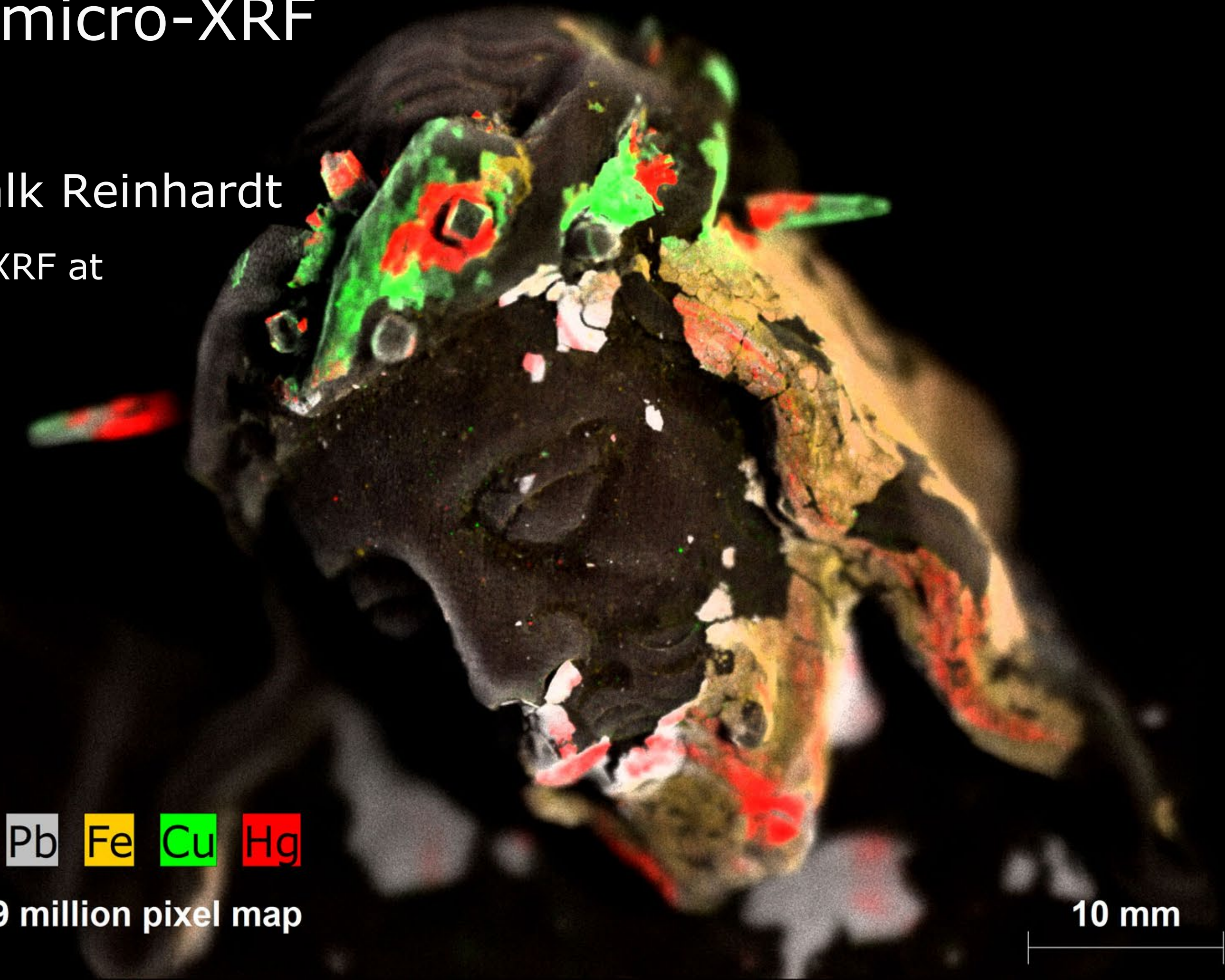
New Horizons of micro-XRF

Dr. Roald Tagle and Falk Reinhardt

Application Scientists micro-XRF at

Bruker Nano Analytics



Introduction
Presenters / Moderators

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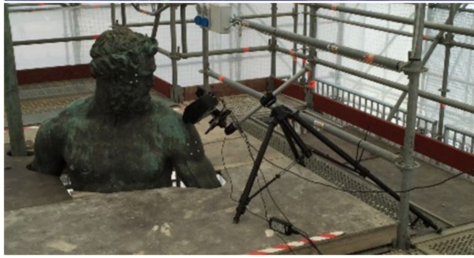
Overview

- XRF in Art & Conservation
- Using the M4 Tornado for studying old photographs
  - The object
  - The instrument
  - The different options and their effect
- M6 Jetstream
  - A short history
  - Improvements over time
  - Most recent improvements
- Live part
  - Some features of the upgraded M6 Jetstream
- Q&A session

Supporting Art and Conservation
XRF and Art a Hand-in-Hand partnership

- XRF has proven to be a core analytical technique in Cultural Heritage studies.
- XRF provides key information on the studied objects in a reliable fast and non-invasive way.
- **But** the needs are not always the same. They differ in crucial ways with respect to the **what**? , the **where?**, and the **how**?
- One analytical principle but several instruments.



Art & Conservation strategy

Solutions Portfolio

The BRUKER unique instrument portfolio –
to offer the perfect instrument for
any specific need

Performance & Features

Tracer

ELIO

CRONO

M4 Tornado

M6 Jetstream

Data evaluation strategy
Unification of sophisticated tools


ARTAX


M4 Tornado


EDS QUANTAX

M6 Jetstream

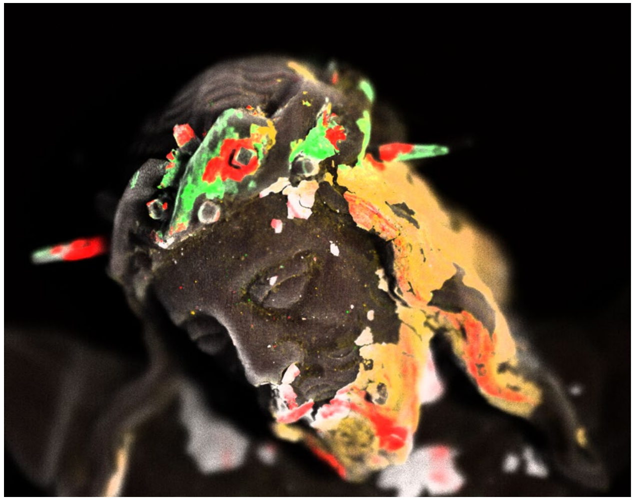

Data evaluations toolbox

CRONO



ELIO

Developments & Innovations
Motivation for improvement

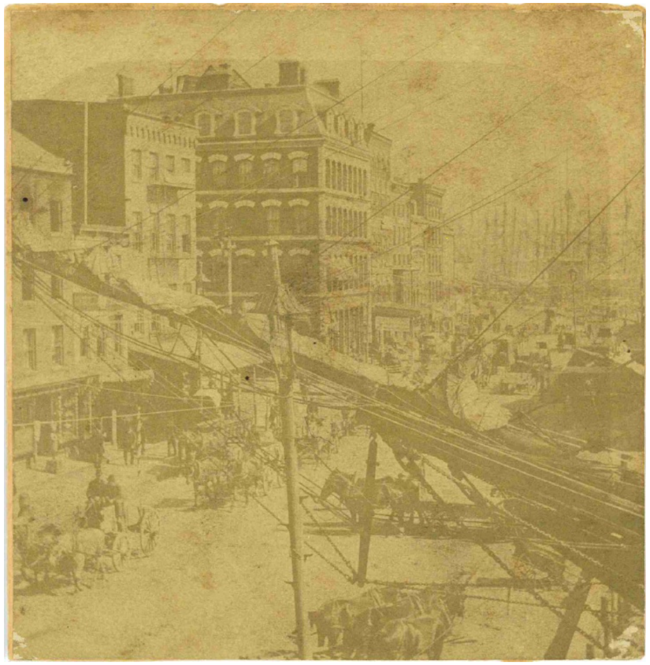


Visualization of objects composition by micro-XRF mapping strongly supports the multidisciplinary research and evaluation of complex samples.

However, despite the advances in micro-XRF instrumentation and analysis in recent years, some **limitations** remain:

- Objects with topography or a complex surface shape
- Long scan times required to achieve sufficient accumulated counts over large areas
- X-ray tube configurations can lead to non-ideal X-ray line overlaps and analysis environment may lead to damage to sensitive objects (e.g. vacuum)

A degraded photograph
Possibilities of micro-XRF



The studied object is an old photograph of a harbor, with horse carriages and sailing ships.

