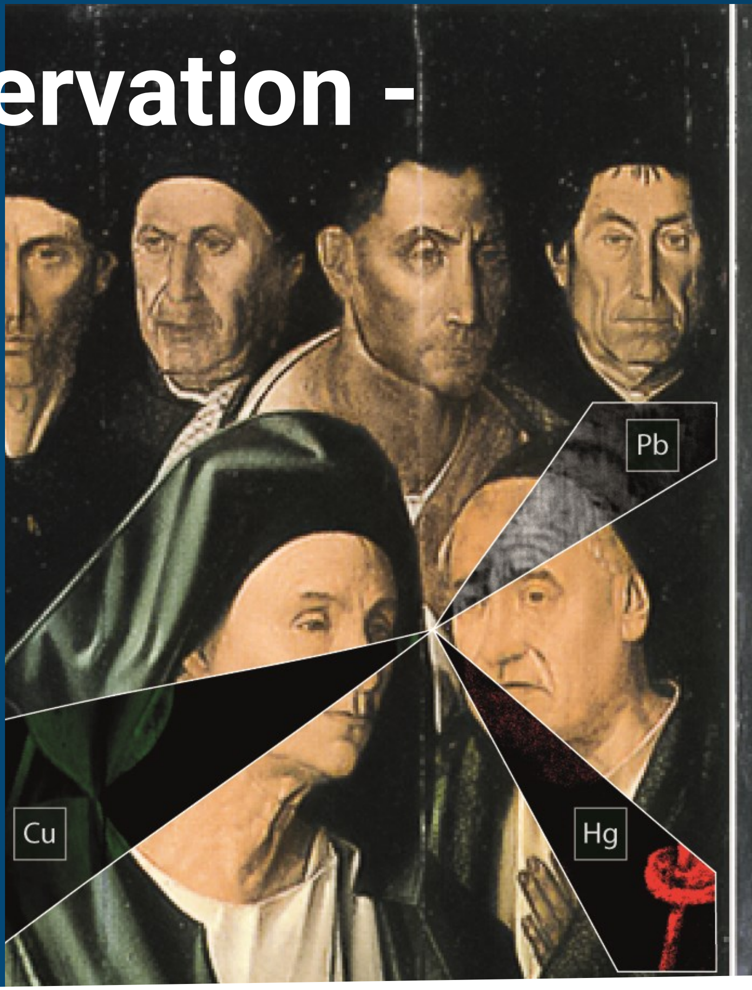
ART & CONSERVATION WEBINAR SERIES – PART VII

XRF Data Processing in Art and Conservation - Advanced Features of ESPRIT Reveal



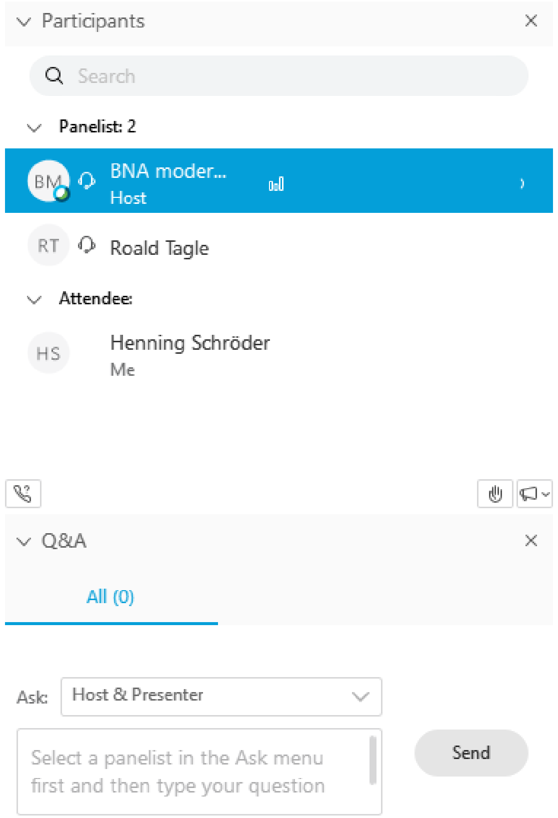
Dr. Henning Schroeder
Dr. Roald Tagle
Michele Gironda

23.09.2021

Bruker Nano Analytics

Questions and Answers

- 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 personal session.



Speakers

Dr. Henning Schröder

Product Manager
Micro-XRF

Bruker Nano GmbH

Dr. Roald A. Tagle Berdan

Senior Application Scientist
Micro-XRF

Bruker Nano GmbH

Michele Gironda

Global Market
Segment Manager
Art & Conservation

Bruker Nano GmbH

Agenda

1 Introduction

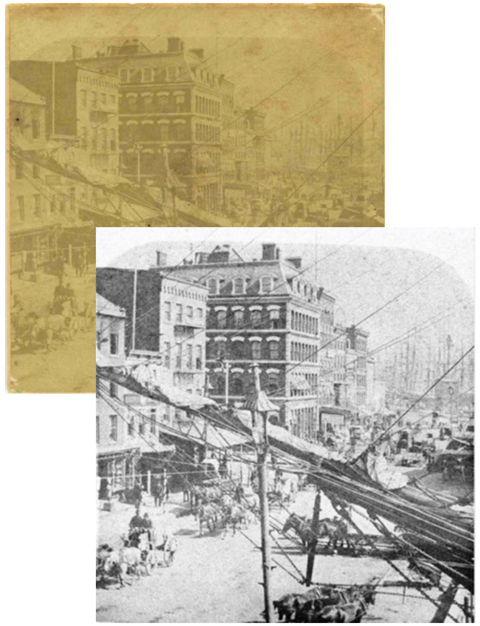
2 Composition Analysis
A Lydian Gold Coin

