Questions, Thoughts, or Comments?

To contact us during the Webinar please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

Please accept our sincere apologies if we can’t discuss all comments and questions within the session!

We will of course answer and discuss those later on by e-mail or in another Webex meeting.

M4 TORNADO^{PLUS} – A New Era in Micro-XRF

Bruker Nano Analytics, Berlin, Germany
Webinar, September 19th 2019

Introduction
Presenters / Moderators

Falk Reinhardt

Application Scientist,
Bruker Nano Analytics, Berlin, Germany

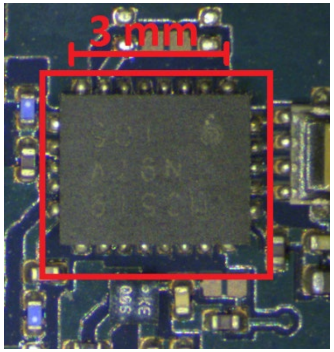
Dr. Max J.L. Bügler

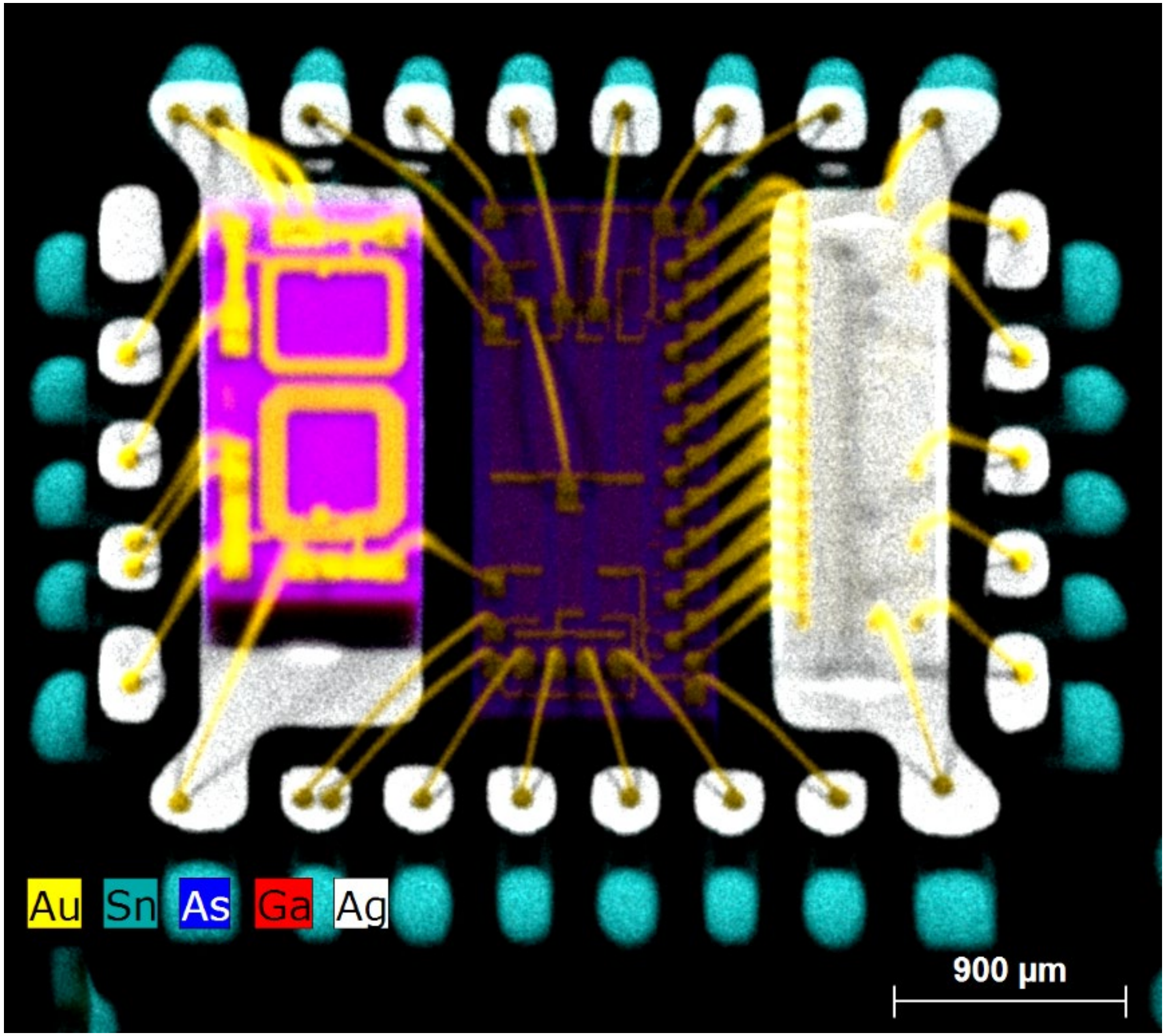
Applications Specialist,
Bruker Nano Analytics, Berlin, Germany

Introduction
The method – micro-XRF

- Little to no sample preparation
- Non-destructive
- Elemental information
- Small spot analysis
- Information from within the sample

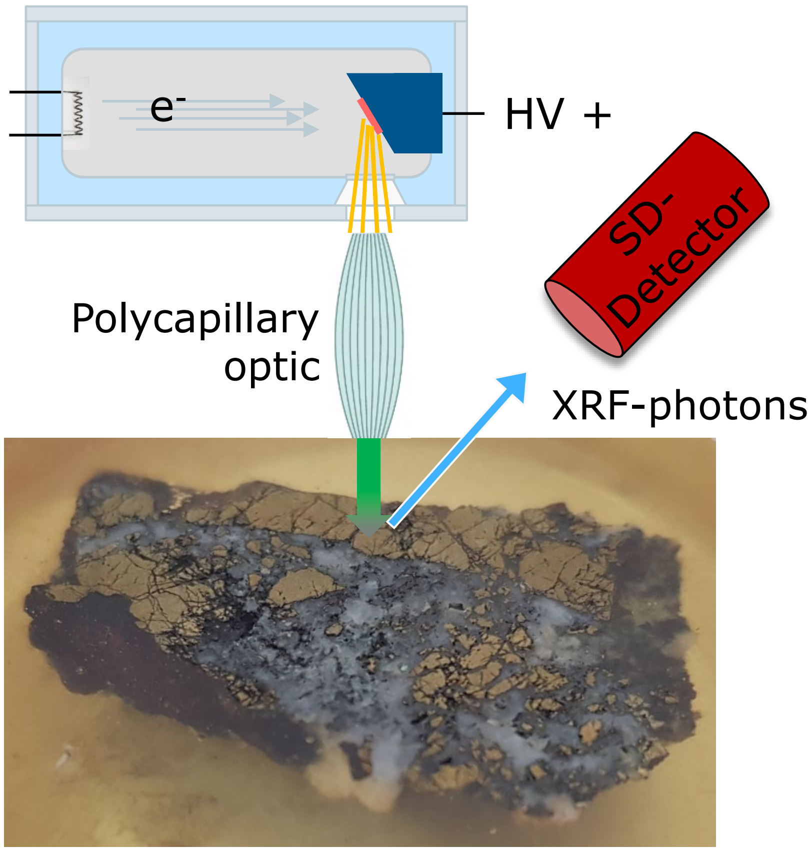
- Large-scale
- Quantification



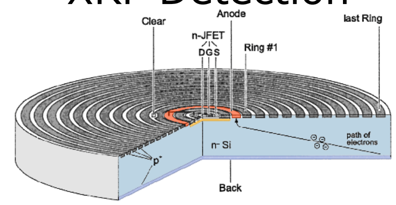


Introduction
…in other words

Excitation



XRF Detection



Silicon **D**rift **D**etector with XFlash® Technology

- X-rays can be guided onto a small spot
- Spatially resolved element-specific signal
- Intensity ratios of observed elemental lines can be used for quantification

The instrument
M4 Tornado

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)

Optional 40 W micro-focus W tube with collimator
for excitation of 'heavy' elements, embedded in lighter matrices (not used here)

Up to two Silicon drift detectors (SDD)
with 30 or 60 mm² active area each
energy resolution < 145 eV
optional with light element window
(for Mn-Kα @ 130 kcps throughput)

Sealed sample chamber with adjustable pressure between 1 mbar and atmospheric pressure
for detecting elements down to Na
(down to C with LEW)

Sample stage with measureable area of 200 mm x 160 mm, maximum sample height 120 mm, maximum sample weight 7 kg, and sample stage speed up to 100 mm/s, minimum step size 4 µm

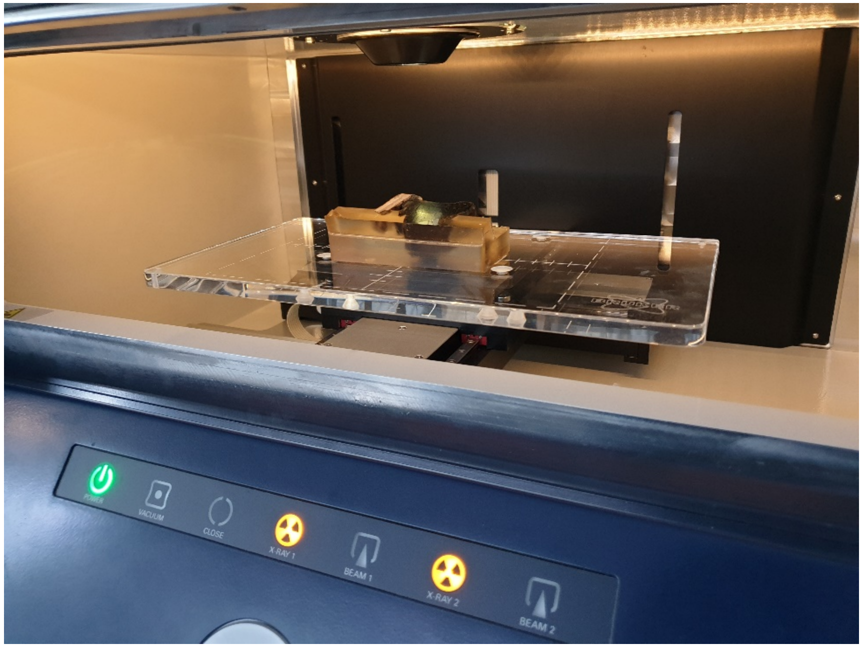
The novel instrument
M4 TORNADO^{PLUS}

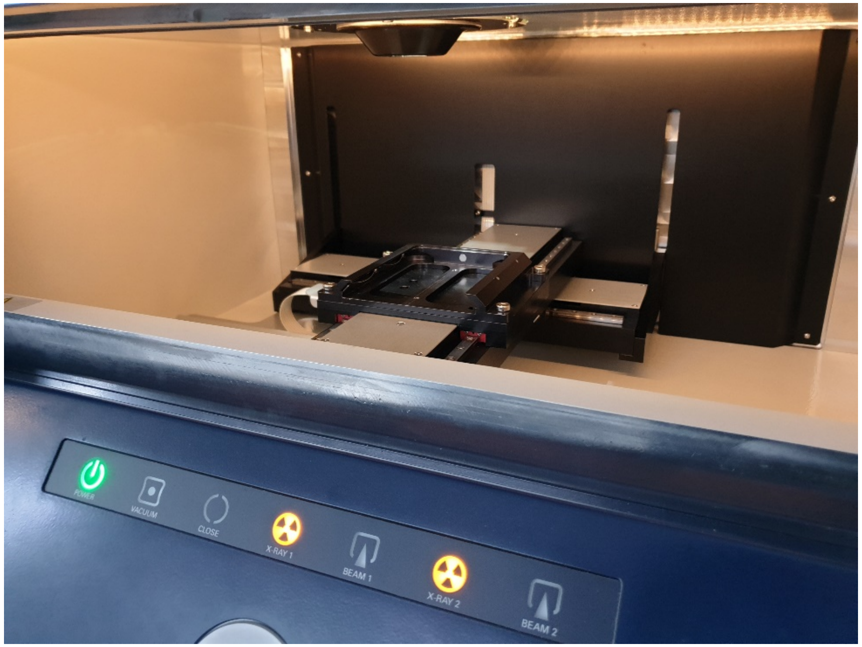
State-of-the-Art Hardware and Firmware

Includes all novel M4 features

- Quick exchange sample table
- Aperture Management System (AMS)
  (increased depth of field)
- Light Element Detector Window
  (detecting elements down to Carbon)
- Helium purge system
  (vacuum performance at atmospheric pressure)
- Collimator Changer for 2nd tube
  (adaption of spot size to the analytical task)
- High Pulse throughput
  (processing of up to 550.000 counts per second)