This photograph has lost lots of its contrast. The paper turned yellow; the silver is tarnished.

Nevertheless, the pictures, i.e. the Ag atoms on the paper are still there.

Can micro-XRF be used to map the distribution of Ag on the paper?

- Non-invasive multi-element technique
- Spatial resolution below 20 µm
- Minimal, almost no sample preparation required

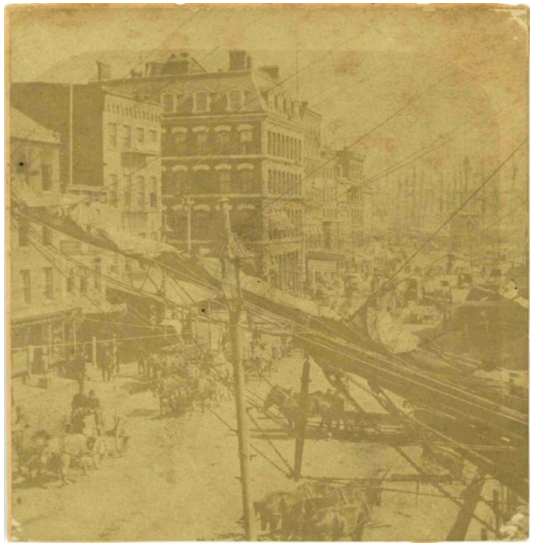
A degraded photograph
Challenges for micro-XRF

Several challenges arise when looking for Ag in a photograph:

- The Ag-K lines are almost invisible, because the Ag layer is extremely thin
- The Ag-L lines overlap with the signal from 1 % Argon in the air
- The typical Rh source yields very inefficient excitation

What features would we need?

- Efficient excitation of Ag-L lines
  → Use different anode materials (W or Cr)
- Removing the Ar background
  - Vacuum → puts sample under strain
  - N_2-atmosphere, only 20 % less signal* than vacuum but sample-friendly



*calculated for 800 mbar N_2 using https://xrfcheck.bruker.com/FilterTransmissions

The M4 Tornado
Standard configuration

Micro-XRF table-top instrument:

- Primary tube with polycapillary optic with < 20 µm spot size for Mo-Kα (usually with Rh-target)
- Optional second tube, with collimator
- 1 or 2 SDD(s), 30 mm^2 or 60 mm^2
- fast servo-driven stage
- Membrane pump, pressure down to 1 mbar, usually 20 mbar
- Excitation and detection under 50°
- Two optical microscopes under ~90°

Introduced with M4 Tornado Plus:

- Light-element window detectors
- Aperture Management
- High signal throughput
- He-purge system

The M4 Tornado
…for studying photographs

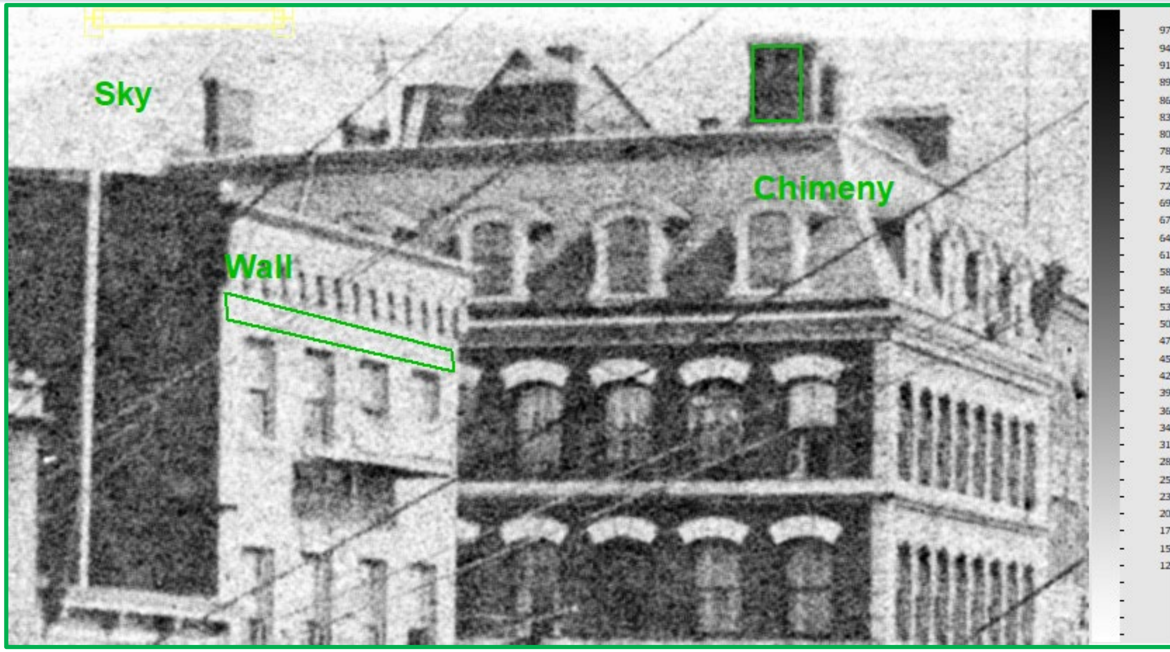
Micro-XRF table-top instrument:

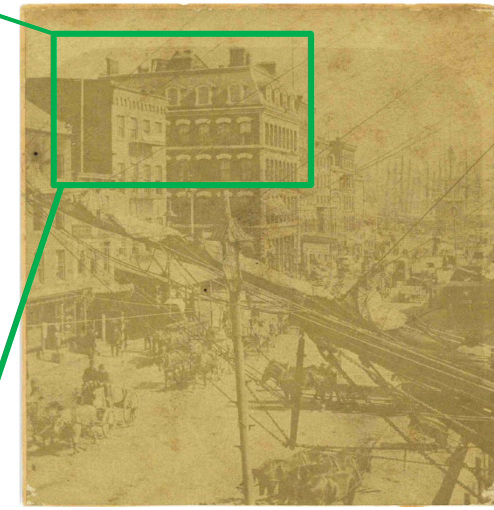
- Primary tube with polycapillary optic with < 20 µm spot size for Mo-Kα (usually with Rh-target) ← **which target is optimal?**
- Optional second tube, with collimator
- 1 or 2 SDD(s), 30 mm² or 60 mm²
- fast servo-driven stage
- Membrane pump, pressure down to 1 mbar, usually 20 mbar
- Excitation and detection under 50°
- Two optical microscopes under ~90°

Introduced with M4 Tornado Plus:

- Light-element window detectors
- Aperture Management
- High signal throughput
- He-purge system ← **used for N_2**

M4 Tornado for photographs
Anode comparison





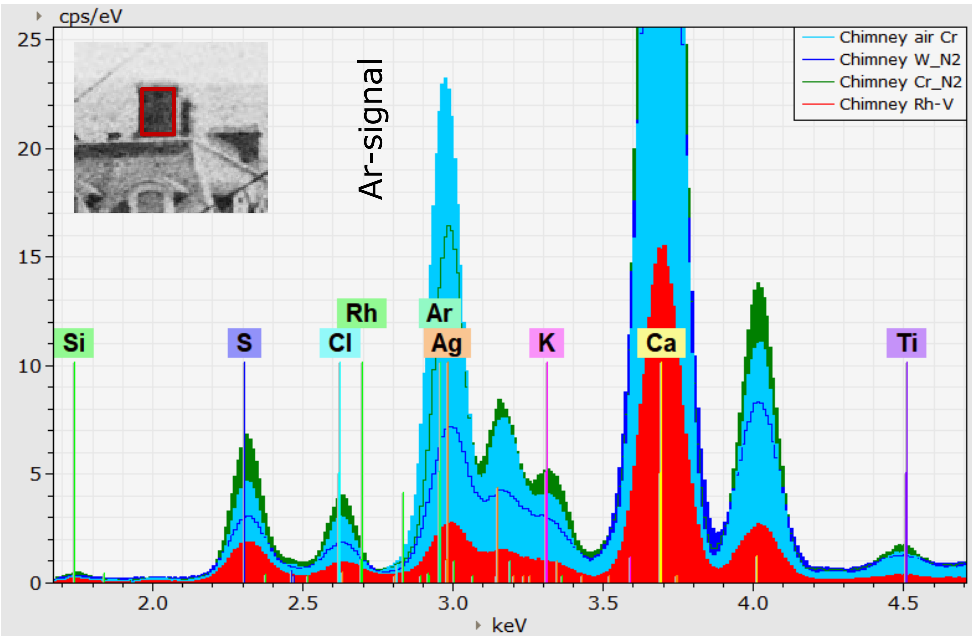
Conditions:
35 kV 800 µA
W-anode
N_2-atm at 830 mbar
50 µm, 30 ms

For a "quantitative" comparison between the measurement conditions, defined areas of different contrast were selected from the maps:

Dark → Chimney
Medium → Wall
Light → Sky

The sum spectra of these areas were extracted for comparison

M4 Tornado for photographs
Anode comparison



The Ag-L signal is, as expected, much better for Cr and W excitation than for Rh.