3 Restauration vs. Original Artwork
The Saint Vincent Panels

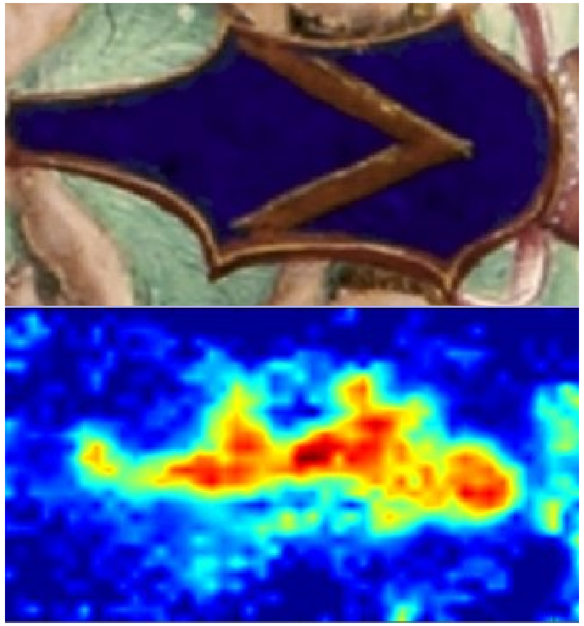
4 Summary

5 Questions and Answers

XRF in Art & Conservation



Trace element sensitive



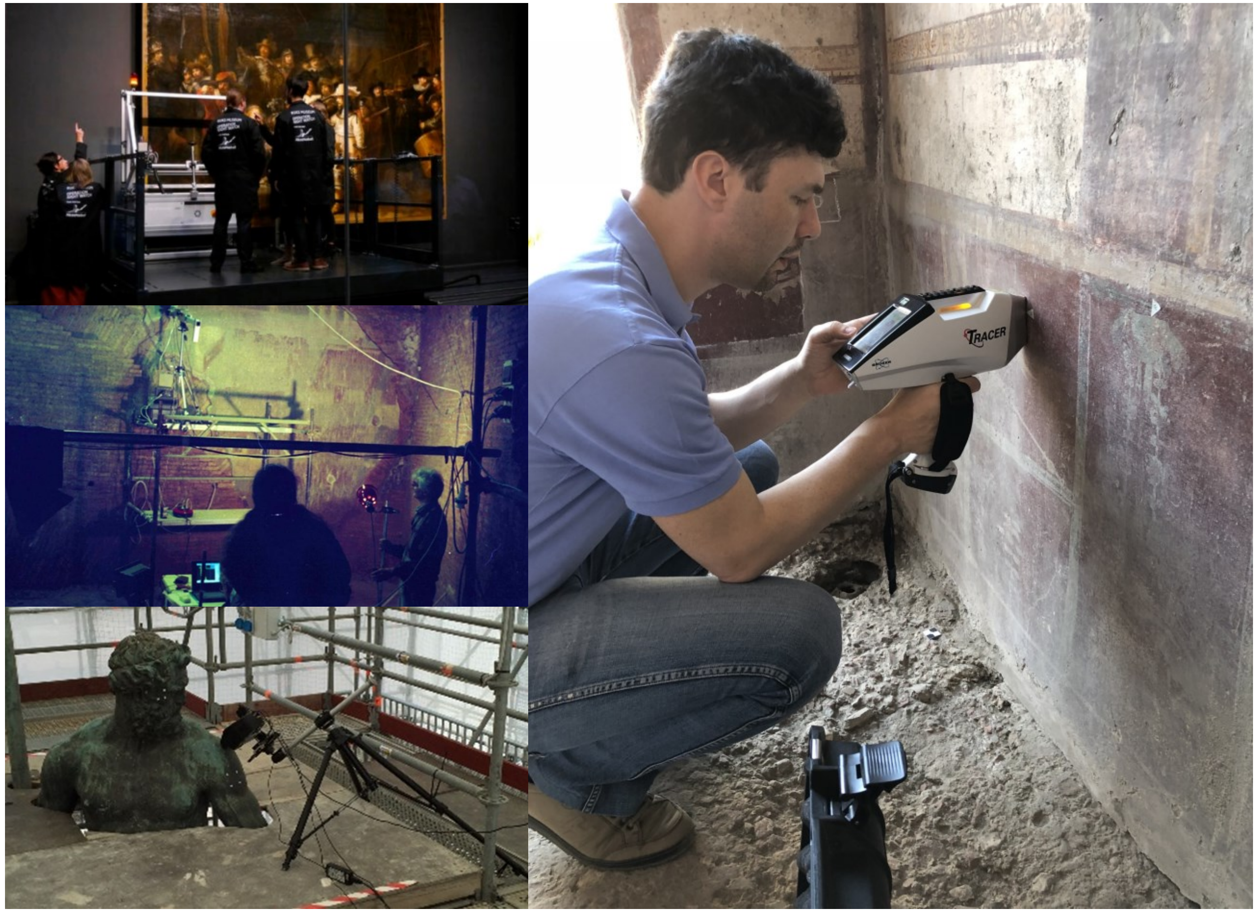
Information from depth in the sample

No sample preparation

- XRF is an element specific technique as each element absorbs and emits fluorescence at its individual energy
- The element concentration can be determined from this data as XRF spectrometers analyze the fluorescence
- An XRF scanner records the fluorescence on multiple points to determine the element distribution
- In most cases X-rays can penetrate deeper into matter than visible light allowing identification of hidden paintings or faded colors

XRF in Art & Conservation

- XRF has proven to be a core analytical technique in Cultural Heritage studies
- XRF provides key information on objects: reliable, fast, and non-invasive
- But application needs are not always the same. They differ in crucial ways with respect to the what, the where, and the how.
- Bruker offers several instruments for one analytical principle



Bruker offers the perfect instrument for your specific needs

mapping

spot

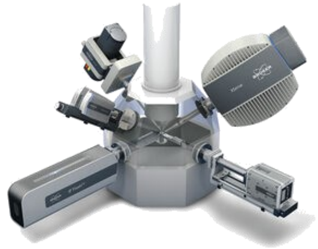
TRACER Family

ELIO

CRONO

M6 JETSTREAM

M4 TORNADO



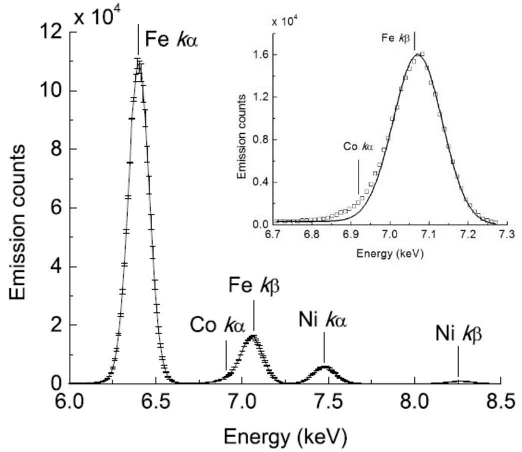
Electron microscope analysers:
EDS-WDS-EBSD-micro-XRF

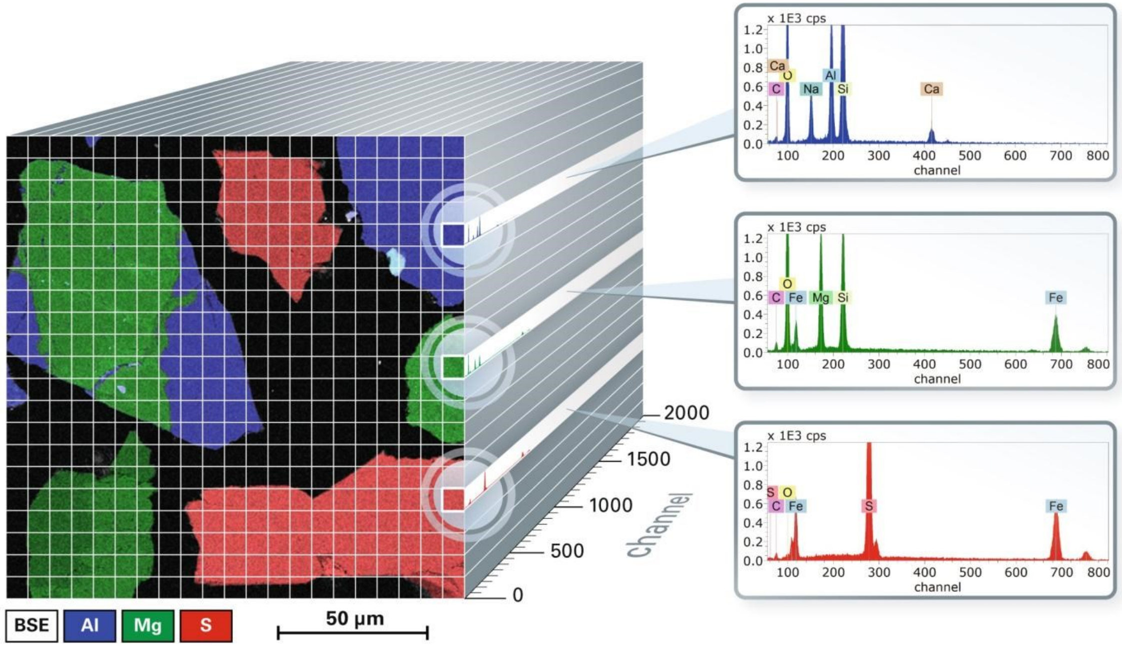
portable

laboratory based

X-Ray Fluorescence Data

- XRF-spectra show the fluorescence as a function of detector channel or energy
- Each element can have several peaks
- The peak position is characteristic for each element
- The intensity can be related to the concentration of the element
- Extending the measurement from a single point to multiple points allows to identify patterns of elements offering additional and, sometimes, unexpected information to the art object study





A Universe of Data

- The latest technology developments and the flexibility in the design available in our portfolio of instruments give access to a universe of data depicting the magic link between chemistry and art.