Quick exchange sample stage

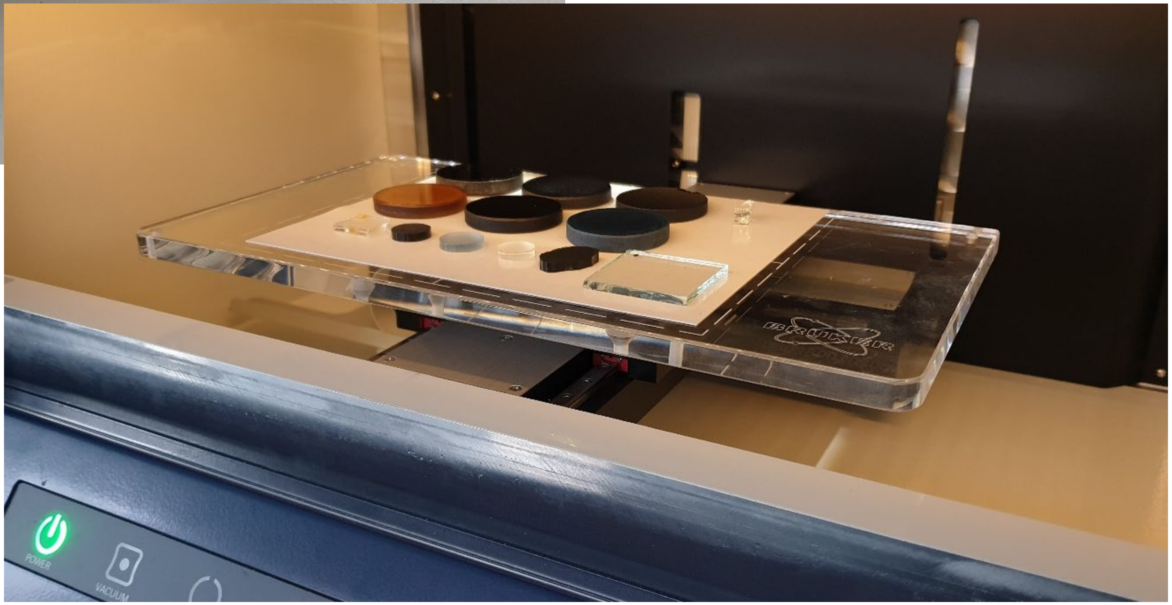




Easy-to-take-out dove tail sample stage can be fastened/unfastened in a second.

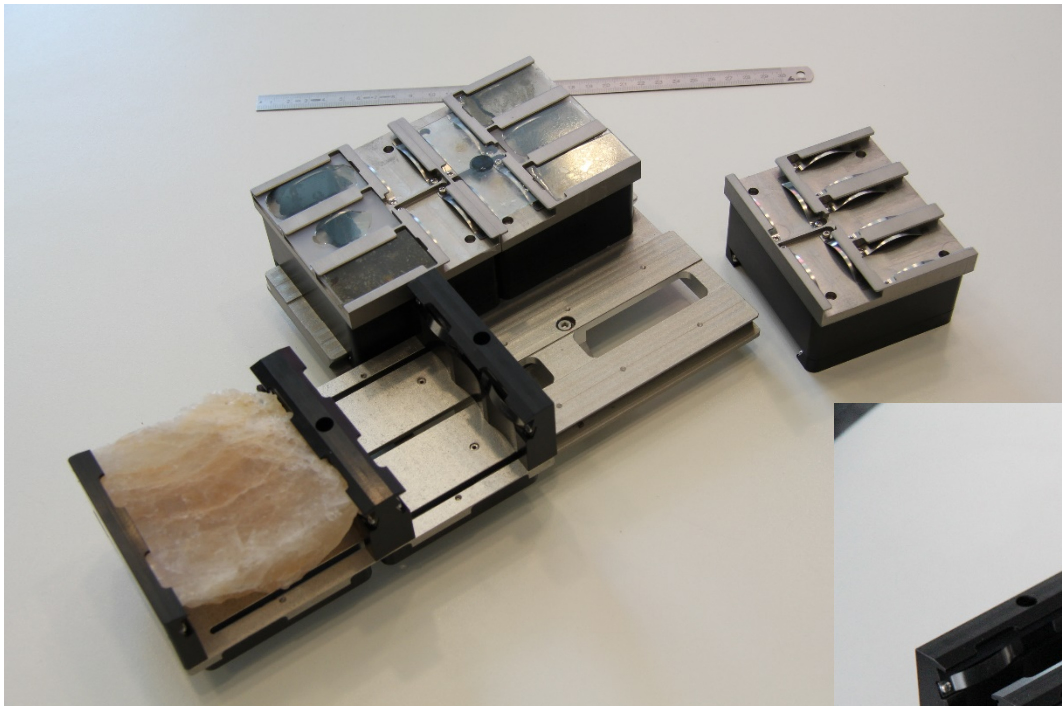
Quick exchange sample stage

Easy sample arrangement



Quick sample stage mounting

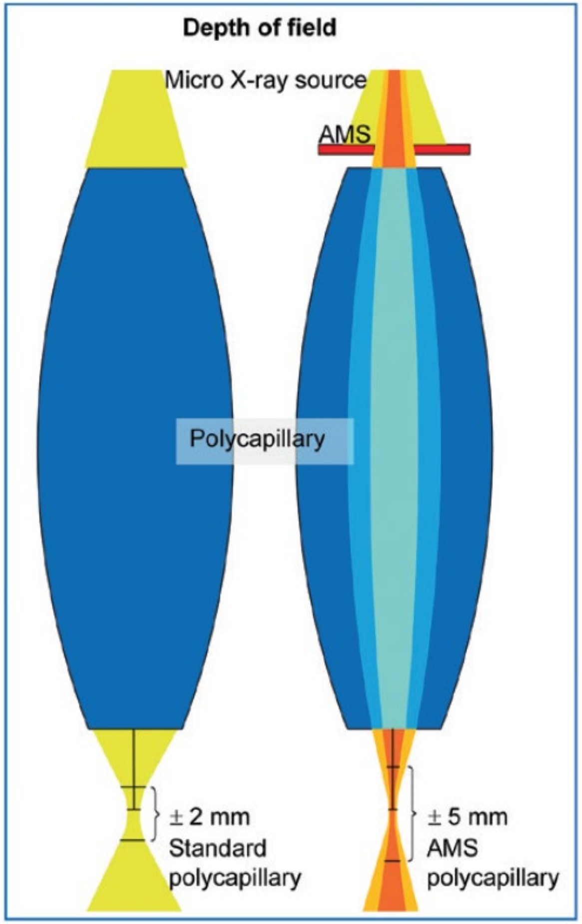
Quick exchange sample stage
Different options

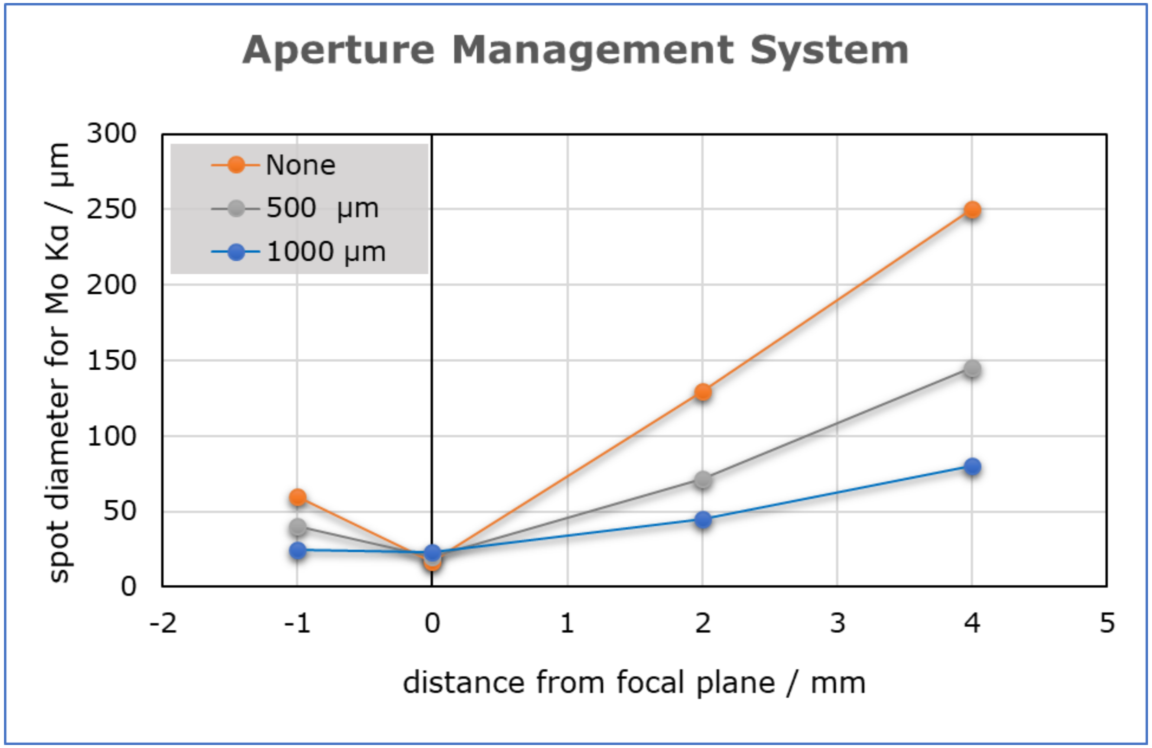


Drill core holder and thin section holder available. Design idea here is the same surface plane of both sample types.

The standard acrylic glass stage is available as an accessory → users can customize the stage for their specific samples.