Net intensity [cps] live time			
Spectrum	Conditions	Ag-L	Ag-Int. rel to Cr
Sky	Cr_N2	1154	1.0
Sky	W_N2	801	0.7
Sky	Rh_Vac	82	0.1
Wall	Cr_N2	1826	1.0
Wall	W_N2	1387	0.8
Wall	Rh_Vac	211	0.1
Chimney	Cr_N2	3878	1.0
Chimney	W_N2	3043	0.8
Chimeney	Rh_Vac	518	0.1
Cr--> (30 kV 400 µA) W--> (35 kV 800 µA) Rh --> (50 kV 600 µA)			

The Cr-tube gives ~20 % more intensity for the Ag-L line than a W-tube.

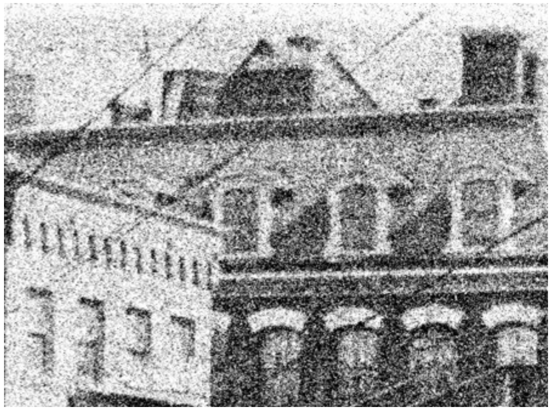
The Rh tube is very inefficient even though it has been used under Vacuum condition.

Is a Cr-anode better than a W-anode?

M4 Tornado for photographs
Anode comparison

Cr-tube

W-tube



Differences are surprisingly small.

Possible explanation:
The spot of a Cr tube is slightly larger than that of a W tube due to the lower energy of the photons (and the larger angle of total reflection).

So … which one is better, Cr or W?

- Cr is slightly better in terms of Ag-signal
- W offers more versatility (especially when used with different filters).
- W is a very robust X-ray source but lacks light-element performance.

Conditions:
35 kV 800 µA
W-anode, N_2-atm. 830 mbar
50 µm, 30 ms

30 kV 400 µA
Cr-anode, N_2-atm. 806 mbar
50 µm, 30 ms

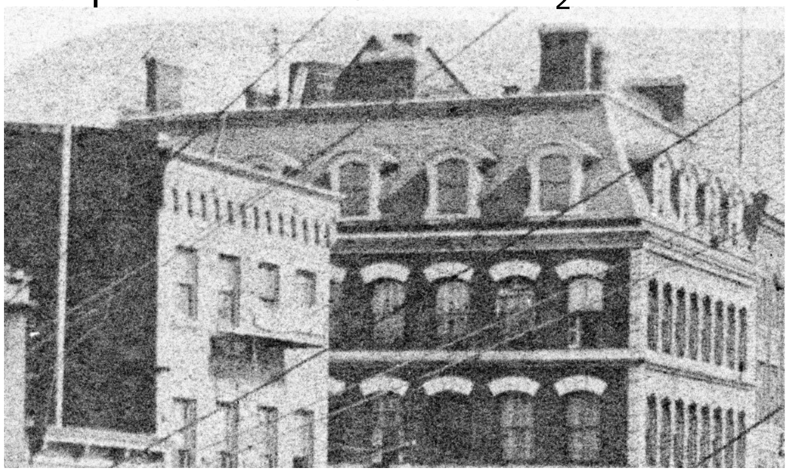
M4 Tornado for photographs

Resolution comparison

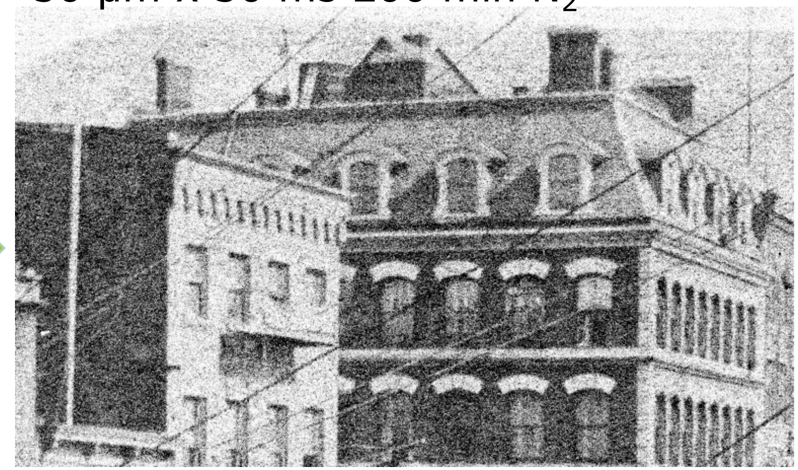
25 µm x 30 ms 800 min N_2

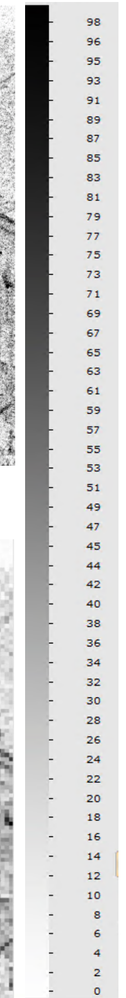
50 µm x 30 ms 200 min N_2

Best



OK

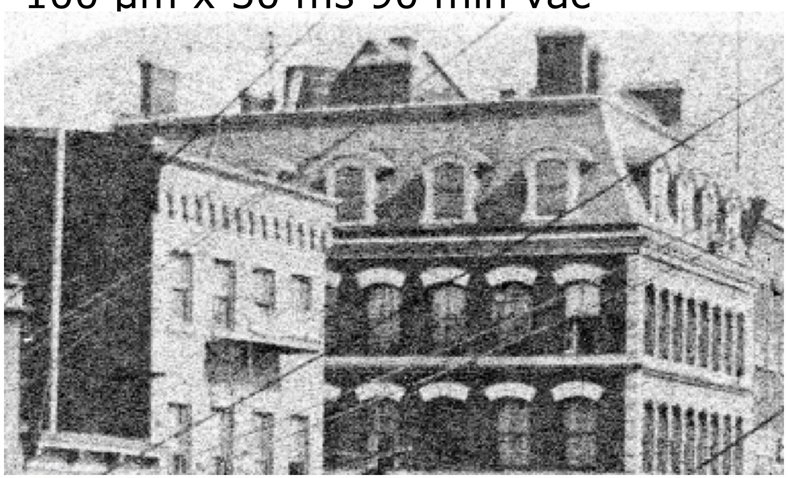




100 µm x 50 ms 90 min vac

200 µm x 100 ms 40 min vac

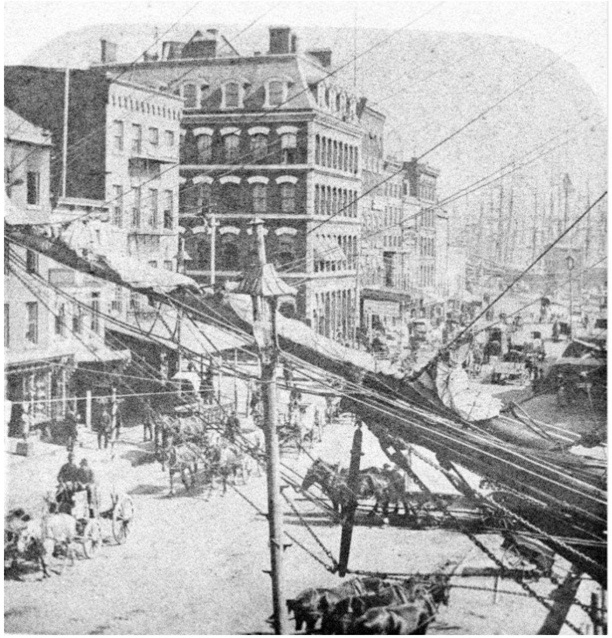
Comparison



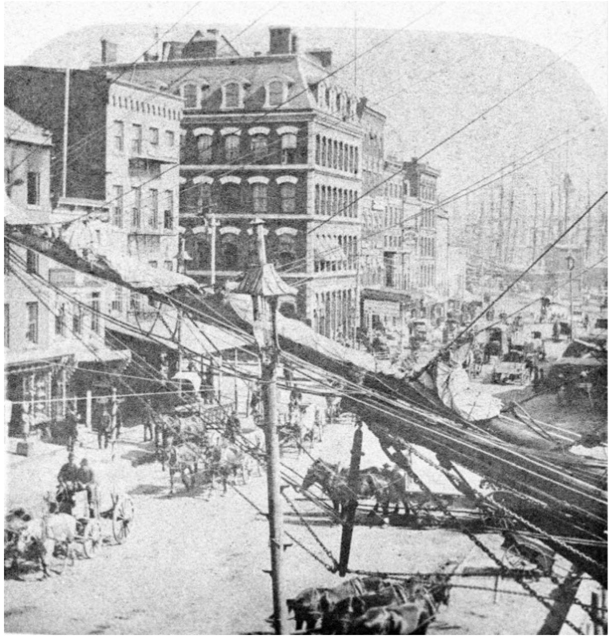
M4 Tornado for photographs
Time comparison

