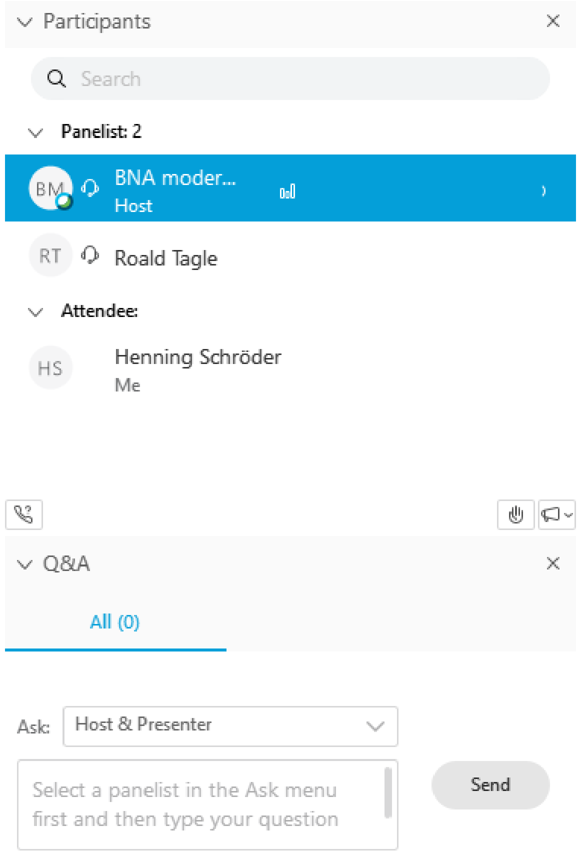
BRUKER NANO ANALYTICS' CULTURAL HERITAGE WEBINAR SERIES 2023

Analysis of non-infinite samples in Cultural Heritage

Micro-XRF Applications Team
Bruker Nano Analytics

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.

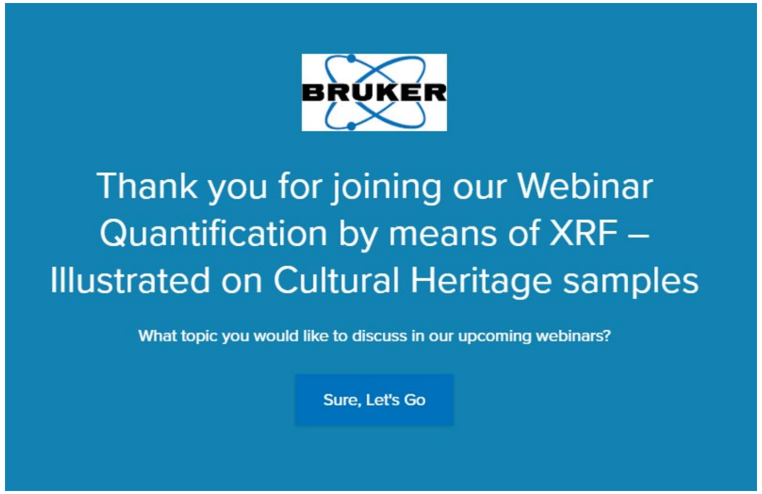
Any unanswered questions or comments will be answered and discussed by e-mail or in another WebEx session.

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

There are many topics involving XRF in Cultural Heritage!

We are interested to know which topic(s) you would like to learn more about in upcoming webinars?

- For live sessions: follow the QR code on the right.
- For on-demand: You can find a link in the video description or follow the QR code on the right.



The Speakers

Dr. Roald Tagle

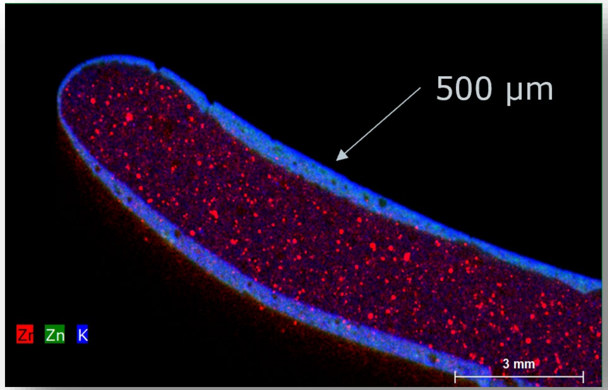
- Head of XMP Application,
  Bruker Nano Analytics, Berlin, Germany

