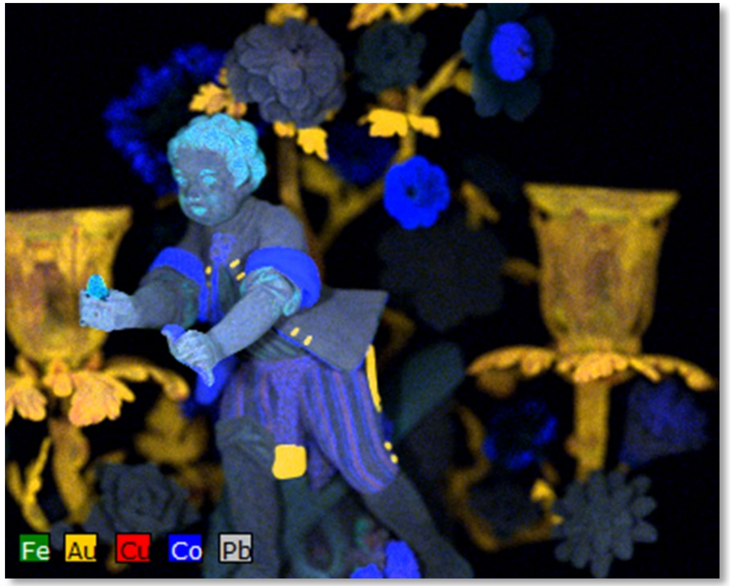
BRUKER NANO ANALYTICS' CULTURAL HERITAGE WEBINAR SERIES 2024

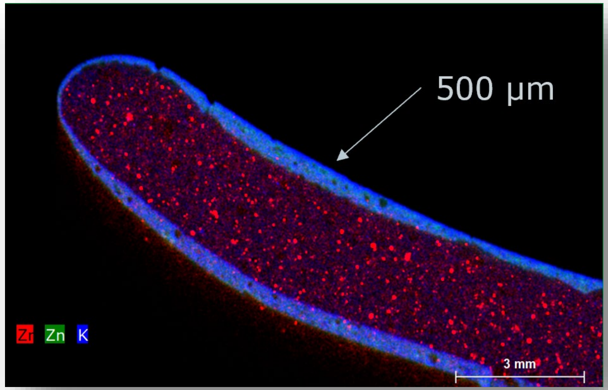
Tracing craftsmanship: Analyzing archaeological objects and handcraft using micro-XRF analysis

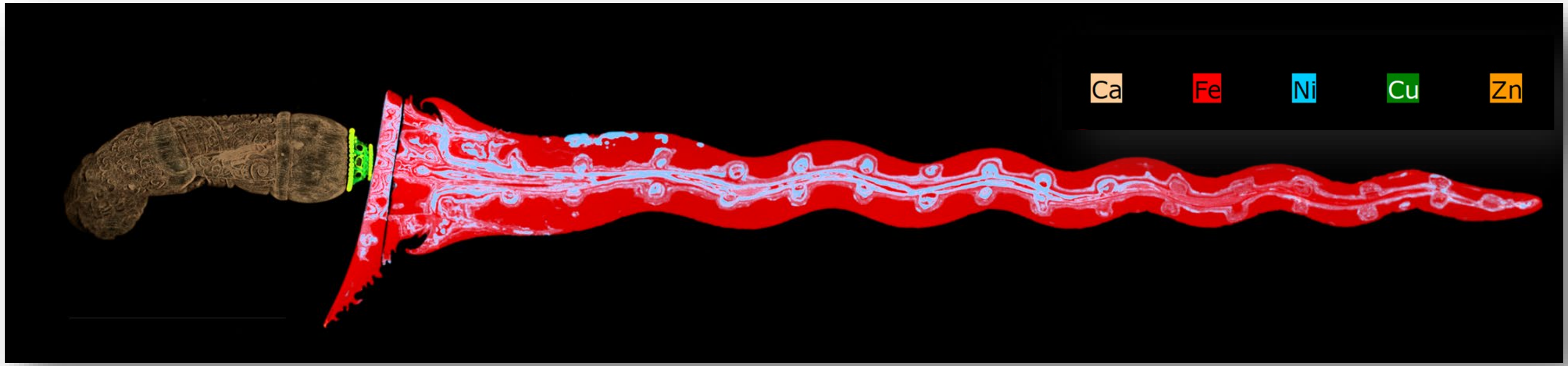
Bruker Nano Analytics

Overview

- This webinar discusses the **analysis of three-dimensional objects**
- Beginning of 2025, we will dedicate a webinar to the **analysis of porcelain and ceramics using micro-XRF**
- Further next year, we will explore the analysis of **manuscripts and written Heritage**







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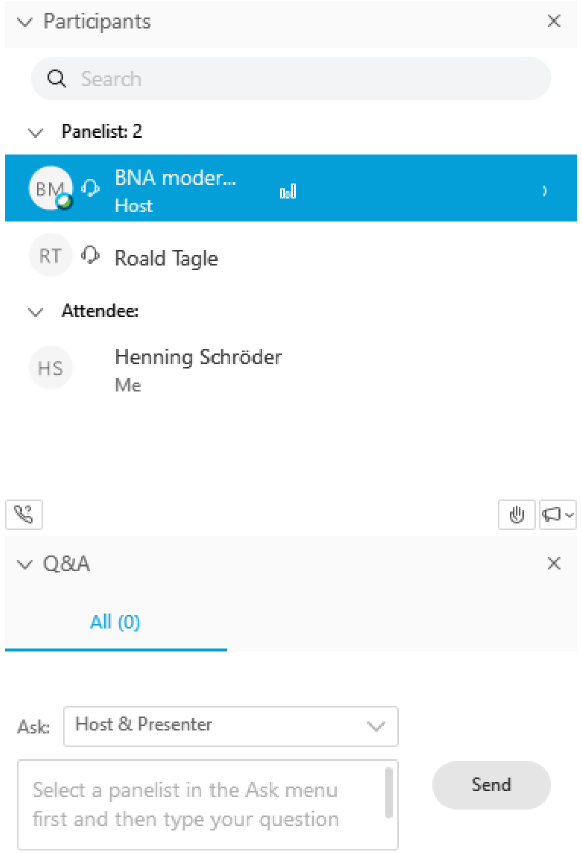
Art & Conservation Webinar Series
Analysis of non-infinite samples in Cultural Heritage

If you have questions during this webinar,

please **type your questions**, thoughts, or comments in the

Q&A box and **press Send**.



We ask for your understanding, if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another WebEx session.

Art & Conservation Webinar Series
The Speakers

Mareike Gerken M.A.

- Application Scientist XMP specialized in Cultural Heritage
  Bruker Nano Analytics, Berlin, Germany

Dr. Roald Tagle

- Global Manager of Application Science, Bruker Nano Analytics, Berlin, Germany

BRUKER NANO ANALYTICS' CULTURAL HERITAGE WEBINAR SERIES 2024

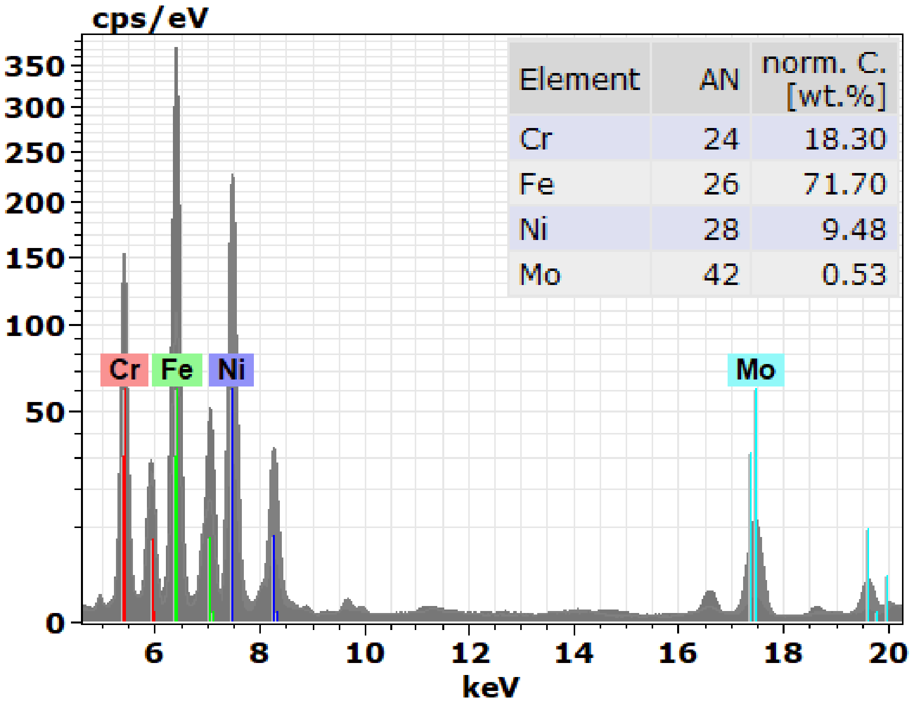
What is micro-XRF?

What is micro-XRF?
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.

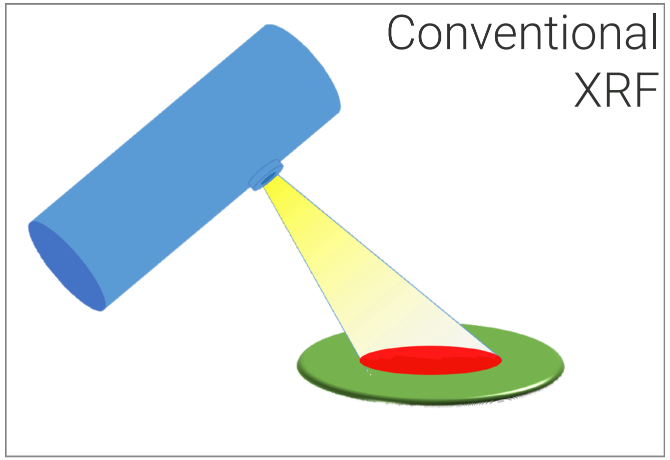
Information is lost!

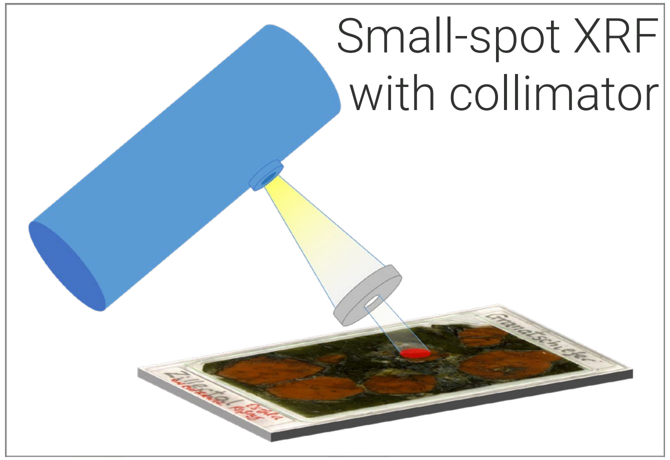
The compositional variations in a sample may be a crucial property of the material

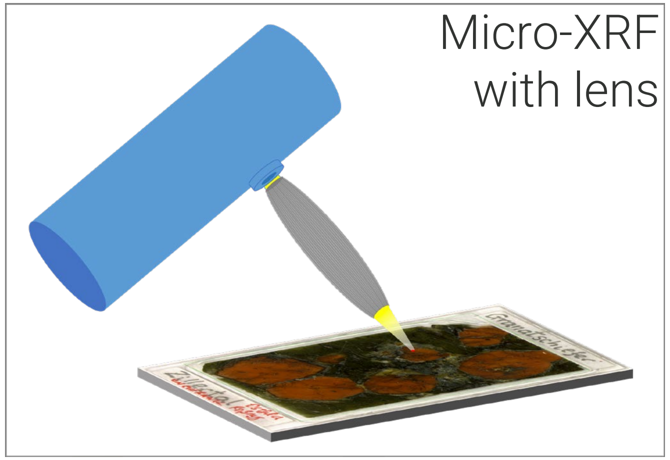


Element	AN	norm. C. [wt.%]
Cr	24	18.30
Fe	26	71.70
Ni	28	9.48
Mo	42	0.53

What is micro-XRF?
From XRF to micro-XRF





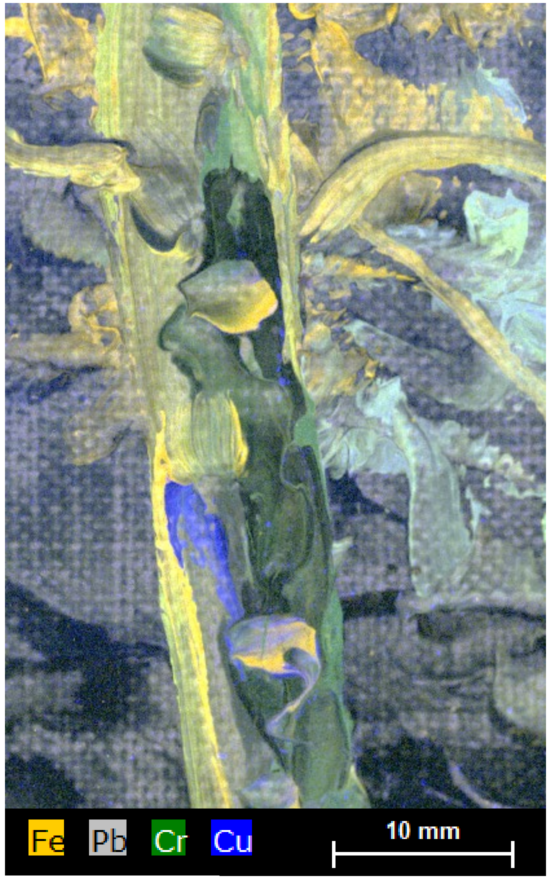


Composition

Compositional variations

What is micro-XRF?
Micro-XRF

- Micro-XRF is spatially resolved XRF.
  - →Micro-XRF reveals where elements are.
  - →Micro-XRF is ideal for non-homogeneous samples.
- It usually requires minimal or no sample preparation.
- Qualitative and semi-quantitative analysis is always possible
- 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.



The challenge
Highly-topographic Cultural Heritage objects

What types of objects are we talking about?

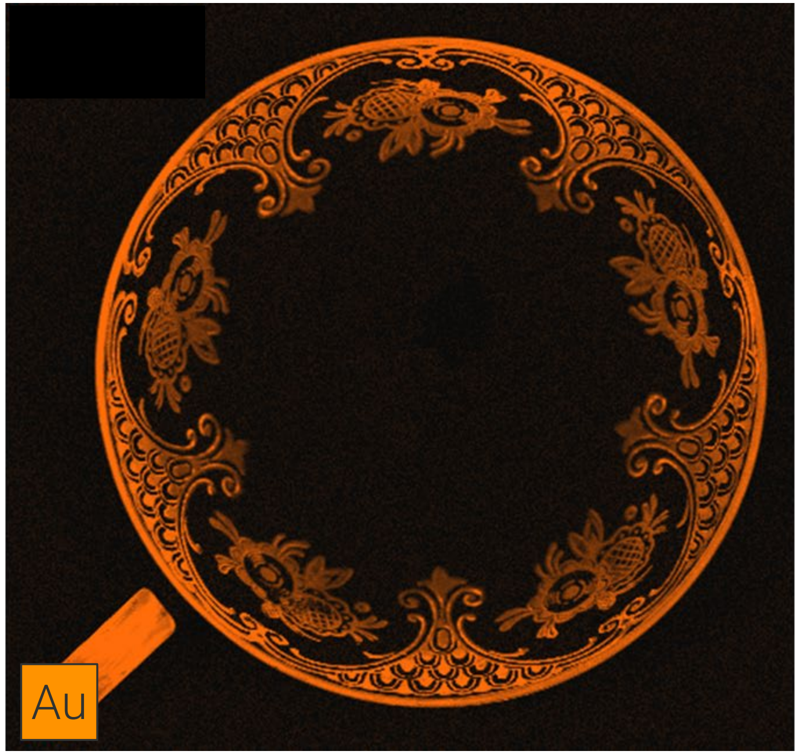
- Metals
- Porcelain and ceramics
- Glass
- Decorated wooden or stone objects
- …

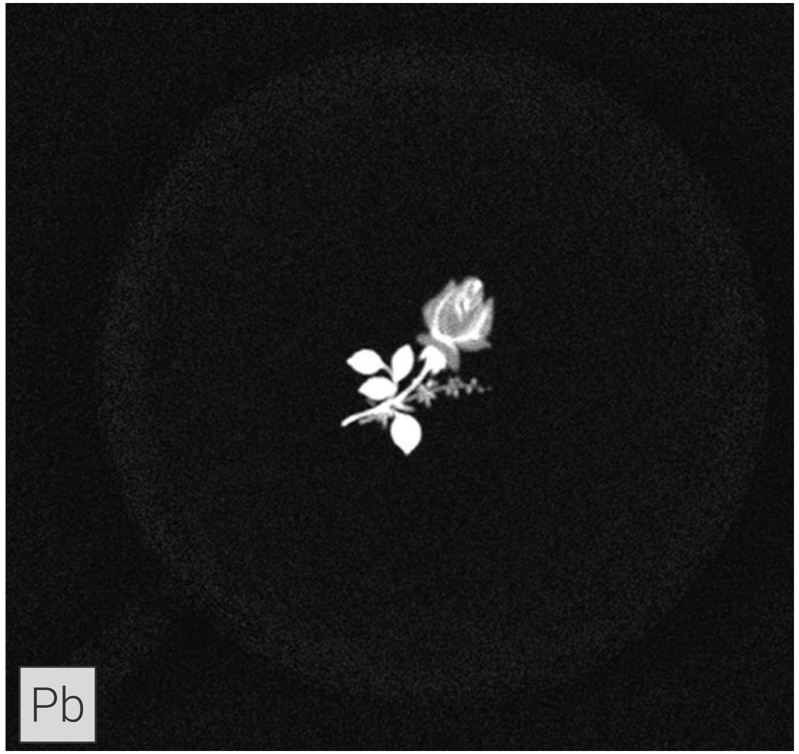
Which research questions can be answered using XRF?

- Provenance (origin and dating)
- Composition
- Technology and production
- State of preservation and previous treatments




How can we get the information difficult to reach?
A porcelain teacup





The finely painted flower motiv and gold decoration is located down to 4 cm deeper than the cups edge.

