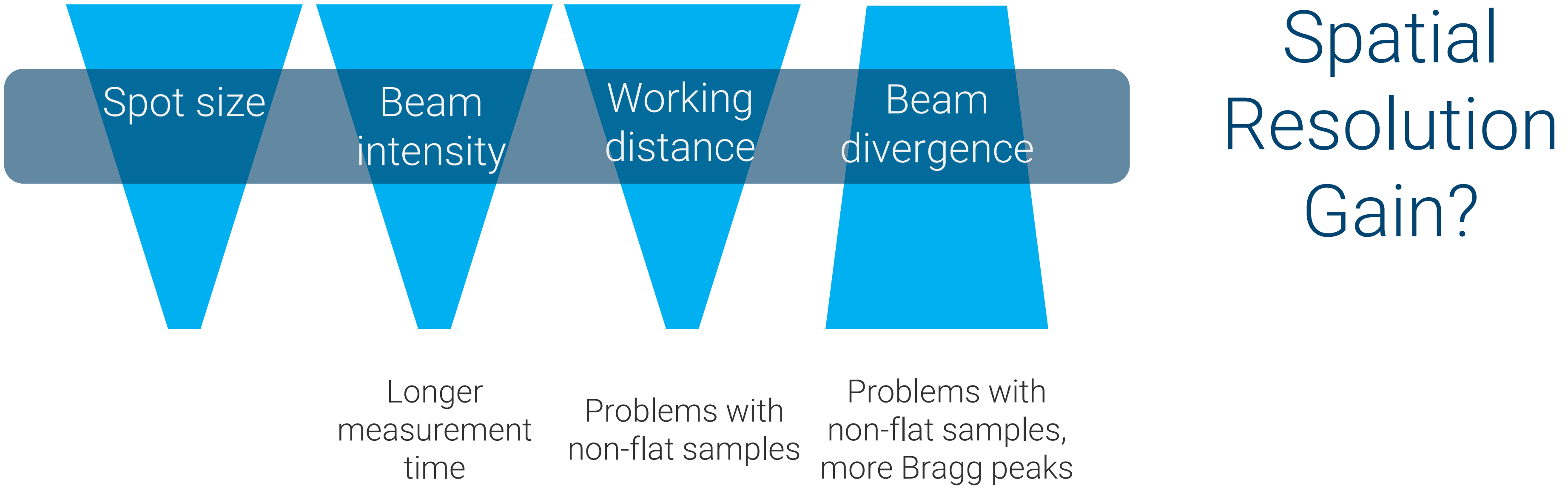
Spatial resolution

- The spatial resolution in micro-XRF depends on the spot size of the polycapillary lens.
- Therefore, reducing the polycapillary spot size seems to be a straight-forward way to further increase the spatial resolution of the method.
- Is this "logical" step fully valid? Is there a limit for the attainable spatial resolution, as there is for SEM-EDX?



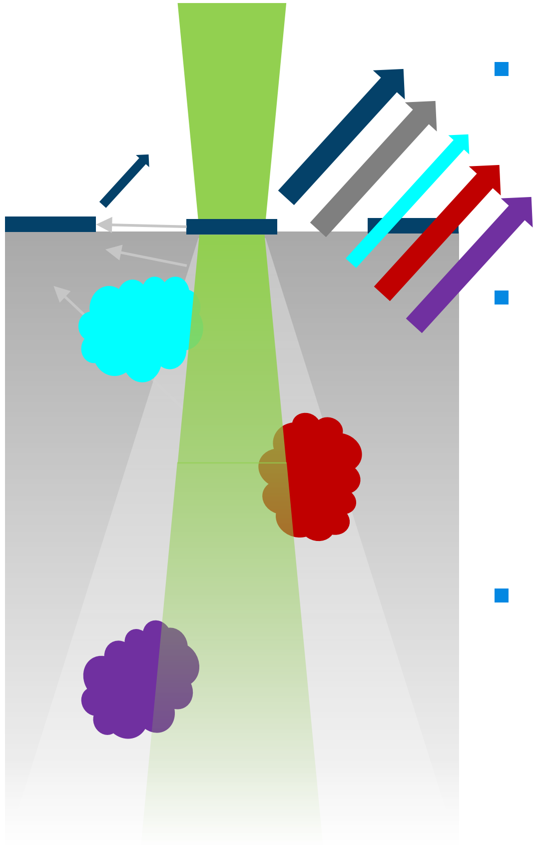
Spatial resolution ... and its effects

- It is possible to attain smaller spot sizes, but it comes at a price: **intensity** is sacrificed, **working distance** is lost, and the X-ray beam **divergence** is increased.
- What is the gain in spatial resolution?



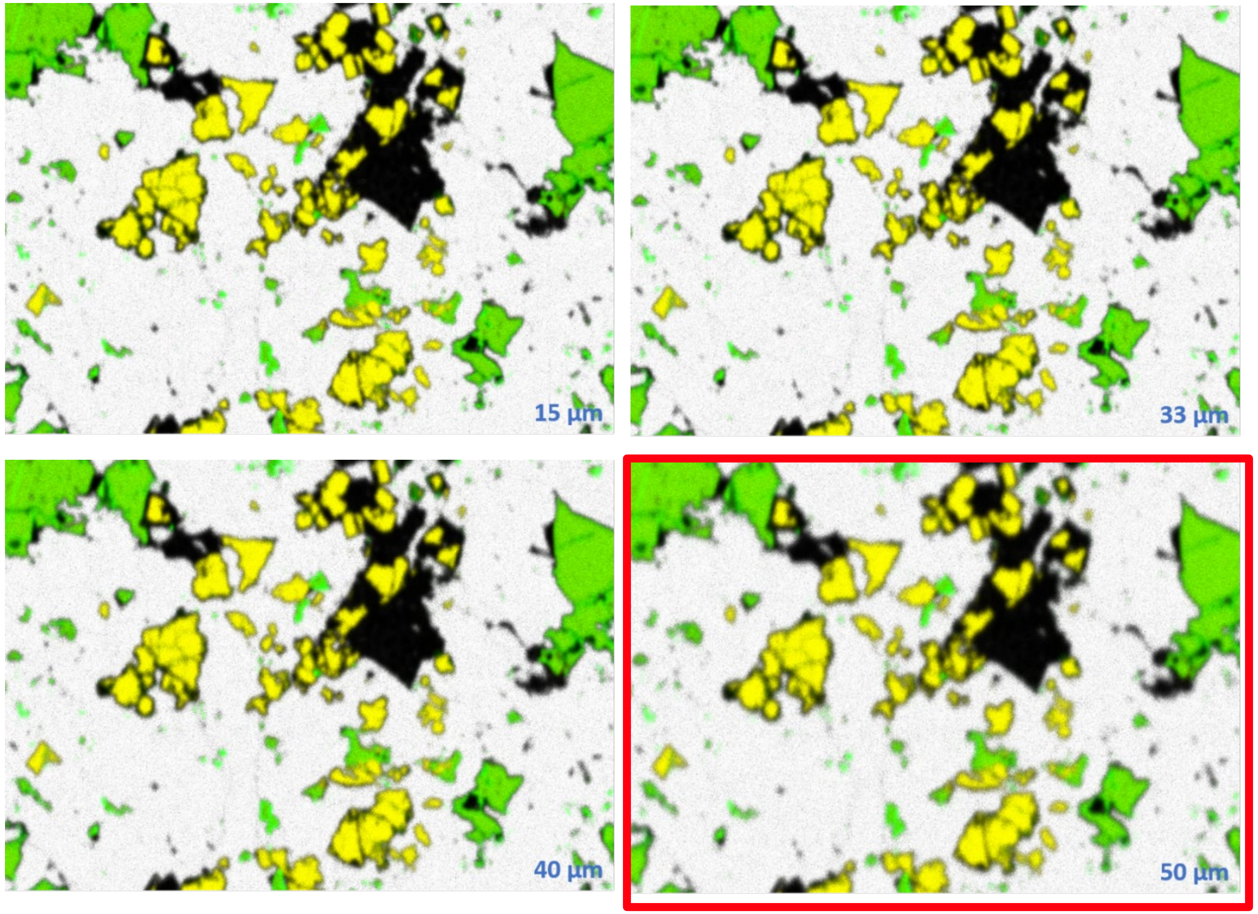
Spatial resolution
Experimental findings

- Micro-XRF is not exclusively probing the surface!