Aperture Management System
Introduction



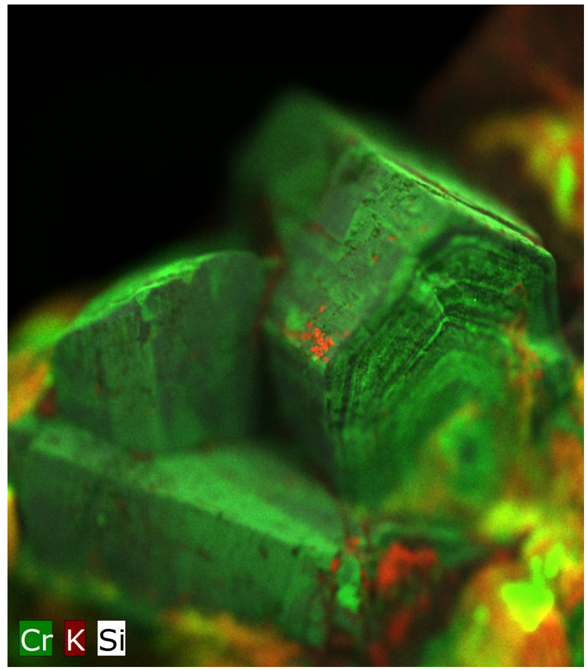


at 4 mm out of focal plane the spot size is reduced from ~ 250 µm down to ~ 75 µm

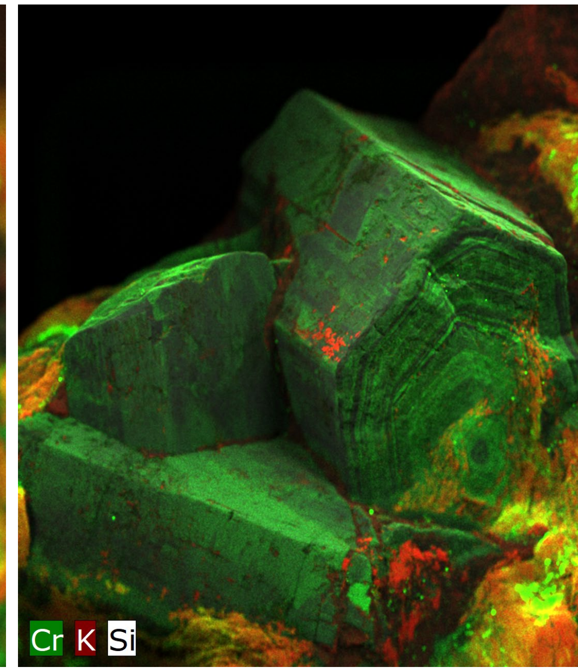
Aperture management – patent pending

Aperture Management System
High-topography samples


Emerald crystal, Brazil



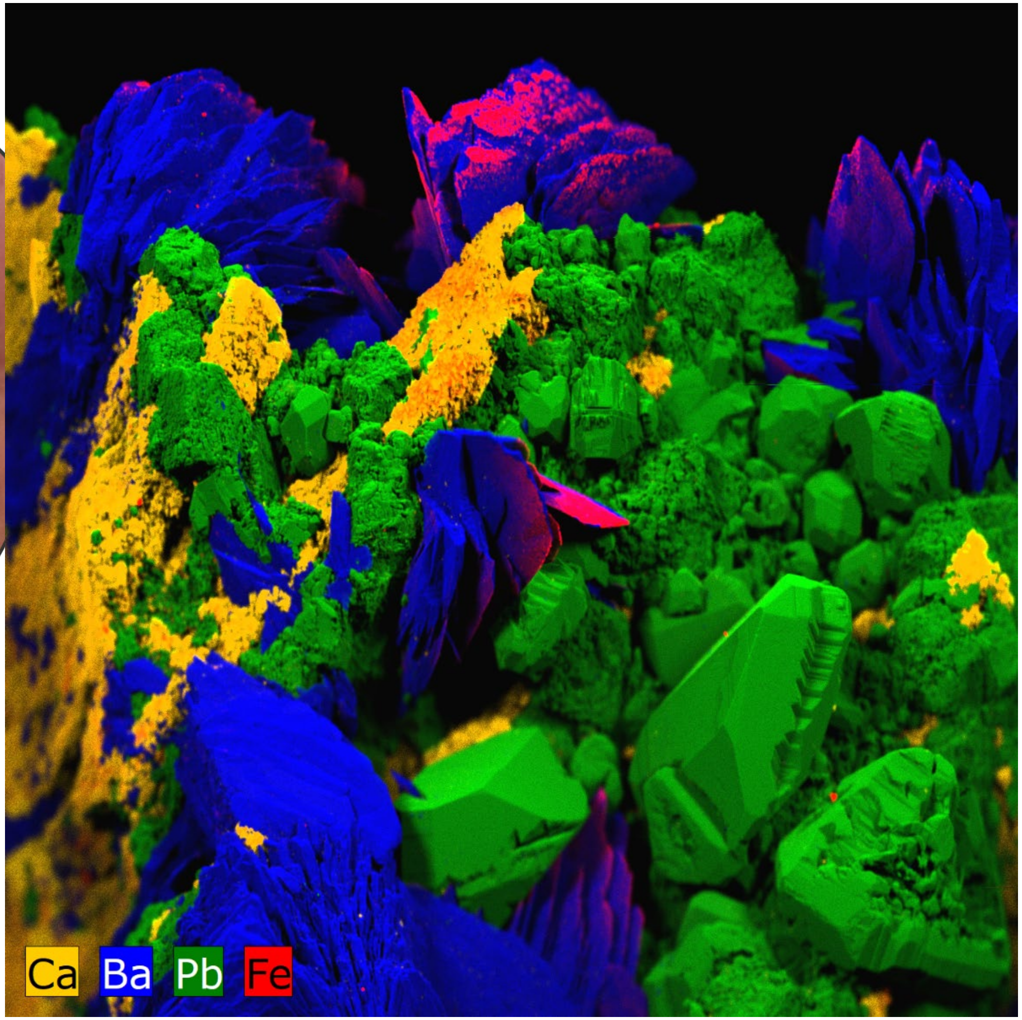
without AMS



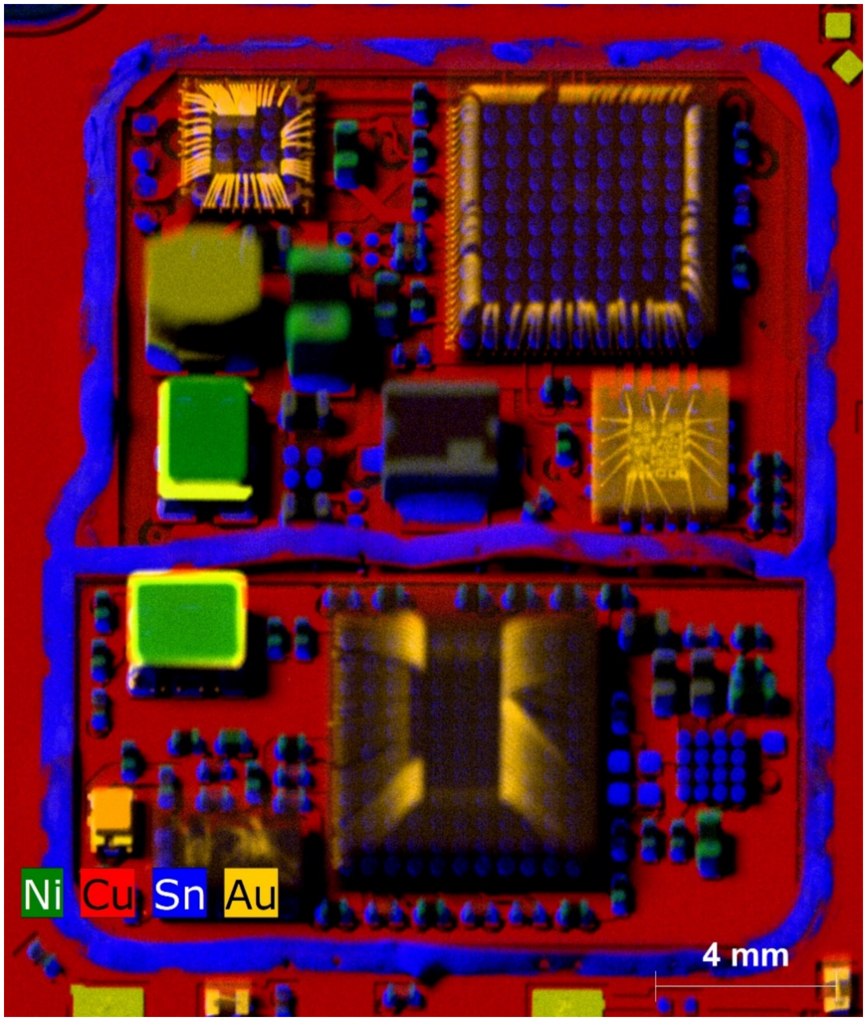
with AMS

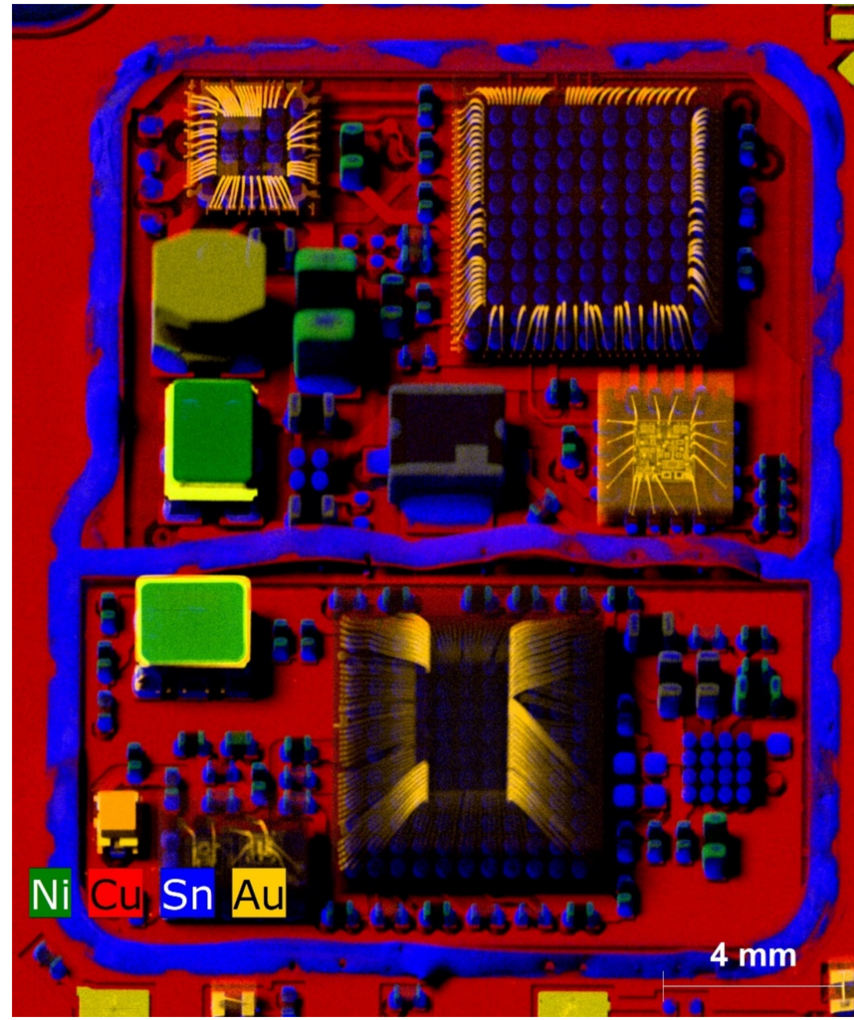
Aperture Management System
High-topography samples