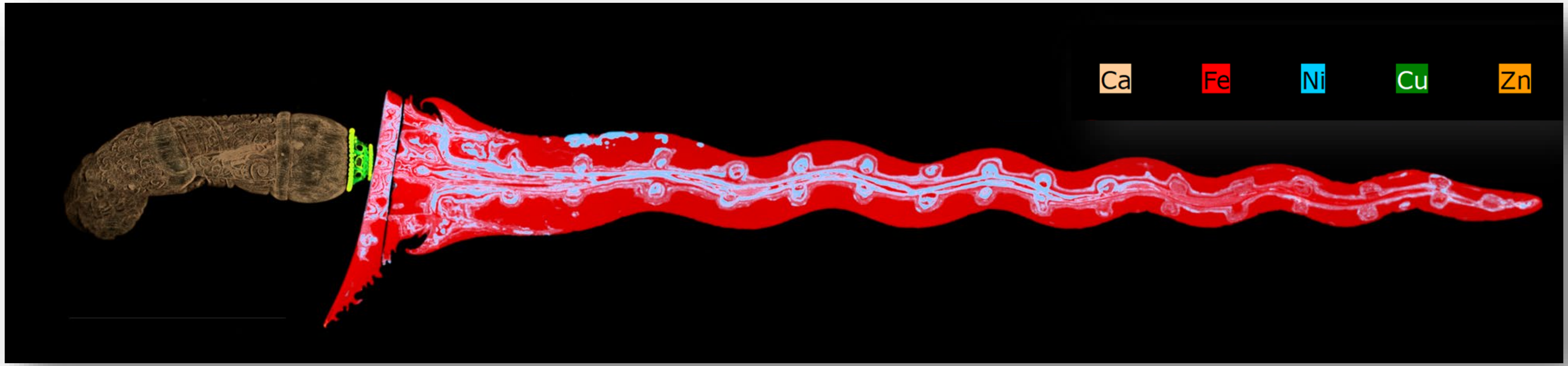
Mareike Gerken M.A.

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

Overview

- This webinar focuses on quantitative XRF analysis of non-infinite samples.
- If you want to know more about **quantification of Cultural Heritage related materials** subscribe for the on-demand webinar session from October 12th 2023.
- Further next year, we will continue discussing the analysis of **three-dimensional objects,** aiming on qualitative and quantitative analysis, its potentials and limitations.





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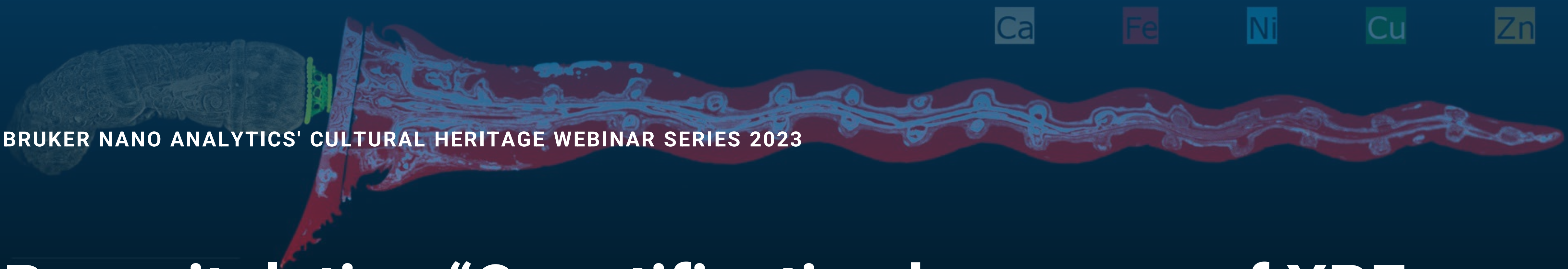


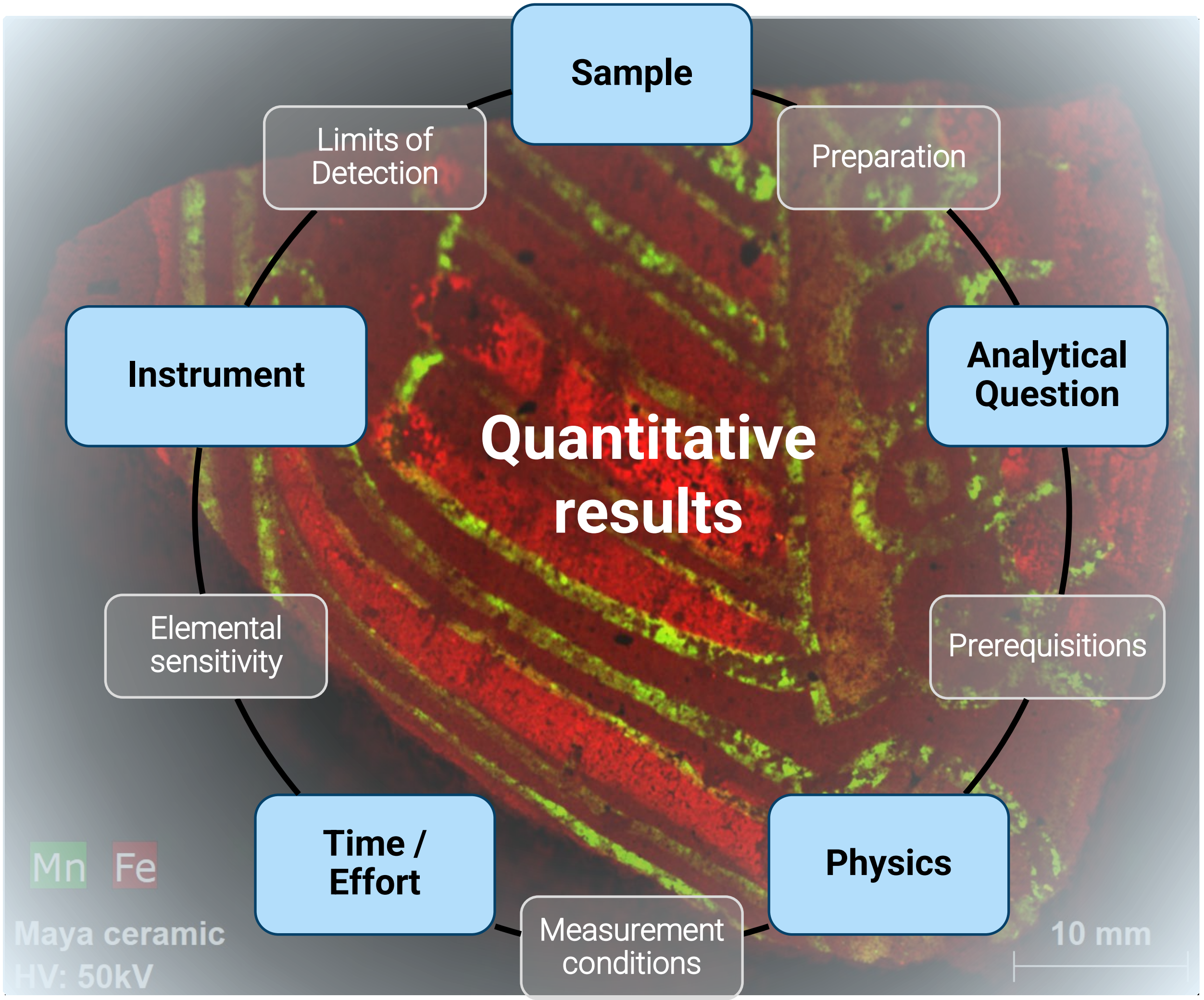
Recapitulating “Quantification by means of XRF in Heritage Science”