From Point to Area Measurement

- This generates an extremely high degree of complexity when it comes to move from data to information
- It is important to:
  - interrogate
  - sort
  - analyze the data set
- with a fast and reliable tool about aspects that are under investigation.
- Mining into data becomes a necessity and it is in this activity Bruker is investing important engineering efforts to complete its instruments designed for art studies.

From Raw data to Scientific Narrative

Data

Sorting
& processing

Presenting

All the way to a rich and correct Scientific Narrative it is crucial to consider

1) Accurate data reduction and information extraction
   a. Correct identification of element peaks vs artifacts
   b. Robust deconvolution of peak overlaps and background subtraction
   c. Robust and accurate quantification algorithms (FP) in software
2) Consistency
   a. Application of the same data reduction procedure across multiple measurements and objects

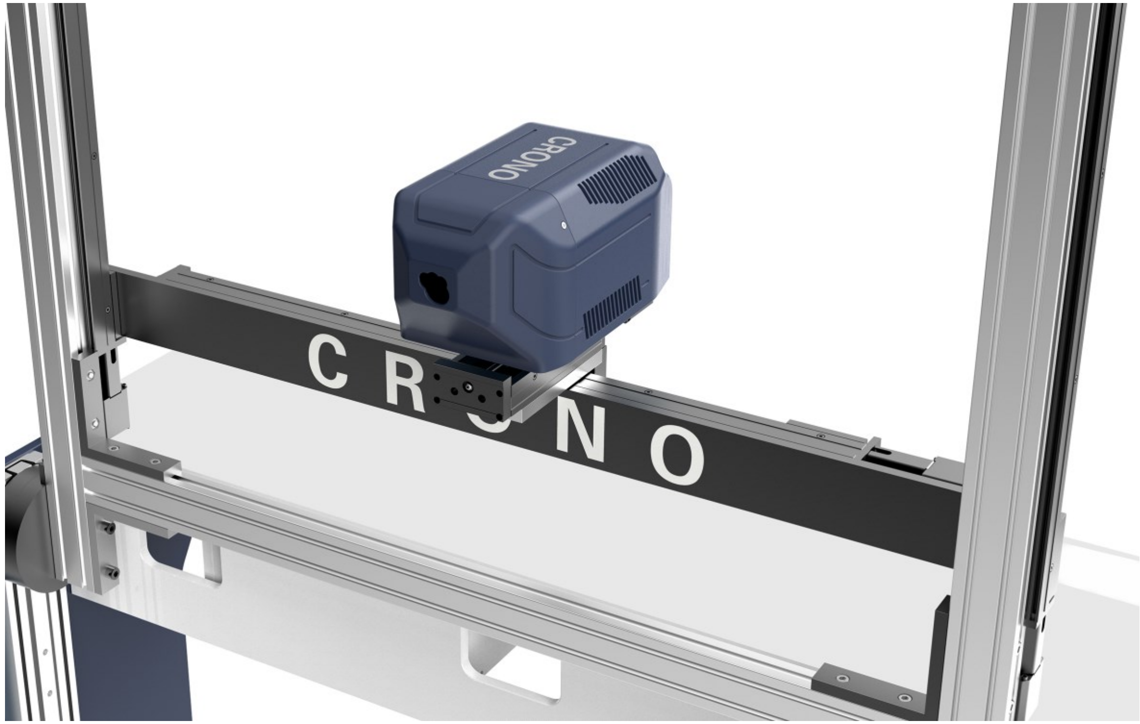
- In our solutions (including ESPRIT Reveal) we aim to provide the tools for advanced and robust data reduction for characterization and provides the tools for consistent application for data reduction protocols.

ELIO - The Only Portable micro-XRF Scanner on the Market

- Ultra-portable solution
  2.1 kg total weight of the measurement head
- Elemental composition via spot analysis
  1 mm collimator size (Ø)
- Elemental distribution via spatially resolved micro-XRF
  10 cm x 10 cm travel range

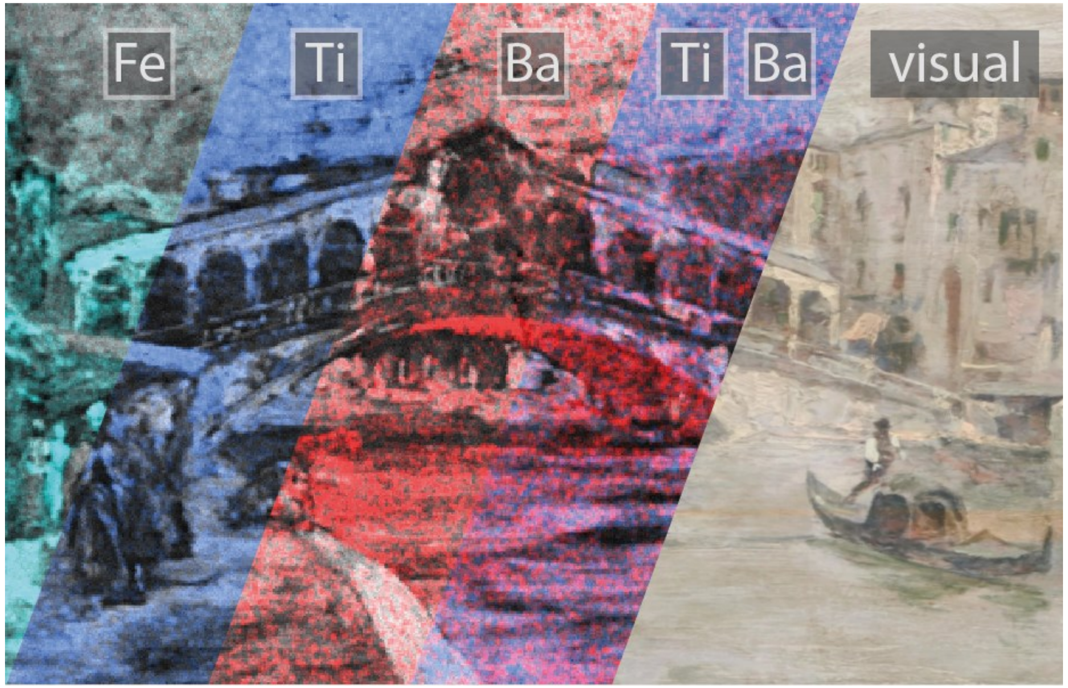
CRONO - Fast Scanner for Large Areas

- Elemental composition via spot analysis (0.5 / 1.0 / 2.0) mm collimator size (Ø)
- Elemental distribution via spatially resolved micro-XRF 600 mm x 450 mm travel range
- Fast travel speed of 42 mm/s