Not much improvement from here

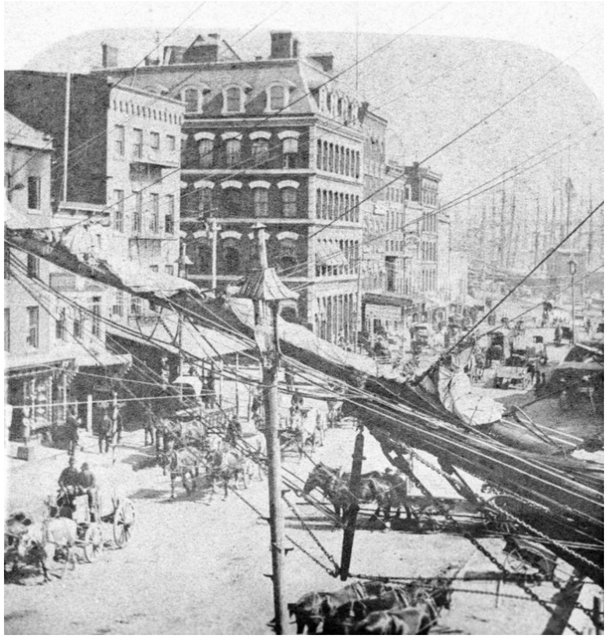
Conditions:
35 kV 800 µA
W-anode, vac 20 mbar
50 µm



50 ms, ~6 h



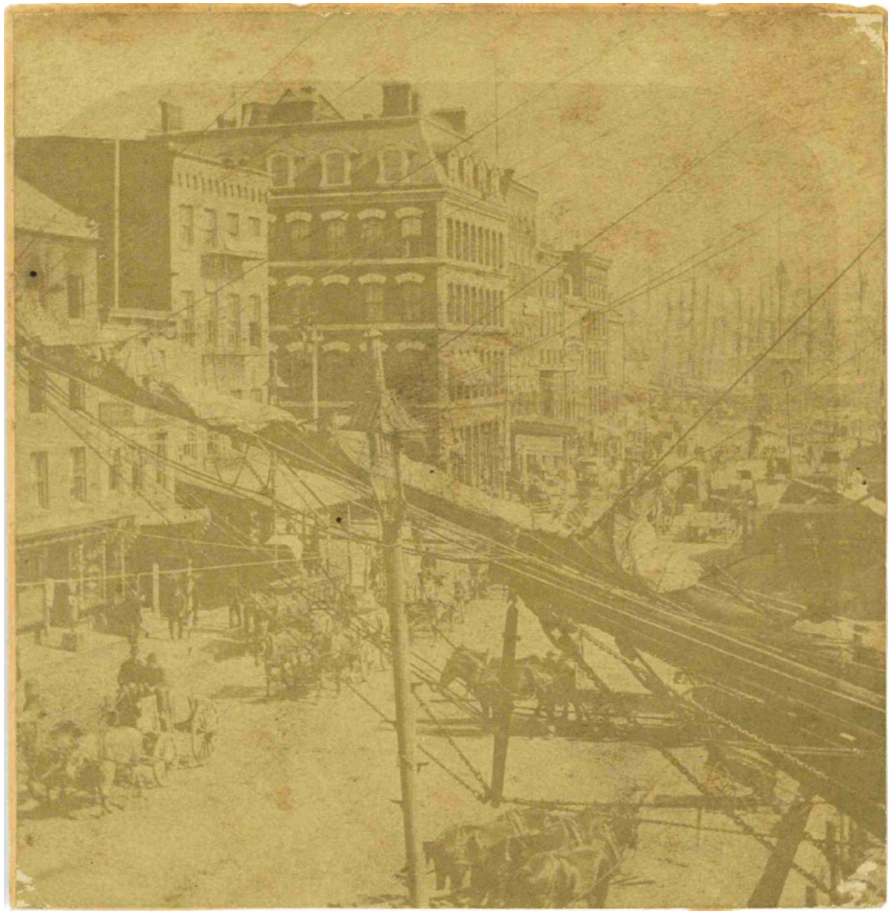
100 ms ~ 12 h



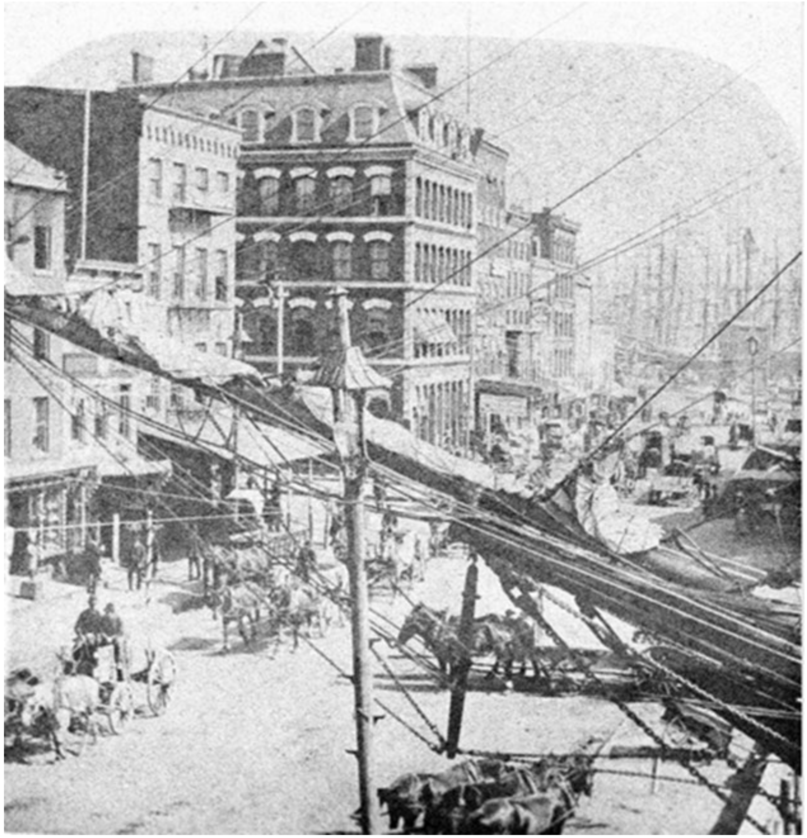
830 ms ~ 90 h

Only little difference for this object.
→ Measurement times around 50 ms are sufficient.

M4 Tornado for photographs
A “quick” scan



~3 h scan **W**-source



M4 Tornado 35 kV 800 µA, 2x 30 mm² SDD,
air 20 mbar, 50 ms, and 100 µm.

Summary
M4 Tornado for photographs

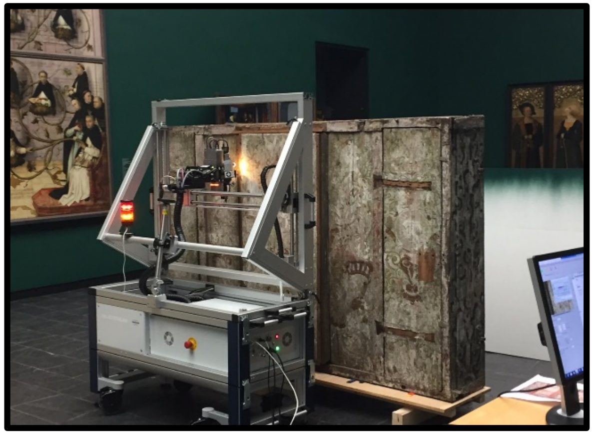
Micro-XRF allows to study the Ag distribution in old photographs.