Quantitative X-ray fluorescence analysis
A complex matter…

*"Physics unveils possibilities,
technology harnesses potentials,
while the synergy between the sample and
the analytical query forges the path."*

Quantitative results emerge as a convolution of:

- the sample
- the analytical question
- the applied effort
- the available time
- the analysts' talent
- the capabilities of the available instrumentation



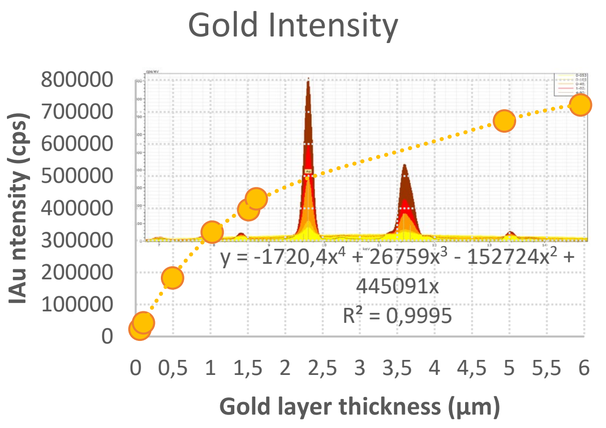
Quantitative X-ray fluorescence analysis
Understanding your sample… from the XRF point of view

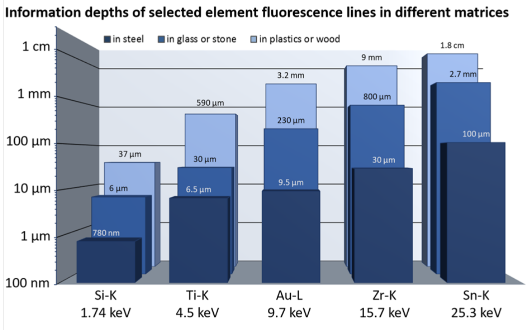
Each material has its own intrinsic structure and composition that impacts not only the analysis itself but also its outcomes. Likewise, each instrument has its own specifications that equal its performance.
Understanding both is the key to getting significant and analytically relevant results!

Sample Determinants

Information depth

Homogeneity





The Copper CHARM set: 10.1111/arcm.12117

Quantification
…With standards or without?

Ideally, for a Quantification the samples are:

- Homogeneous
- Infinitely thick
- All matrix-relevant elements in the sample are either detectable and their amount known, or they are in a fixed ratio to a detectable element.

?

→ If this IS the case, standard-less or reference material-free (FP) methods are well suitable with possibilities to increase performance by using reference materials

→ If this is NOT the case, reference samples are recommended. Otherwise, the complexity of the task increases significantly together with the uncertainty of the results

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Non-infinite samples in Cultural Heritage
An overview

What types of materials are we talking about?

- Gildings
- Alloys
- Corrosion layers
- Ink
- Glazes (Ceramics)

Which research questions can be answered using XRF?