- There always is a 3D component to be considered.
- Even if the excited surface area is getting smaller, the probed depth doesn't change.
- Depending on the matrix and the probed element, the depth may define the probing volume.

Thin section of ~ 25 µm thickness



Spatial resolution
... and information depth

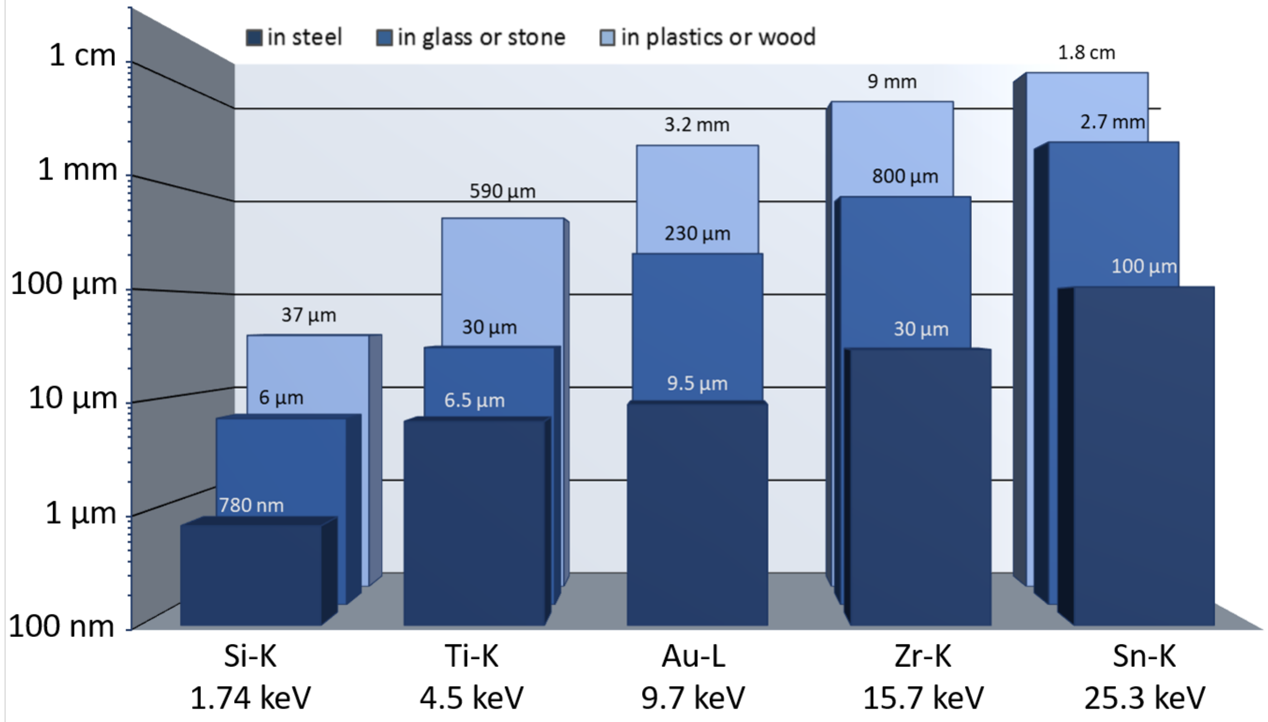
- Ultimately, the maximum achievable resolution depends on the matrix of the sample and the **information depth** of the elements to be resolved.
- In a rock sample, the maximum achievable resolution should be ≥ 40 µm.
- In a metal sample, the maximum achievable resolution should be ≥ 10 µm.
- A smaller excitation spot will not necessarily lead to increased resolution.
- The drawbacks, however, will be noticeable:

Longer measurement time

Problems with non-flat samples

Problems with non-flat samples, more Bragg peaks

Information depths of selected element fluorescence lines in different matrices



BACK TO THE ROOTS – PART I

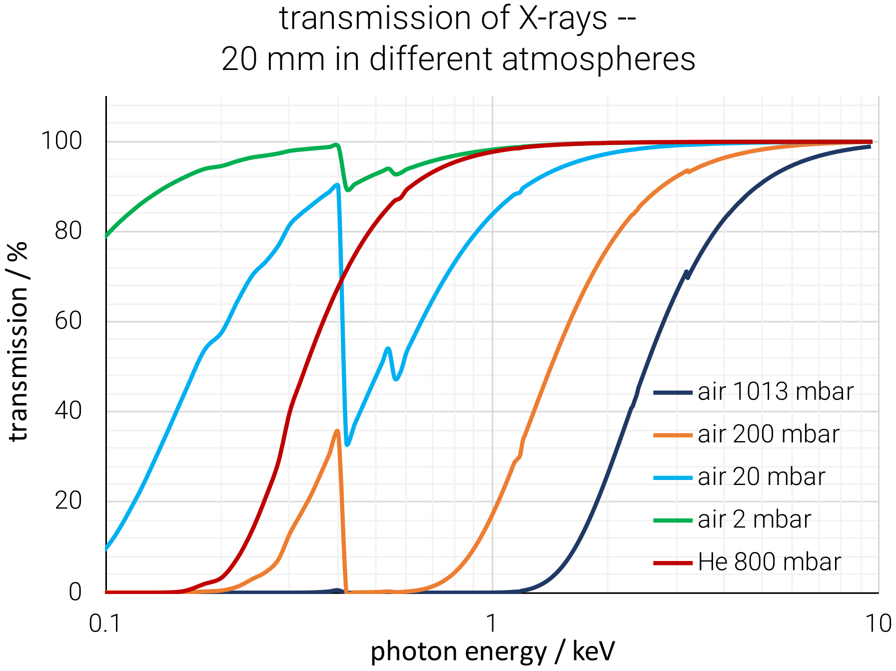
4. Atmosphere

Atmosphere
An overview

- The atmosphere surrounding the sample is an important measurement parameter, especially when light elements are of interest.
- Of utmost importance for (map) analysis will be a stable pressure. Otherwise, any fluctuation in pressure will manifest in varying measured element sensitivities!

Element	Energy in keV	Air 1000 mbar	Air 200 mbar	Air 20 mbar	Air 2 mbar	He 800 mbar
C	0.3	0.0	11	80	98	43
N	0.4	0.4	33	90	99	71
O	0.5	0.0	0	54	95	87
F	0.7	0.0	1	65	96	94
Na	1.0	0.1	23	86	99	98
Ca	3.7	80	96	100	100	100
Fe	6.4	96	99	100	100	100

calculated for 20 mm distance betwenn sample and detector
Air = 78.115 % N2; 20.95 % O2; 0.934 % Ar