The resulting picture's quality depends on the measurement conditions

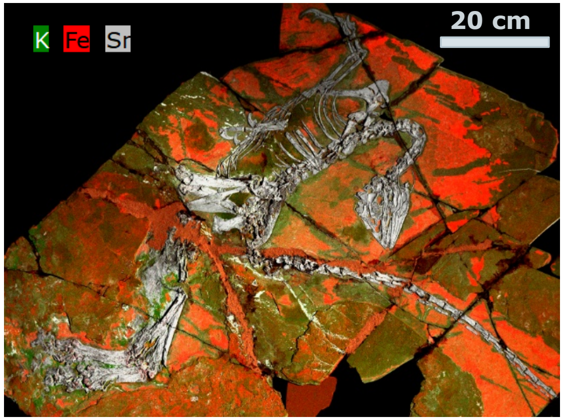
- Spatial resolution, i.e. step width
  - Optimum was found to be between 50 µm and 100 µm
- Measurement time per pixel
  - No significant improvement for more than 50 ms/pixel
- Atmosphere
  - Vacuum, if sample allows, otherwise N_2 flush
- The anode material
  - Cr seems self-evident because most efficient for Ag-L excitation
  - W is almost as good but by itself a more versatile tube

M6 Jetstream at work
Working around the planet

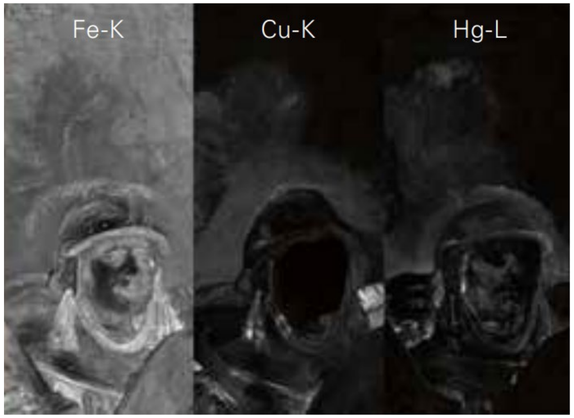
Staedel Museum, Frankfurt



Xinghai Museum, Dalian



Rijksmuseum, Amsterdam



M6 Jetstream – a short story
Introduction (2012)

Prototype M6 Jetstream

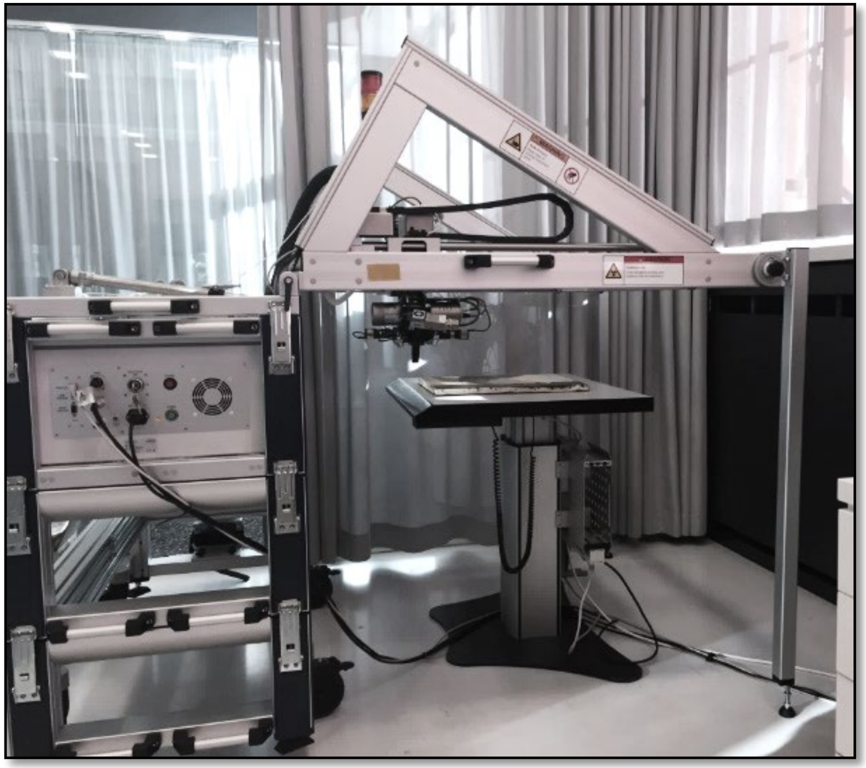
- Developed in cooperation with the Delft University of Technology
- Unique instrument, operational at the Rijksmuseum, Amsterdam
- Some features:
  - **800 mm x 600 mm** scan area
  - **30 W** Rh tube with polycapillary optic
  - **30 mm²** SDD
  - Instrument for vertical scanning
  - Sample stage speed up to **100 mm/s**, and **200 mm/s²**

Development Phase I
M6 Jetstream

M6 Jetstream - introducing novel features

- Vertical and horizontal sample analysis option
- Tilting mechanism for inclination adjustment
- Diffuse LED Illumination for better sample visualization
- Ultrasonic sensor for non-contact sample protection
- **60 mm²** SDD
- Helium flush for light element detection
- Flight case option for transport

Development Phase I
M6 Jetstream



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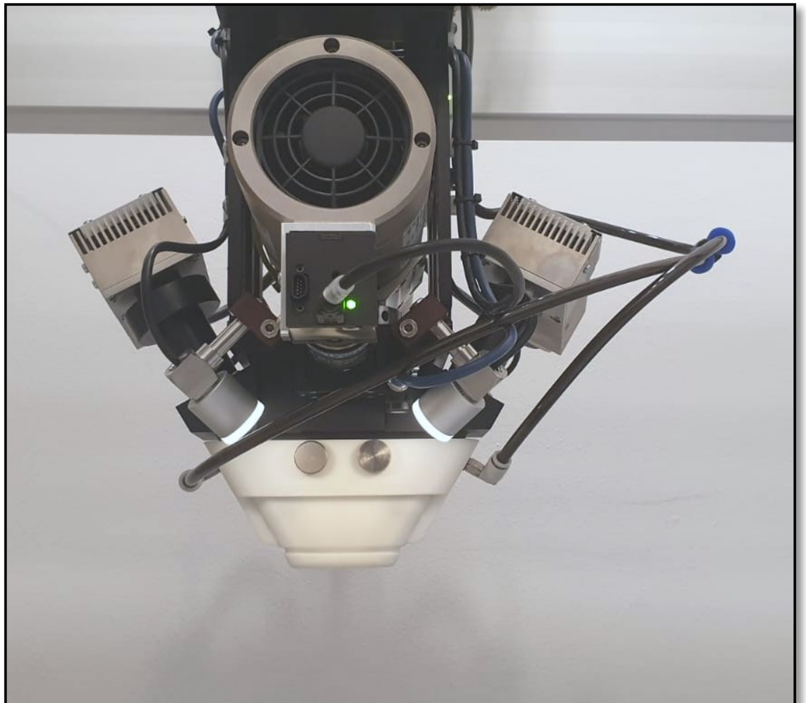
Development Phase II
M6 Jetstream



M6 Jetstream - introducing novel features

- **Double detector technology** with 2x60 mm² SDD (4x the detector area of the prototype)
- **High throughput technology** to improve data acquisition rate (550 kcps data acquisition rate for scanning)
- **Aperture management system** for improved spatial resolution
- Additional **complex filters** including options to filter out Rh-K lines

Development Phase II
Double detector for the M6 Jetstream

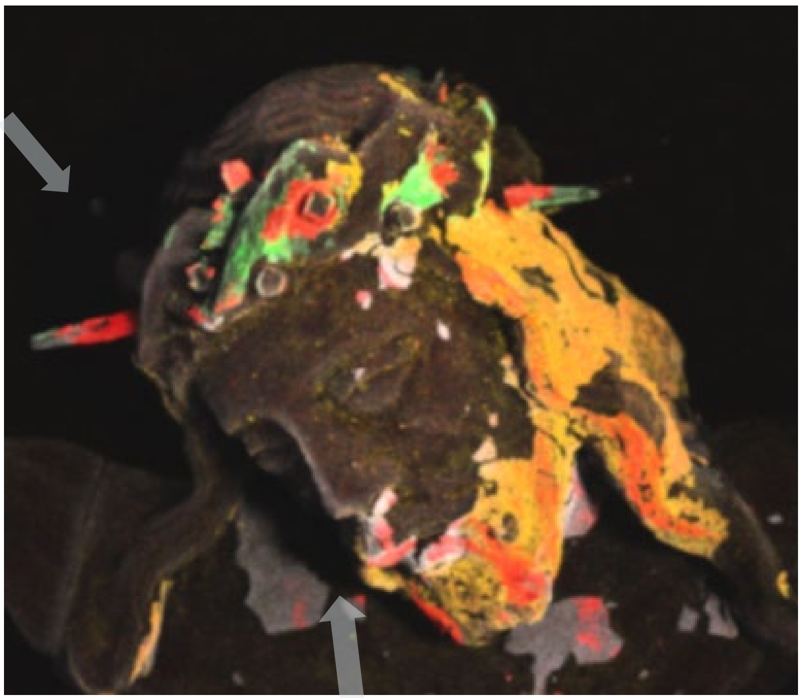
Using 2x 60 mm² SDDs results in a significant improvement of signal acquisition