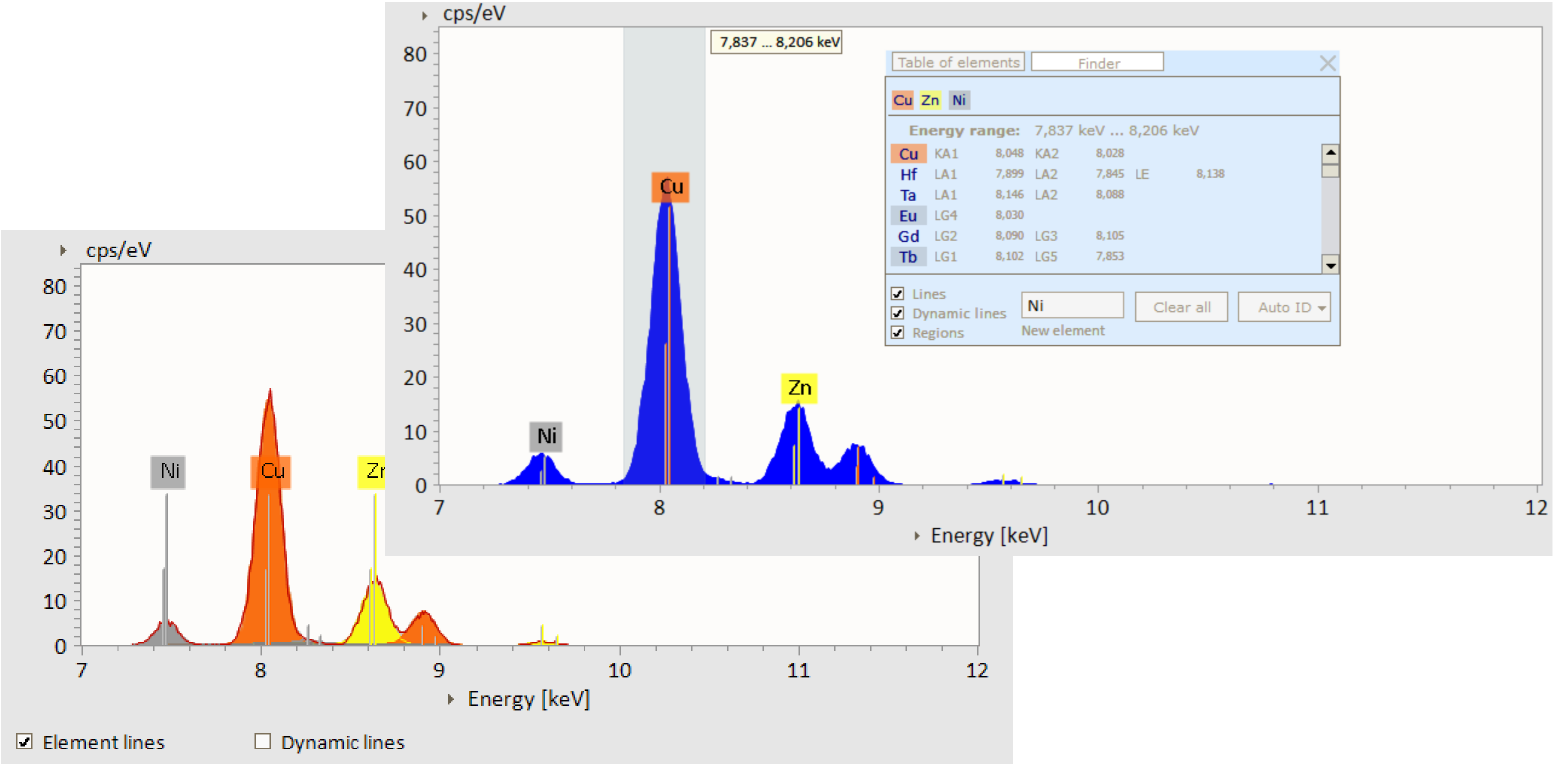
ESPRIT Reveal

- ESPRIT Reveal is a high-performance software for processing X-ray fluorescence spectra and hypermaps
- User friendly design
- No instrument control, no instrument connection required
- Introductory webinar at https://www.bruker.com/en/news-and-events/webinars/2020/xrf-data-processing-in-art-and-conservation-with-esprit-reveal



ESPRIT Reveal

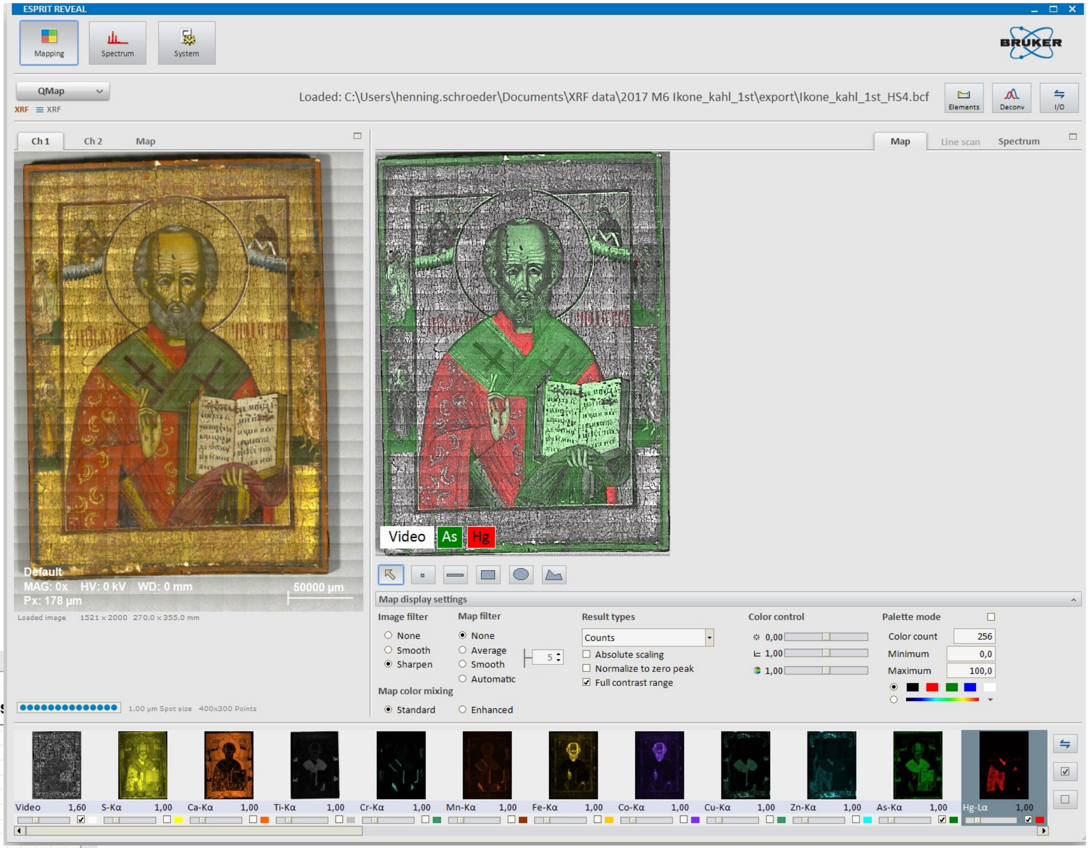
- Easy manual and automatic peak identification
- Automatically optimized ROI setting for selected elements
- Compare spectra
- Background subtraction and deconvolution / peak fitting
- Spectra quantification with selectable and customizable evaluation methods

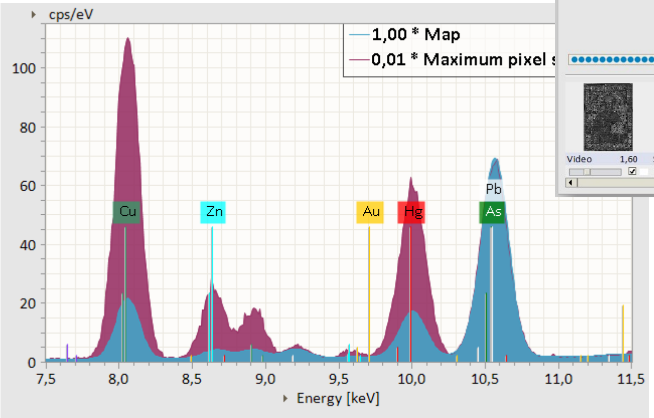


Element	At. No.	Netto	Mass Norm. [%]	rel. error [%] (1 sigma)
Cu	29	60899	75,7	0,7
Zn	30	14829	19,2	0,2
Ni	28	5539	5,2	0,1
Rh	45	38	0,0	0,0
		Sum	100,0	

ESPRIT Reveal

- Visualization and overlay of sample images and hypermaps for multi-element display
- Cut and extract object spectra
- Background subtraction and deconvolution
- Maximum pixel analysis





Qualitative and Quantitative Analysis

Presentation
ELIO: Quantitative analysis of Gold alloys

Lydia electrum coin from 610 BC – 561 BC
1/12th stater, ⌀ 8 mm, 1.16 g

Practical Part
CRONO: Semi-Quantitative painting analysis

The Saint Vincent Panels

Qualitative vs. Quantitative Analysis Where, What and How much

Qualitative analysis identifies 'what' is in a sample, while Quantitative analysis is used to determine 'how much' of 'what' is in a sample.