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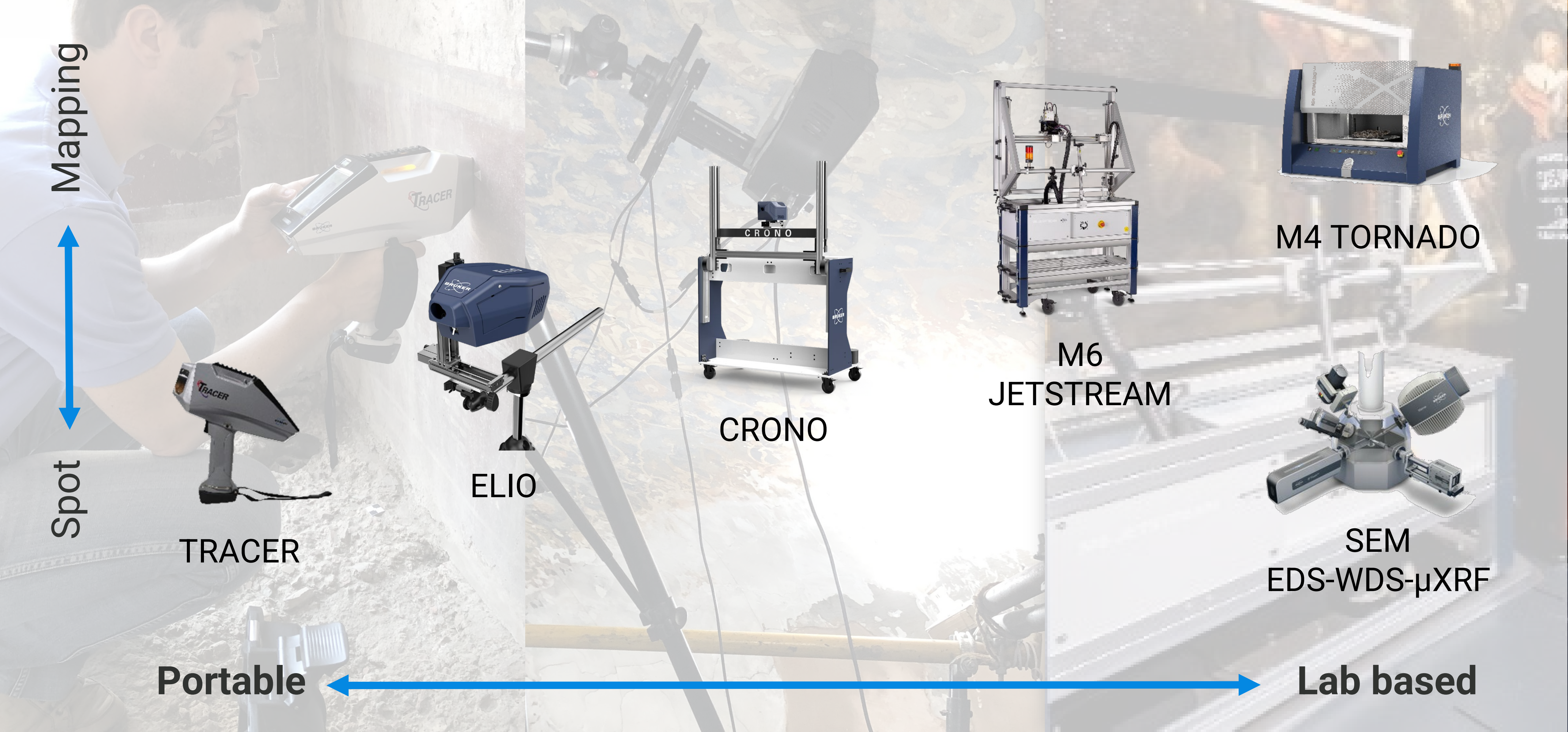
Introducing the instrumentation

XRF, Art and Collections Management



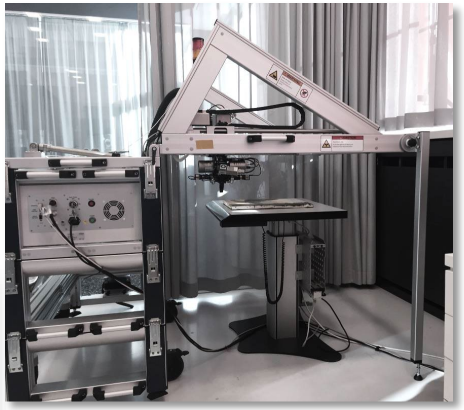
ELIO mapping XRF

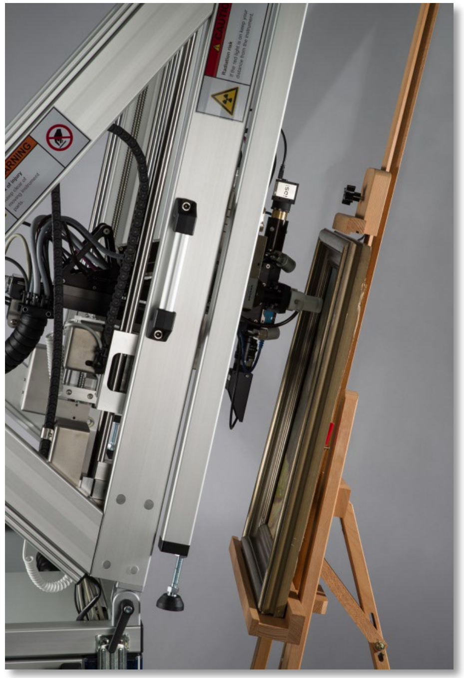
Flexibility of approach and positioning – ideal for different objects on-site and in the lab

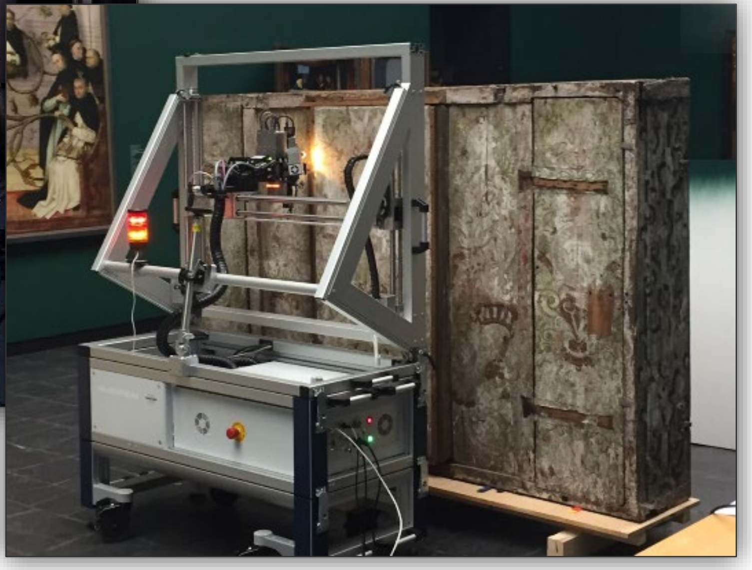
Mesoamerican manuscripts, Bodleian Library Oxford *(see Grazia et al. 2019)*

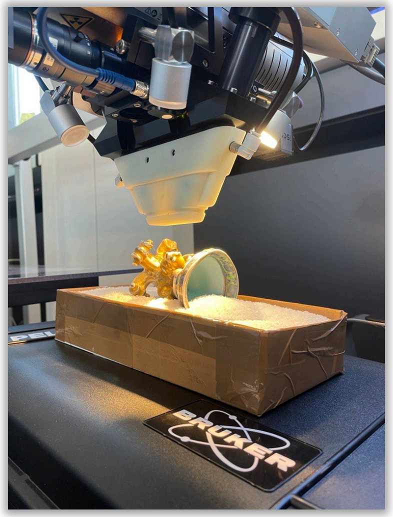
M6 JETSTREAM large-area micro-XRF mapping

Museum- & lab-based mapping solution





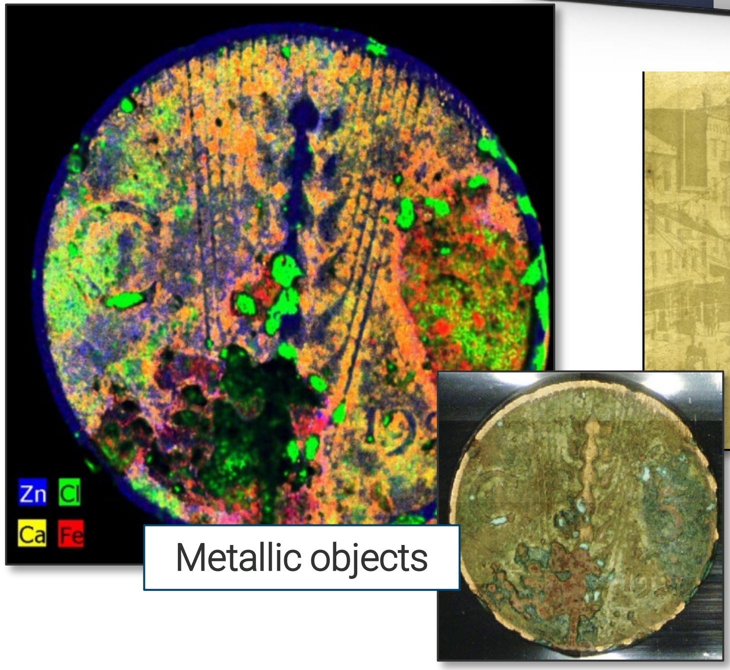




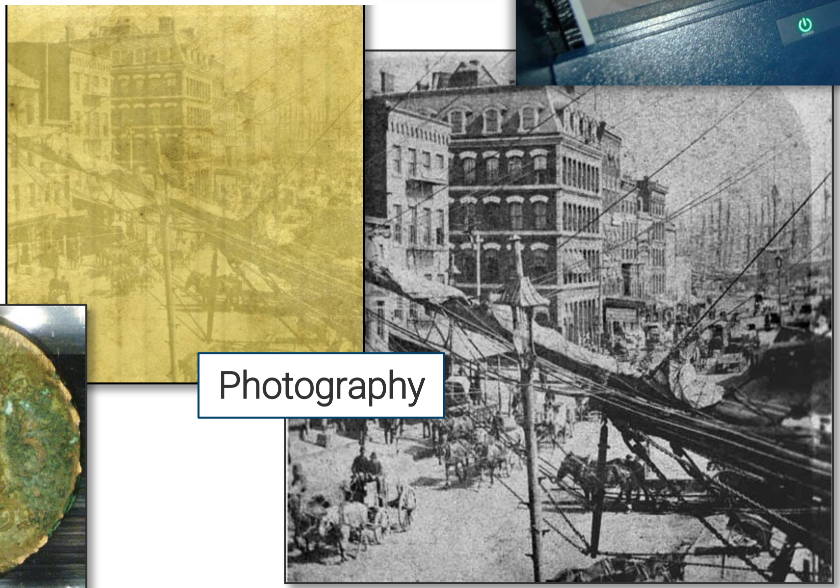
M4 TORNADO micro-XRF

Small spot, closed-beam µXRF

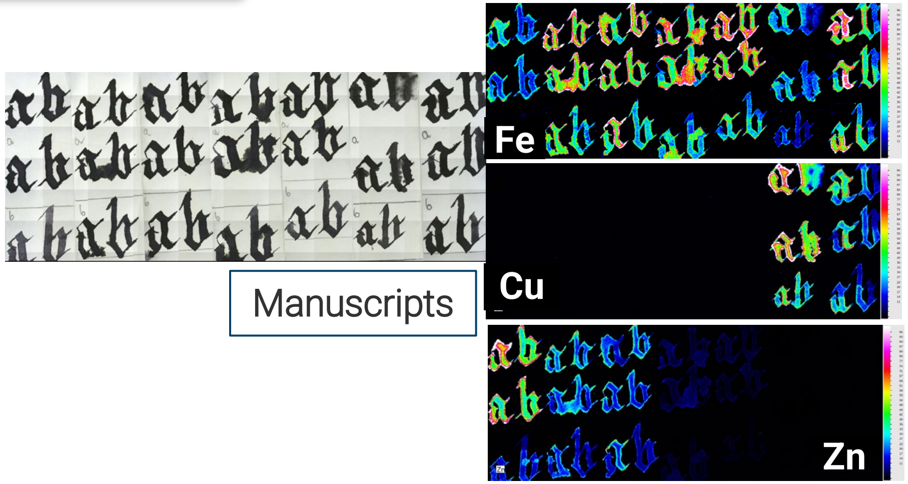
Painted artwork



Metallic objects



Photography



Manuscripts

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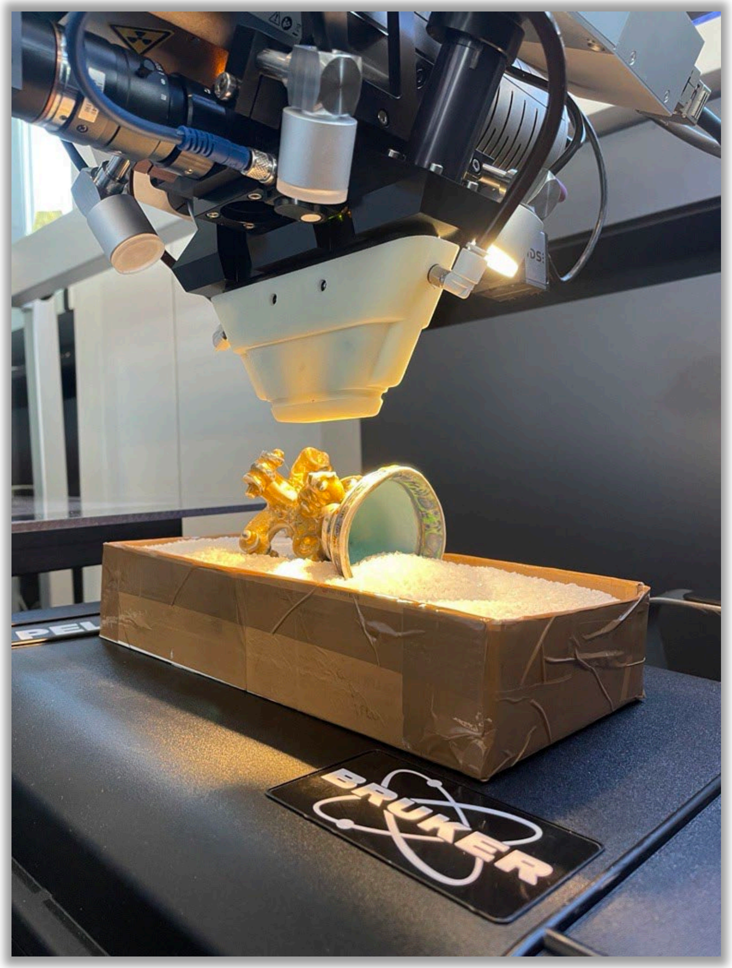
Micro-XRF analysis
An Introduction to Porcelain studies