Cerussite with bladed Barite on Galena, Morocco



Aperture Management System
High-topography samples





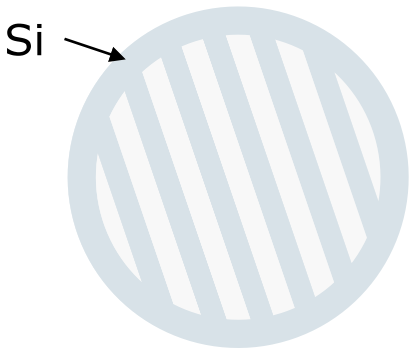
Light element detector windows
Sensitivity

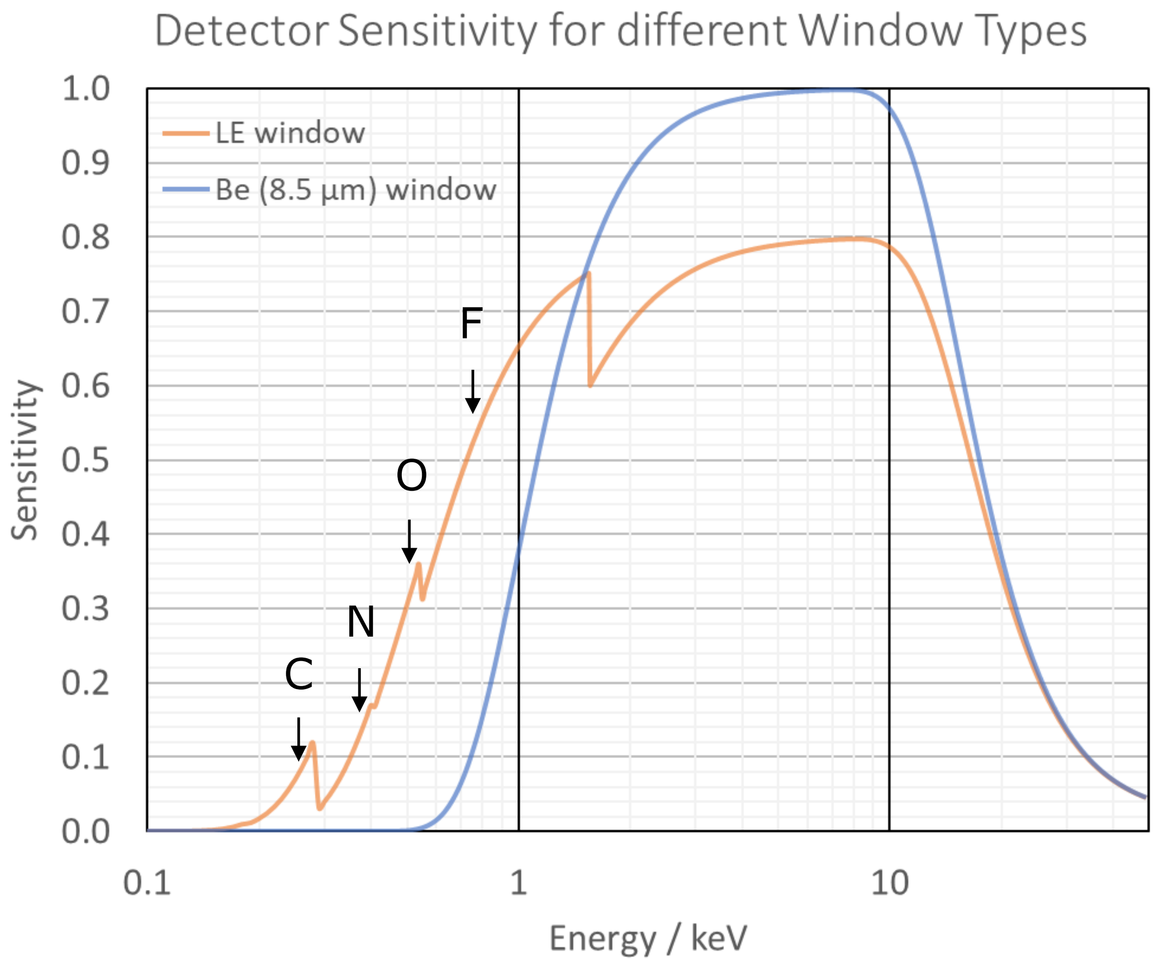
Conventional window:

Be window with thickness between 8.5 µm and 12 µm

Light element window:

Thin polymer foil supported by a Silicon grid

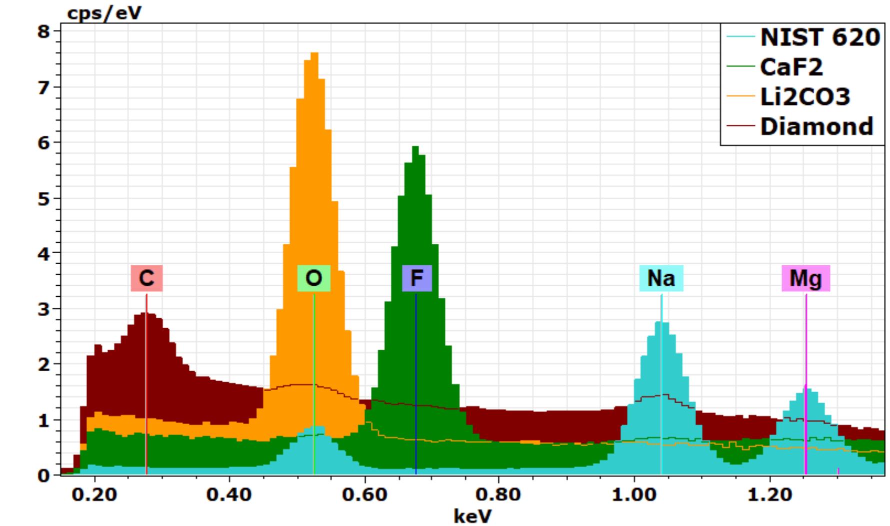


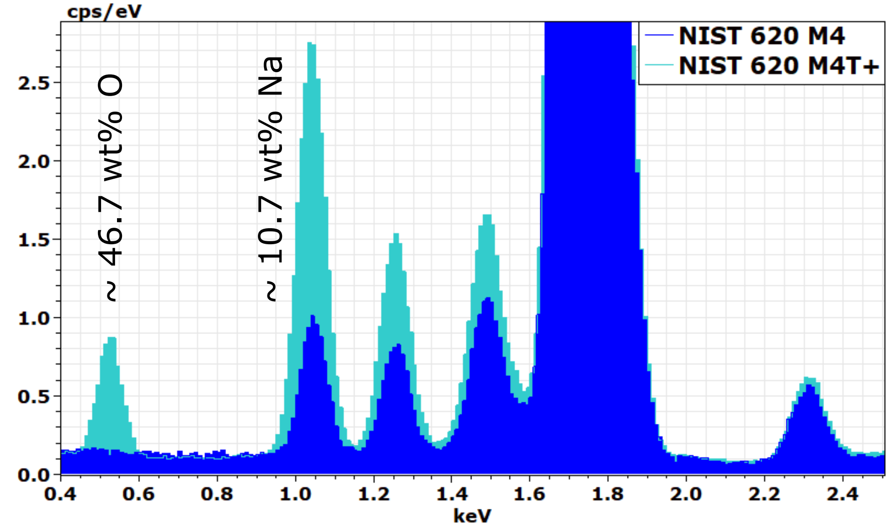


Light element detector windows
Spectra

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, information depth is too different from the other elements.

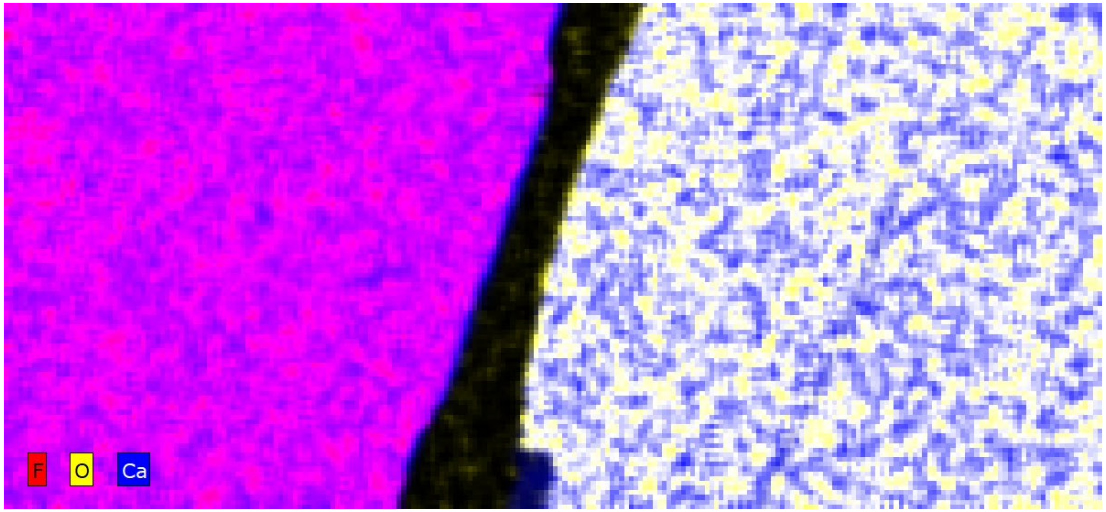




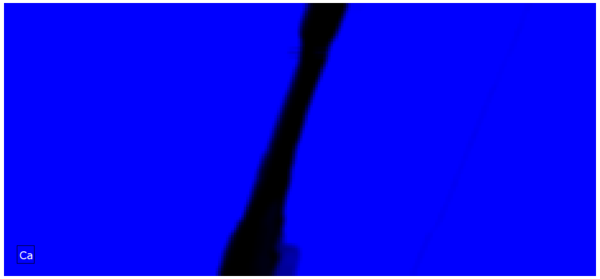
Light element detector windows
Maps

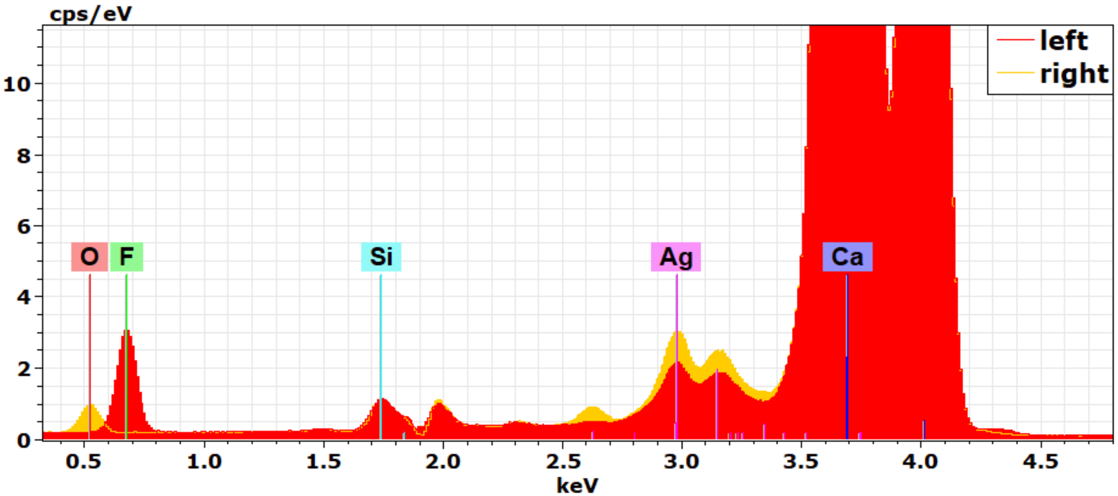
Calcite and Fluorite can hardly be discerned by usual micro-XRF (restricted to elements above and including Na).