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




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Measuring gildings

Studying gildings
An introduction to… the art-technology

Historically, different gilding techniques have been used:

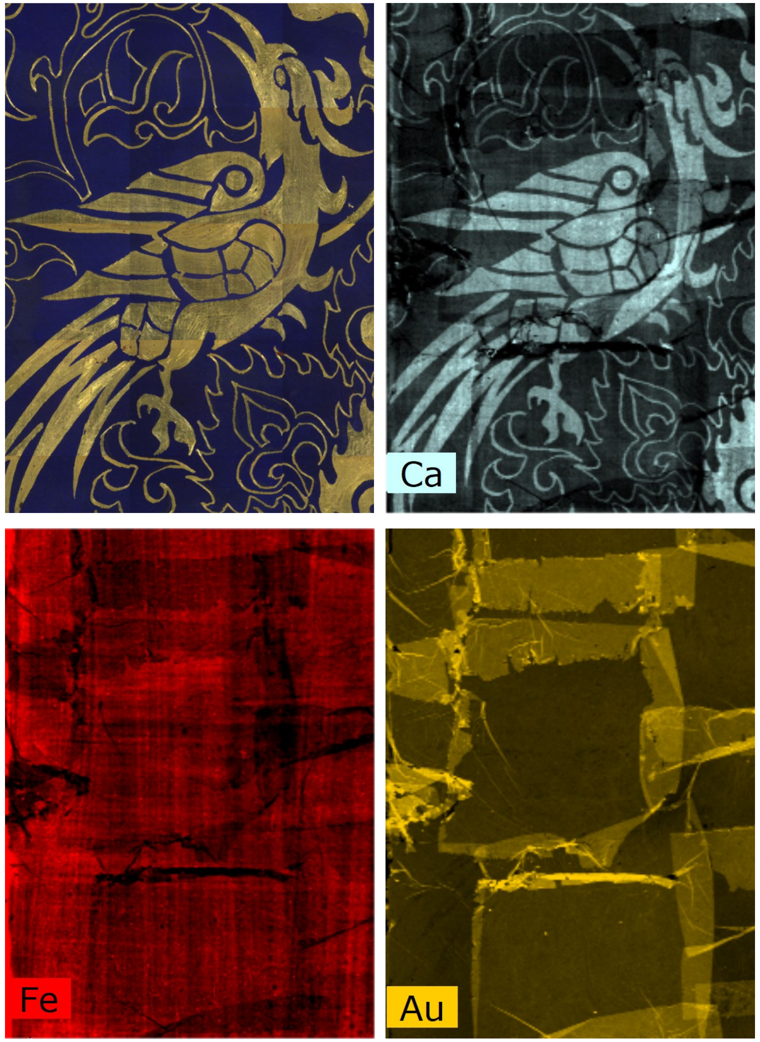
- **Water/ poliment gilding**: gold leaf applied on a layer of bole that covers a gesso ground and afterwards burnished.
- **Mordant/ oil gilding**: gold leave applied on an adhesive (oil-resin) and not burnished.
- **Shell gold**: Powdered gold bound with gum arabic or any other medium applied with a brush.

Plus, additional techniques that imitate gold

- Varnished or burnished silver or tin foil
- …

And multiple decoration techniques…

*https://courses.shtyrmer.com/renaissance/techniques/gilding-techniques/



Micro-XRF mapping of a *sgraffito* decorated gilding.

Studying gildings
An introduction to… ongoing research

What can we learn from spatial resolved micro-XRF analysis?

Information	Research question
Application technique	Attribution
Application quality	Skill level
Size of gold leaves	Origin & Provenance

But what if we could extend the amount of information to…

- Gold material
- Gold leaf thickness

} Compositional analysis

MacLennan *et al. Herit Sci* (2019) 7:25
https://doi.org/10.1186/s40494-019-0271-0
Heritage Science

RESEARCH ARTICLE Open Access

Check for updates

Visualizing and measuring gold leaf in fourteenth- and fifteenth-century Italian gold ground paintings using scanning macro X-ray fluorescence spectroscopy: a new tool for advancing art historical research

Douglas MacLennan[1*], Laura Llewellyn[2], John K. Delaney[3], Kathryn A. Dooley[3], Catherine Schmidt Patterson[1], Yvonne Szafran[2] and Karen Trentelman[1]

Studying gildings
An introduction to… ongoing research

A historical overview about analytical approaches to determine the leave thickness

Invasive approaches

- SEM/EDX on cross-section samples.
  doi.org/10.1111/arcm.12287

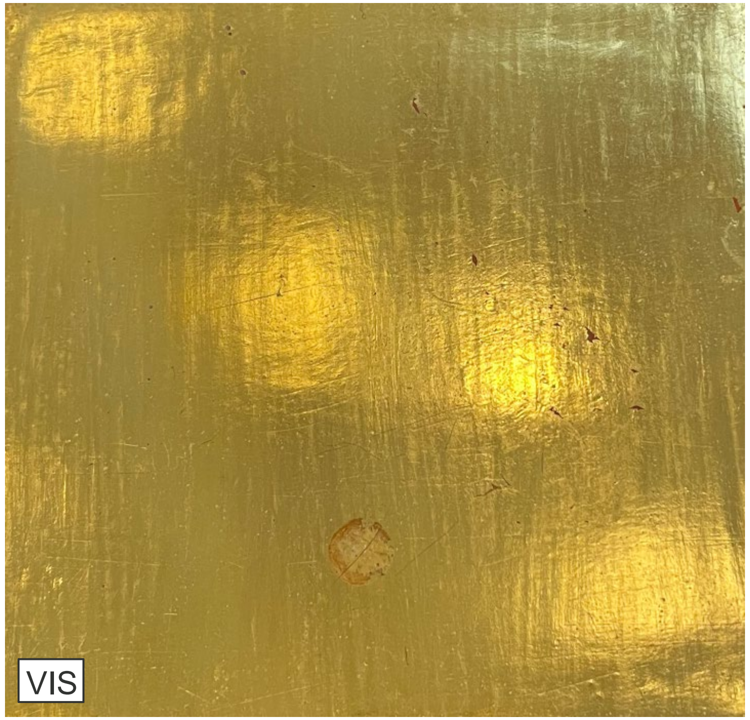
Non-invasive approaches:

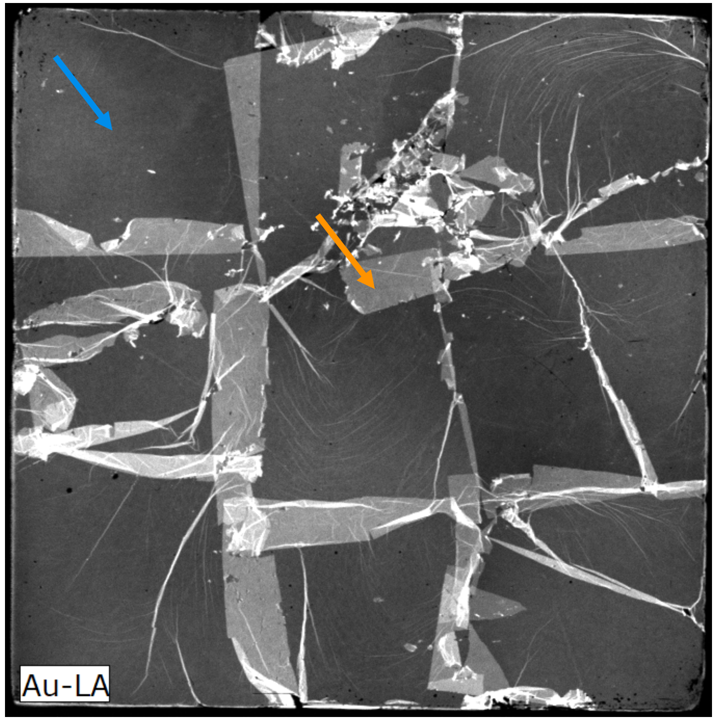
- Using the intensity ratio of Pb-Lα/Lβ of the adhesive layer of a mordant gilding.
  doi.org/10.1002/xrs.2518
- Calculating from the weight and composition of *ducat* or *florin* used.
  “The Market for Painters' Materials in Renaissance Florence.” Kubersky-Piredda, Susanne. (2010) - In: Trade in artists' materials. Markets and commerce in Europe to 1700 p. 223-244

Studying gildings
Non-infinity of gold leaves

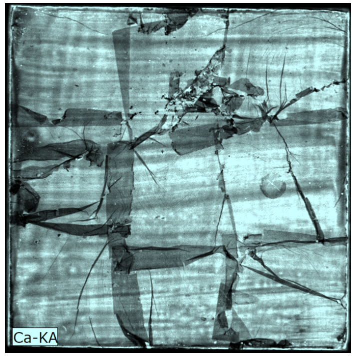
Looking at the Au-Lα distribution of a gilded surface, intensity differences are clearly notable between areas covered with a single gold layer or overlapping leaves.

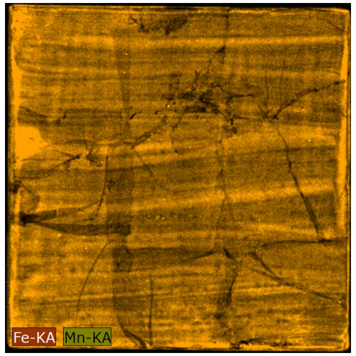
The common gold leave thickness is ca. 100 – 300 nm.

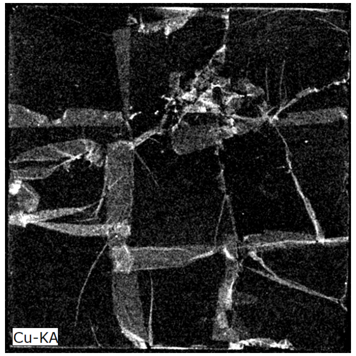




M6 JETSTREAM, 50 kV 600 µA, 100 µm spot, 150 µm pixel size, 25 ms/px dwell time.