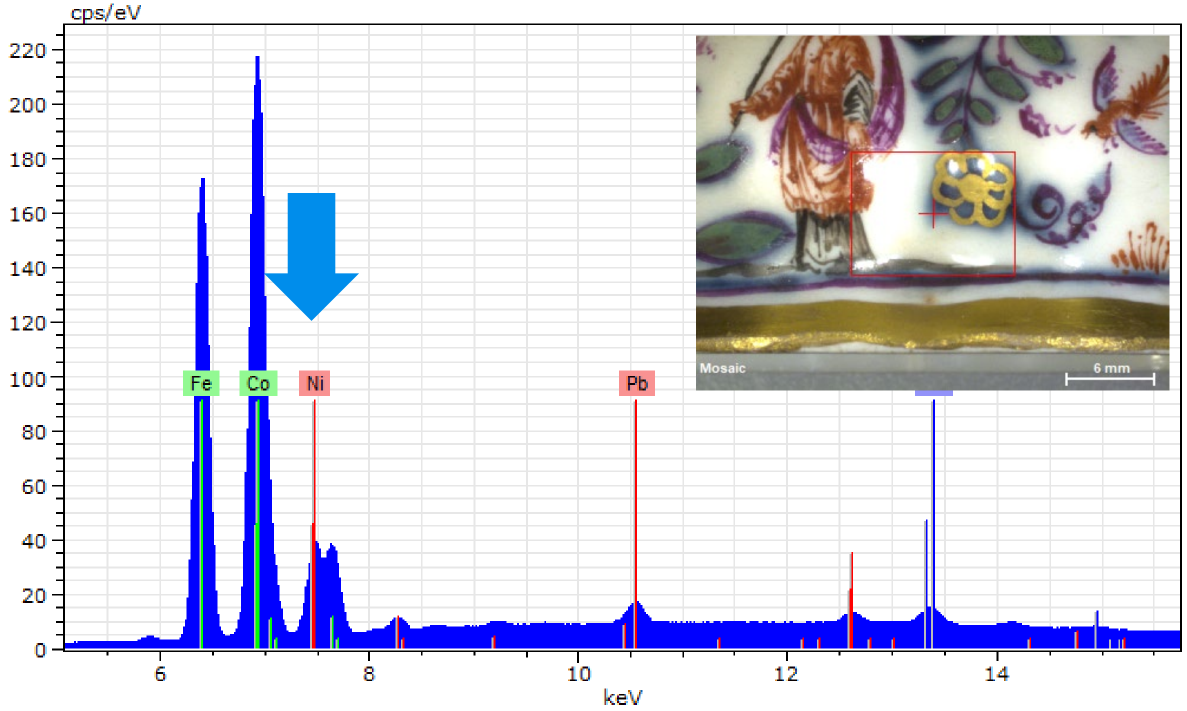
Porcelain analysis
Sample positioning

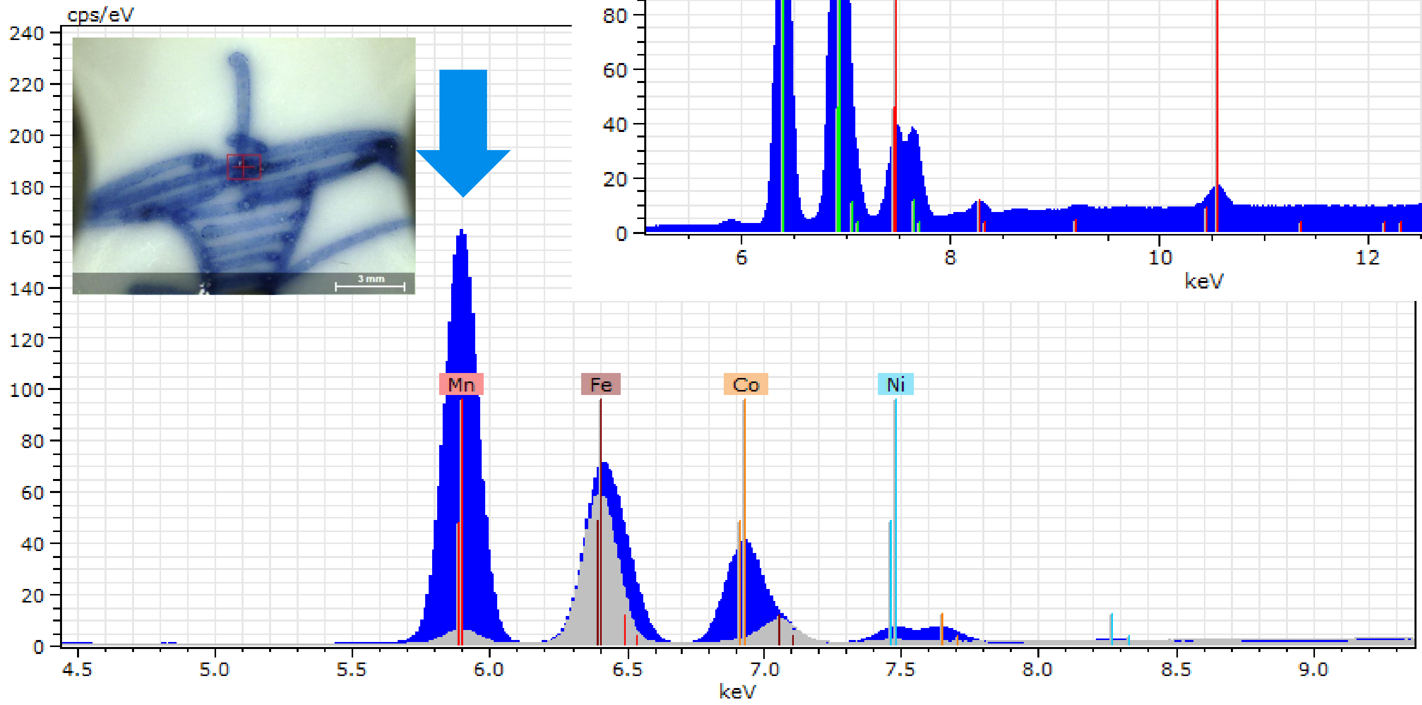
- Pigments
- Glaze
- Composition



Porcelain analysis
An Introduction

- Pigments
  - Pitfalls: Non-infinitely thick
  - Qualitative analysis
  - Common questions:
    - Colour components
    - Trace elements
    - Additives
- Glaze
- Composition



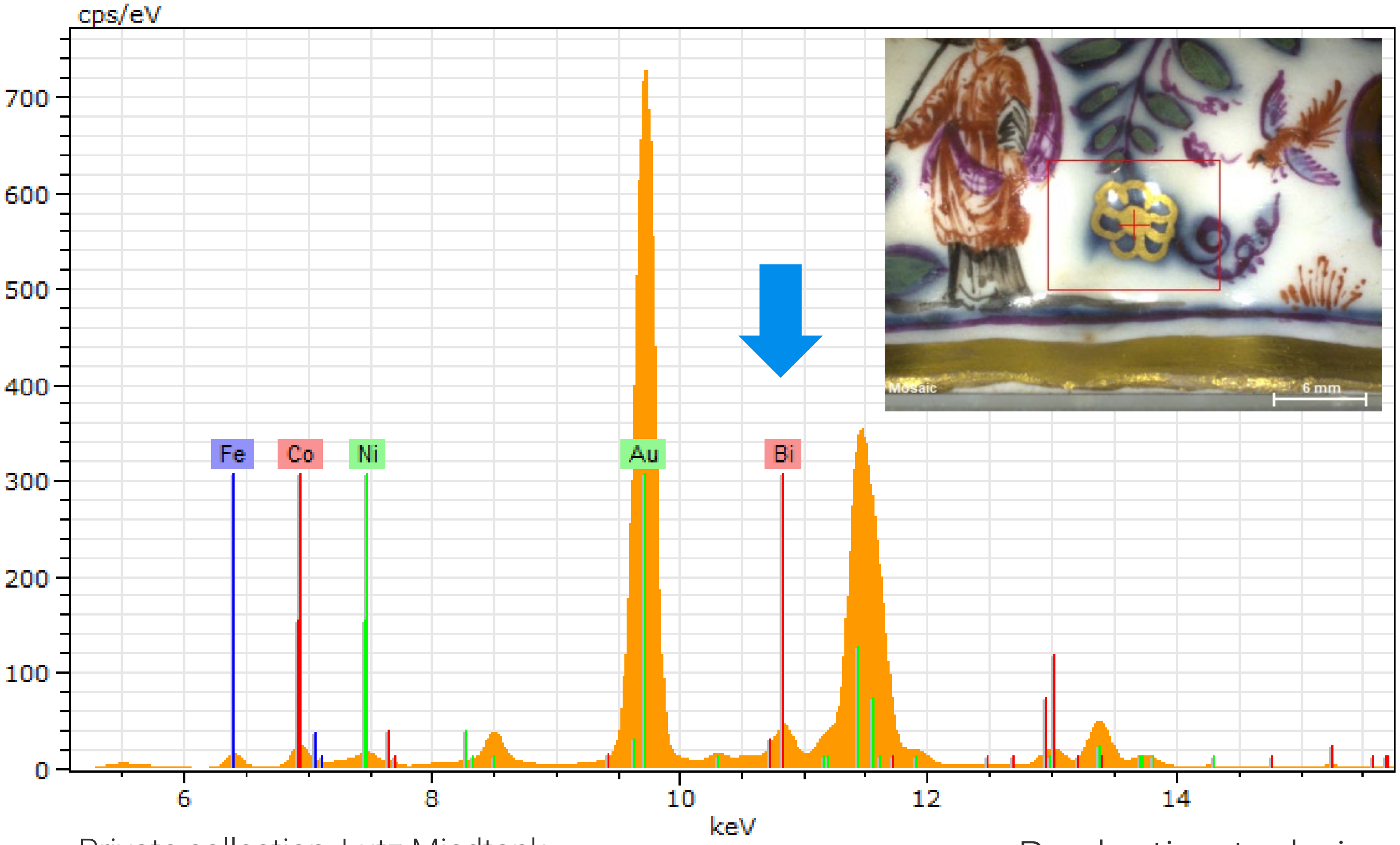


Provenance studies on cobalt blues

Private collection, Lutz Miedtank.

Porcelain analysis
An Introduction

- Pigments
  - Pitfalls: Non-infinitely thick
  - Qualitative analysis
  - Common questions:
    - ➢ Colour components
    - ➢ Trace elements
    - ➢ Additives
- Glaze
- Composition

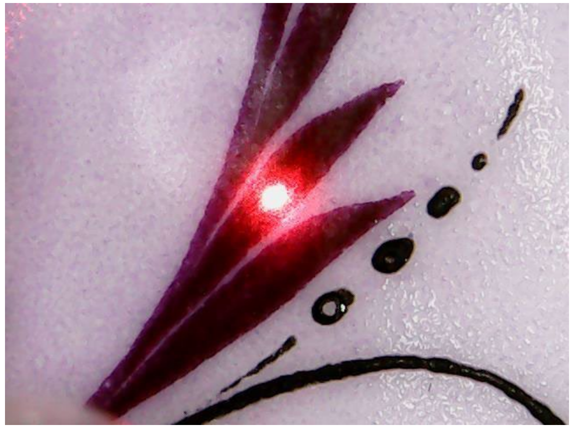


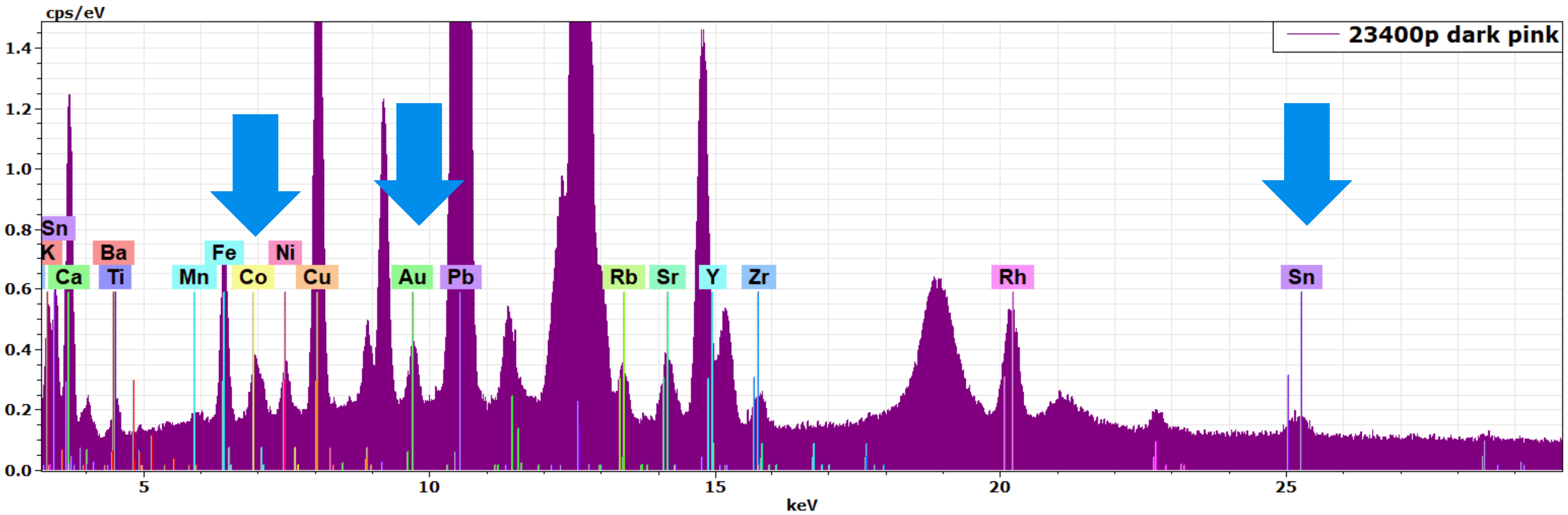
Private collection, Lutz Miedtank.

Production technique of the gilding

Porcelain analysis
An Introduction

- Pigments
  - Pitfalls: Non-infinitely thick
  - Qualitative analysis
  - Common questions:
    - Colour components
    - Trace elements
    - Additives
- Glaze
- Composition

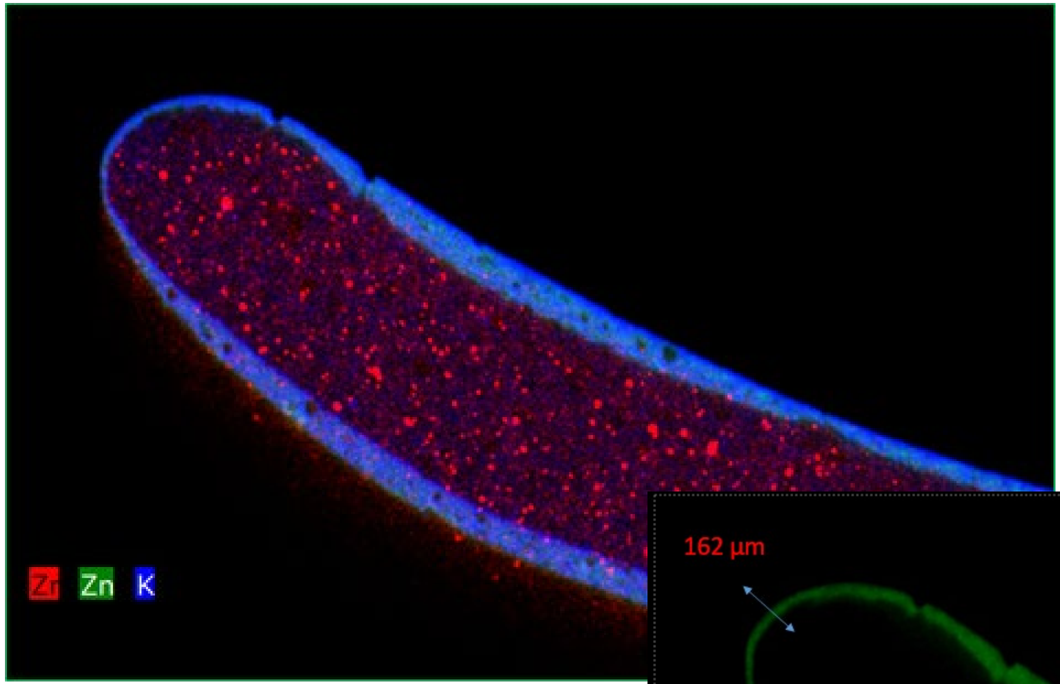


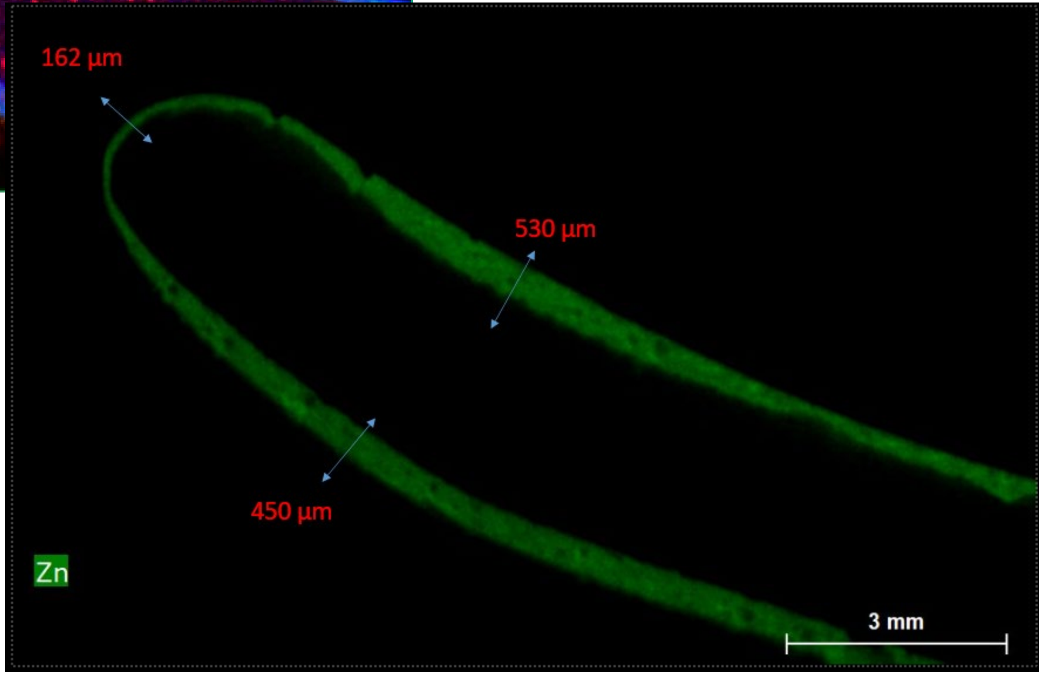


Sèvres Manufacture and Museum.

Porcelain analysis
An Introduction

- Pigments
- Glaze
  - Pitfalls: Non-infinitely thick
  - Qualitative analysis
  - Common questions:
    - ➢ Porcelain technology: e.g. hard or soft past
    - ➢ Composition and additives
    - ➢ Thickness determination
- Composition





Approaches to quantitative analysis will be discussed in the next webinar!

Porcelain analysis
An Introduction

24 Meissen 1730-1735 | Kangxi 1700-1720 Export-Porzelain | Yongzheng, 1730 Export-Porzelain | Qianlong 1760 Export-Porzelain | 20 century?

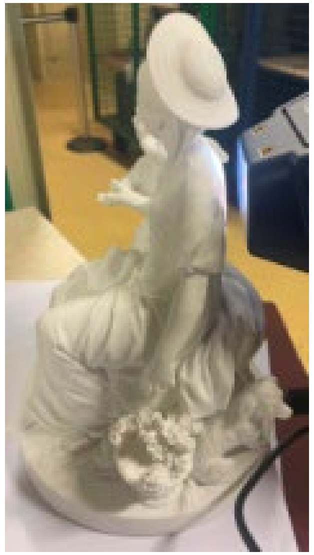
- Pigments
- Glaze
- Composition
  - Pitfalls: Non-glazed area of the body
  - Quantitative analysis
    - ➢ Vacuum is a plus as also light elements can be quantified without references
    - ➢ Relative abundancies can also be measured at air indicating provenance or standard-based approaches
  - Common questions:
    - ➢ Provenance studies

Spectrum	Al2O3	SiO2	SO3	K2O	CaO	TiO2	MnO	Fe2O3
4	25.4	65.2	0.61	5.29	1.11	0.21	0.16	1.59
5	26.3	64.7	0.51	4.65	1.82	0.10	0.17	1.64
6	30.6	62.7	0.17	4.11	0.91	0.06	0.11	1.30
8	18.8	71.9	0.13	4.49	3.20	0.05	0.12	1.25
11	25.8	66.2	0.21	4.91	1.22	0.06	0.15	1.31
12	25.1	66.0	0.00	5.41	1.62	0.09	0.13	1.54
14	23.5	68.8	0.14	4.47	1.24	0.07	0.14	1.42
23	36.7	58.6	0.34	2.96	0.69	0.02	0.01	0.60
24	34.0	60.0	0.35	4.23	0.60	0.07	0.01	0.52
29	26.2	65.7	0.63	5.71	0.37	0.22	0.02	0.93

Private collection, Lutz Miedtank.