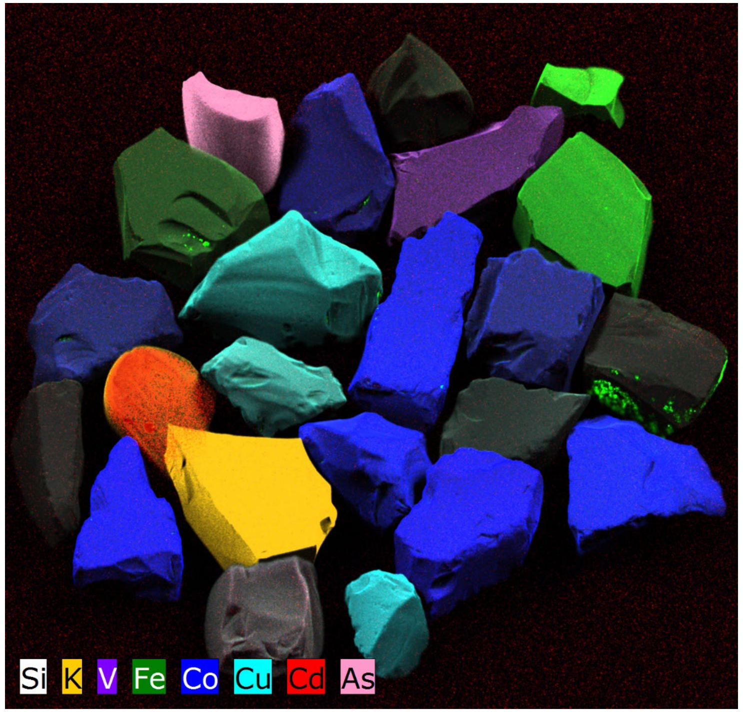


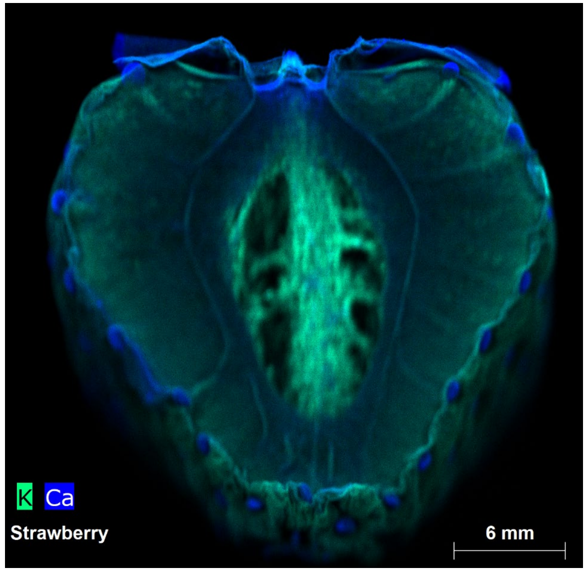
BACK TO THE ROOTS – PART I

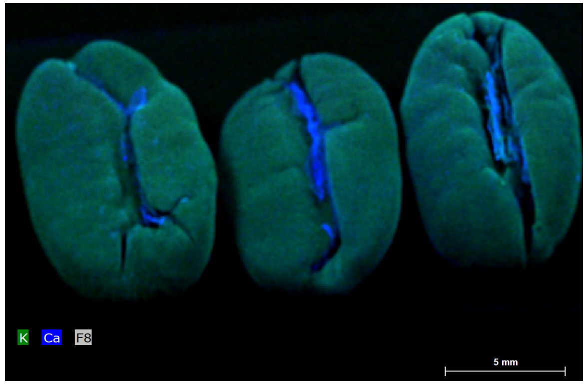
5. Samples

Samples

Anything from 7 kg of massive samples to powders and liquids can be measured with micro-XRF.







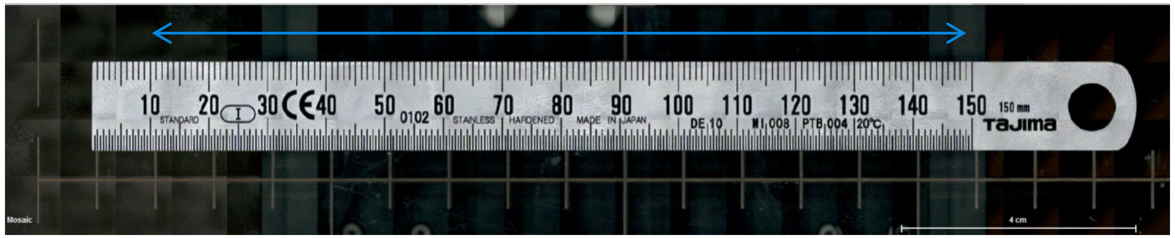
BACK TO THE ROOTS – PART I

6. Sample stage

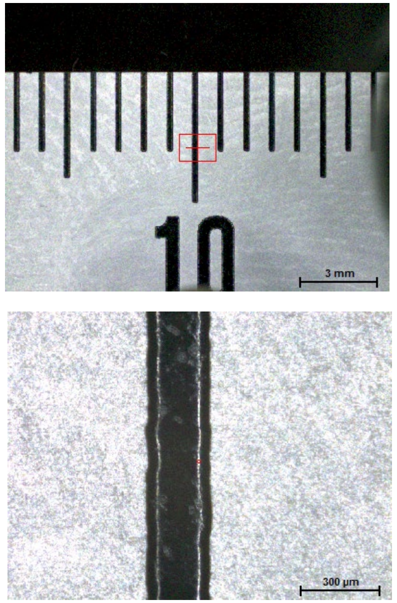
The stage
Fast and precise

- The sample stage needs to fulfill (at least) three conditions:
  - It should be able to move **large samples** (which may get heavy).
  - It must be **fast** (to allow for short measurement times).
  - It needs to be **precise** (at least more precise than the spot size).

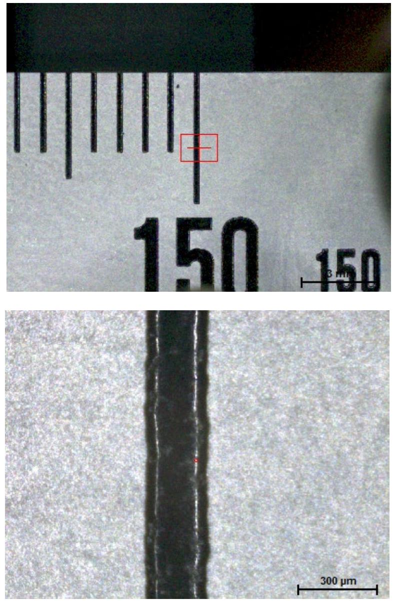
  - Reproducible positioning is needed for multi-frame-measurements!