The Fluorine signal is needed to discriminate the two minerals.



Example: CaF_2 on the left, $CaCO_3$ on the right side.





Helium purge system
Why?

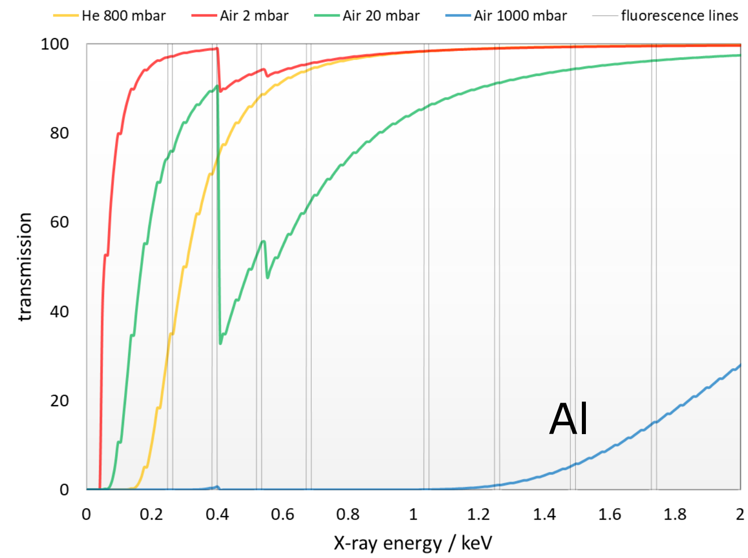
Analyzing light elements (< Al) is practically impossible at ambient pressure.

Evacuating the measurement chamber is a prerequisite.
Standard measurement conditions are at 20 mbar (down to Na, M4 TORNADO) or 2 mbar (down to C, M4 TORNADO^{PLUS}).

BUT: Evacuation of the measurement chamber will lead to a quick evaporation of any water and other volatiles contained in a sample.

→ not suitable for wet samples or hazardous materials

→ Flow-controlled Helium purge as an option



Usual approach:
carefully pump down to 800 mbar to seal the chamber and then exchange atmosphere with He (or other gases)
→ minimum He consumption for long-time measurement