- The Geometry reduces the “shadow” effect
- The dual-detector setup with independent signal processing units allows for maximizing the detectable counts while retaining good spectroscopic resolution and low dead times

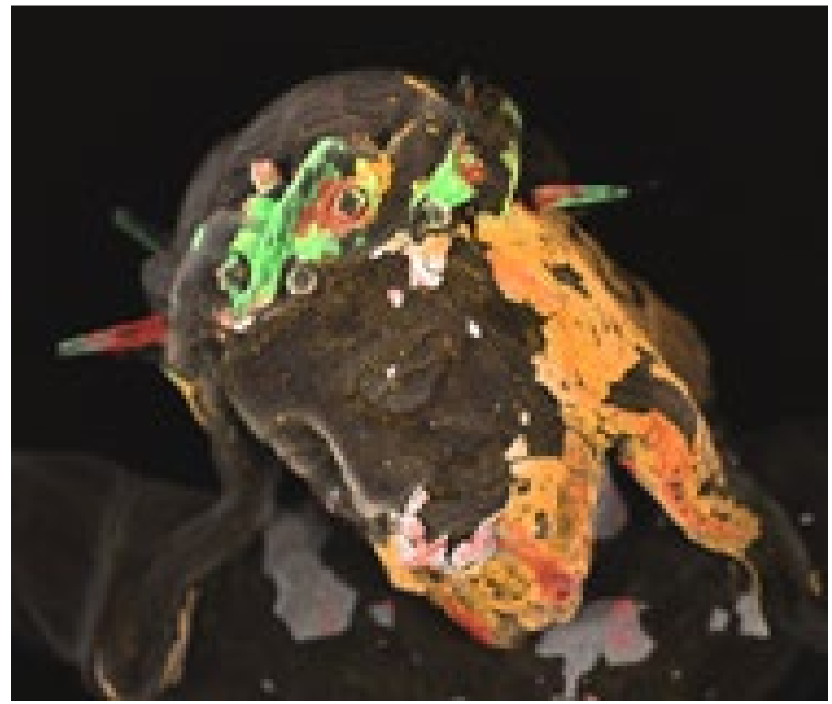
More signal per time → faster scanning and/or better signal to noise ratio and lower sample dose → passive improvement without increasing sample irradiation

Double detector for the M6 Jetstream
Reducing measurement shadow

Single detector "looking" from the right



Double detector "looking" from both sides



Detection "shadow"

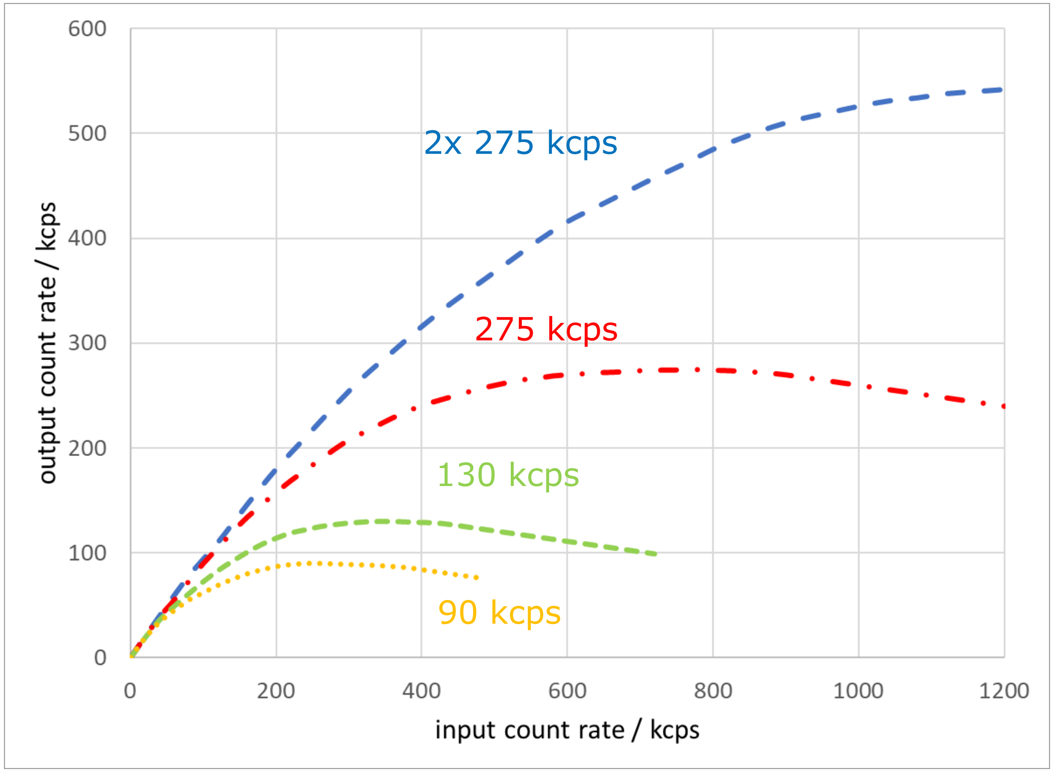
Double detector for the M6 Jetstream

High pulse throughput

Using 2x 60 mm² SDDs lots of photons hit the detector(s)

Independent signal processing is an advantage, as each detector must deal with “only” its own half of the count rate.

State-of-the-Art detector technology allows the use of signal processing units that allow to create 275 kcps as maximum output count rate.



More in the live part!

Double detector for the M6 Jetstream
Radiation dose in the sample

Tube power 30 W → 99.99996 % of power lost in beam path → $1.25 \cdot 10^{-5}$ W on the spot

We know the **Power** (in the spot)

WIKIPEDIA
The Free Encyclopedia

Absorbed dose is a dose quantity which is the measure of the energy deposited in matter by ionizing radiation per unit mass

$$D = \frac{E}{m} = \frac{E}{A \cdot d \cdot \rho}$$

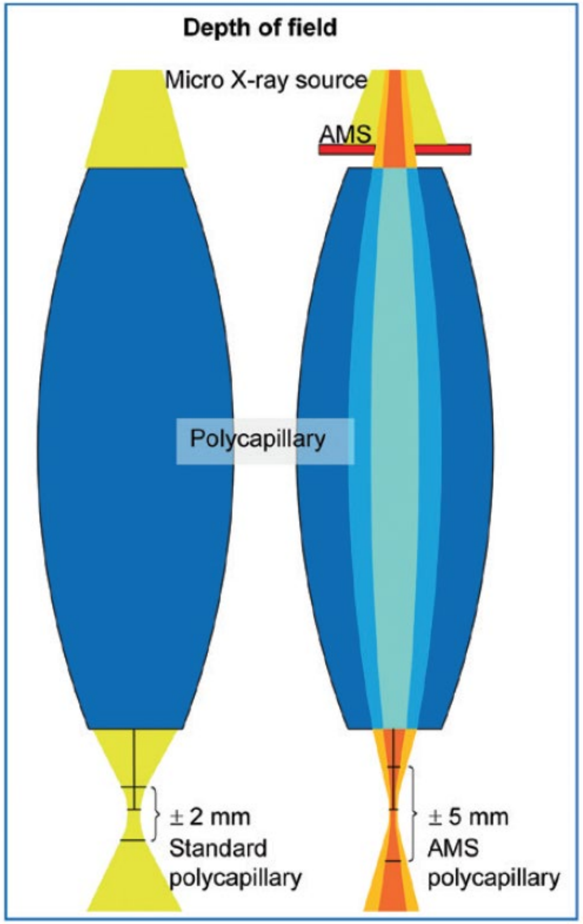
We are concerned about the **Energy** (per sample mass)

Power is given in W (Watt), Energy is given in J (Joule).

Power is Energy per time (1 W = 1 J/s), put otherwise 1 J = 1 W·**s**

With a fixed tube power, the dose on the sample can directly be tuned by **changing the time** the sample is irradiated.