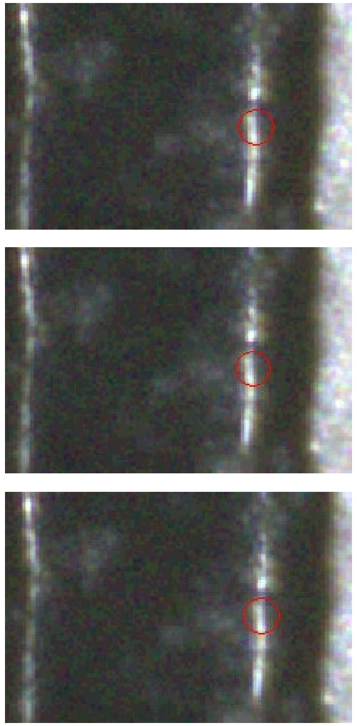


Position 1



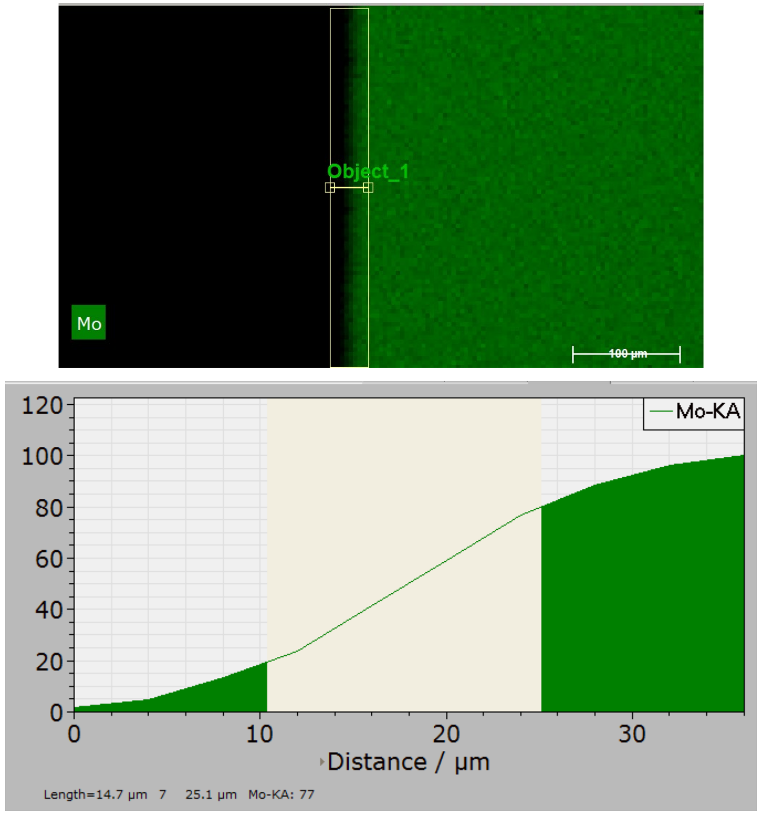
Position 2





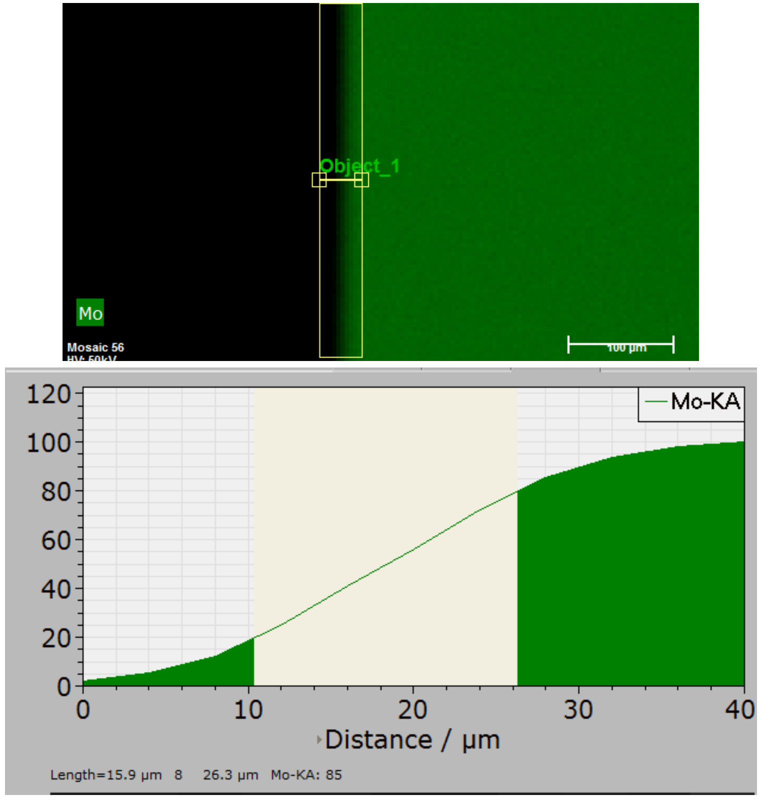
The stage
Reproducible positioning

One cycle



(14.6 ± 0.3*) µm

10 cycles



(15.9 ± 0.3*) µm

Mapping parameters		
Width:	151	pixel
	603	µm
Height:	85	pixel
	340	µm
Pixel Size:	4	µm
Total number of pixel:	12835	pixel
Acquisition parameters		
Frame count:	1/1	
Pixel time:	5	ms/pixel
Measure time:	52 s	
Overall time:	3:13 min	
Stage speed:	800	µm/s
Tube parameter		
High voltage:	50	kV
Anode current:	599	µA
Filter:	Empty	
Optic:	Lens	
Chamber at:	Air 1050.7	mbar
Anode:	Rh	
Detector parameters		
Selected detectors:	1	
Max. pulse throughput:	130000	cps

* For each set of data, different users derived values with 0.3 µm deviation.

BACK TO THE ROOTS – PART I

7. Detectors and “clean spectra”

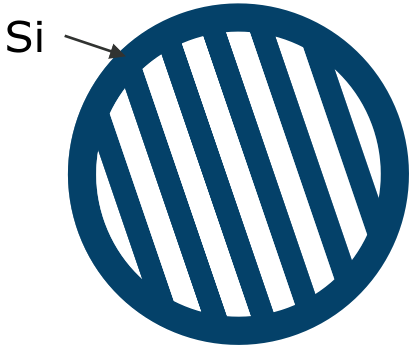
Detectors
... and their entrance window

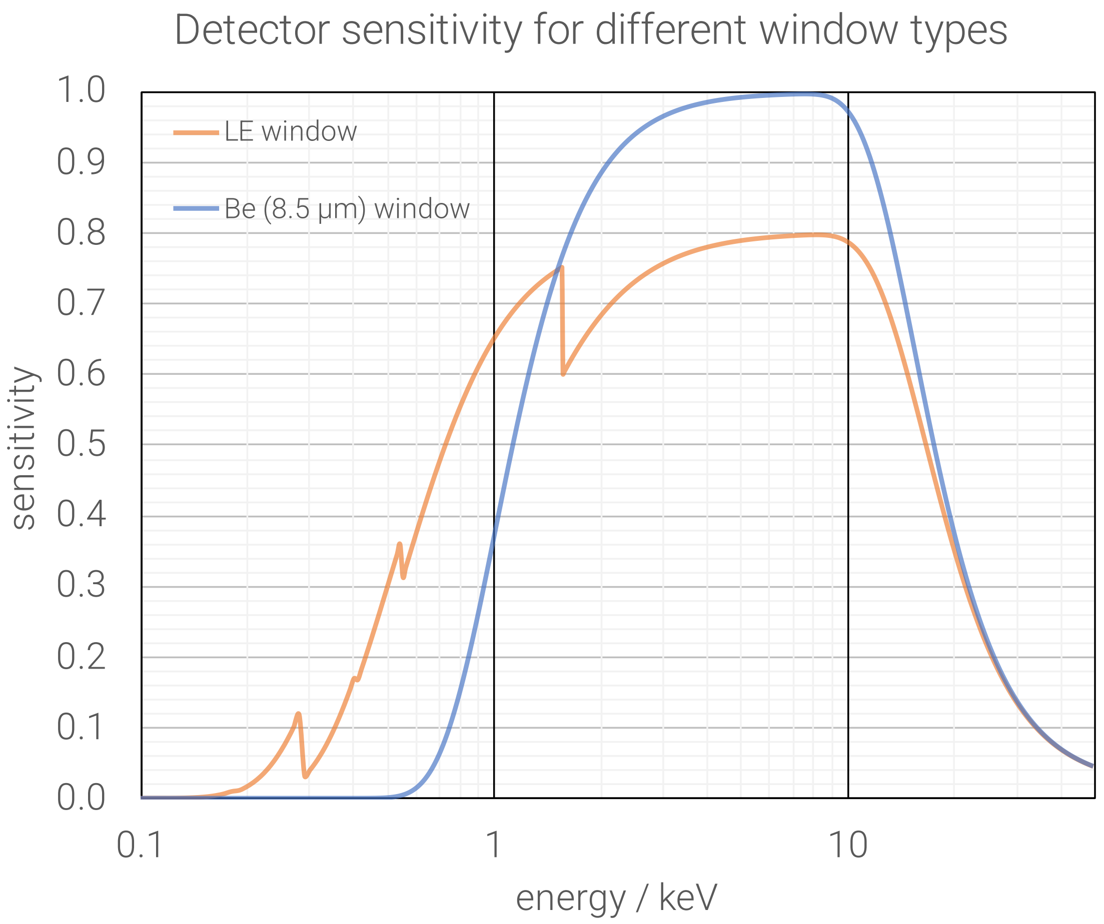
Conventional window:

Be window with thickness between 8.5 µm and 12 µm

Light element window:

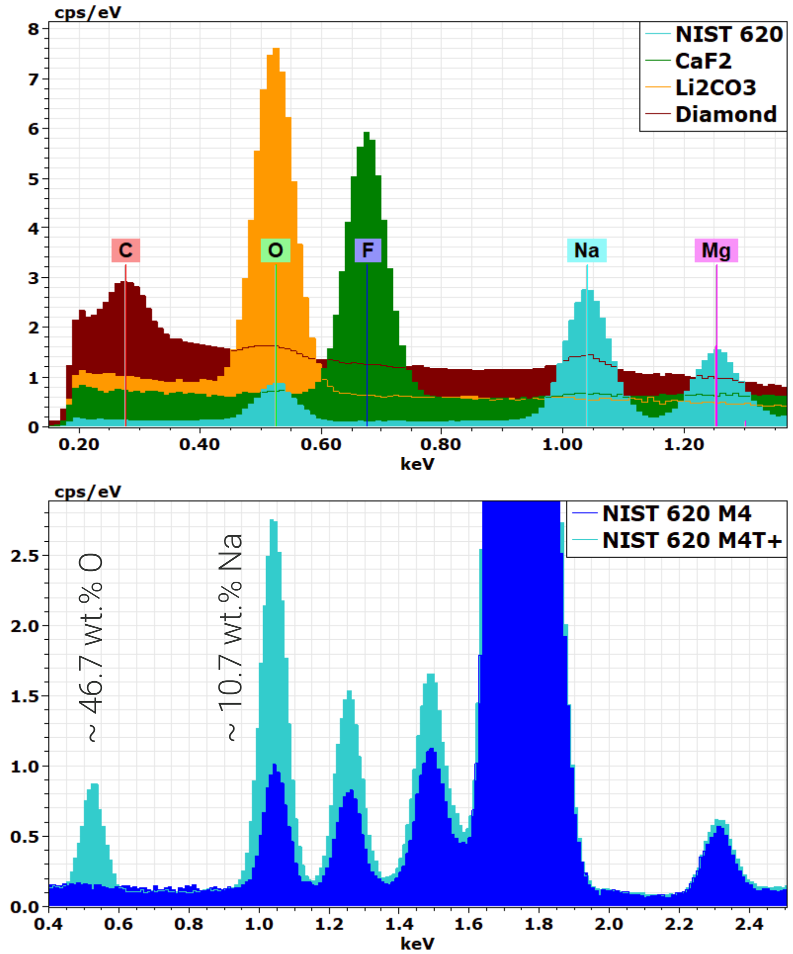
Thin polymer foil supported by a silicon grid



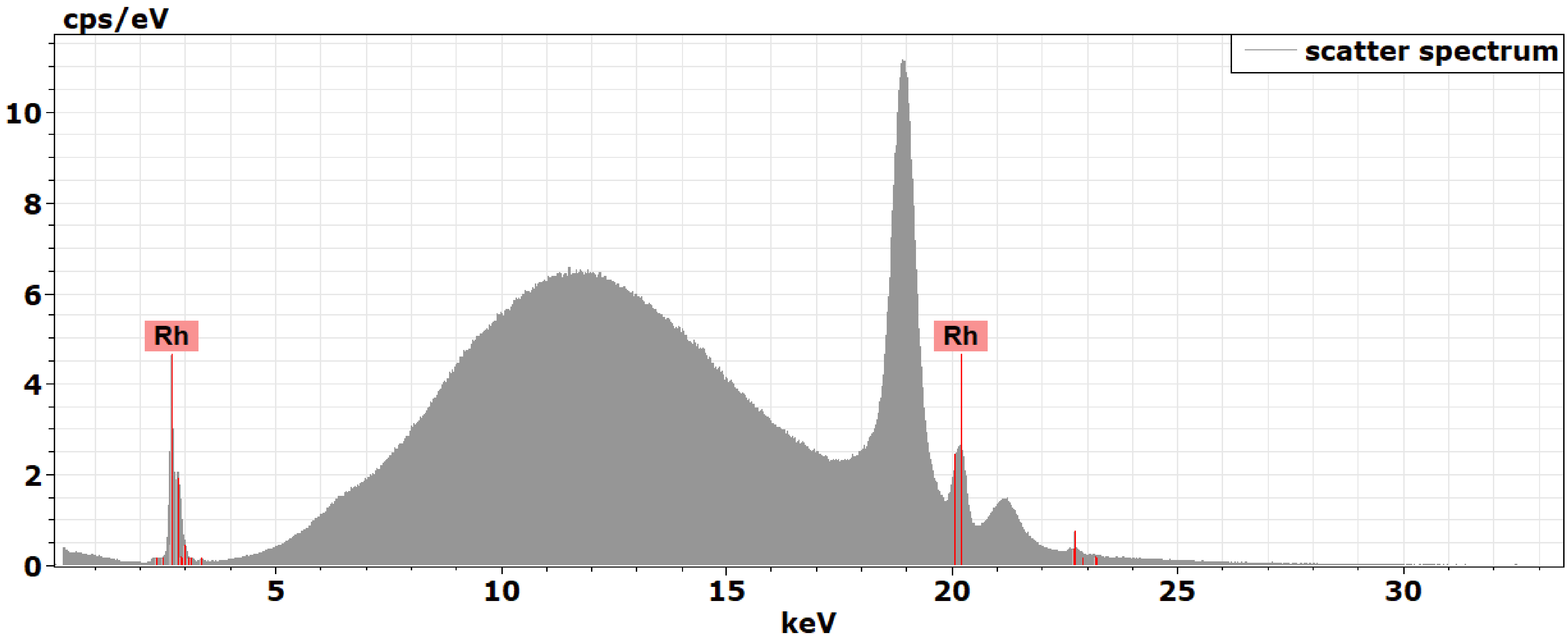


Detectors
... and their entrance window

- The ability to see the carbon Kα fluorescence is to be considered a benchmark for the sensitivity of the instrument.
- The M4 TORNADO PLUS is not well-suited for quantitatively analyzing carbon! Especially not when scanning.
- In this spectral region the sensitivity is low, line overlap and inter-element effects are very pronounced and the information depth is very different from the other elements.
- A detector that can see the X-ray fluorescence of carbon is, of course, more sensitive for all light elements than a conventional detector.
- It's twice as sensitive for Mg-Kα (at 1.25 keV).
- For higher energies, the Si support grid still acts as a filter.