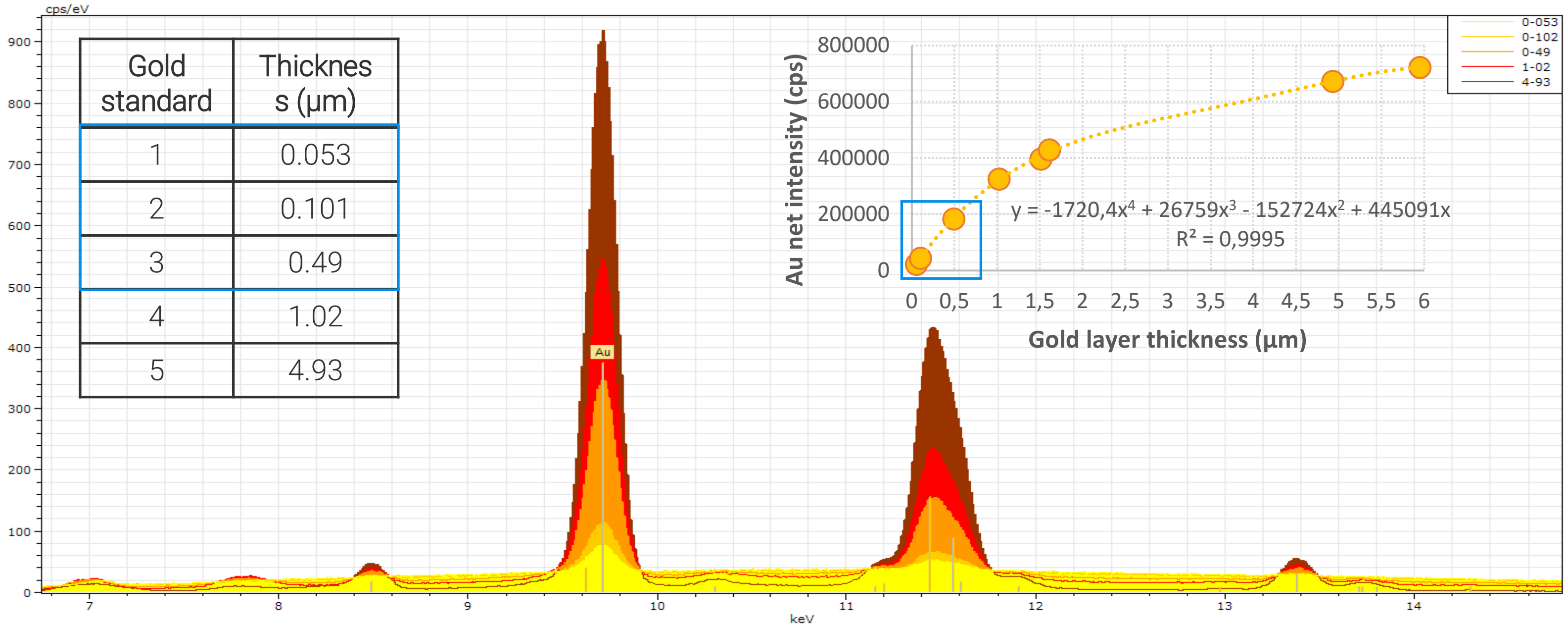




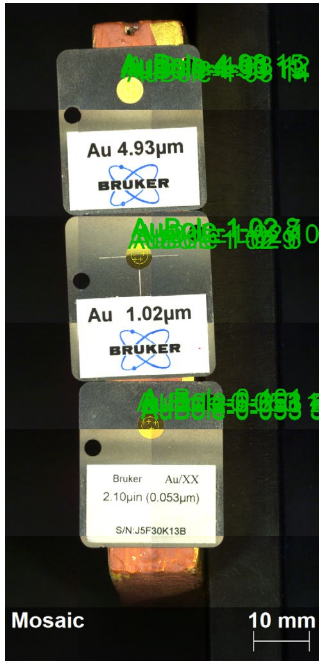


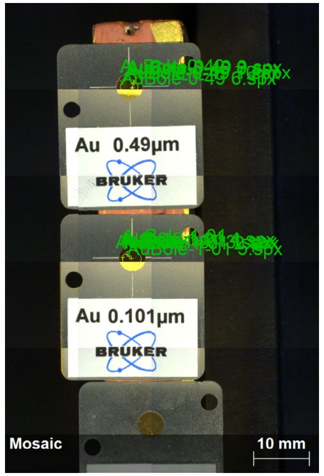
Studying gildings
Non-infinity of gold leaves: Using reference materials

- Thin gold foils were measured on top of the prepared priming and bole to simulate the same background: The plot of net intensity (cps) vs. gold layer thickness (µm) shows a linear correlation in the sub-500 nm range.
- We cannot determine the actual coating thickness, but the number of atoms measured. The thickness is just a function of density!