Both types of analysis are often done simultaneously and are considered examples of analytical chemistry(1).

Due to the spatially resolving X-ray beam, micro-XRF provides an additional dimension of information:

the 'where'.

Thus, with micro-XRF, it is possible to evaluate 'where' in the sample is 'what' and 'how much' of it.

Qualitative

Quantitative

Semi-Quantitative

Semi-quantitative analysis is more than poor quality quantitative analysis

→ It is often the smartest and quickest option to address complex questions

(1) Helmenstine, Anne Marie, Ph.D. "Understanding Quantitative Analysis in Chemistry." ThoughtCo, Aug. 25, 2020, thoughtco.com/definition-of-quantitative-analysis-604627.

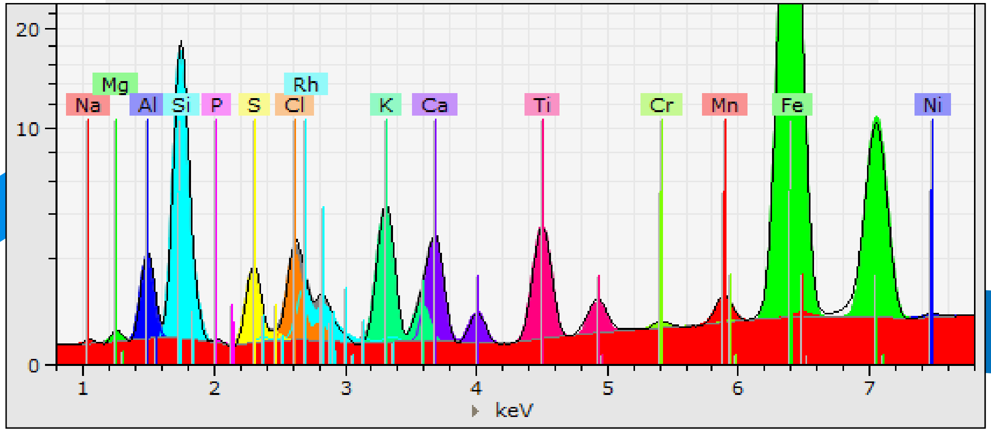
Qualitative or Semi-Quantitative Analysis

Pre-requisites for qualitative or semi-quantitative analysis: Calibrated spectrometer

Measured energy peaks can be identified as Elements present in the sample (qualitative analysis)

A state-of-the-art software supports this work by including tools such as peak fitting, deconvolution, and corrections of detector artifacts.

The spectrum provides the information about elements and their intensity

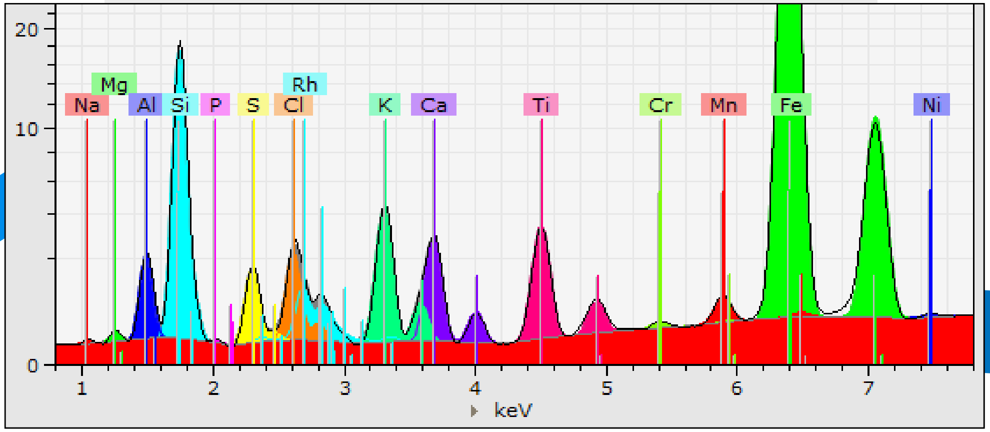


The relative peak heights (or the area under the peaks) identifies major, minor and trace element components

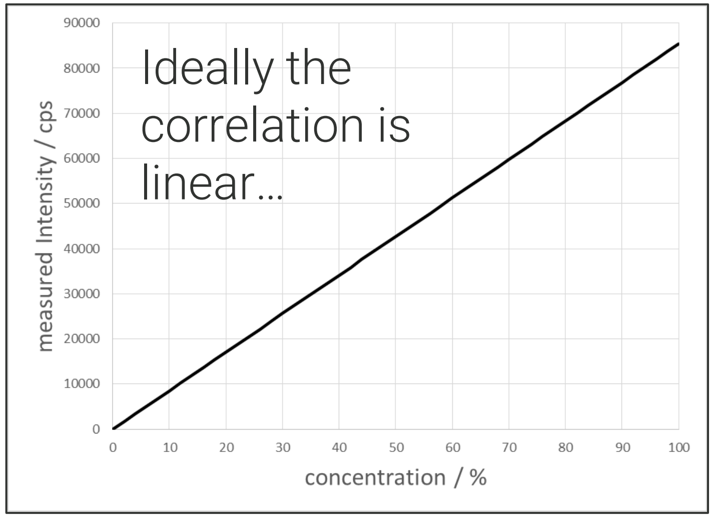
e.g. in this example, there is more Fe (green) than Mn (red), whilst there is similar amounts of K (green) and Ca (purple)….

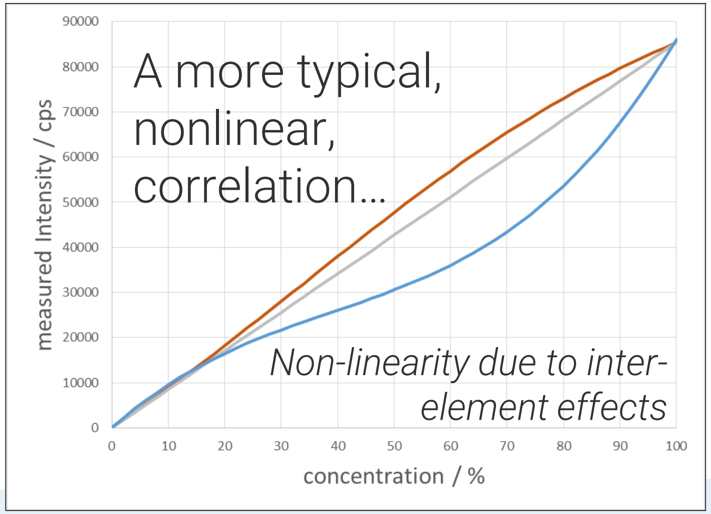
Quantitative analysis

The spectrum provides the information about elements and their intensity



Pre-requisites for quantification:
Some type of correlation between concentrations of elements in the sample and measured fluorescence intensity





Quantification Models

1. **Physical models** also called fundamental parameters quantification (FP-models)
   - Quantification based on known cross sections and probabilities as well as most physical processes taking place from the X-ray generation over the excitation to the detection
   - No standards needed
   - Sample must fit the model
2. **Mathematical models** (Empirical methods)
   - Some sort of correlation between measured element intensities and concentrations
   - Standards are required
   - Sufficiently** similar between unknowns and reference samples

** this depends on the sample matrix

3. **Mixed models** (we use it)
   - Combination of physical models (FP) and empirical sample evaluation resulting in **standard-supported FP**

FP-Quantification

The ESPRIT Reveal Software includes an FP quantification option
This option is based on the Sherman approach(2) of full forward spectra calculation. Based on an assumed sample composition, a spectrum are calculated. In an iterative process the assumed composition is varied until the measured and calculated spectra are matched.