Detectors
... and clean spectra

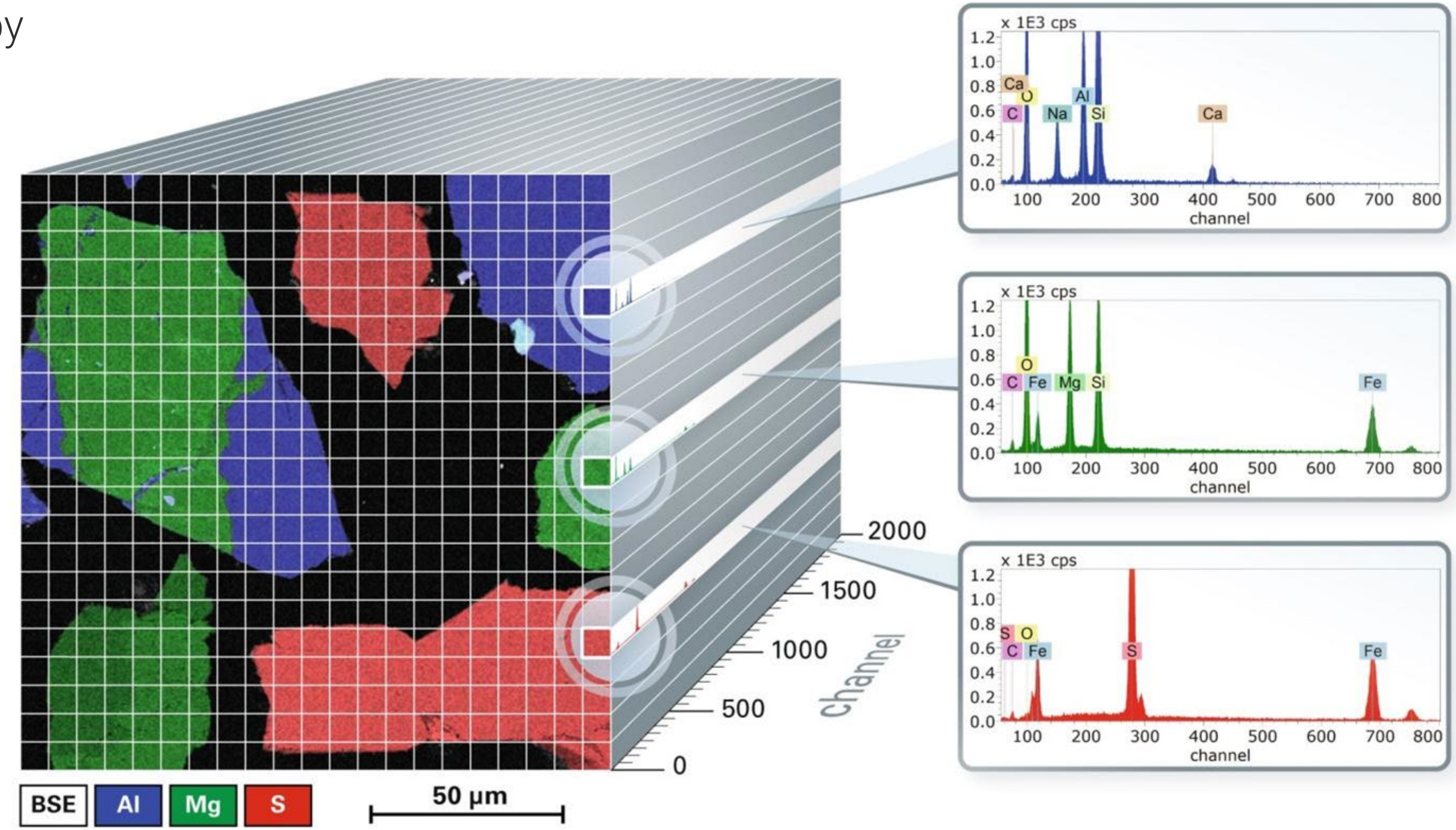


BACK TO THE ROOTS – PART I

8. Data mining possibilities

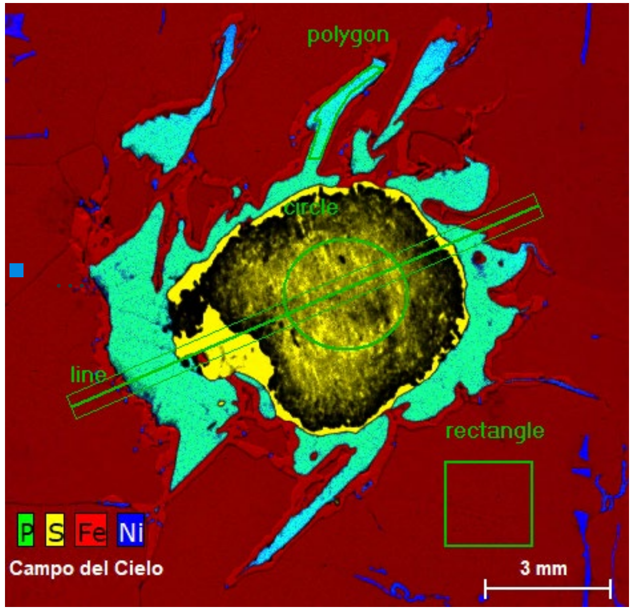
Data mining
The HyperMap datacube

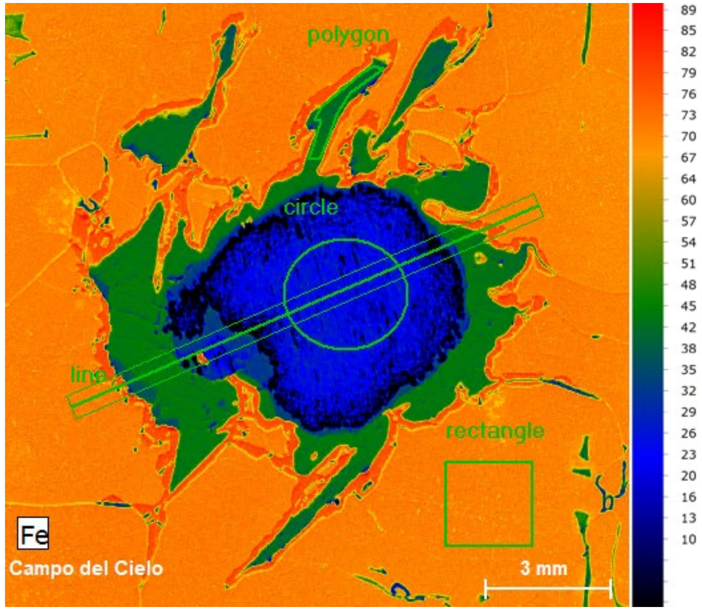
- Position tagged spectroscopy is state of the art.
- We call our dataset "HyperMap".
- For each pixel in a map, the complete spectral data is saved.
- The data are then available for offline analysis – even years later.