He purge
Prevent drying of wet samples

Fresh cut strawberry –
a wet sample

Scan size: 31.2 mm x 30.5 mm

Step width: 20 µm

Map: 2.379.000 Pixel

Measurement time: 10 ms/Pixel

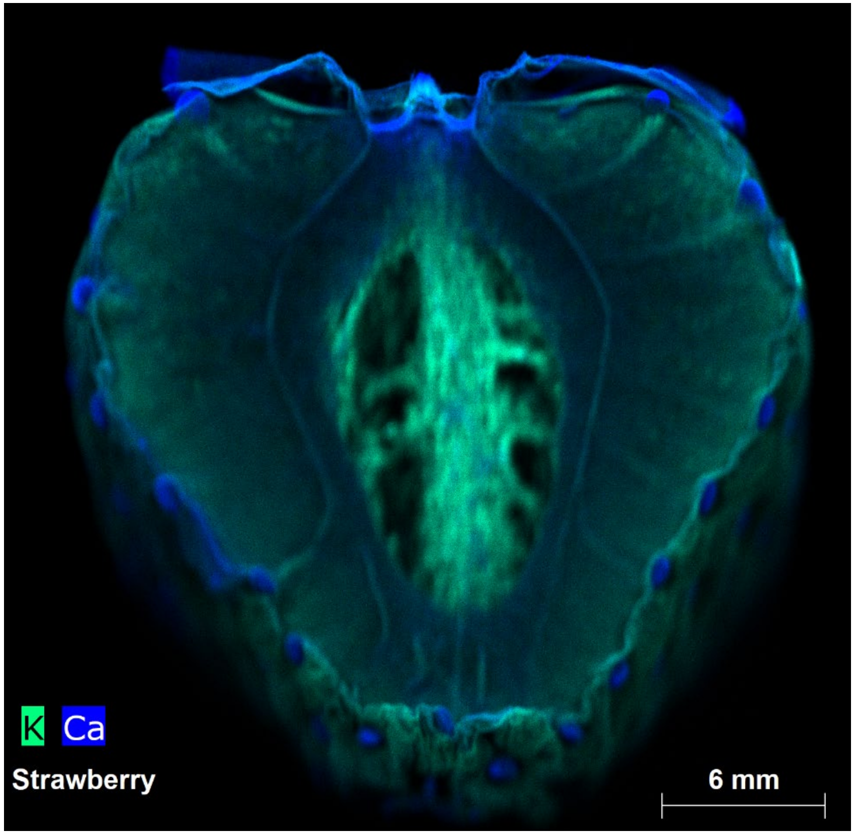
Overall time: 8:34 h

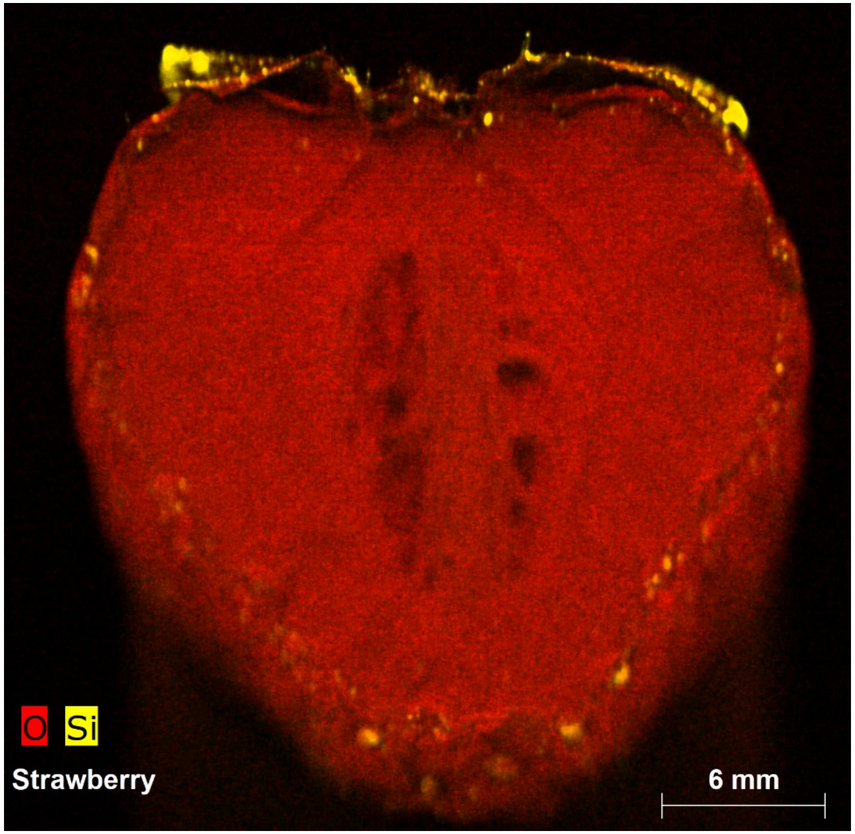
Tube: 50 kV / 600 mA

2x 60 mm² SDDs

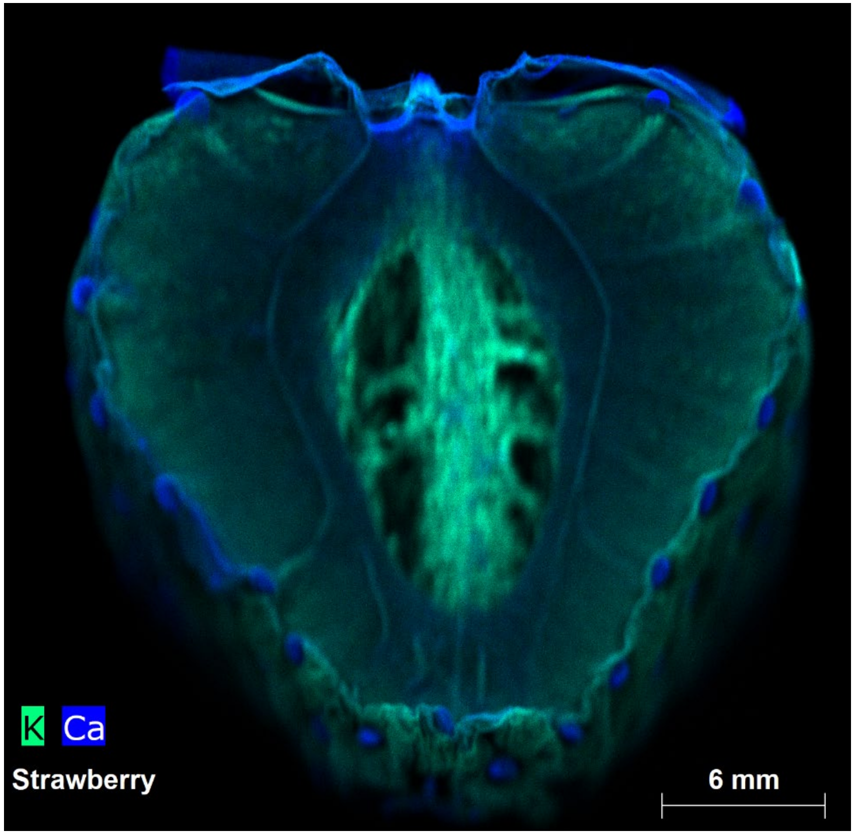
He purge
Prevent drying of wet samples

Oxygen can be detected in He atmosphere

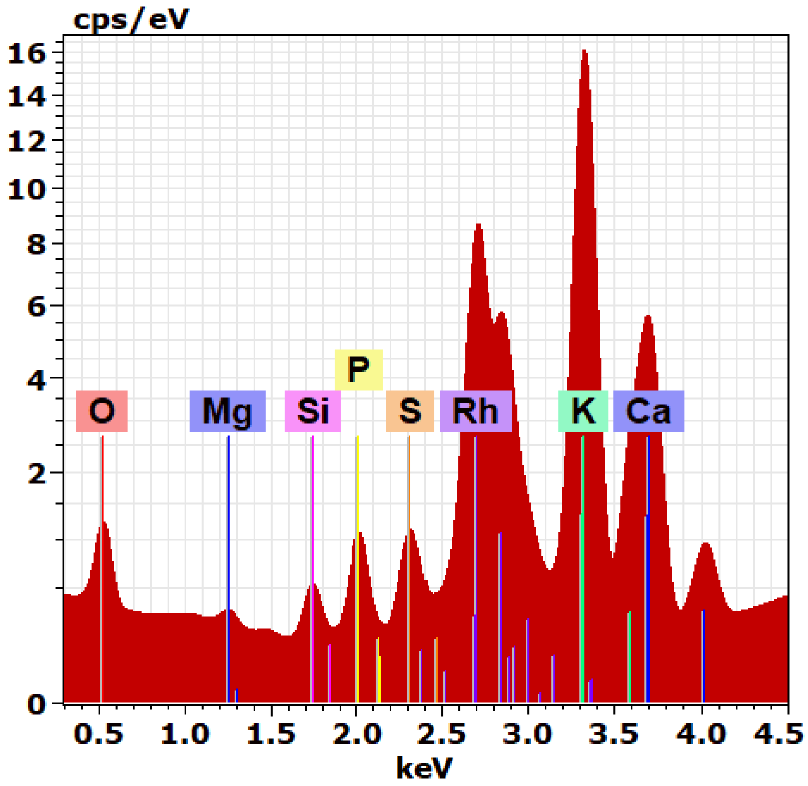




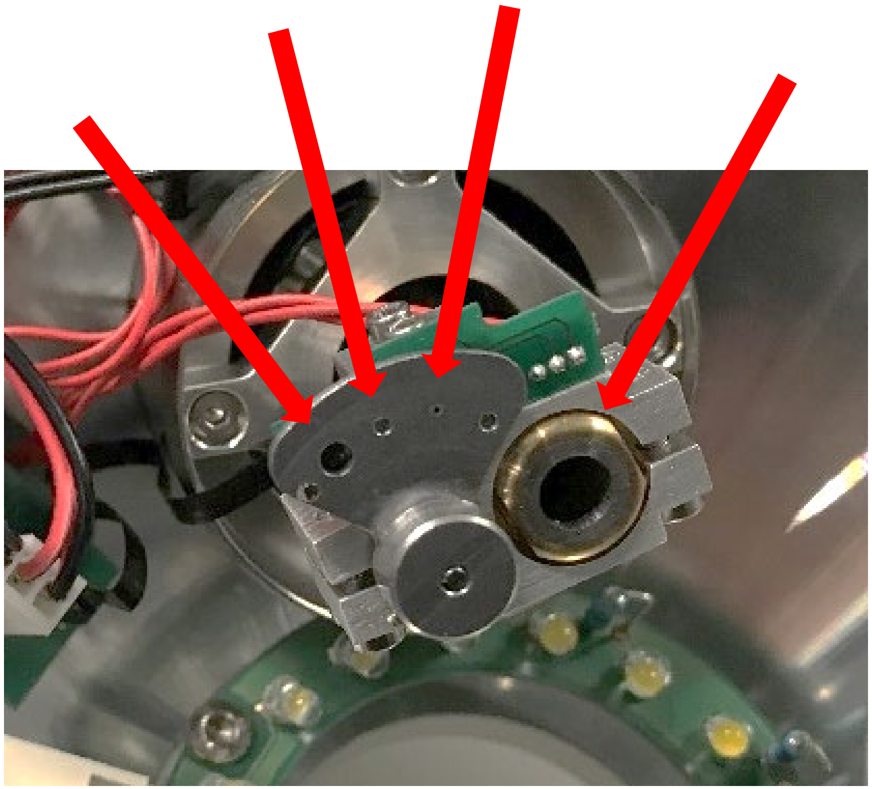
He purge
Prevent drying of wet samples



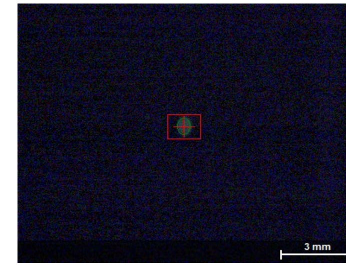
Oxygen can be detected in He atmosphere



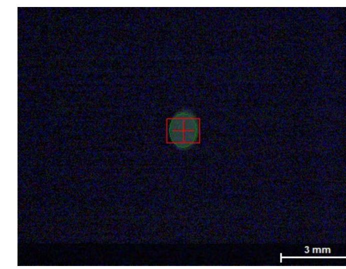
Collimator Changer
Introduction



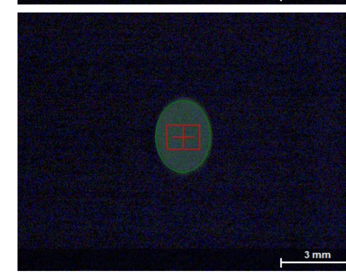
0.5 mm
0.6 mm x 0.75 mm



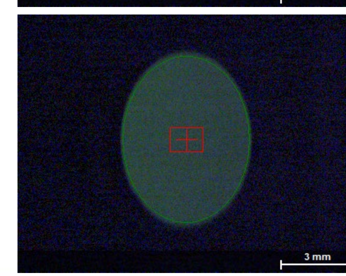
1 mm
1.2 mm x 1.5 mm



2 mm
2.4 mm x 3.1 mm

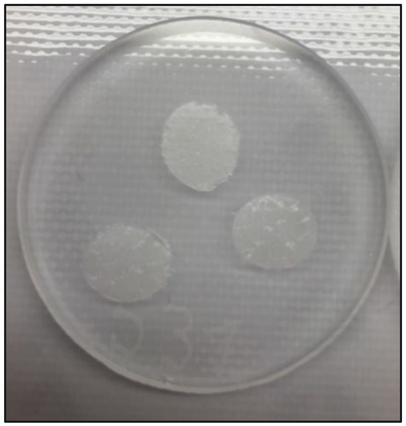


4.5 mm
5.5 mm x 7.2 mm



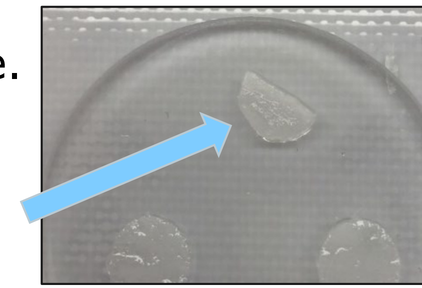
Application example
Soaked-up liquids – Map approach

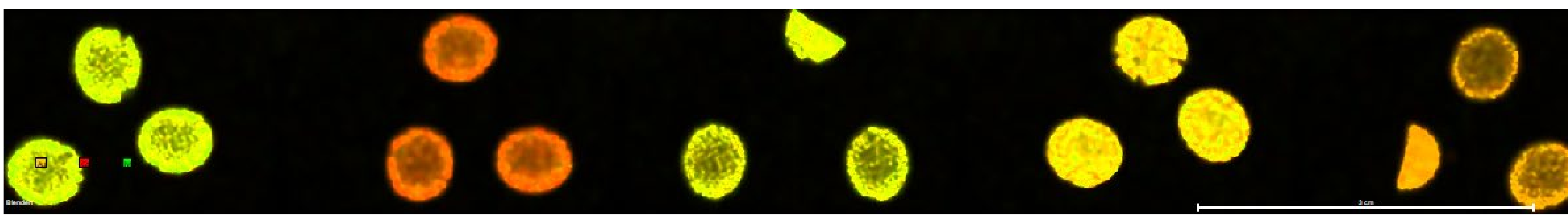
Idea: deposit a **defined amount of solution in a defined area**, scan, and sum up the integral detected fluorescence intensity

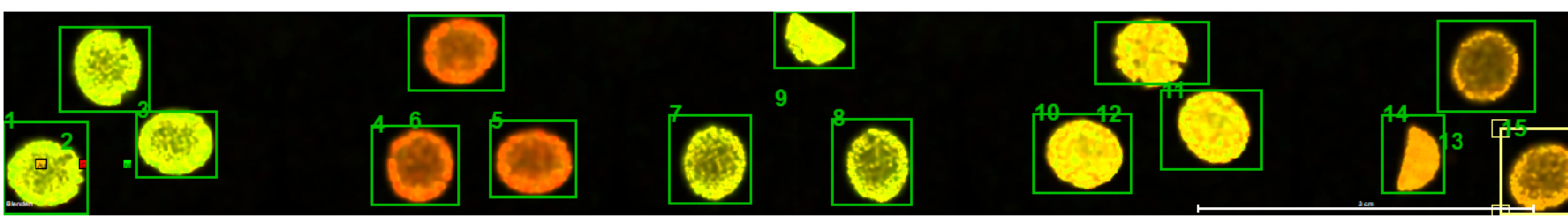


For the analysis 5 µl-droplets were deposited on a ~ Ø 6 mm absorbent tissue.

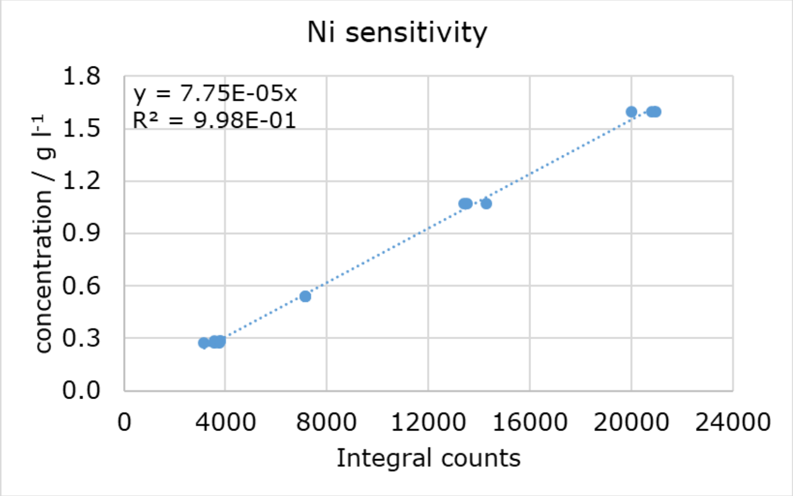
To evaluate effects of poor sample preparation, two samples were folded.