Sévres Porcelain Manufacture
Biscuit: Provenance studies

Sèvres
MNC 2641



Sèvres
MNC 21134

Unknown
MNC 2024.4.1

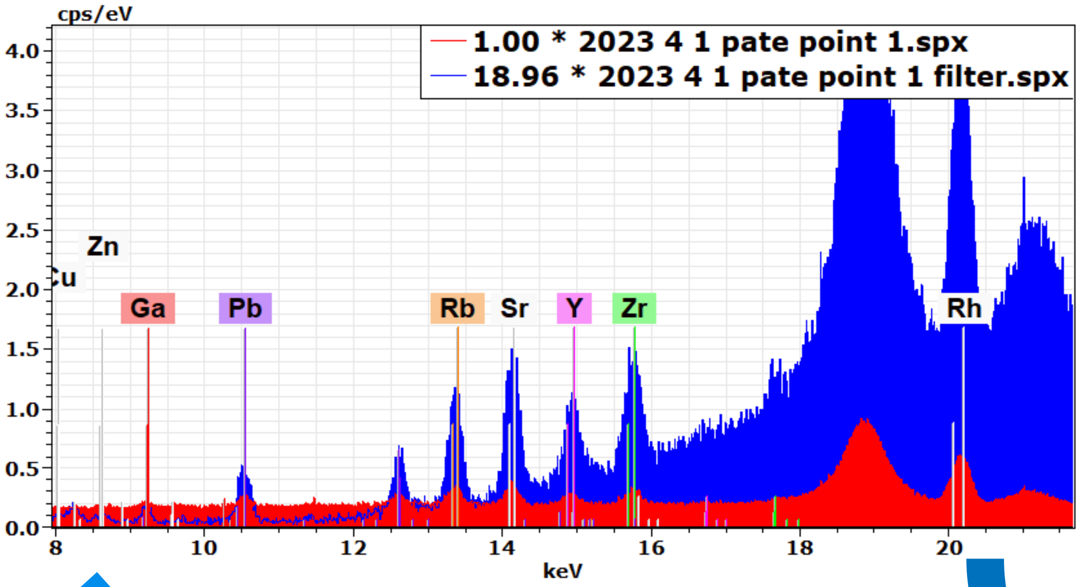
Limoges
MNC 25341

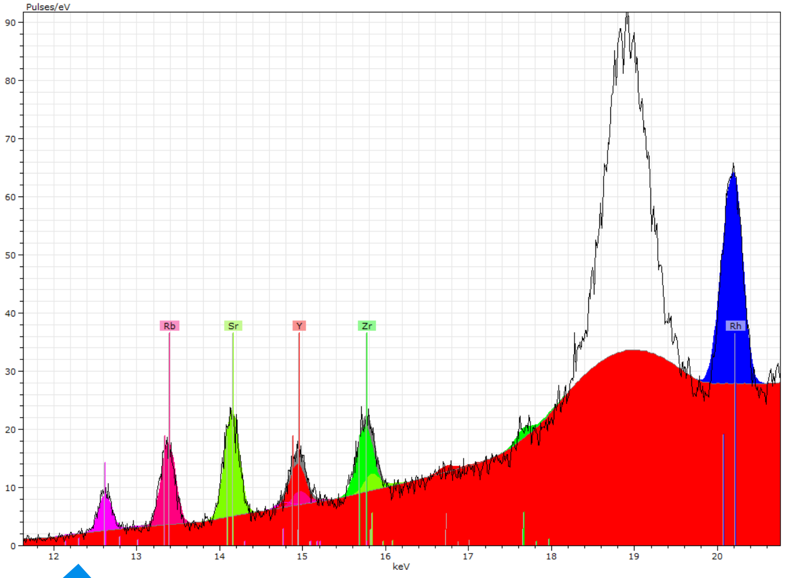
Sèvres?

Limoges?

Porcelain analysis
Tuning excitation conditions

Unknown
MNC 2024.4.1





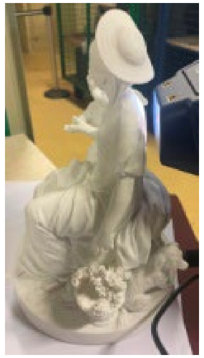
Using a strong filter to enhance peak-to-background ratio for high-energy trace elements

Extracting net intensities for ratio analysis

Porcelain analysis
Biscuit: Provenance studies

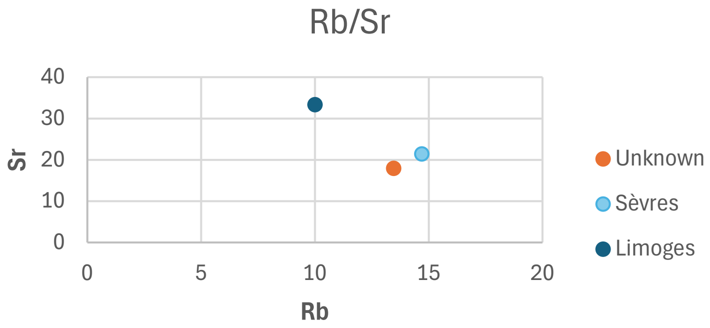
Unknown
MNC 2024.4.1

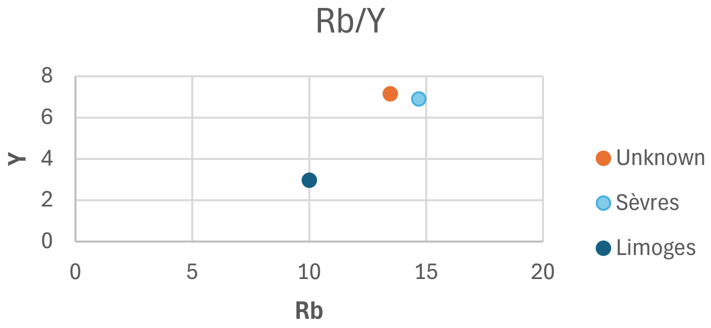
Sèvres
MNC 2641

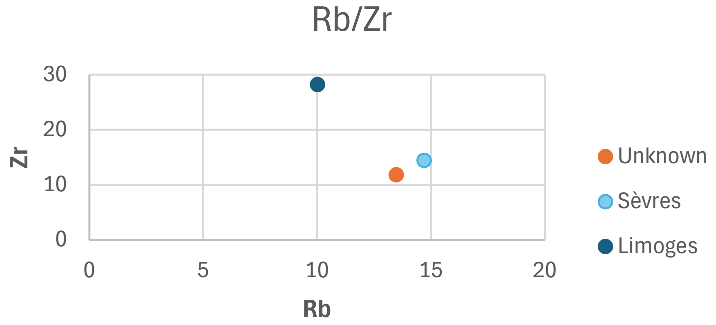


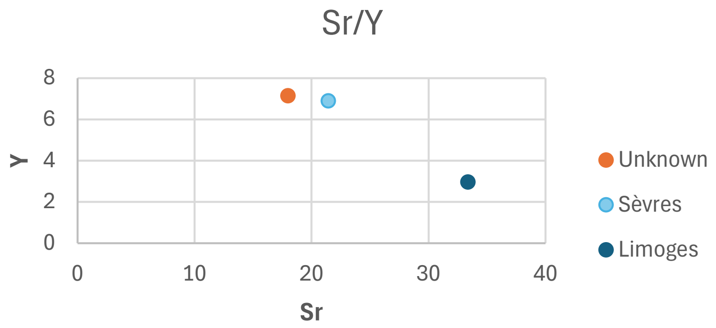
Sèvres
MNC 21134

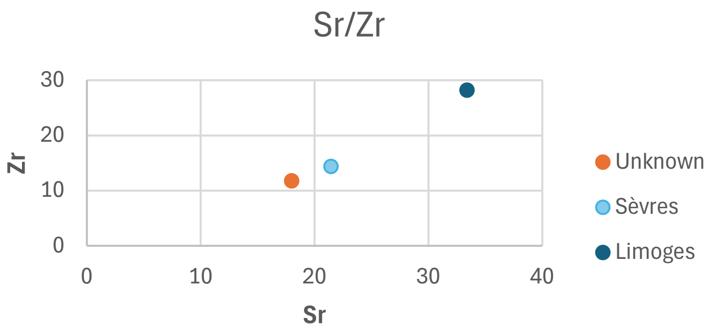
Limoges
MNC 25341

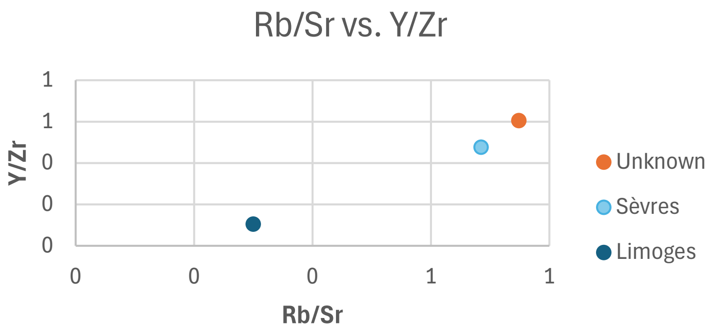












The unknown object is from the Sèvres workshop!

Mapping intricate three-dimensional objects
Do we need to keep a constant distance to the object's surface?

Private collection, Lutz Miedtank.

1. Topography cannot be followed.
2. Danger for the object as well as the instrument due to crash.
3. Increase of measurement time due to task complexity.
4. Simpler data interpretation and visualization.

We use a different approach!

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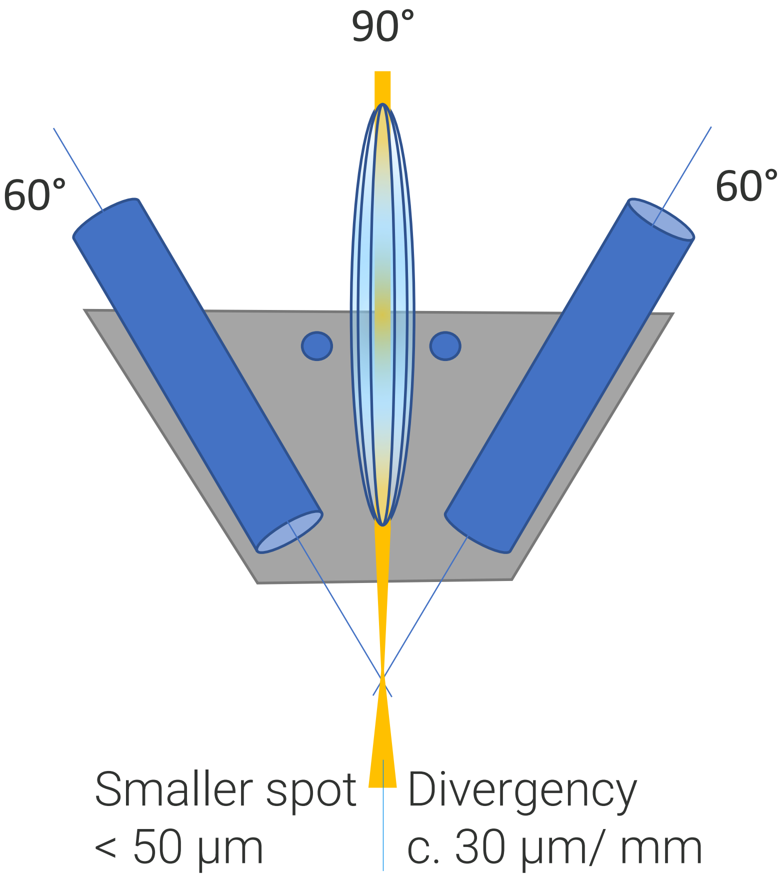
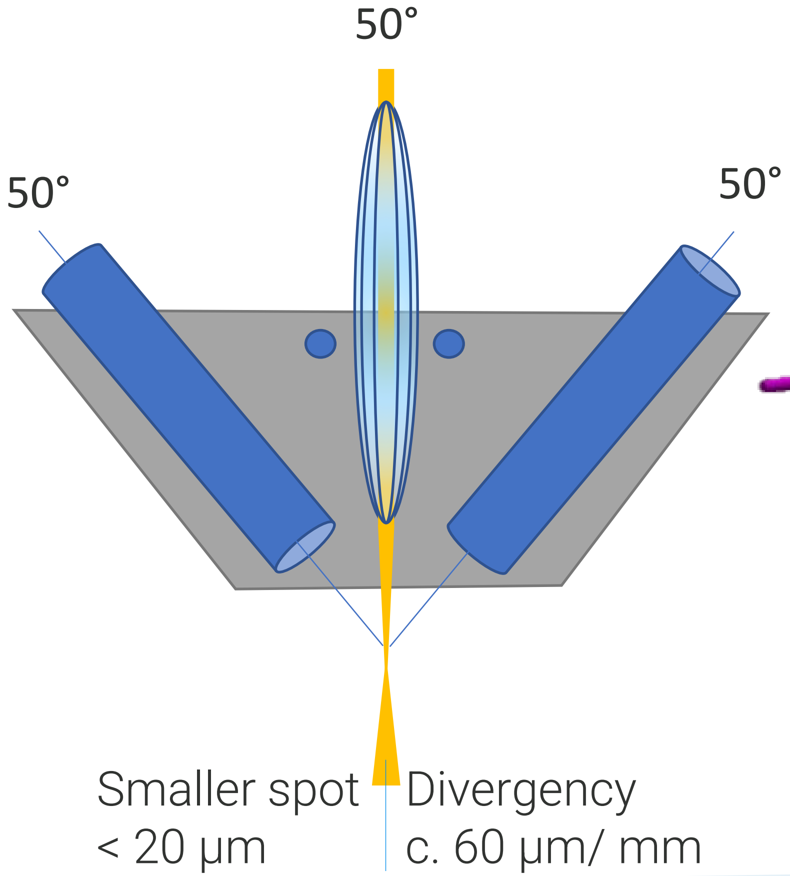
Introducing the AMS feature for measuring highly-topographic samples

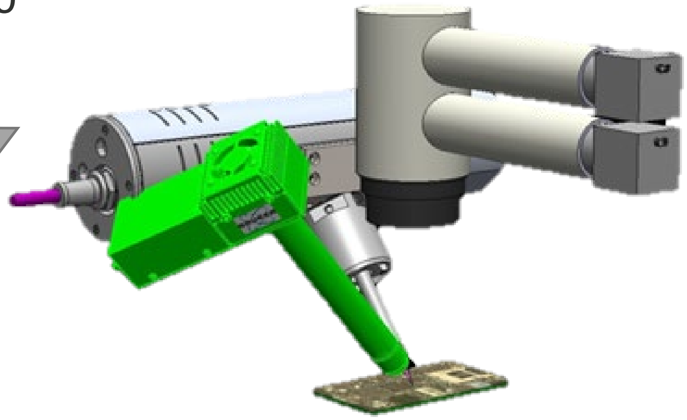
Understanding your instrument
Hardware geometry of excitation and detection

M6 JETSTREAM



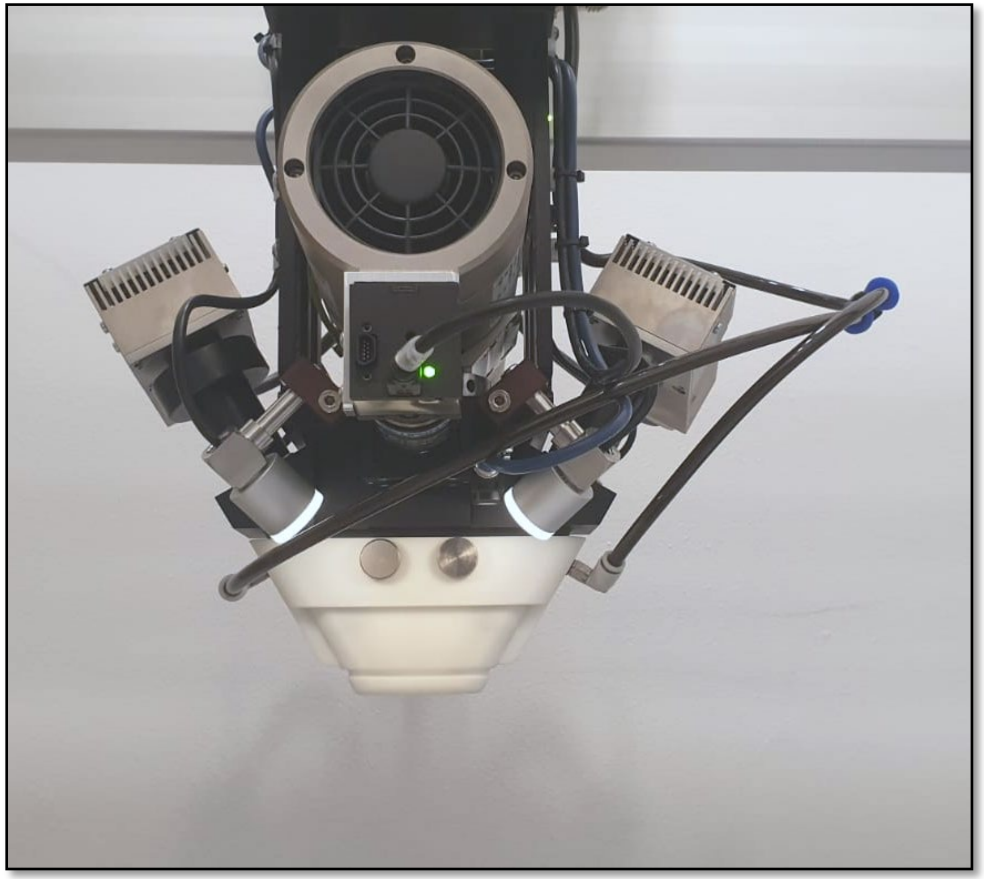
M4 TORNADO





Dual detector technology
…as implemented in the M6 JETSTREAM

- Double detector technology with 2x60 mm² SDD (**4x the detector area of the prototype**)
  30 mm² → 60 mm² factor **~1.7 intensity improve**