Gold standard	Thickness (µm)
1	0.053
2	0.101
3	0.49
4	1.02
5	4.93





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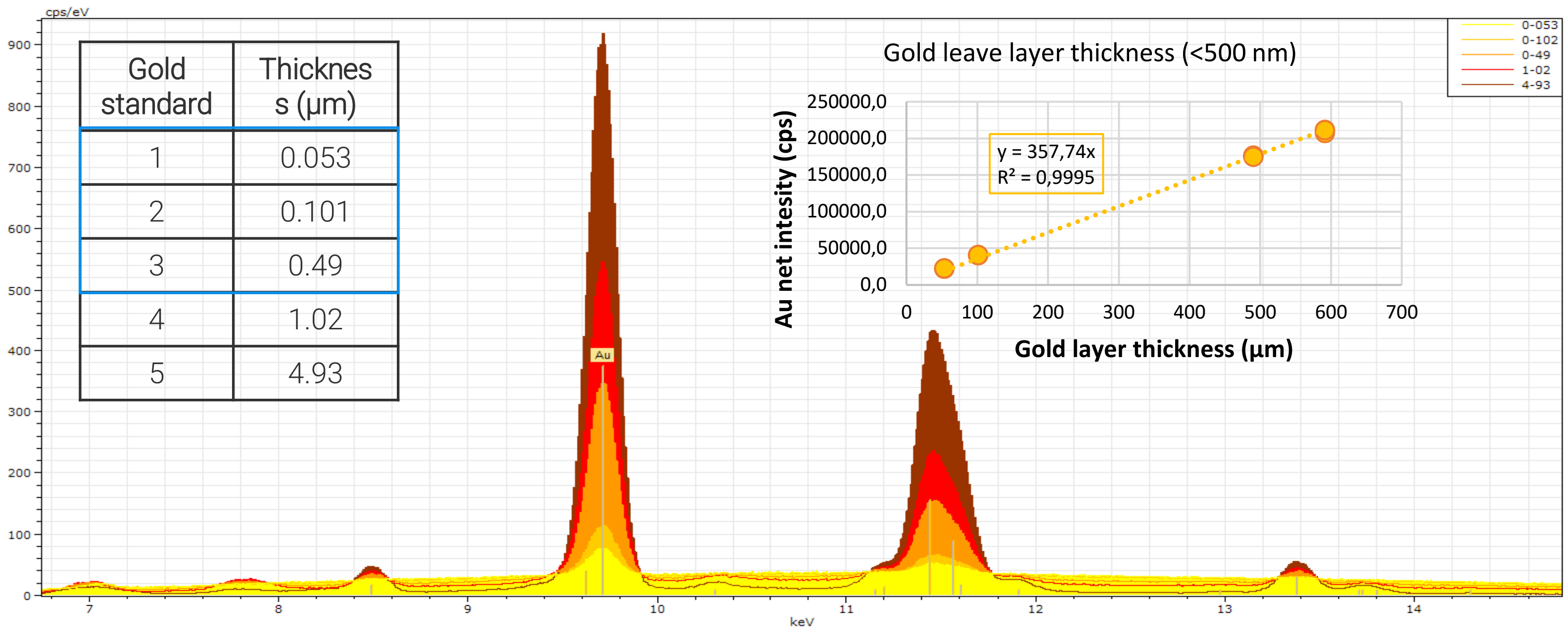
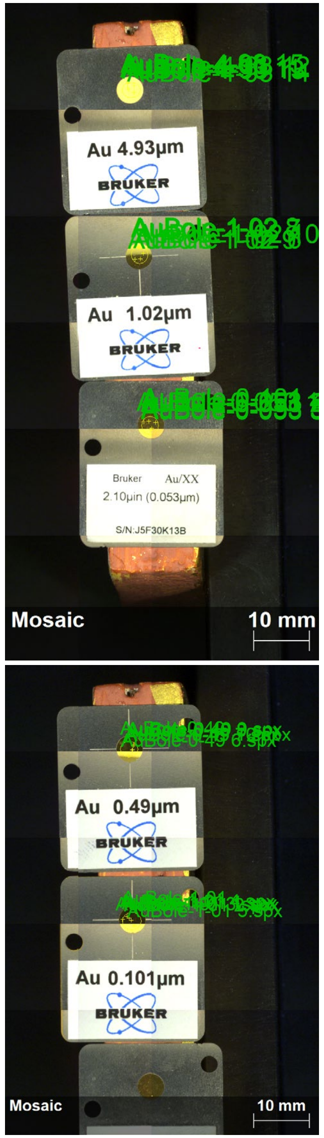