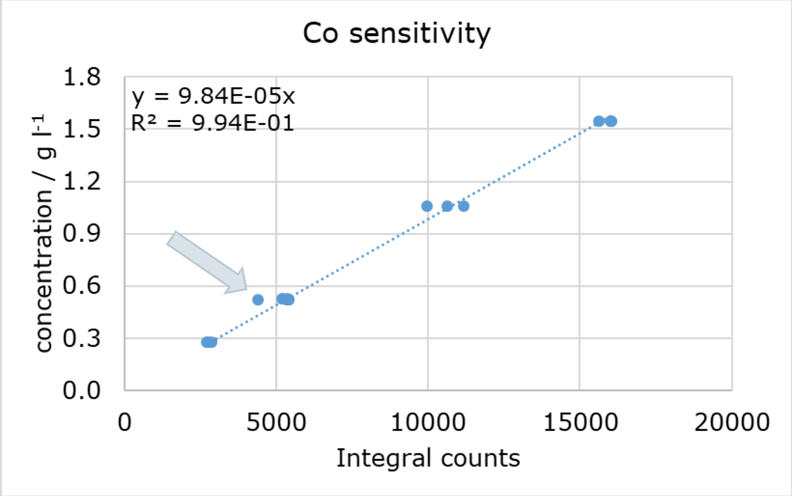


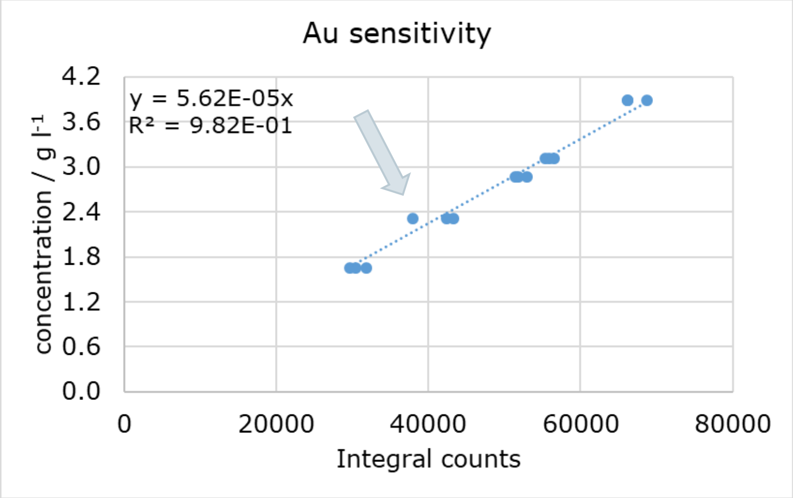




Application example
Soaked-up liquids – Map approach





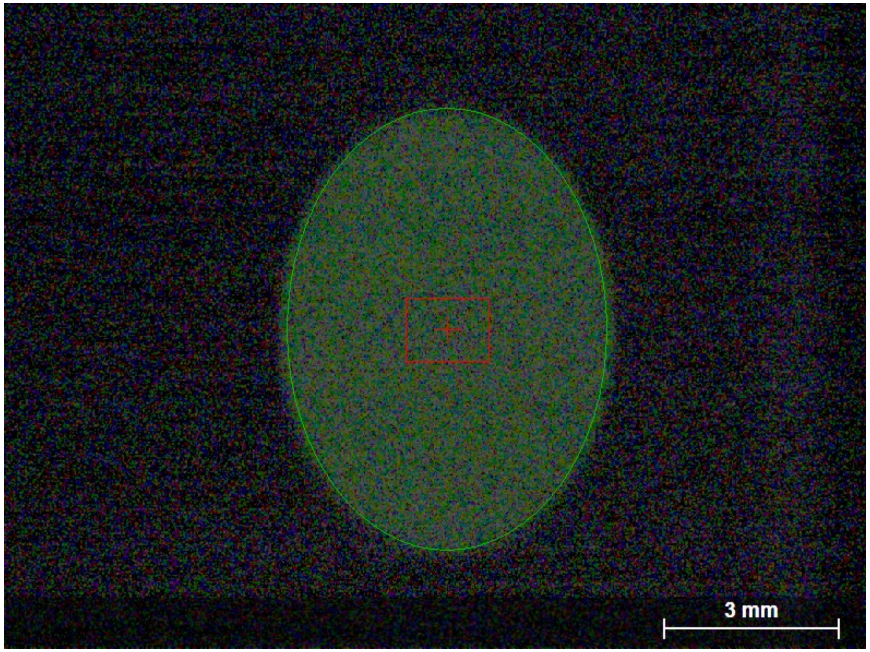


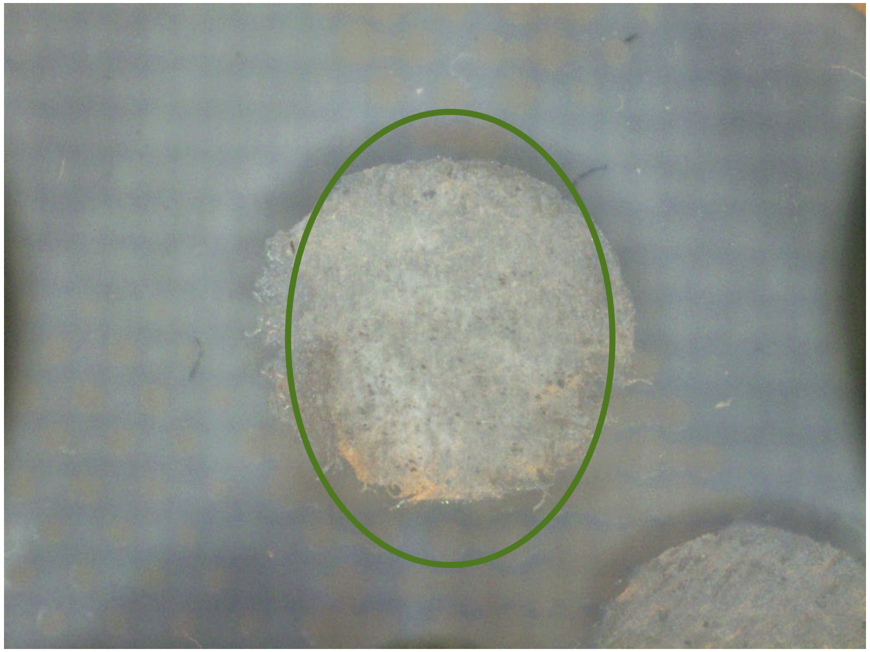
There is a very good linear correlation between the extracted intensity and the concentration. From the slope (sensitivity) the concentration in the sample can be derived. The main uncertainty results from the droplet preparation (see the deviation in the 3 dots for the same concentration).

The folded samples also results in small deviations (see arrow).

Application example
Soaked-up liquids – with collimator

Alternatively: single spot measurement with very large collimator



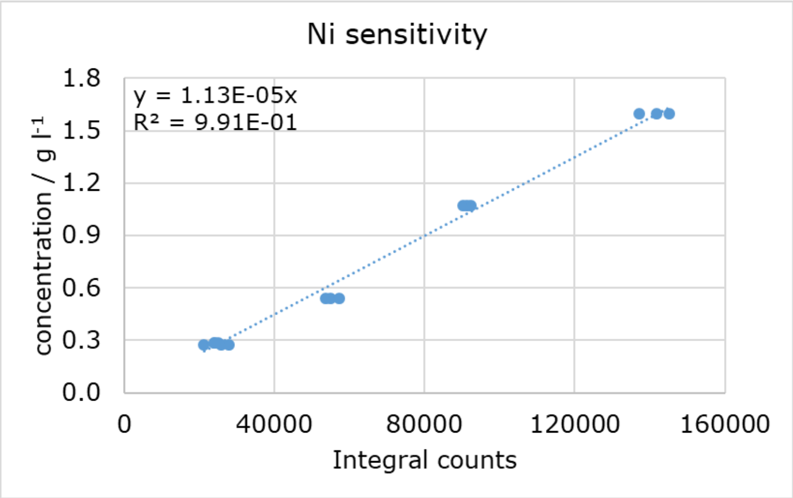


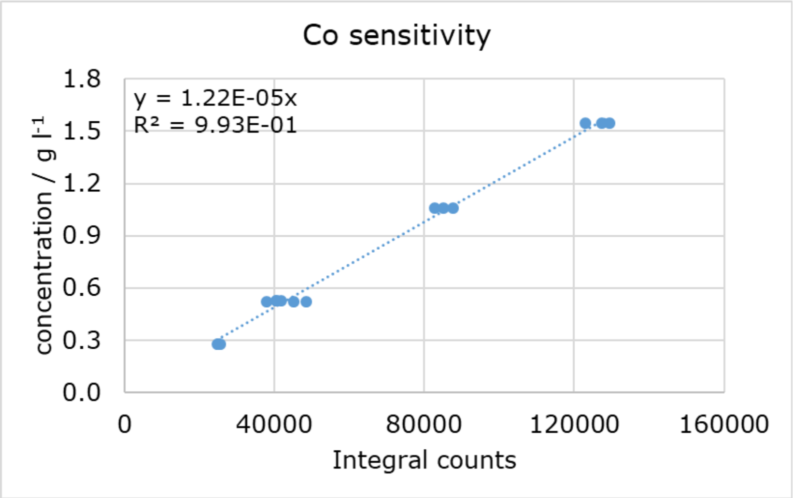
Using the 4.5 mm collimator the size of the X-ray beam on the sample is ~ 5.4 mm x 7.2 mm.

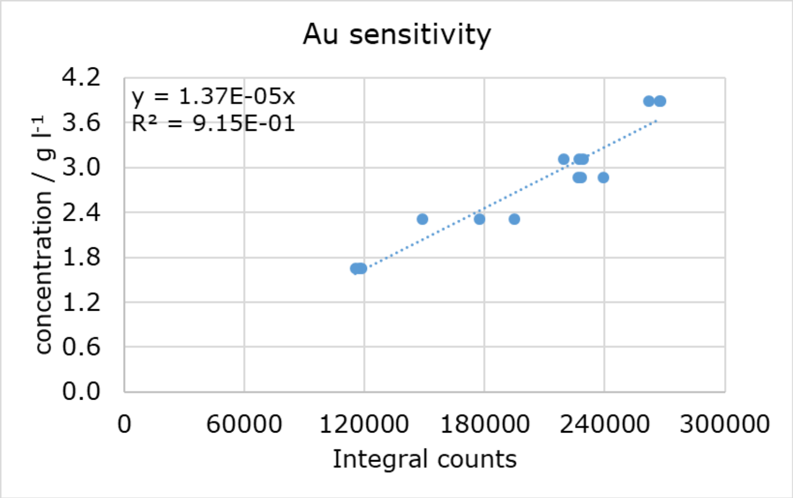
The spots overlaps reasonably well with the sample.

60 s realtime measurements per sample.

Application example
Soaked-up liquids – with collimator







Again there is a good linear correlation between the extracted intensity and the concentration. The slope is different from the prior measurements, in line with different excitation conditions.

As some of the samples are not fully covered by the X-ray spot the correlation is not as good, especially since the elements are enriched at the edges of the tissue.

Application example
Soaked-up liquids – comparison

Rh tube 20 µm lens spot and map

Spectrum	Co counts	Co [g/l]	Ni counts	Ni [g/l]	Au counts	Au [g/l]
S1	5099	0.50	6534	0.51	53746	3.02
S2	4996	0.49	6436	0.50	52392	2.95
S3	5147	0.51	6740	0.52	55375	3.11
S4	5980	0.59	7491	0.58	60326	3.39
average		**0.52**		**0.53**		**3.12**
s		0.04		0.03		0.17
s%		7.41		6.08		5.41
		0.52 ± 0.04		**0.53 ± 0.03**		**3.12 ± 0.17**

Rh tube 4.5 mm collimator spot and single spot

Spectrum	Co counts	Co [g/l]	Ni counts	Ni [g/l]	Au counts	Au [g/l]
S1	42249	0.52	46978	0.53	222252	3.03
S2	42240	0.52	46556	0.52	220602	3.01
S3	50818	0.62	56899	0.64	268763	3.67
S4	43497	0.53	48651	0.55	229864	3.14
average		**0.55**		**0.56**		**3.21**
s		0.04		0.05		0.27
s%		7.98		8.42		8.32
		0.52 ± 0.04		**0.56 ± 0.05**		**3.21 ± 0.27**