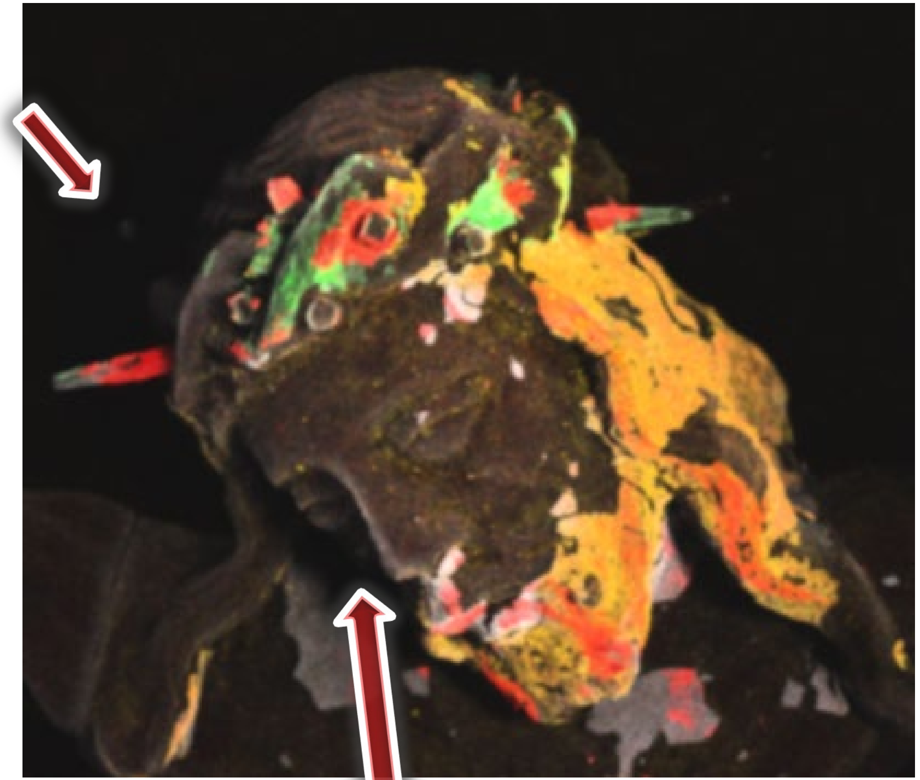
- **High throughput technology**
  to improve data acquisition rate over 300 kcps

- Better visualization of non-flat samples

- **Patented Aperture management system**
  for improved spatial resolution

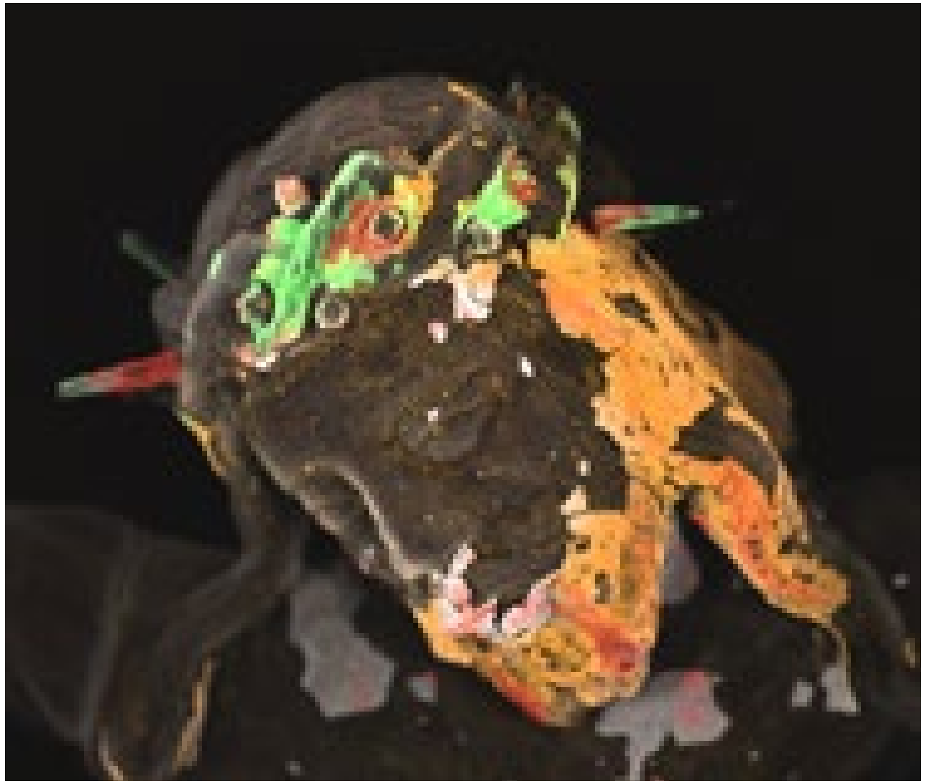
Dual detector technology
Shadow effects of a single SDD system

Single detector
“looking” from the right



Detection “shadow”

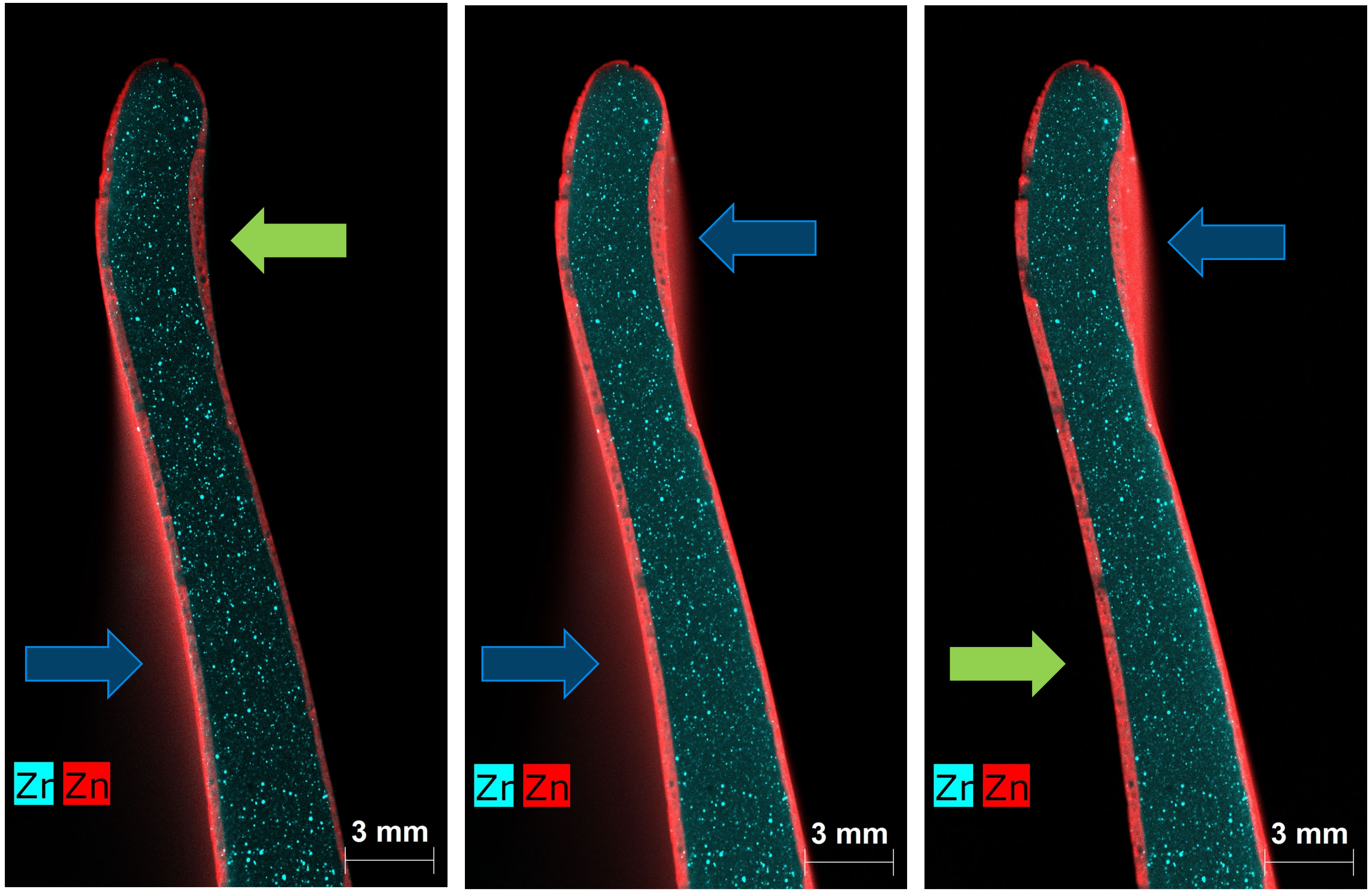
Double detector
“looking” from both sides



M4 TORNADO: Dual detector technology
Benefits of choosing the point of view

The polished edge of a ceramic sample placed vertically.

Left detector | Both detectors | Right detector



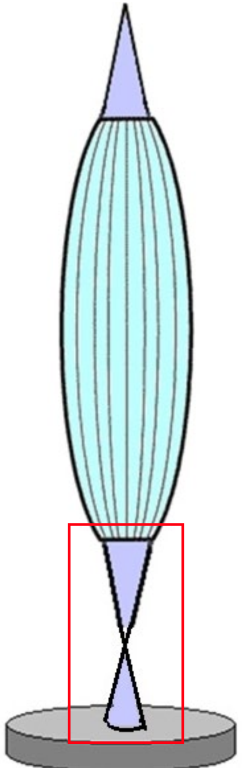
Choice of detector enables “cleaner” edges

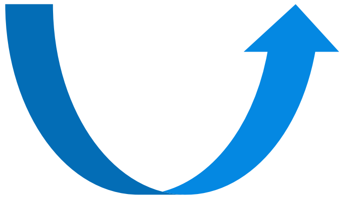
M6 JETSTREAM: Lens divergency
Spot size and working distance

Instrument has 5 configured working distances. Spot sizes between 100 µm and ~500 µm can be selected. Maximum spot size depends on lens.

The distance between one and the next configured spot size is ~ 3.2 mm. The WD can is defined by a sharp image in the high magnification camera at the respective camera position.

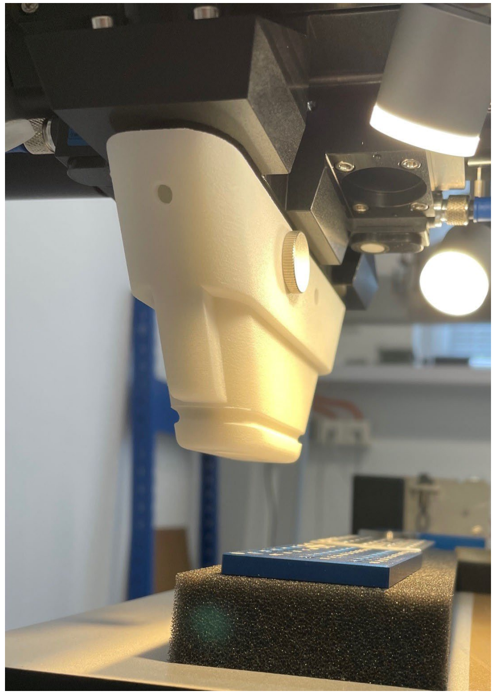
For our used lenses we can defined ~ 100 µm every 3 mm with out the AMS.



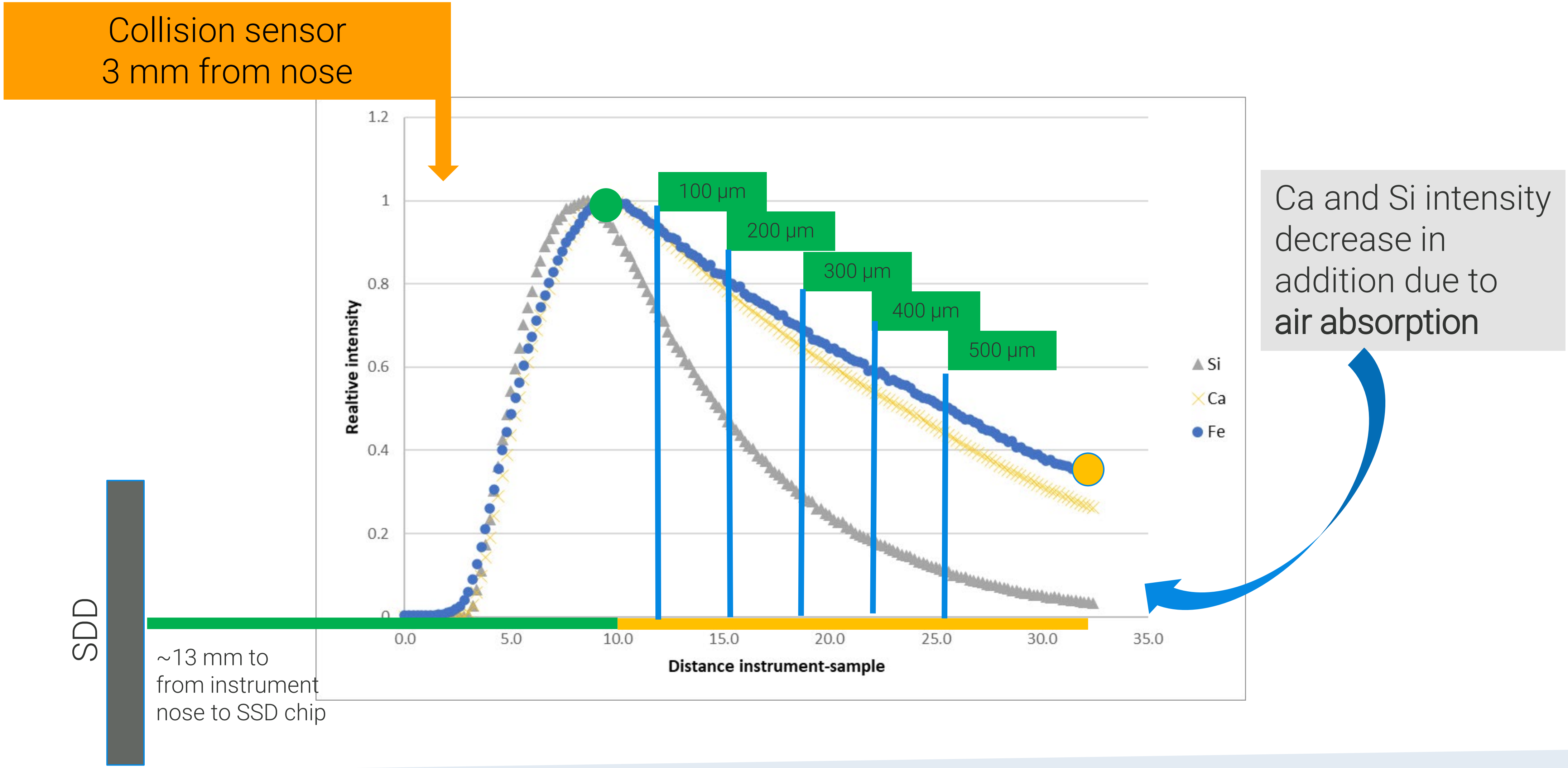


WD @ smallest configured spot size ~ 13 mm

WD @ largest configured spot size ~ 25 mm

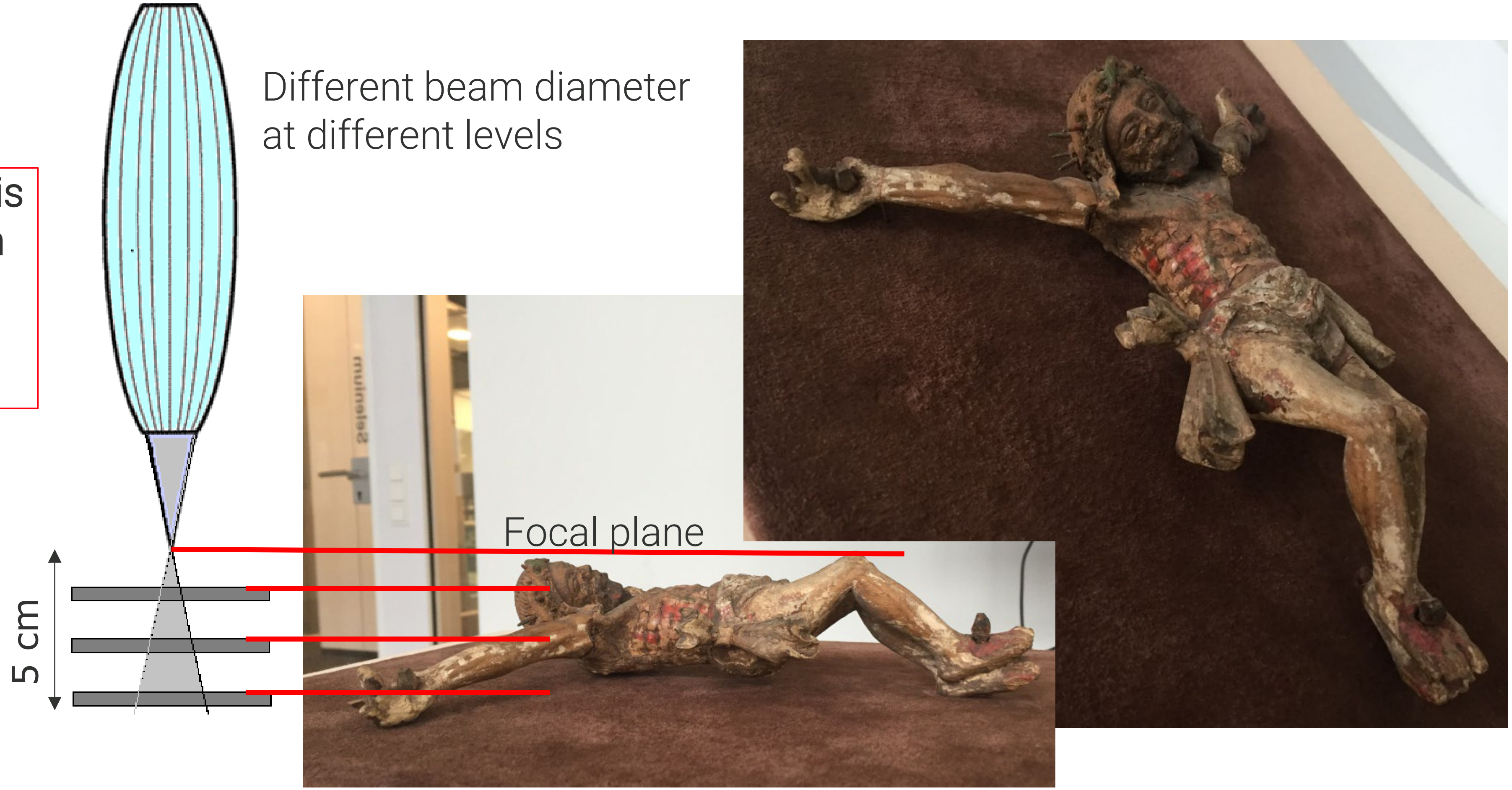


M6 JETSTREAM: Calibrated working distances
Intensity variation on a glass sample

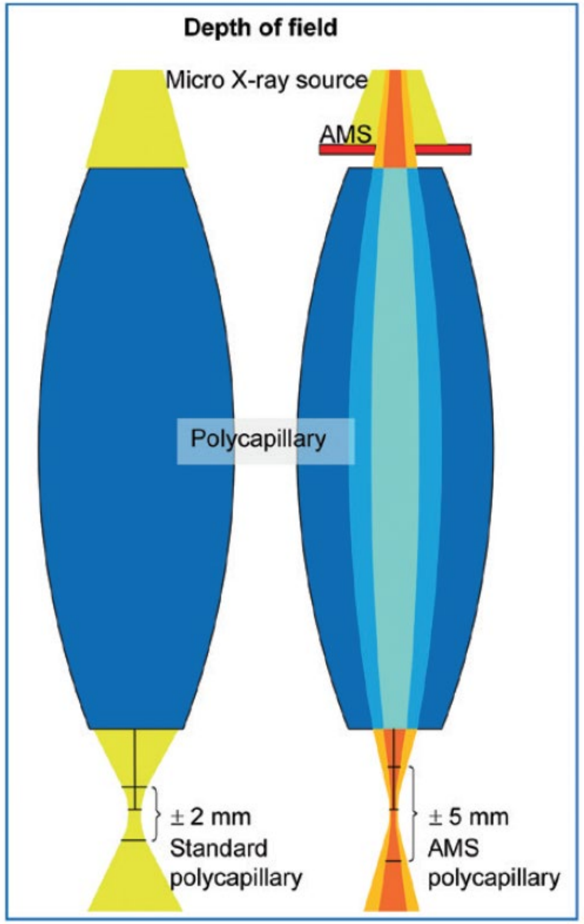


Mapping highly topographic samples with high spatial resolution
Aperture Management System (AMS)