For such a quantification, a physical description of the instrument's geometrical parameters, as well as a series of measurements of samples with known composition, is required to calibrate or describe the instrument sensitivity.

After this, any sample fulfilling the following prerequisites can be quantified:

- all main elements in the sample are detectable or, as for oxygen, in a known relation to a detectable element, e.g. Fe_2O_3
- sample is homogenous
- sample is infinitely thick

For example: Ideal samples are metal alloys, as in our next example.

(2) J. Sherman, The theoretical derivation of fluorescent X-ray intensities from mixtures, Spectrochimica Acta 7, 1955–1956, Pages 283-306

Lydian Stater are the World's First Coin

The Lydian Stater was the official coin of the Lydian Empire, introduced before the kingdom fell to the Persian Empire.

The earliest Staters probably date from the second half of the 7th century BC, during the reign of King Alyattes (r. 619–560 BC).

The Lydian Stater was composed of electrum, a naturally-occurring gold-silver alloy. The measured mix of approximately 55 % gold, 45 % silver, and a small balance of copper is not consistent with natural gold-silver ratios especially considering its variation even withing a single locality.

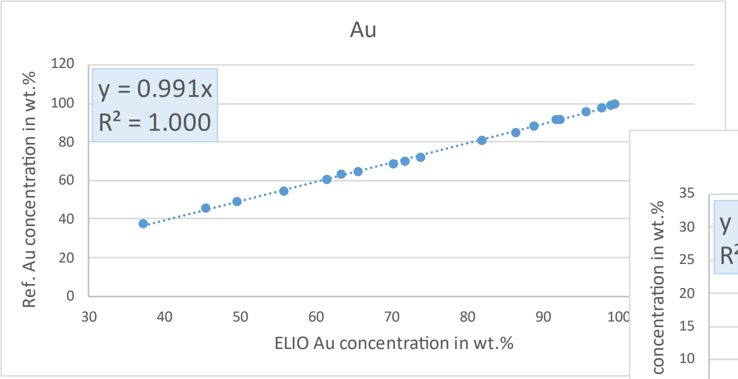
Lydia, Alyattes,
610–561 BC
1/12th Stater
⌀ 8 mm
1.16 g

(3)Millman, E. (2015, March 27). The Importance of the Lydian Stater as the World's First Coin. World History Encyclopedia. Retrieved from https://www.worldhistory.org/article/797/the-importance-of-the-lydian-stater-as-the-worlds/

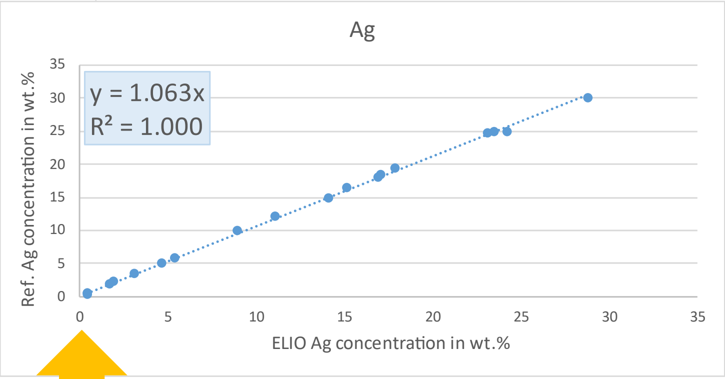
Quantitative metal analysis

The quantitative results for the calibrated ELIO were validated using a series of reference gold samples covering a wide range of concentrations.

The idea is, to validate and improve the results using a standard-supported FP-quantification



Correlation also through the origin



Reference gold samples [%]

	Cu	Zn	Ag	Cd	Au
1			0.5		99.5
2	6.3		2.0		91.7
3	5.1	0.5	2.2	0.5	91.7
4	6.0		5.9		88.1
5	2.2		12.2	0.6	85.1
6	1.7	0.4	0.4		97.5
7			19.5		80.5
8	4.6	3.1	18.4	1.7	72.2
9	5.1		24.8		70.1
10	14.9	1.9	14.9	3.8	64.5
11	15.5		30.0		54.5
12	26.0		25.0		49.0
13	25.0	4.6	25.0		45.5
14	52.5	3.0	5.0	2.0	37.5
15	1.1		3.5		95.4
16	0.5		0.5		99.0
17	4.0	**2.0**	18.0	8.0	68.3
18	26.4		10.0		63.4
19	20.7	**1.9**	16.5		60.8

The results shows a very good agreement between FP-quantification and reference sample compositions.

The linear correlation through the origin allows for a robust and simple sensitivity correction. (as we call it a “type calibration”)

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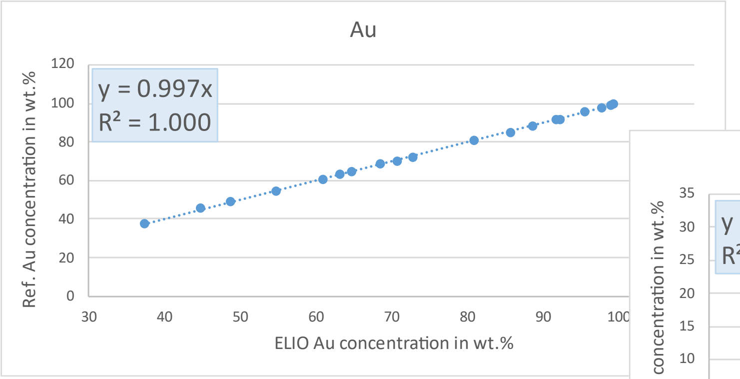
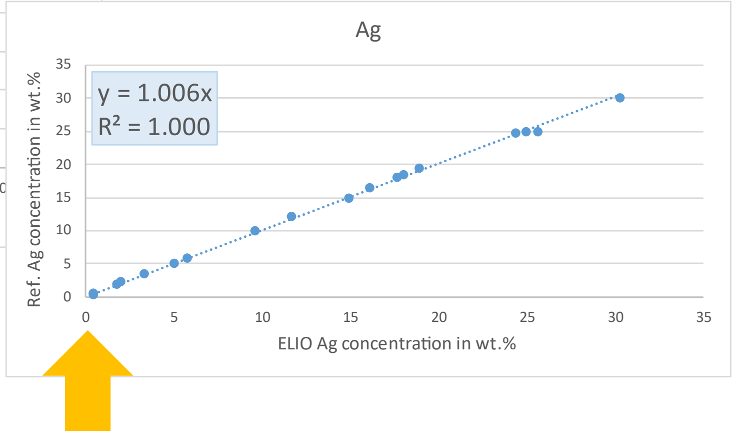


Correlation also through the origin

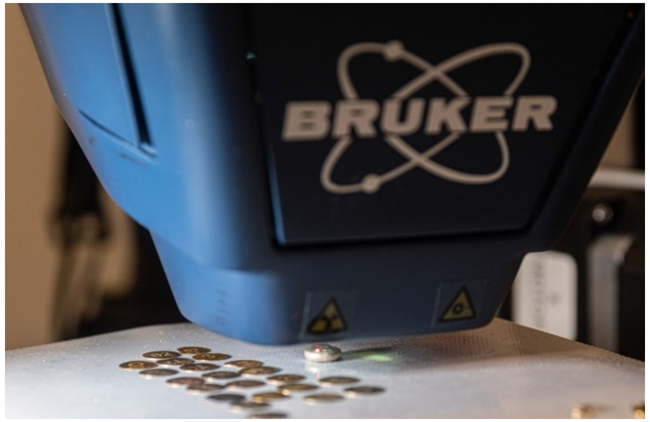


After adjusting the sensitivities for the FP-quantification based on the reference samples, the results improved significantly for the elements Ag and Cu.