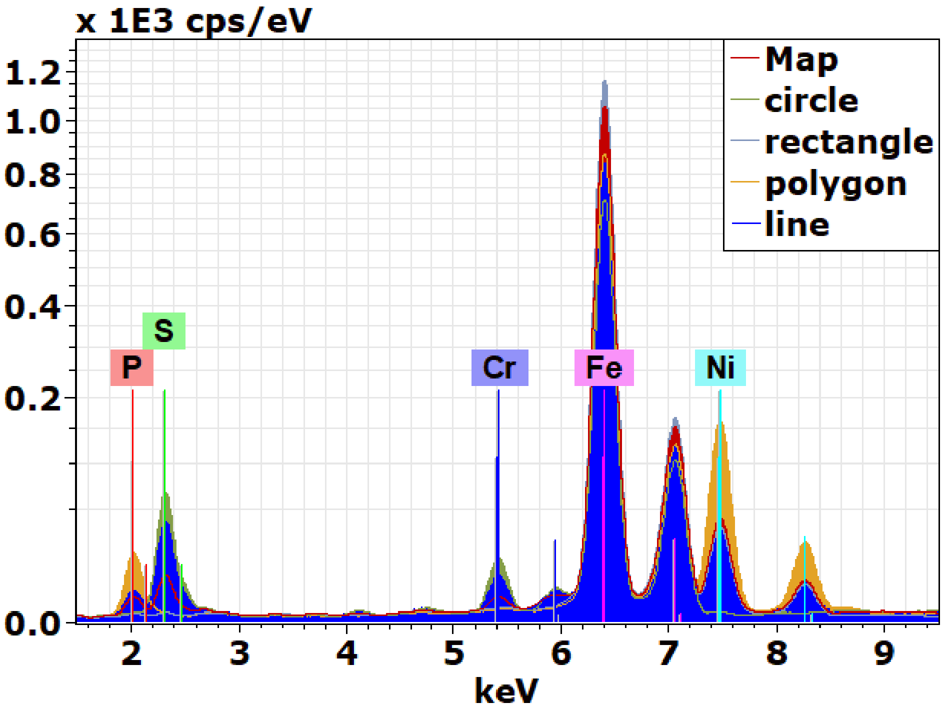


Data mining

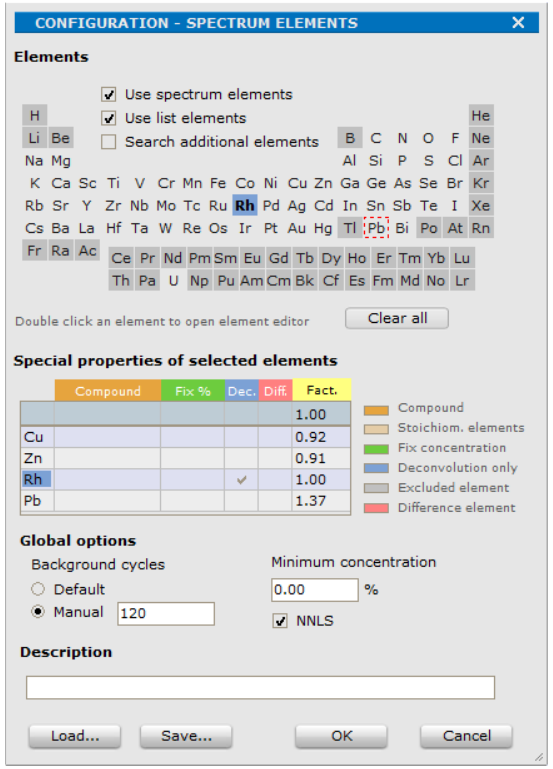
- With the complete spectral data available, multiple ways of data display and evaluation are made possible.





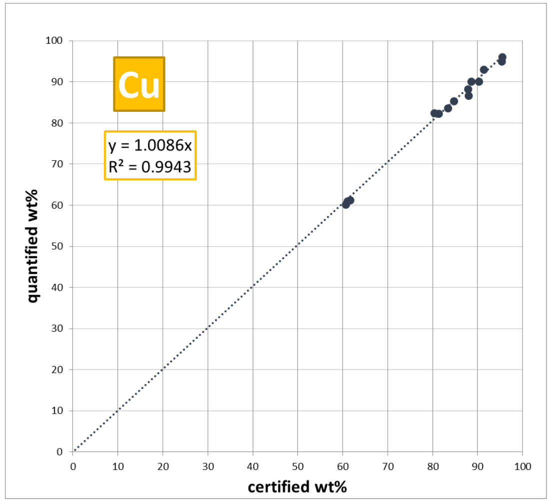


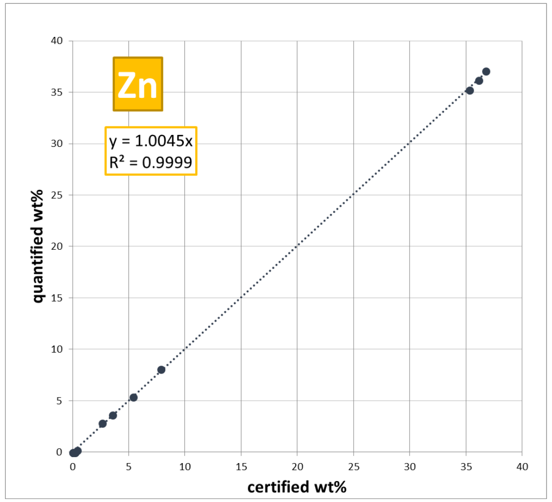
Data mining
FP quantification

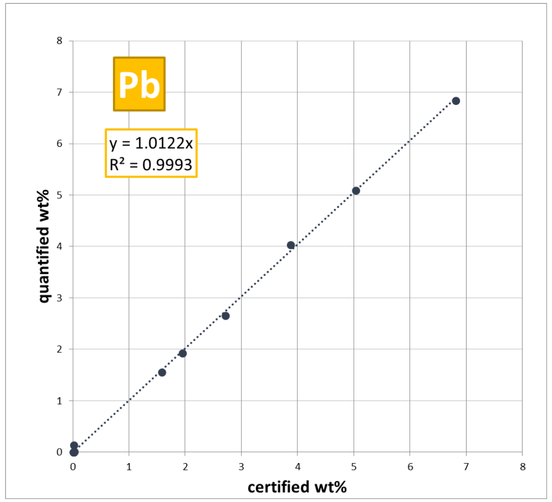


- Type-calibrated FP Quantification.

Grade-IARM	Al	Co	Cr	Cu	Fe	Mn	Mo	Nb	Ni	P	Pb	Si	Sn	Ti	V	W	Zn	Zr
CDA314-72B	T	T	T	90.1	0.0	T	T	T	0.0	0.0	2.0	0.0	0.0	T	T	T	7.8	T
CDA360-73B	0.0010	0.0	T	61.5	0.2	0.0	T	T	0.1	0.0	2.7	0.0	0.2	T	T	T	35.3	T
CDA485-76B	0.0050	0.0	T	60.5	0.1	0.0	T	T	0.0	0.0	1.9	T	0.7	T	T	T	36.7	T
CDA510-77B	0.0010	T	T	95.2	0.0	0.0	T	T	0.0	0.1	0.0	0.0	4.7	T	T	T	0.0	T
CDA544-78B	0.0020	T	T	87.7	0.0	0.0	T	T	0.1	0.2	3.9	T	4.7	T	T	T	3.6	T
CDA623-79B	9.1900	0.0	0.0	88.4	2.1	0.2	T	T	0.1	0.0	0.0	0.0	0.0	T	T	T	0.0	T
CDA630-80B	10.1900	0.0	0.0	81.2	3.3	0.5	T	T	4.7	0.0	0.0	0.0	0.0	T	T	T	0.1	T
CDA642-81B	6.7000	T	0.0	91.2	0.0	0.0	T	T	0.0	0.0	0.0	1.8	0.0	T	T	T	0.2	T
CDA655-82B	0.0020	T	0.0	95.3	0.1	1.0	T	T	0.0	0.0	0.0	3.2	0.0	T	T	T	0.4	T
CDA706-84B	0.0020	0.0	0.0	87.9	1.3	0.6	T	T	10.0	0.0	0.0	0.0	0.0	T	T	T	0.1	T
CDA836-86C	0.0020	T	T	84.6	0.2	0.0	T	T	0.3	0.0	5.0	0.0	4.4	T	T	T	5.4	T
CDA857-87B	0.2000	0.0	0.0	60.9	0.3	0.0	T	T	T	0.0	1.6	0.0	0.8	T	T	T	36.1	T
CDA932-91C	0.0020	T	T	83.2	0.0	0.0	T	T	0.5	0.1	6.8	0.0	6.8	T	T	T	2.6	T
CDA937-BS937B-1	T	T	T	80.2	0.0	T	T	T	0.4	0.0	9.2	T	9.7	T	T	T	0.0	T