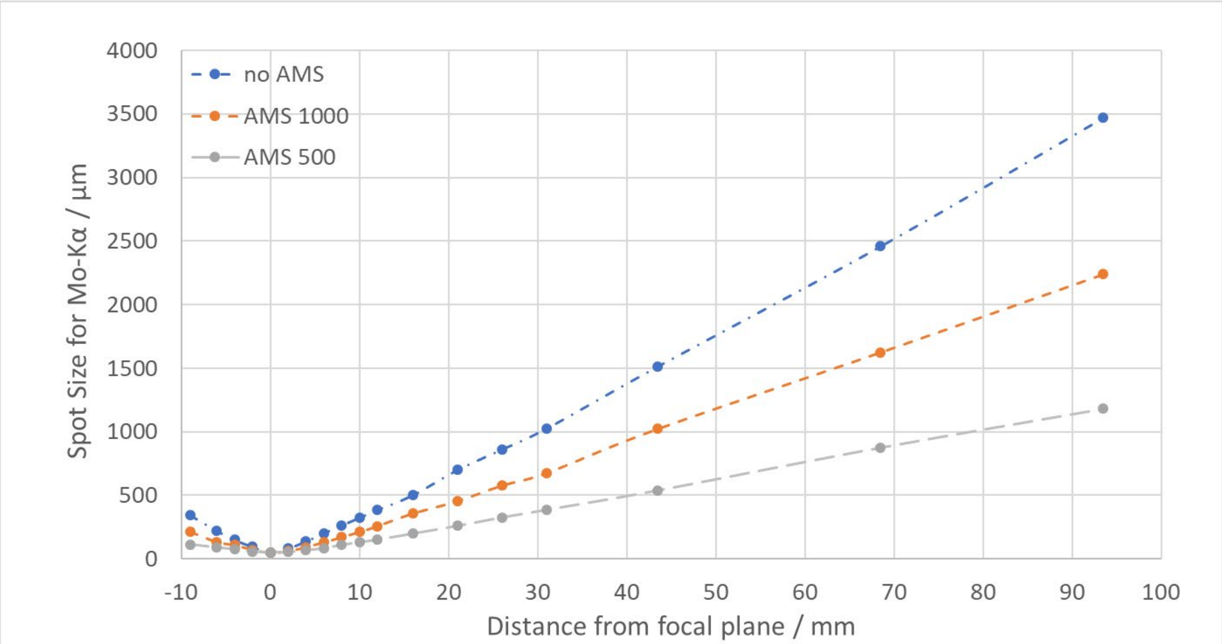
If the object is not flat, each focal plane has its own spot size!



Mapping highly topographic samples with high spatial resolution
Aperture Management System = Almost Monocapillary system (AMS)



Aperture management – patented.

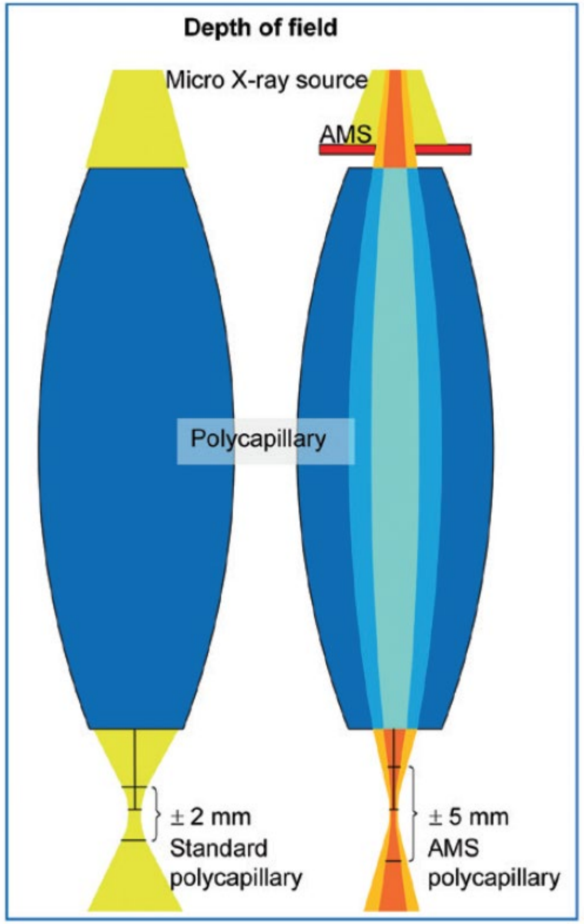


At 10 cm working distance
4 mm
2.5 mm
1.2 mm

3 cm out of focal plane the spot size is reduced

from	1000 µm	(without AMS)
down to	< 700 µm	(for AMS 1000)
or even	< 400 µm	(for AMS 500)

Mapping highly topographic samples with high spatial resolution
Aperture Management System = Almost Monocapillary system (AMS)



Aperture management – patented.

The AMS reduces the number of photons that reach the sample.

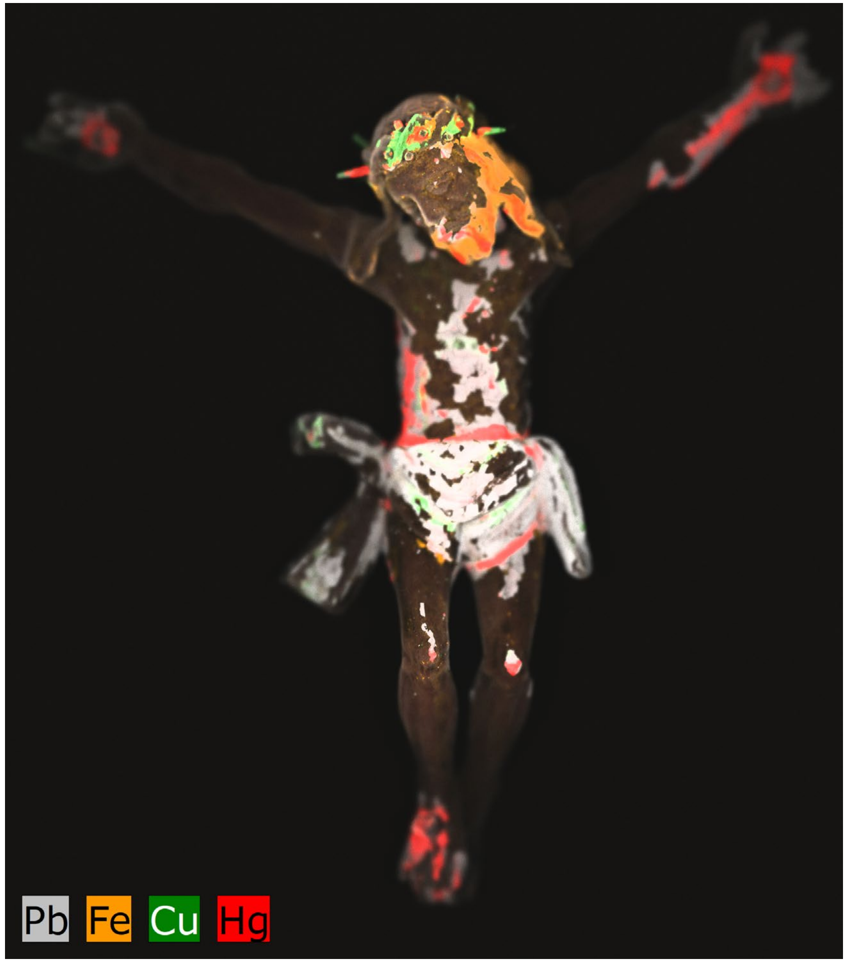
The AMS 1000 (µm opening) reduces the intensity by a factor of ~3,

the AMS 500 (µm opening) down by a factor ~7.

This effect is somehow cushioned by the increased solid angle of detection and signal processing capabilities of the 2x 60 mm² SDDs.


Pb
Fe
Cu
Hg

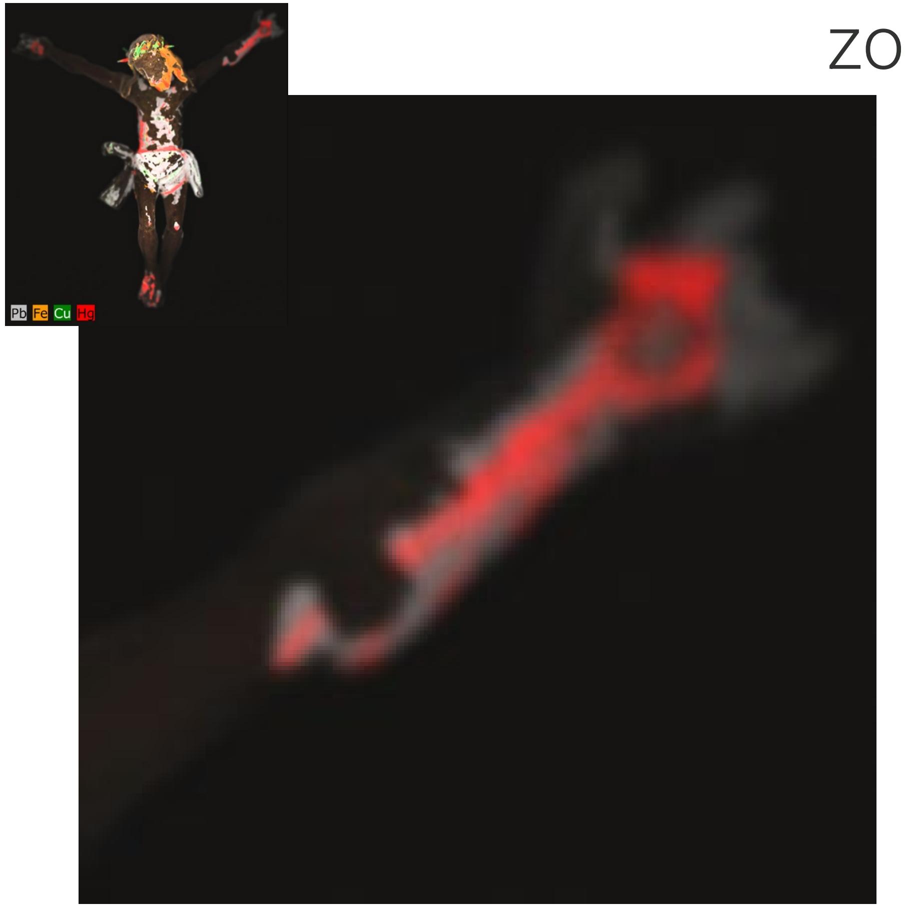
Using the AMS
Maintaining a high spatial resolution across the entire surface