Collimator Changer
Linearity of spectra

Smaller samples call for higher spatial resolution

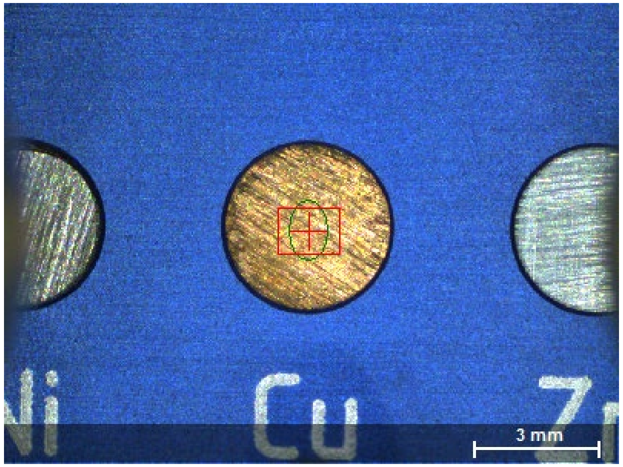
(possible secondary effects should be taken into account)

Sample diameter: 4 mm

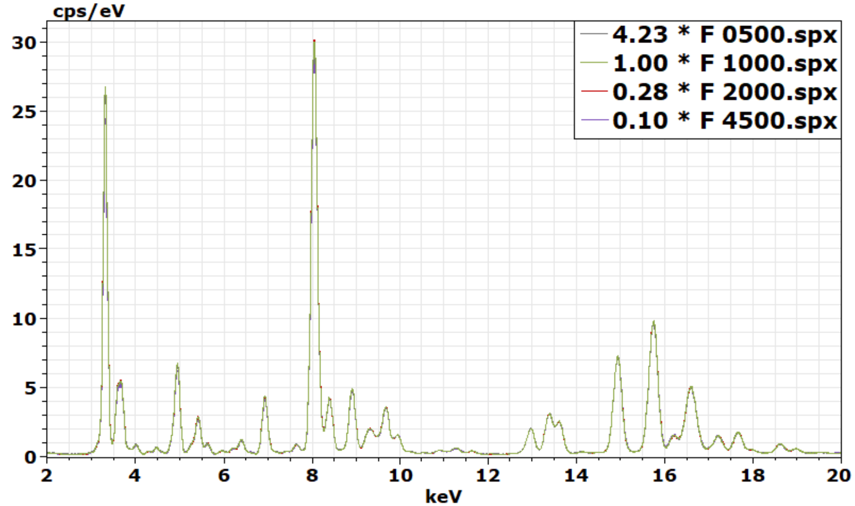
Collimator size: 1 mm

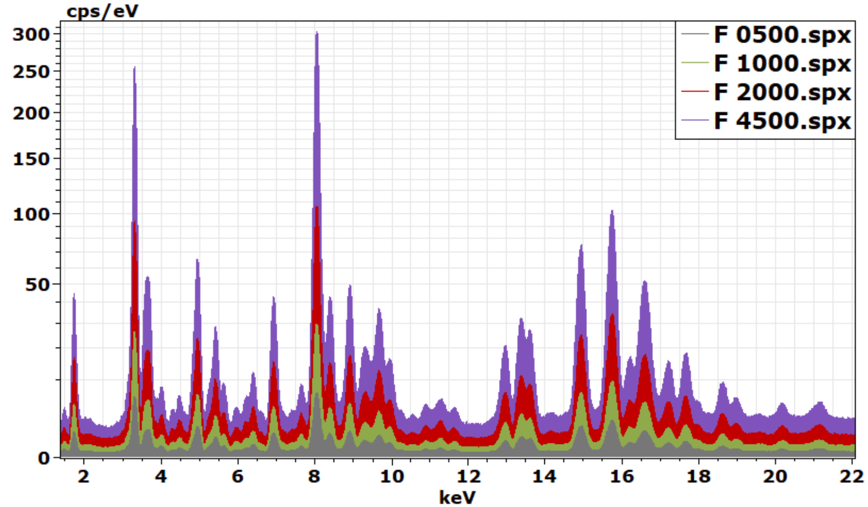
Spot on sample:

1.2 mm x 1.5 mm



Spectra differ only in intensity → easy scaling
Intensity factor equals spot size ratio



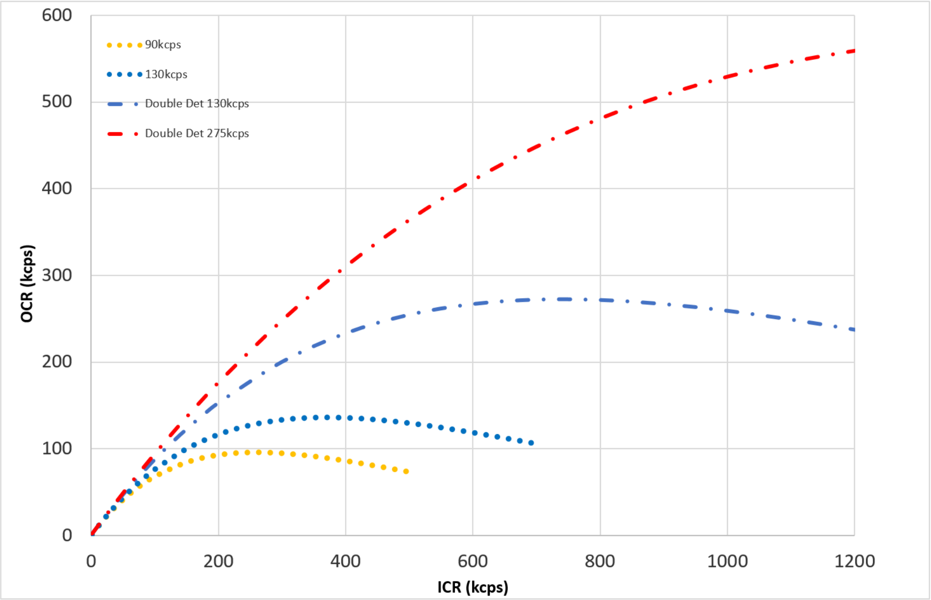


High pulse throughput
Signal processing

Using 2x 60 mm² SDDs the solid angle of detection is huge and, hence, lots of photons hit the detector

Independent signal processing is an advantage, as each detector has to dal with “only” halt the count rate.

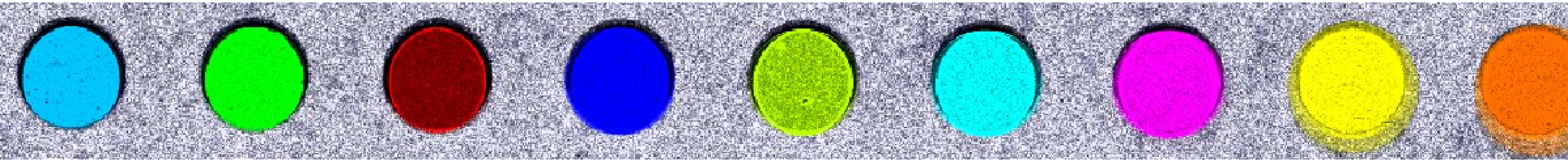
State-of-the-Art detector technology the use of signal processing units that allow to create 275.000 cps as maximum output count rate.



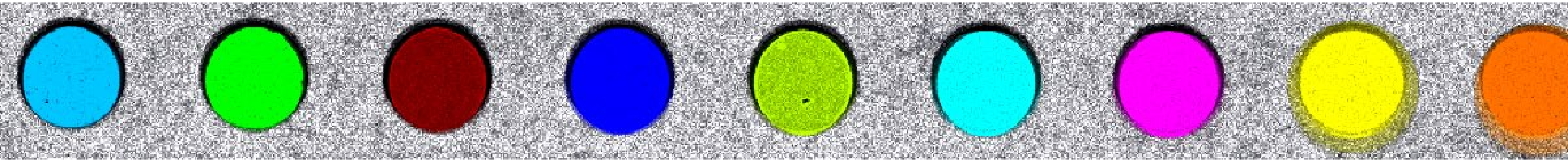
With the dual detector system 550 kcps out put count rate can be generated (at ~ 1.6 Mcps input count rate) while the energy resolution for Mn-Kα is still < 145 eV.

High pulse throughput
Live part

90 kcps



130 kcps



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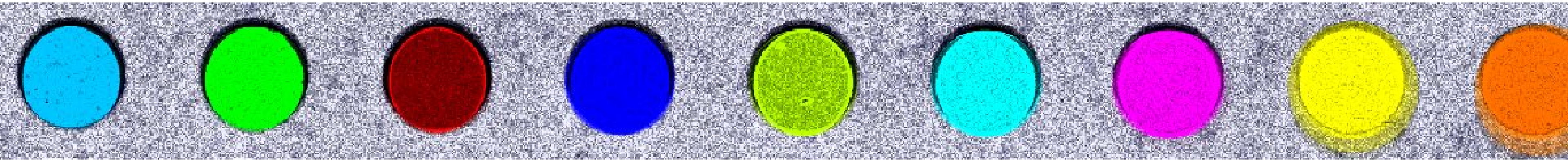
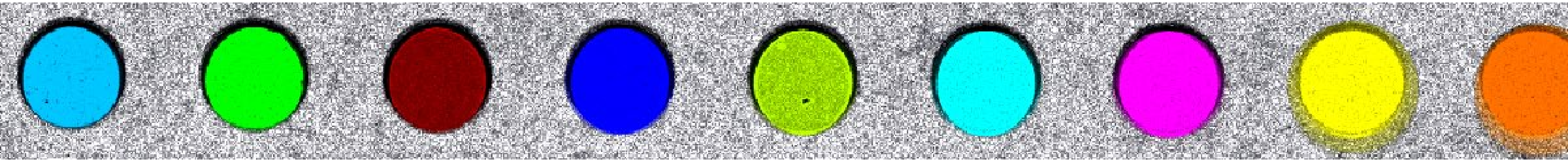
High pulse throughput
Live part

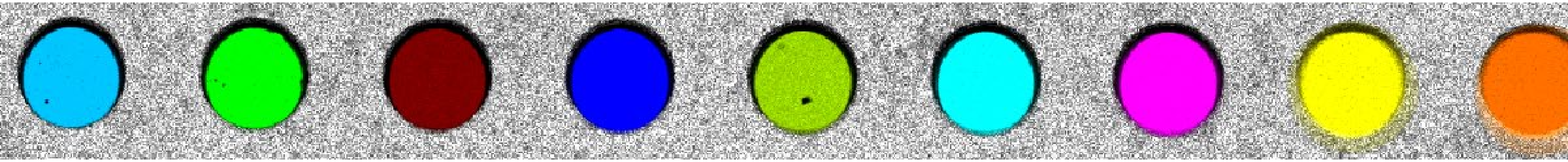
90 kcps



130 kcps



275 kcps



Summary

- The M4 TORNADO^PLUS represents the State of the Art of Bruker's micro-XRF instrumentation
- Several new features, like quick exchange stage, 9-filter-wheel, and high-throughput capability, became standard for the M4 TORNADO, as well
- X-ray tube and detection system of the M4 TORNADO^PLUS are optimized for light element detection
- The lightest detectable element is Carbon, whereas from Oxygen on quantification is feasible
- The collimator changer vastly increases the flexibility of the 2nd X-ray tube
- Flow-controlled Helium purge allows for long-term measurements with minimum sample drying and drastically reduced He consumption
- The Aperture Management System (AMS) increases the depth of field and, thus, allows for better qualitative analysis of uneven surfaces

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Questions, Thoughts, or Comments?

To contact us during the Webinar please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

Please accept our sincere apologies if we can’t discuss all comments and questions within the session!

We will of course answer and discuss those later on by e-mail or in another Webex meeting.