Au from 0.9 wt.% → 0.3 wt.%
Ag from 6.3 wt.% → 0.6 wt.%
Cu from 3.1 wt.% → 1.7 wt.%

Quantitative metal analysis Lydian coin

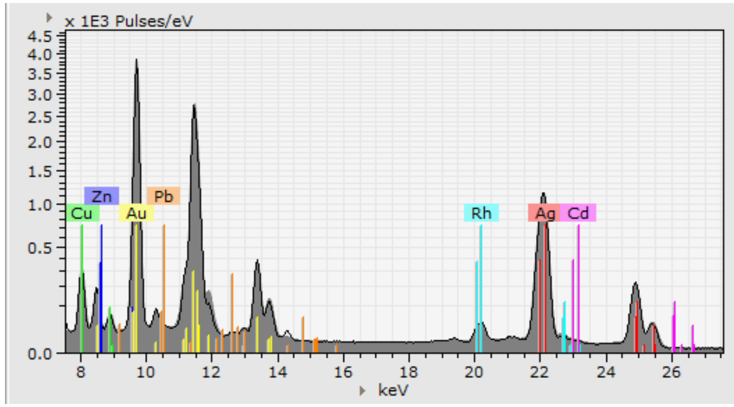
ELIO measuring the coin



Lydian electrum coin

Coin with laser beam for focusing

Best fit calculated and measured spectra

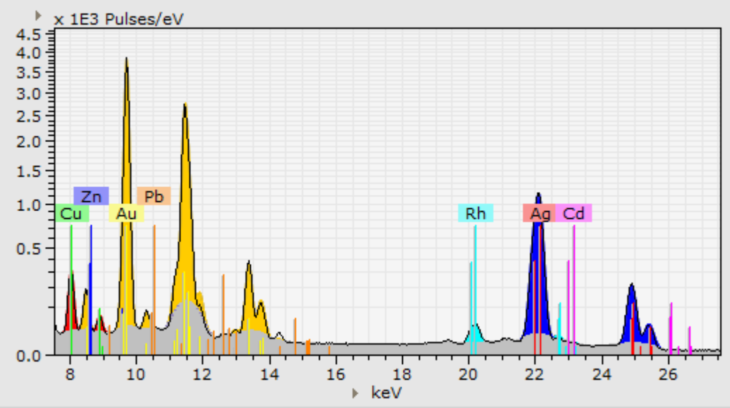


Results of the coin measurement using Esprit Reveal FP and reference samples: Conditions: 50 kV, 80 µA, 120 s real time

Normalized mass concentration [%]

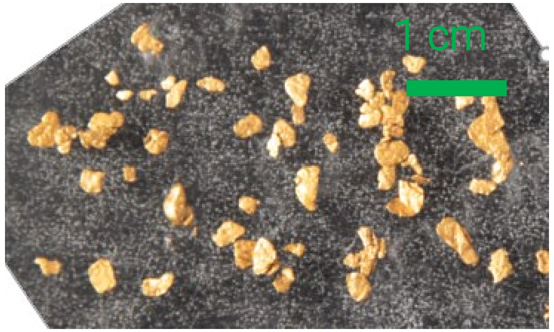
Spectrum	Iron	Copper	Zinc	Rhodium	Silver	Gold	Lead
Au-Coin 120 s II.spx	0.12	1.54	0.00	0.00	45.58	52.70	0.06
Au_Coin 120 s I.spx	0.11	1.53	0.00	0.00	45.83	52.47	0.05
Mean	**0.12**	**1.53**	**0.00**	**0.00**	**45.71**	**52.59**	**0.06**
Sigma	**0.00**	**0.01**	**0.00**	**0.00**	**0.18**	**0.16**	**0.00**
SigmaMean	**0.00**	**0.00**	**0.00**	**0.00**	**0.13**	**0.12**	**0.00**

Single element contribution to the spectrum, in different colors



Quantitative metal analysis
Lydian coin

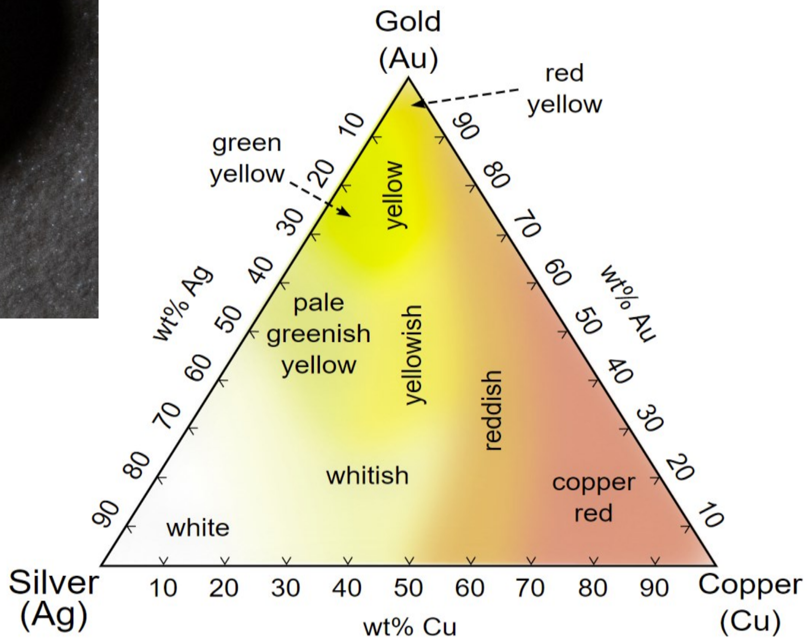
Electrum is a natural Gold-Silver alloy with variable composition.



Coin: Au: 52.6 wt.%
Ag: 45.7 wt.%
Cu: 1.5 wt.%

Values found for Au here are in good agreement with reported values* Au: (55 ± 2) wt.-%

There is debate over whether the coin alloy has a natural origin, or if it is made to this concentration on purpose. Currently, the prevalent theory is that the alloy was casted on purpose.



*Melitz, J. (2016). A model of the Beginning of Coinage in Antiquity.
https://commons.wikimedia.org/wiki/File:Ag-Au-Cu-colours-lt.svg

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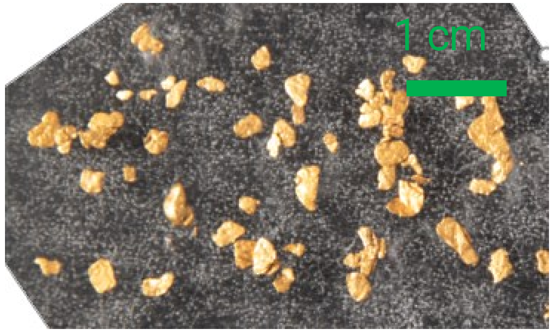
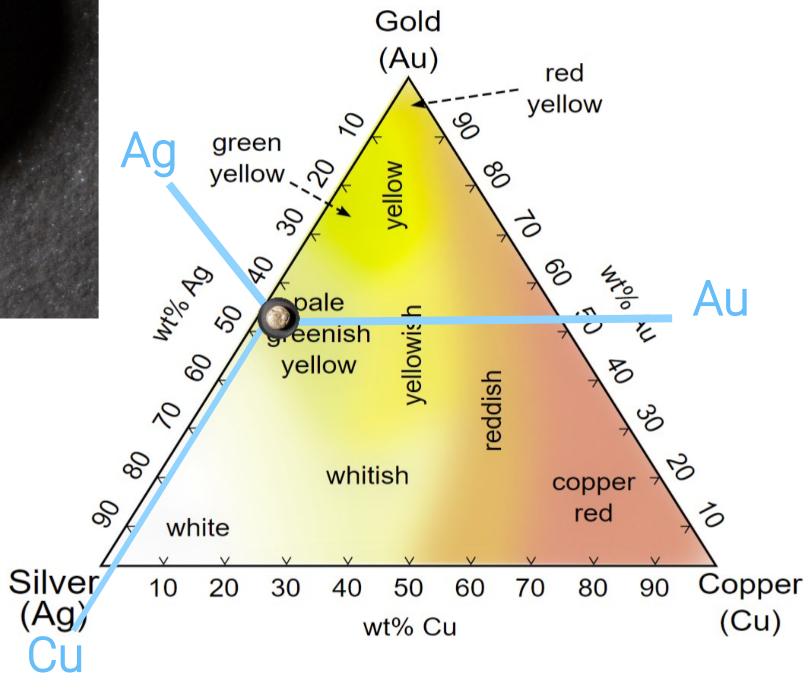