Standard setting

AMS 500 µm

Using the AMS
Maintaining a high spatial resolution across the entire surface



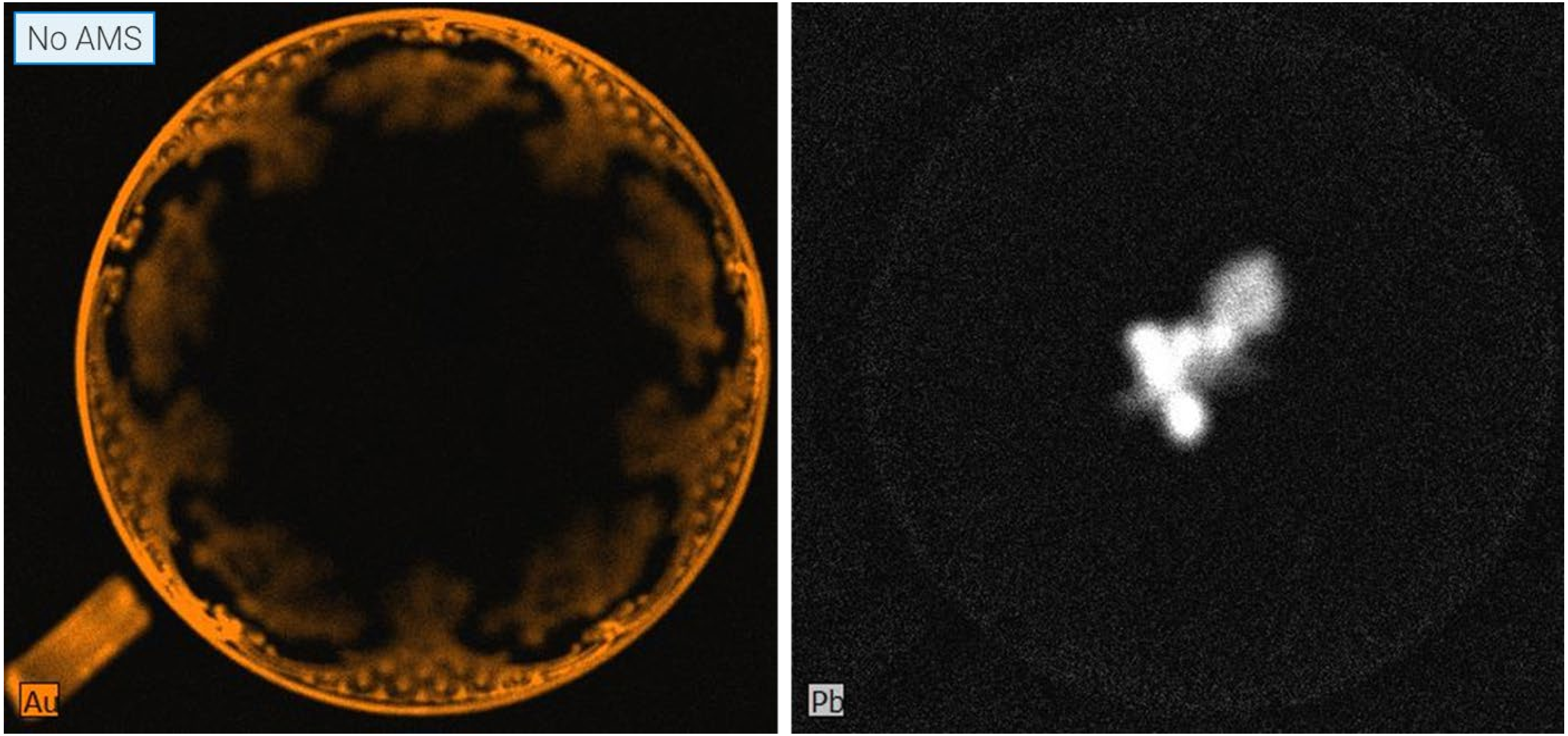
zoom

Standard setting

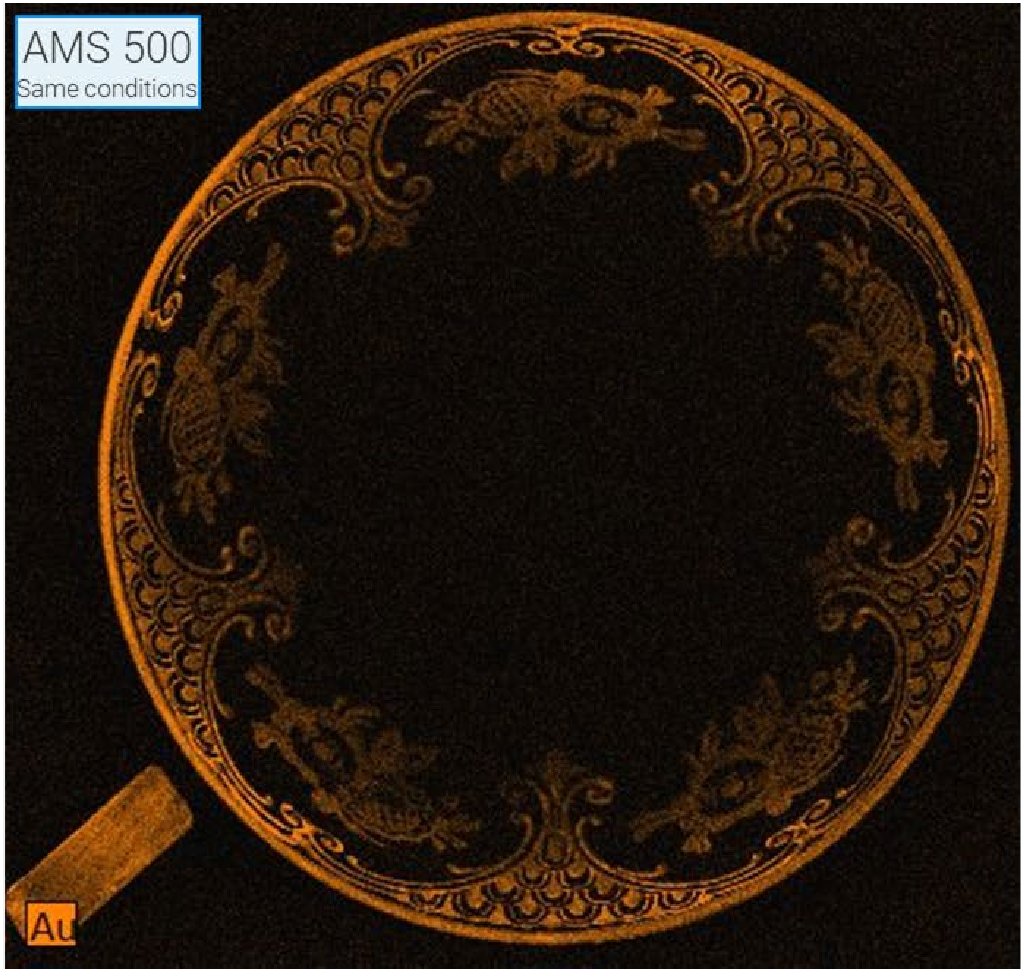
AMS 500 µm

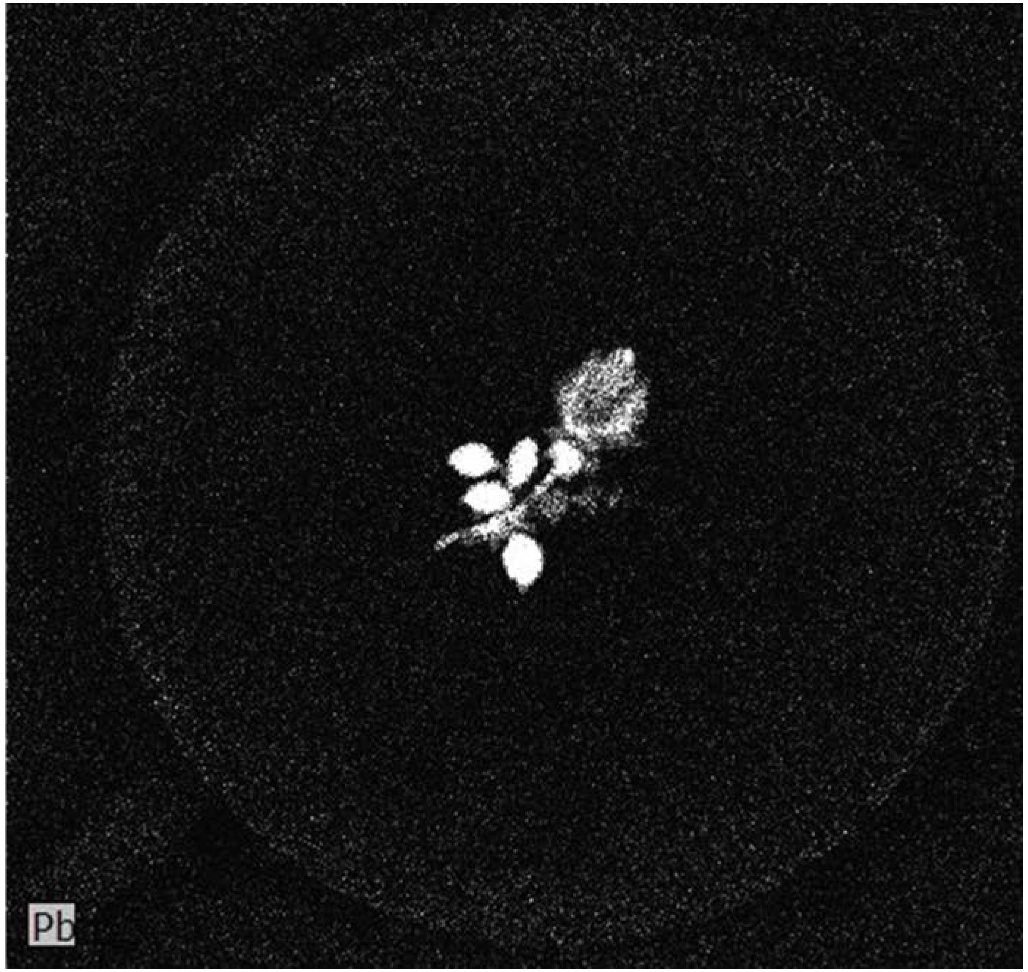
Using the AMS
Measuring areas unreachable to a scanning device

Using the AMS
Measuring areas unreachable to a scanning device



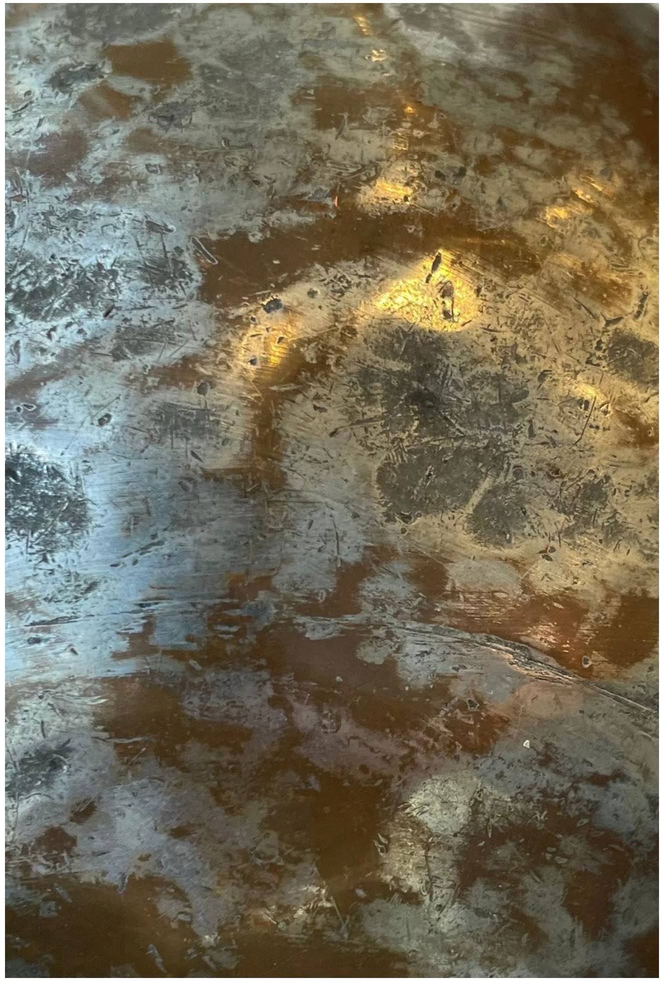
Using the AMS
Measuring areas unreachable to a scanning device





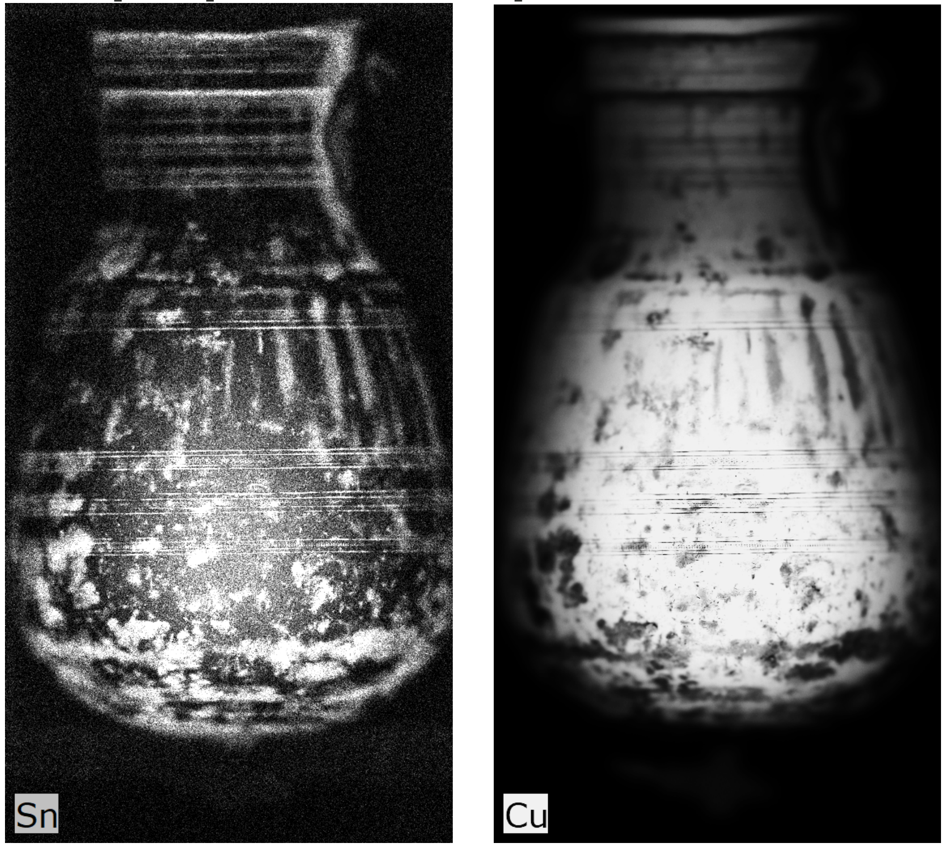
Using the AMS
Measuring areas unreachable to a scanning device