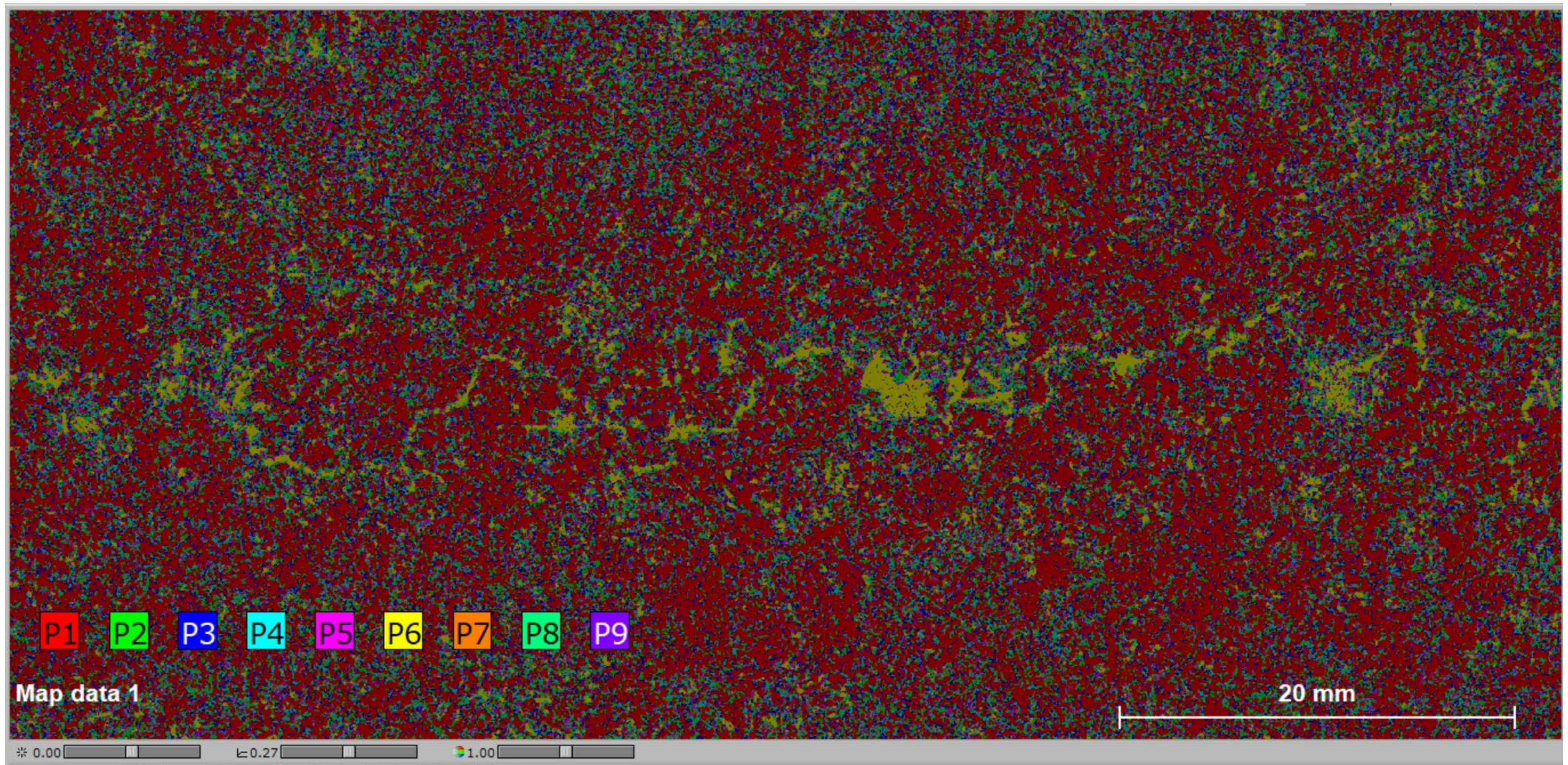






Data mining
Phase analysis

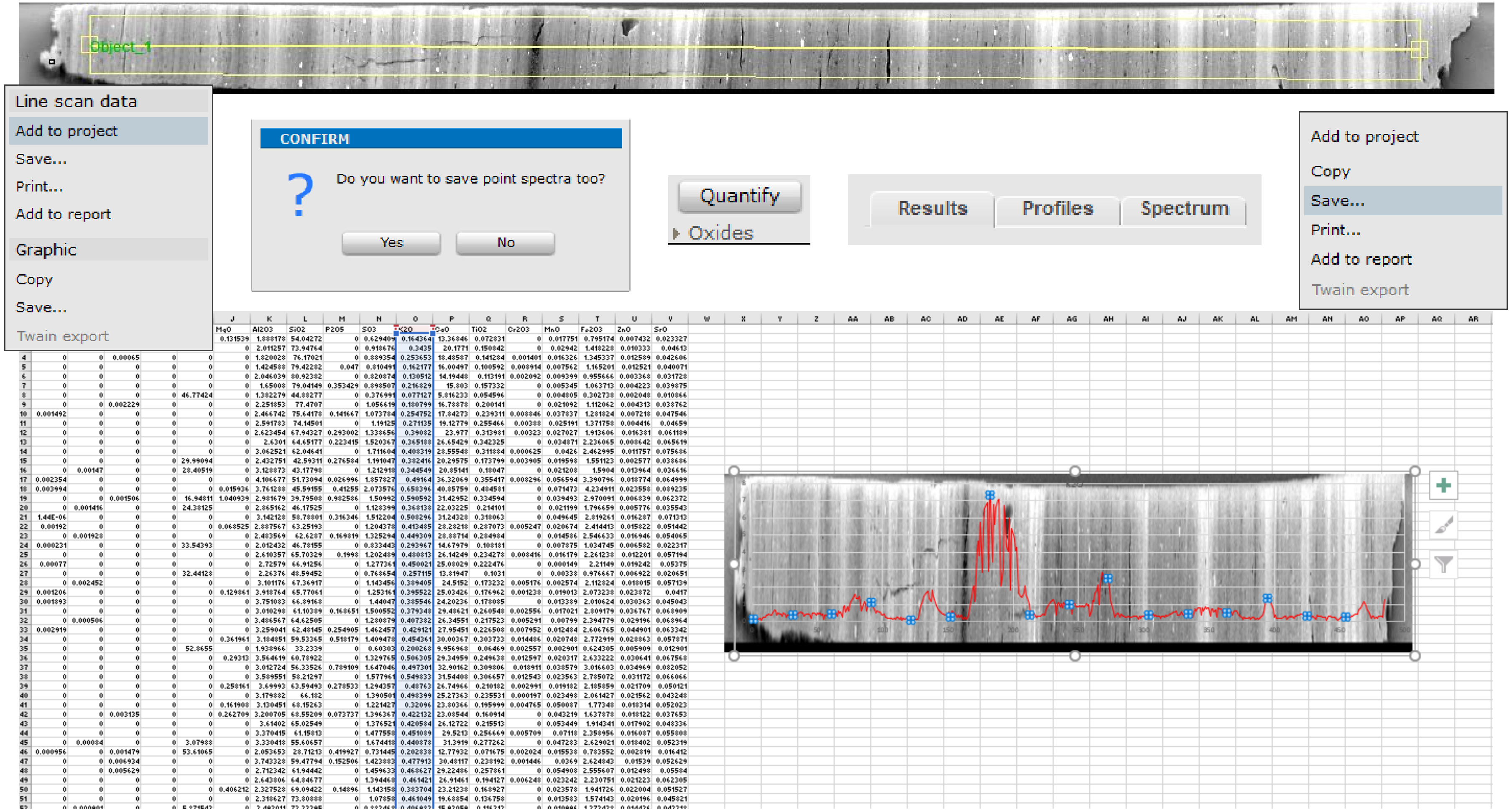
- Pixels of an element distribution map can be sorted into “phases” of similar intensity.
- Sum spectra of these “phases” allow to identify element correlations, to find associated traces, or to generally sum up separate inclusions to get spectra with better statistics.
- Additional information, such as area ratios of the phases, may hold information valuable for quality control.



Counts	Area	Video 1	Al-K	Si-K	S-KA	Ca-KA	Cr-KA	Mn-KA	Fe-KA
P1	50.0 %	--	--	--	--	--	--	16.43	--
P2	12.5 %	--	--	--	--	--	--	19.04	--
P3	11.2 %	--	--	--	--	--	--	18.13	--
P4	9.7 %	--	--	--	--	--	--	19.96	--
P5	6.5 %	--	--	--	--	--	--	20.92	--
P6	4.2 %	--	--	--	--	--	--	25.00	--
P7	2.8 %	--	--	--	--	--	--	21.82	--
P8	2.2 %	--	--	--	--	--	--	22.65	--
P9	0.9 %	--	--	--	--	--	--	23.51	--

Data mining
Displaying complex data

- Some scientific communities are used to certain ways of data display.
- Transferring data to other workspaces within the software allows for different data treatment.
- Export to text files makes it available for analysis and presentation with external software.



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