Interestingly the composition of the coin is very close to the lowest possible Au-Ag alloy with a yellow appearance.



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https://commons.wikimedia.org/wiki/File:Ag-Au-Cu-colours-lt.svg

Quantitative analysis
ELIO

- The ELIO can be characterized and prepared for fundamental parameter (FP) quantification
- For an accurate quantification using an FP model it is required that:
  - Sample is homogenous
  - Sample is infinitely thick
  - All main elements in the sample are detectable, or that the compositions of not detectable elements is known.
  - Alternative the non-detectable element, such as oxygen, comes in a fixed stoichiometric relation to a detectable element, for example Fe_2O_3
- The quantification can be preformed using the ESPRIT Reveal software
- The software allows not only a standard-free quantification but also a mixed quantification model using references samples to improve the precision even further

The Saint Vincent Panels

The Saint Vincent Panels

Live Demonstration

Points to cover

1. Element Identification
   - Spectra fitting
   - Deconvolution
   - Maximum pixel spectra
2. Advance data Mining
   - Element arithmetic
   - Identification of original pigment and repaints
3. Discussion of preliminary results

Live Demonstration

Summary

- The ESPRIT Reveal Software has variety of options allowing to perform complex operation using a user-friendly GUI
- The tools ins the software support basic and complex procedures such as:
  - Element identification, manual or automatic
  - ROI display
  - Fast deconvolution
  - Peak fitting
- In addition, the software has additional tools for data mining:
  - Multiple color and single-color display
  - Contrast optimization tool
  - Intensity arithmetic
  - QMap or full spectra calculation for net peak display

Questions and Answers

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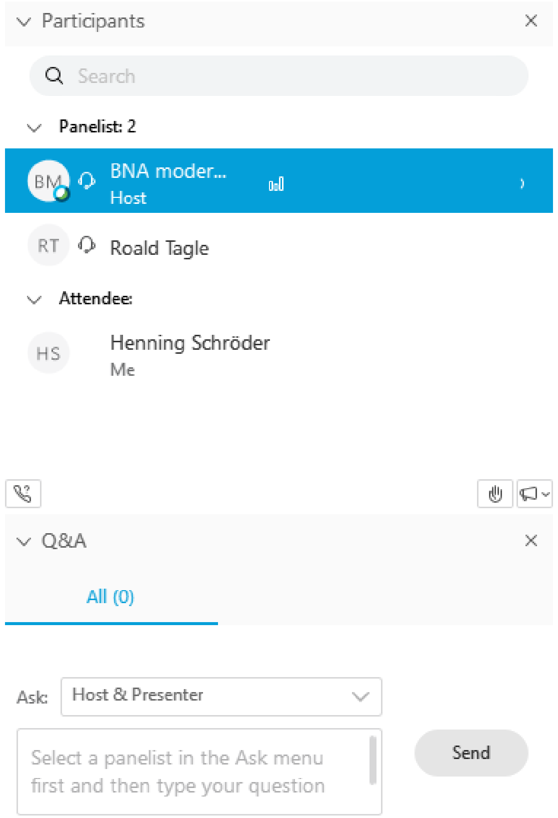
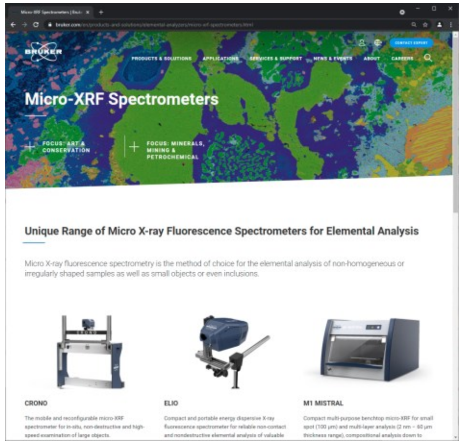
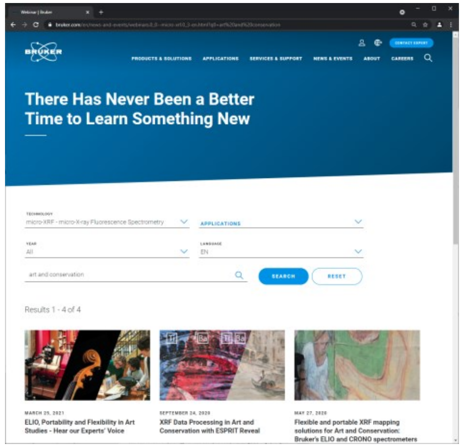


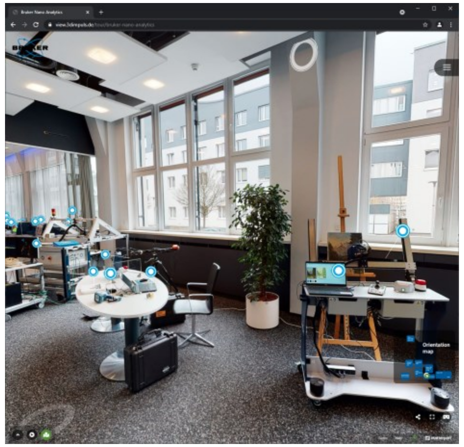
Learn More About our Products



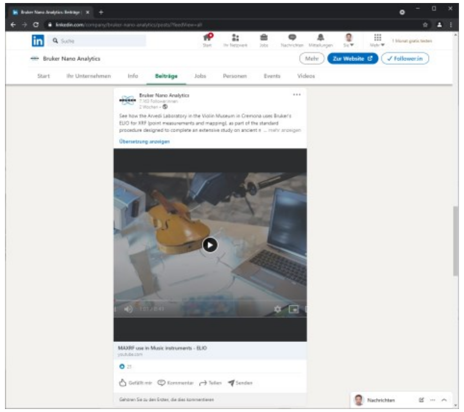
Product Page



Webinars



Virtual Lab



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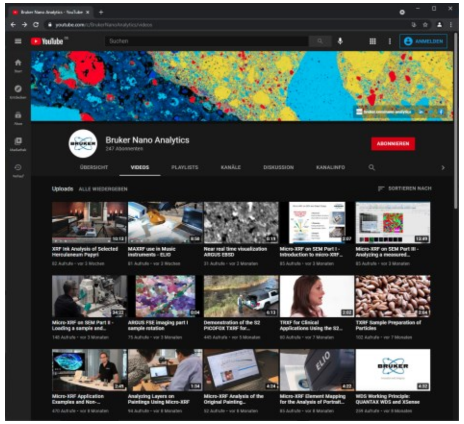

YouTube

For more information, please contact us
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