Development Phase II
Aperture Management System (AMS)

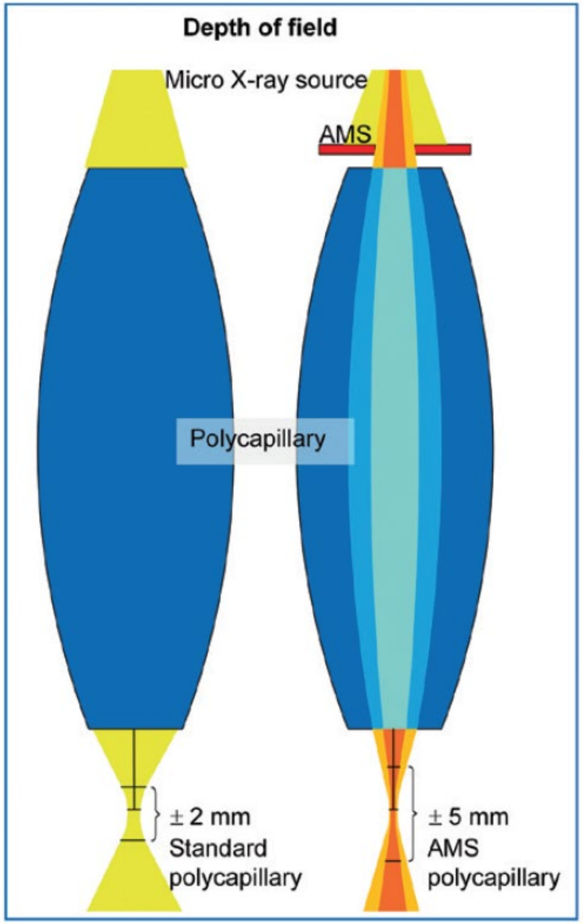


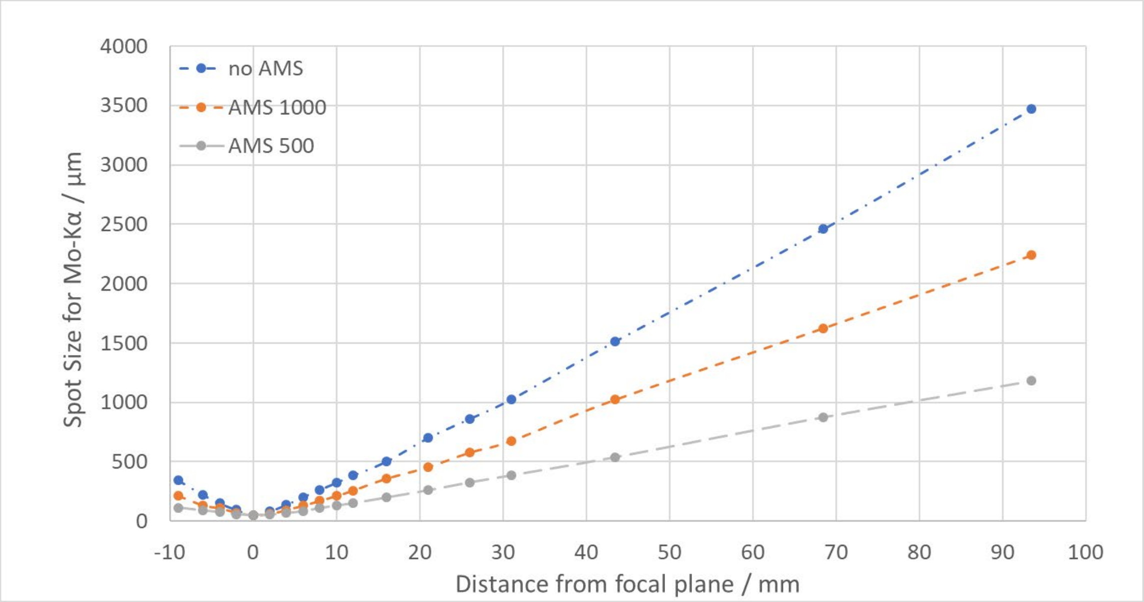
The AMS enables:

- A narrower beam
  - ➔ To keep things in focus, even below and above the analytical distance
- A longer working distance
  - ➔ Less chance of collisions
  - ➔ So variations in sample height are not critical
- Smaller spots for light elements
  - ➔ So lighter elements are resolved better

Aperture management – patent pending

Qualitative analysis
Aperture Management System (AMS)