A tinned bronze cauldron
Enhancing spatial resolution in up to 10 cm depth

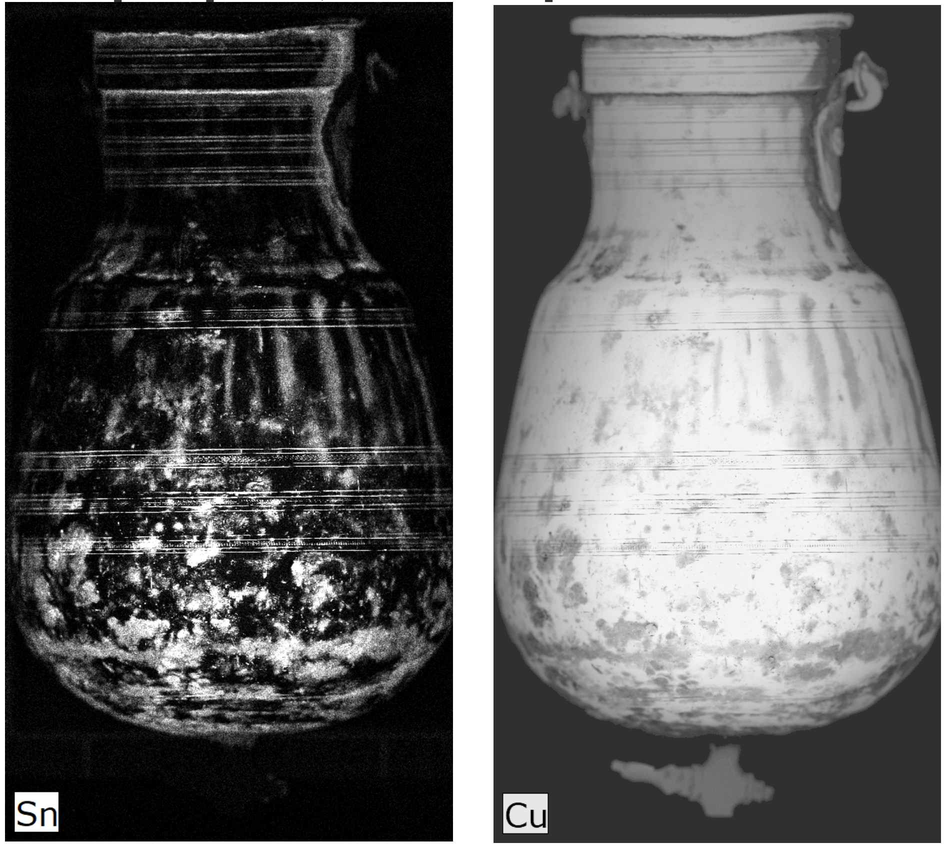


A tinned bronze cauldron
Enhancing spatial resolution in up to 10 cm depth

50 kV, 200 µA, no AMS
300 µm pixel, 50 ms/px dwell time

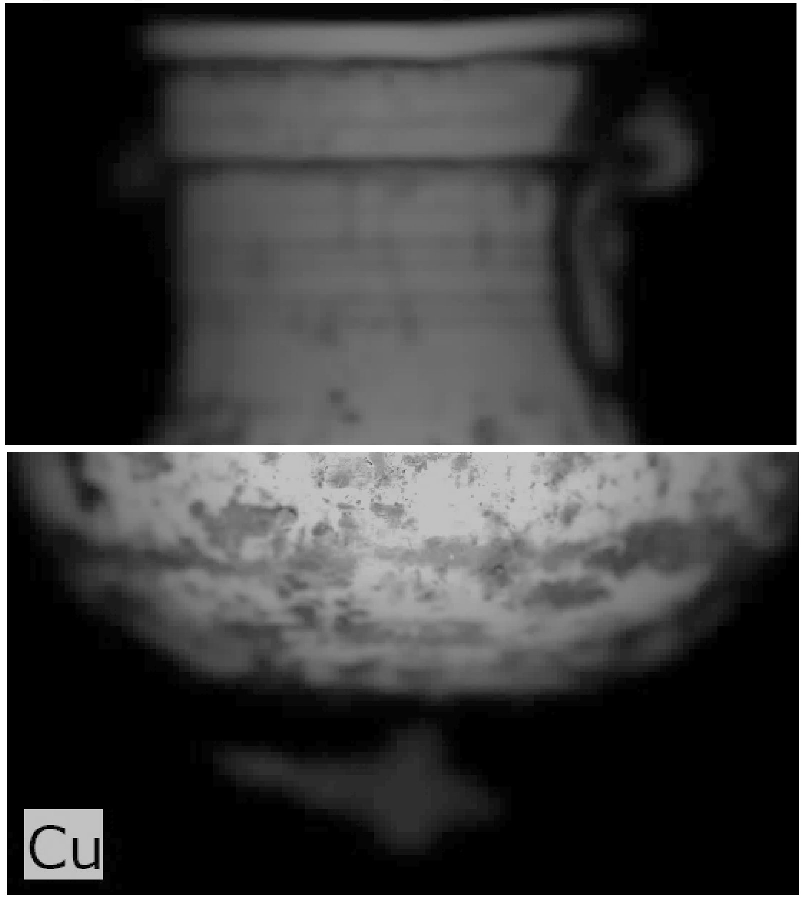


50 kV, 600 µA, AMS 500
300 µm pixel, 100 ms/px dwell time

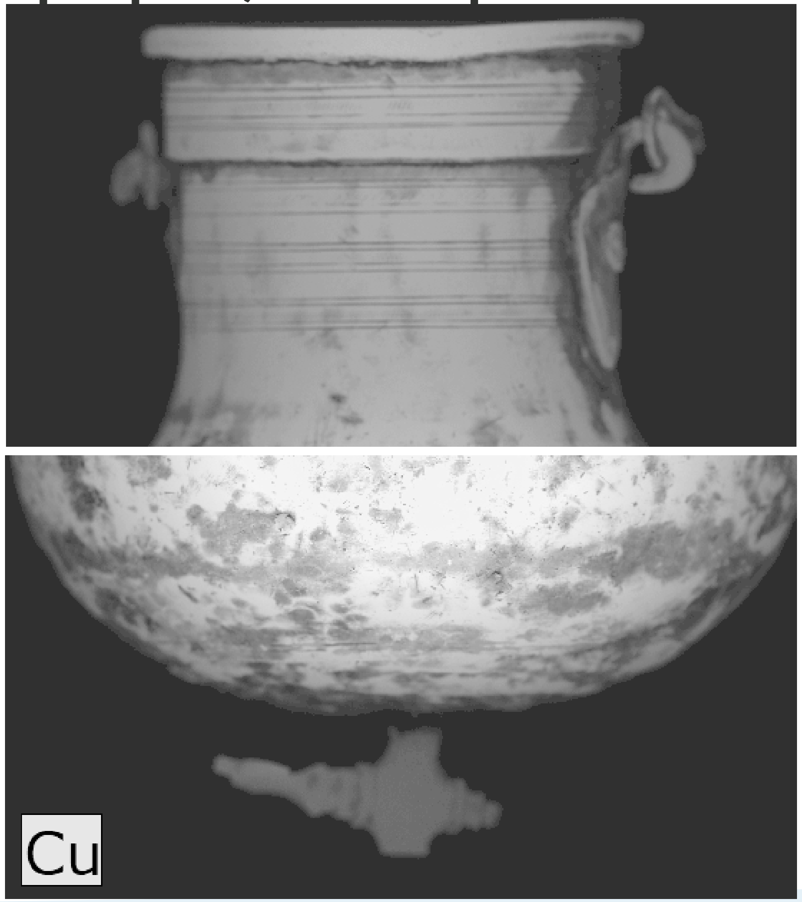


A tinned bronze cauldron
Enhancing spatial resolution in up to 10 cm depth

50 kV, 200 µA, no AMS
300 µm pixel, 50 ms/px dwell time

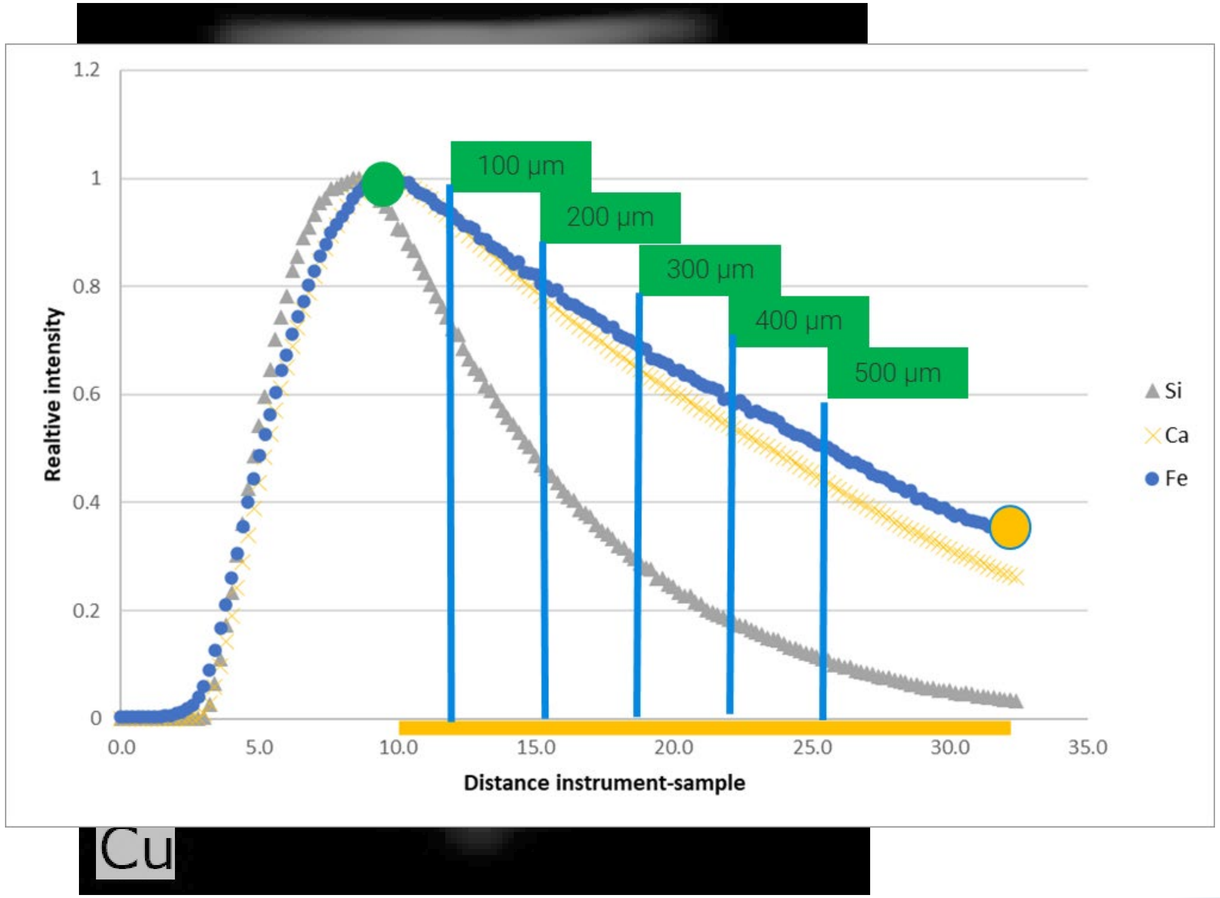


50 kV, 600 µA, AMS 500
300 µm pixel, 100 ms/px dwell time

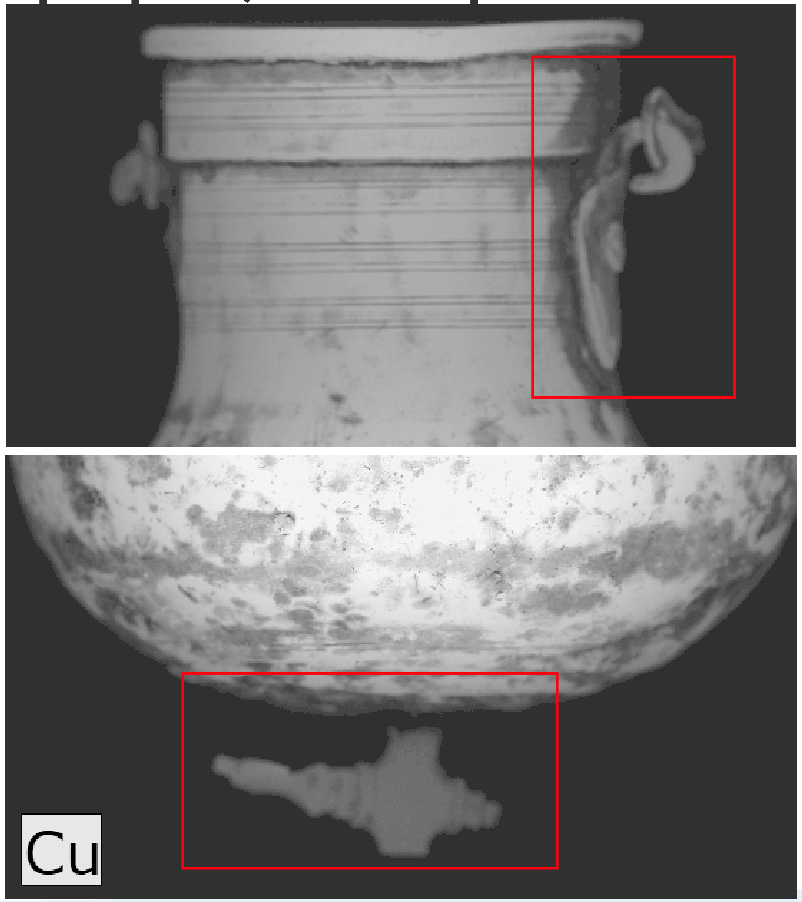


A tinned bronze cauldron
Enhancing spatial resolution in up to 10 cm depth

50 kV, 200 µA, no AMS
300 µm pixel, 50 ms/px dwell time



50 kV, 600 µA, AMS 500
300 µm pixel, 100 ms/px dwell time



c. 10 cm distance

c. 10 cm distance

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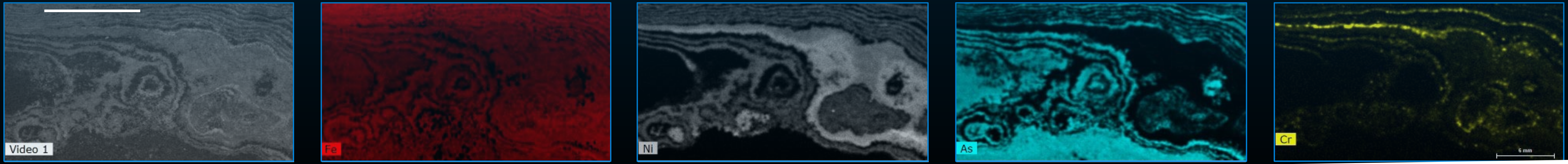
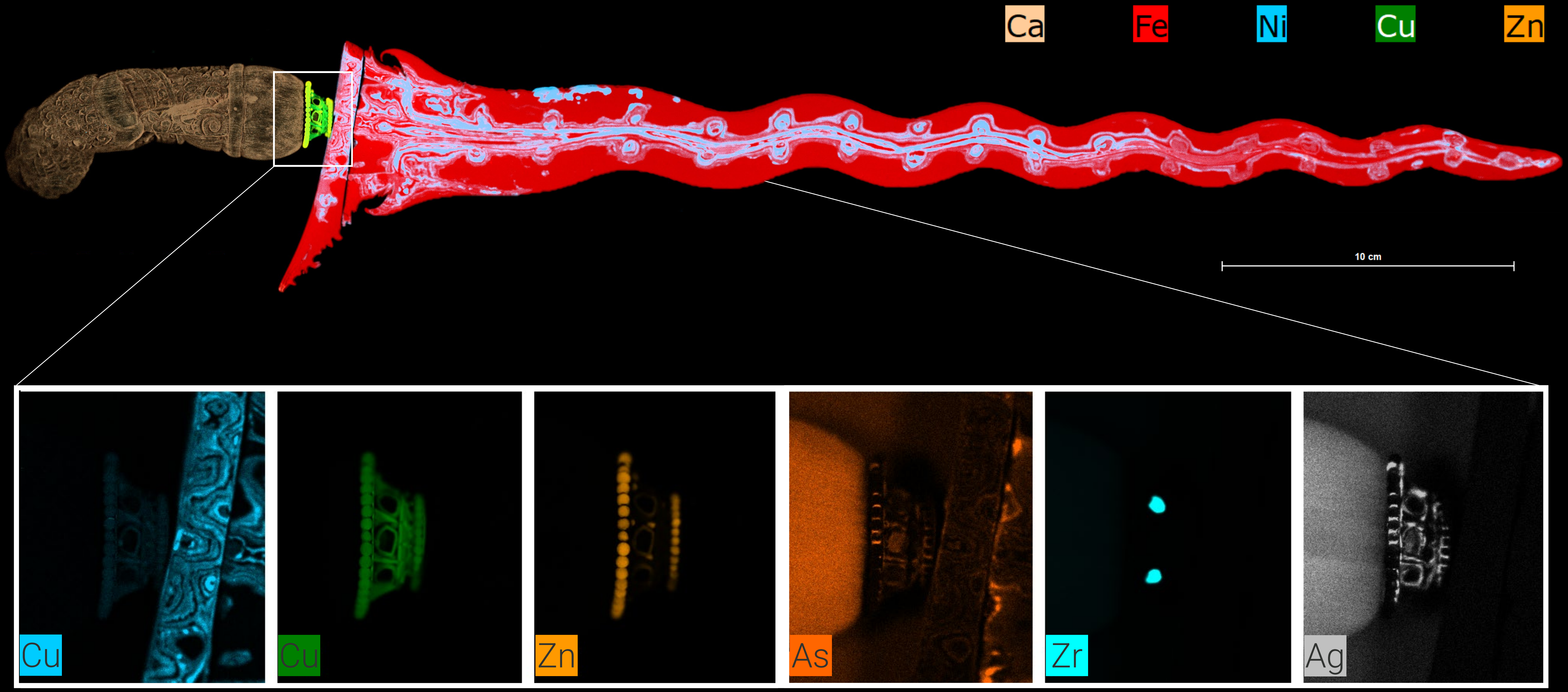
Micro-XRF analysis
An Introduction to quantification of metal objects

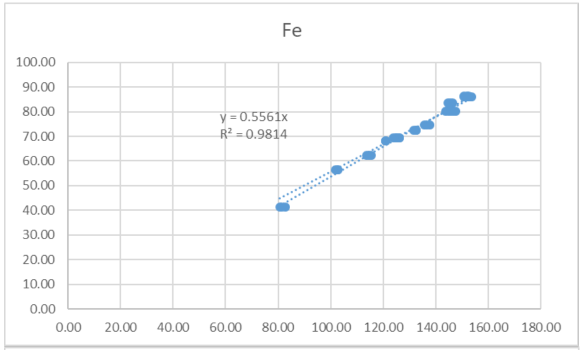


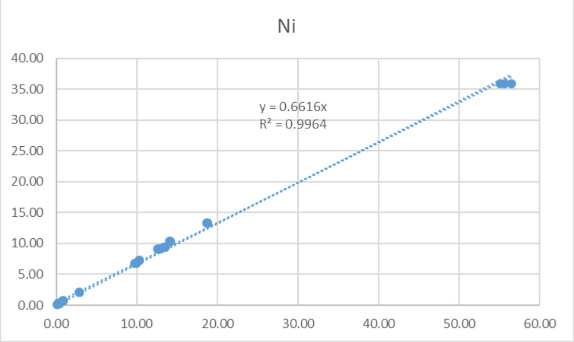


Kris Courtesy of *Bartoschewitz Meteorite Collection*

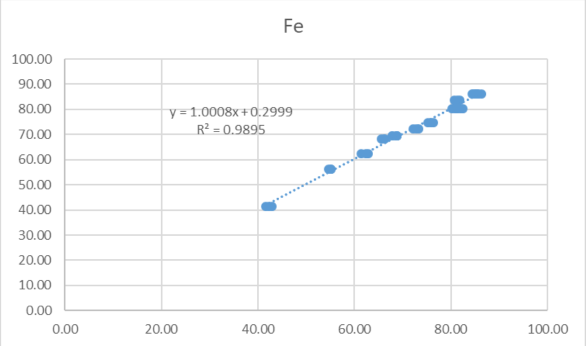
A meteoritic dagger
Quantitative XRF analysis

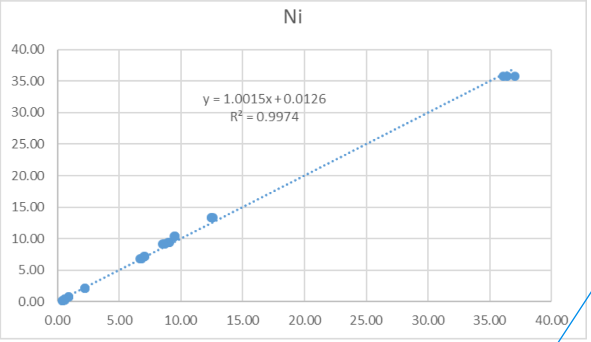
Before TC

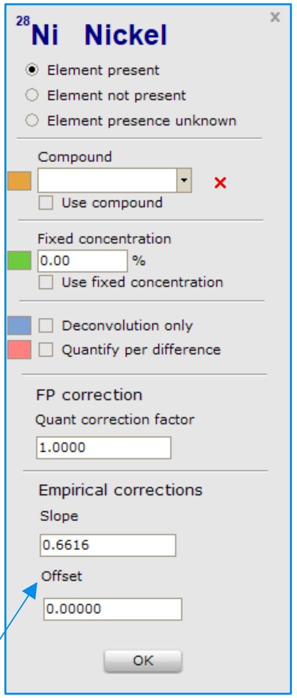


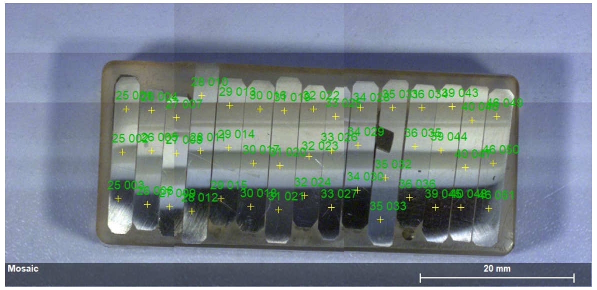


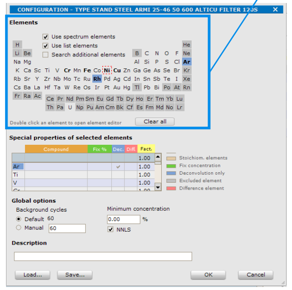
After TC









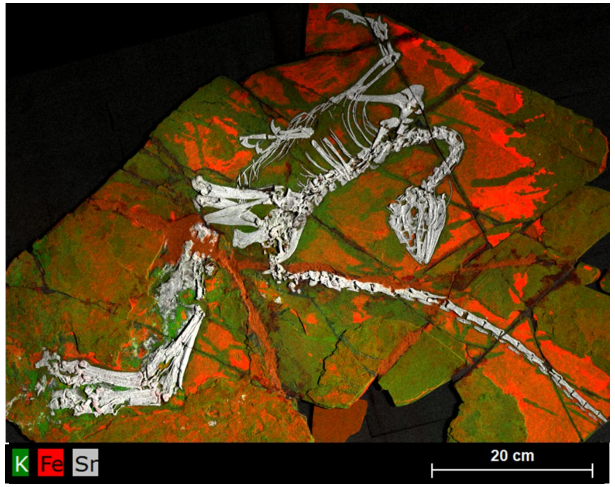


Mass conc. (norm.)

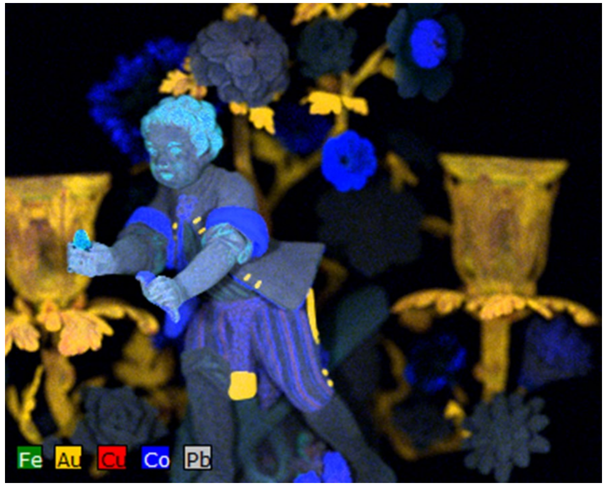
	Ar	Cr	Fe	Ni	Cu	As	Rh	Sum
high Ni 003	0.00	0.03	98.74	1.20	0.02	0.02	0.00	100.00
high Ni 002	0.00	0.03	98.84	1.09	0.02	0.02	0.00	100.00
high Ni 001	0.00	0.03	98.72	1.21	0.02	0.02	0.00	100.00
Mean value:	0.00	0.03	98.77	1.17	0.02	0.02	0.00	
Std dev.:	0.00	0.00	0.07	0.07	0.00	0.00	0.00	
Std dev. rel. [%]:	0.00	12.92	0.07	5.81	15.04	19.57	0.00	
Conf. interval:	0.00	0.00	0.04	0.04	0.00	0.00	0.00	

Micro-XRF analysis of archaeological objects and handcraft
Conclusion

- Micro-XRF offers a vast variety of analyzing archaeological objects and handcraft.
  - Qualitative analysis or semi-quantitative analysis can be done in point as well as scanning mode.
  - Quantitative analysis is more intricate but can be done with standard-free FP or standard-supported.



- The AMS offers to map highly topographic objects with a high spatial resolution.
- Though there is a loss of intensity by both the AMS as well as a larger distance from sample surface to detector, we still get sufficient count rates for mid to high Z elements.

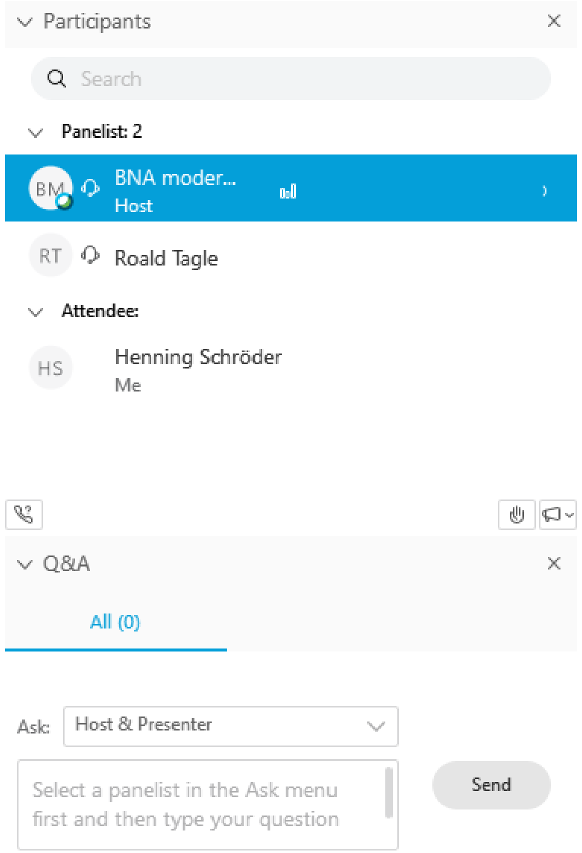


Art & Conservation Webinar Series
Analysis of non-infinite samples in Cultural Heritage

If you have questions during this webinar,

please **type your questions**, thoughts, or comments in the

Q&A box and **press Send**.



We ask for your understanding, if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another WebEx session.

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