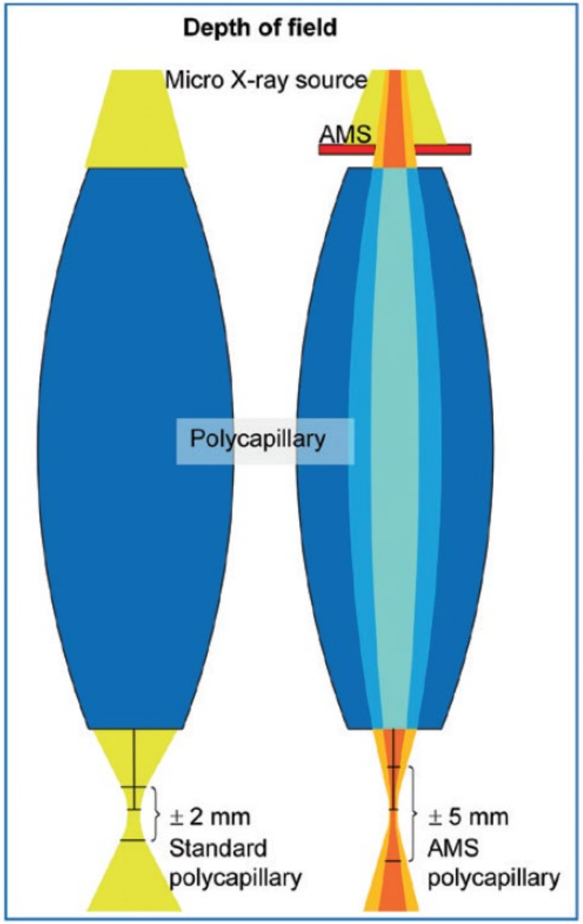


3 cm out of focal plane the spot size is reduced

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

Aperture management – patent pending

Qualitative analysis
AMS and 2x 60 mm² SDDs

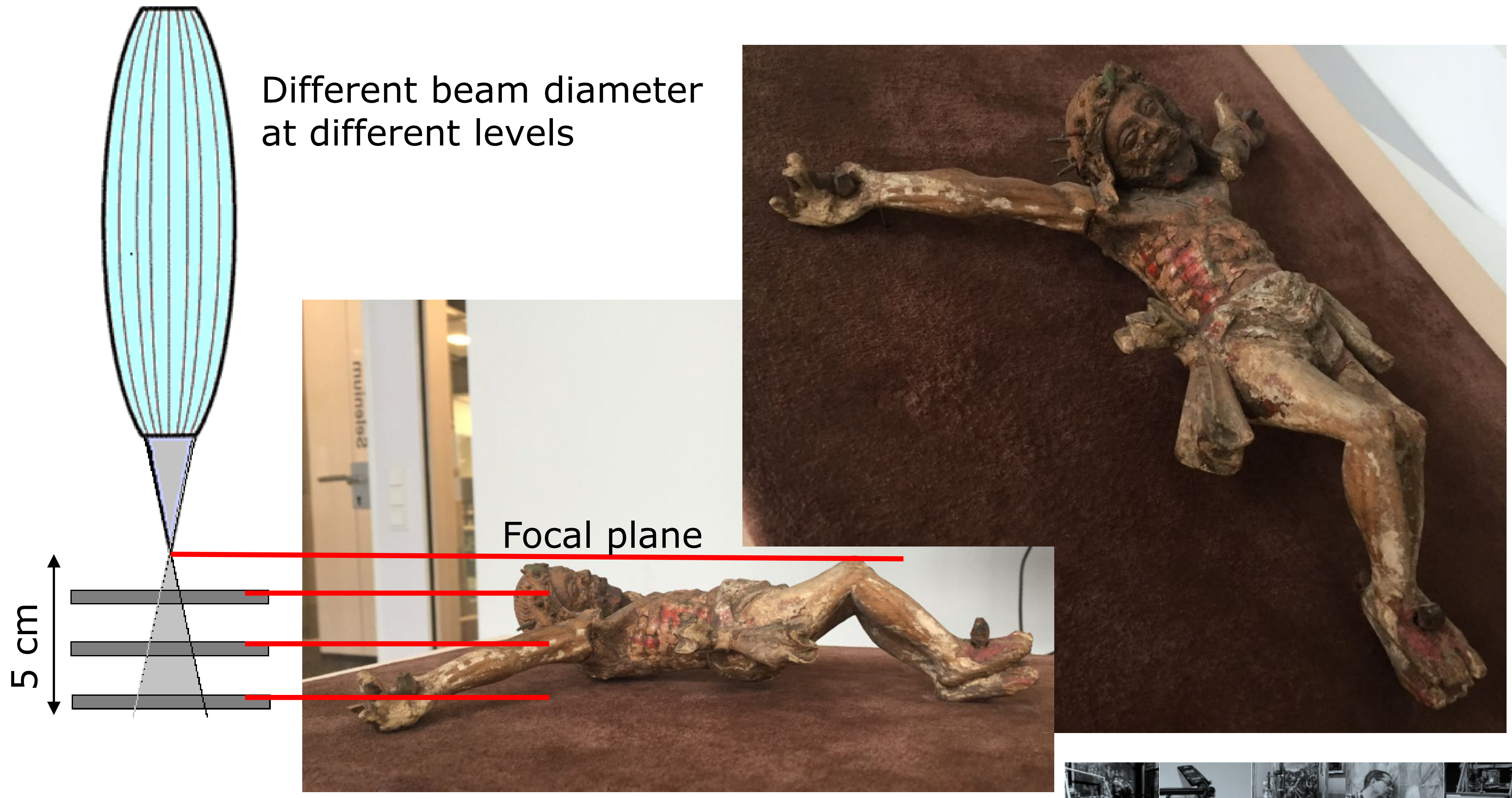


The AMS reduces the number of photons that reach the sample. The AMS 1000 reduces the intensity by a **factor of ~3**, the AMS 500 down to a **factor ~7**.

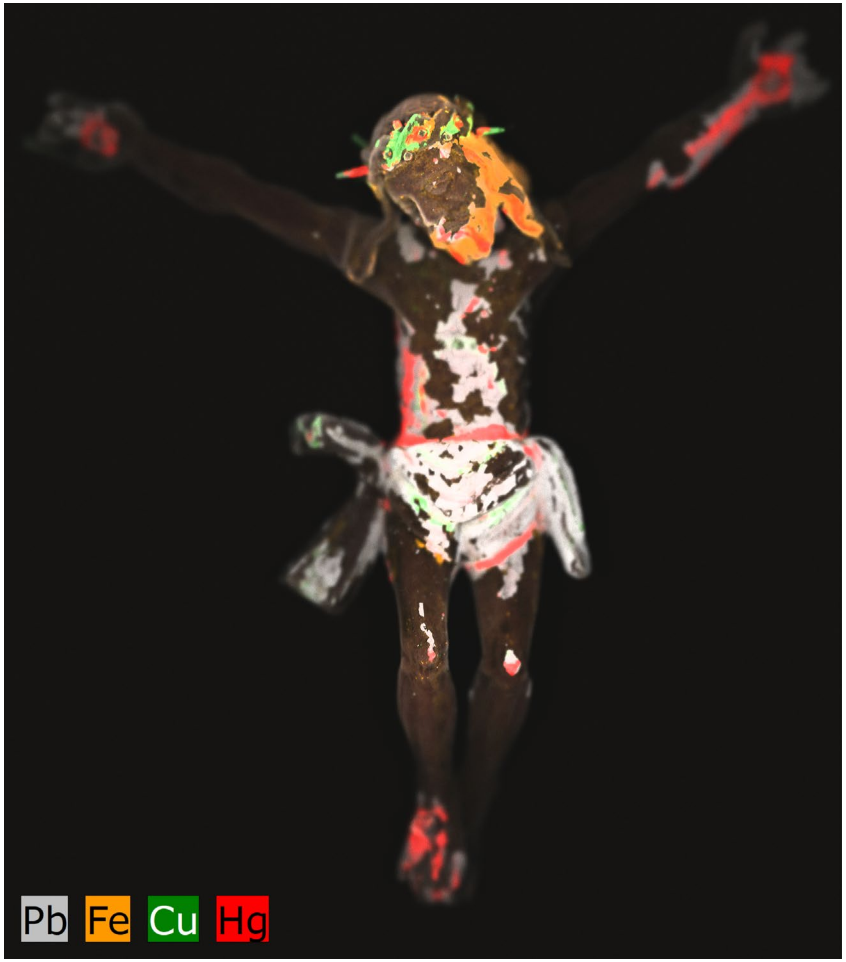
This effect is somehow cushioned by the increased solid angle of detection and signal processing capabilities of the 2x 60 mm² SDDs.

Aperture management – patent pending

Qualitative analysis
Topography and AMS



Qualitative analysis
Topography and AMS

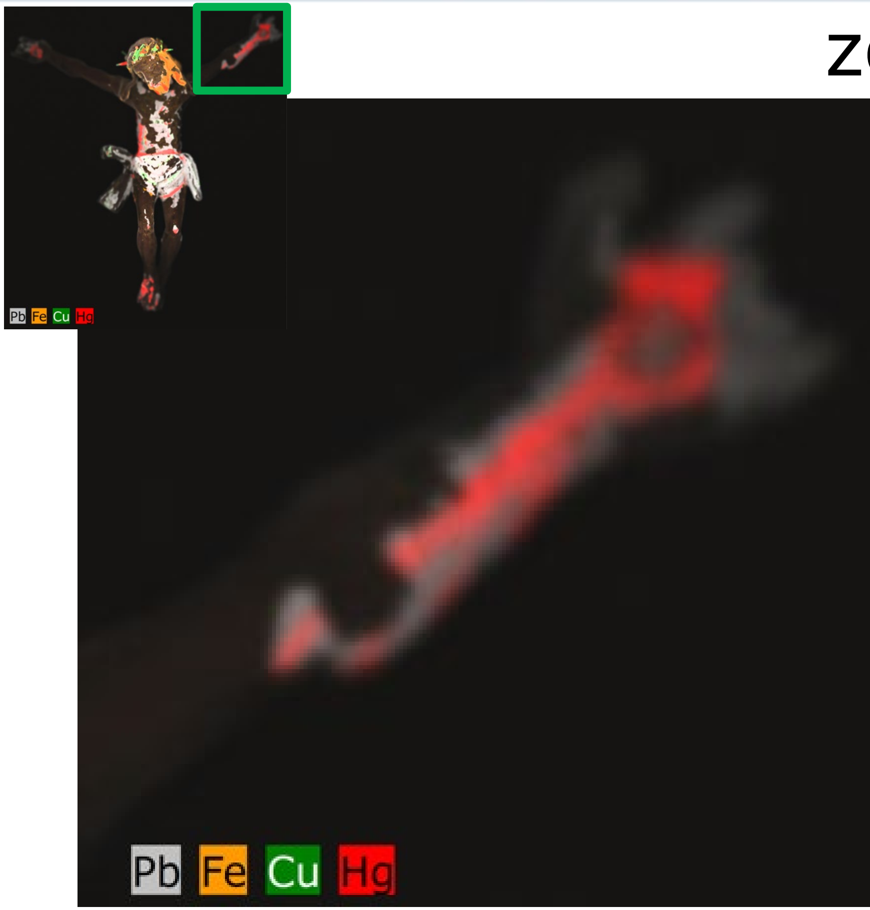


Standard setting

AMS 500 µm

Qualitative analysis
Topography and AMS

zoom



Standard setting

AMS 500 µm

High pulse throughput

Live part

Summary
M6 in Art & Conservation

The M6 Jetstream has been developed for measuring works of Art

After its introduction in 2012 the M6 Jetstream has been upgraded in 2 phases

The most recent developments introduced

- A new set of filters
- The Aperture Management System
- The Dual Detector setup with improved signal throughput

Questions, Thoughts or Comments?

If you have questions or want to contact us during the Webinar, please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

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

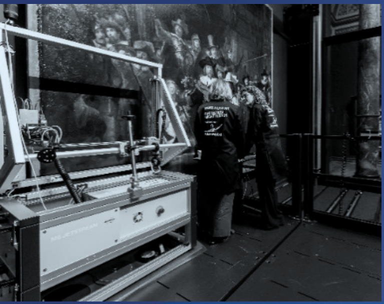
Any unanswered questions or comments will be answered and discussed by e-mail or in another Webex session.

Art & Conservation Webinar Series

Part I – May 6th | **New Horizons of micro-XRF**

Part II – May 27th | **Flexible and portable-XRF mapping solutions: Bruker's ELIO and CRONO spectrometers**

Part III – June 16th | **TRACER: the benchmark in handheld-XRF for cultural heritage**





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