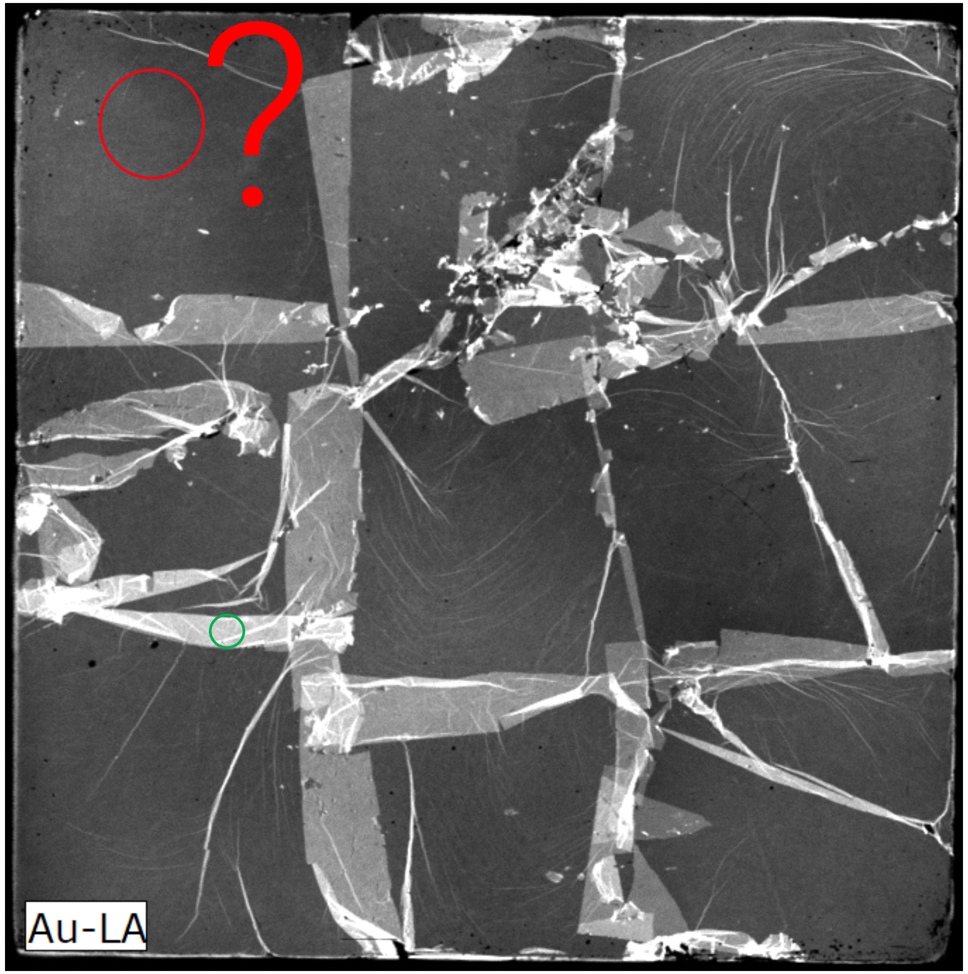
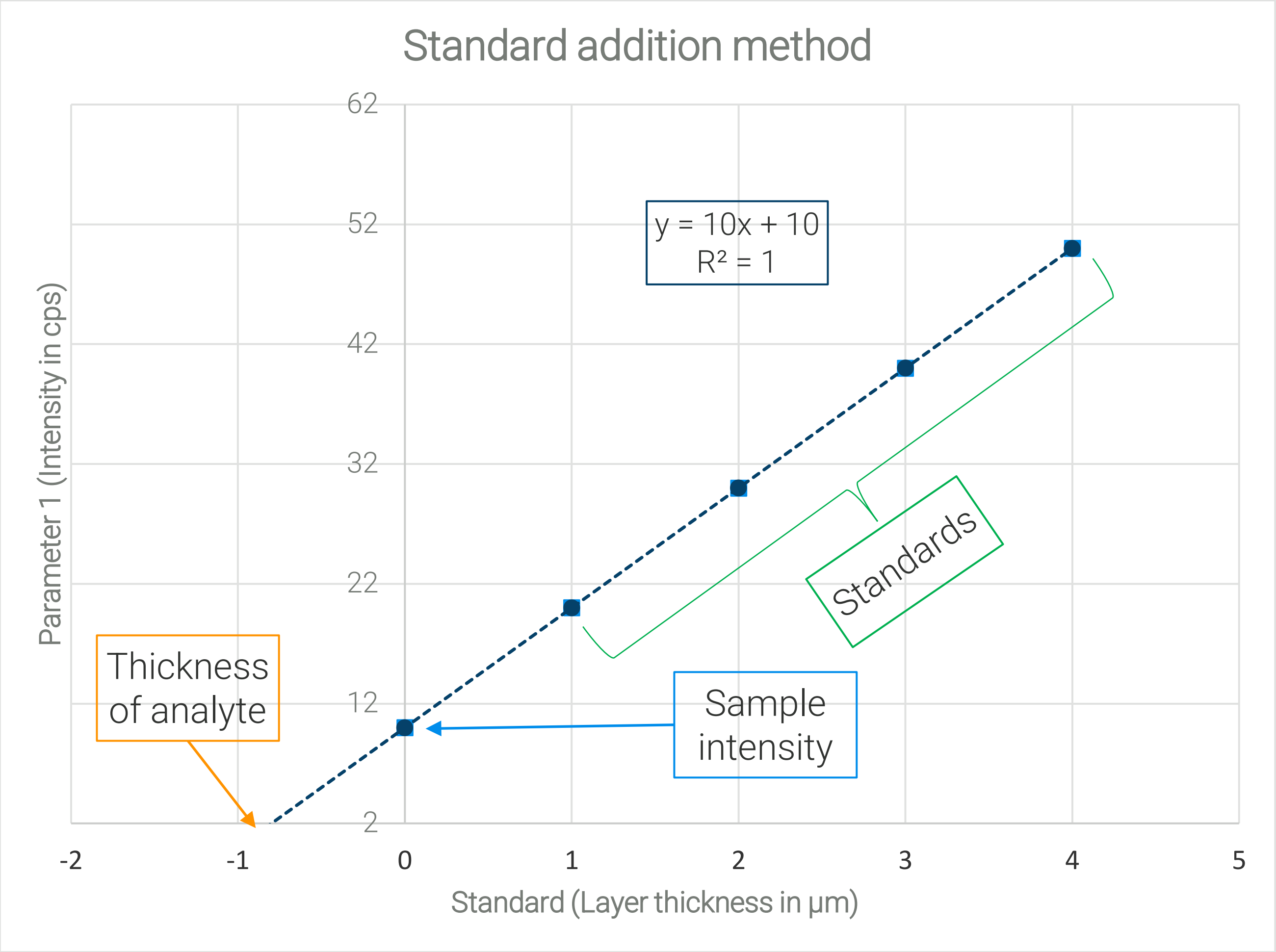




Measuring gold leaf thickness
Standard addition method





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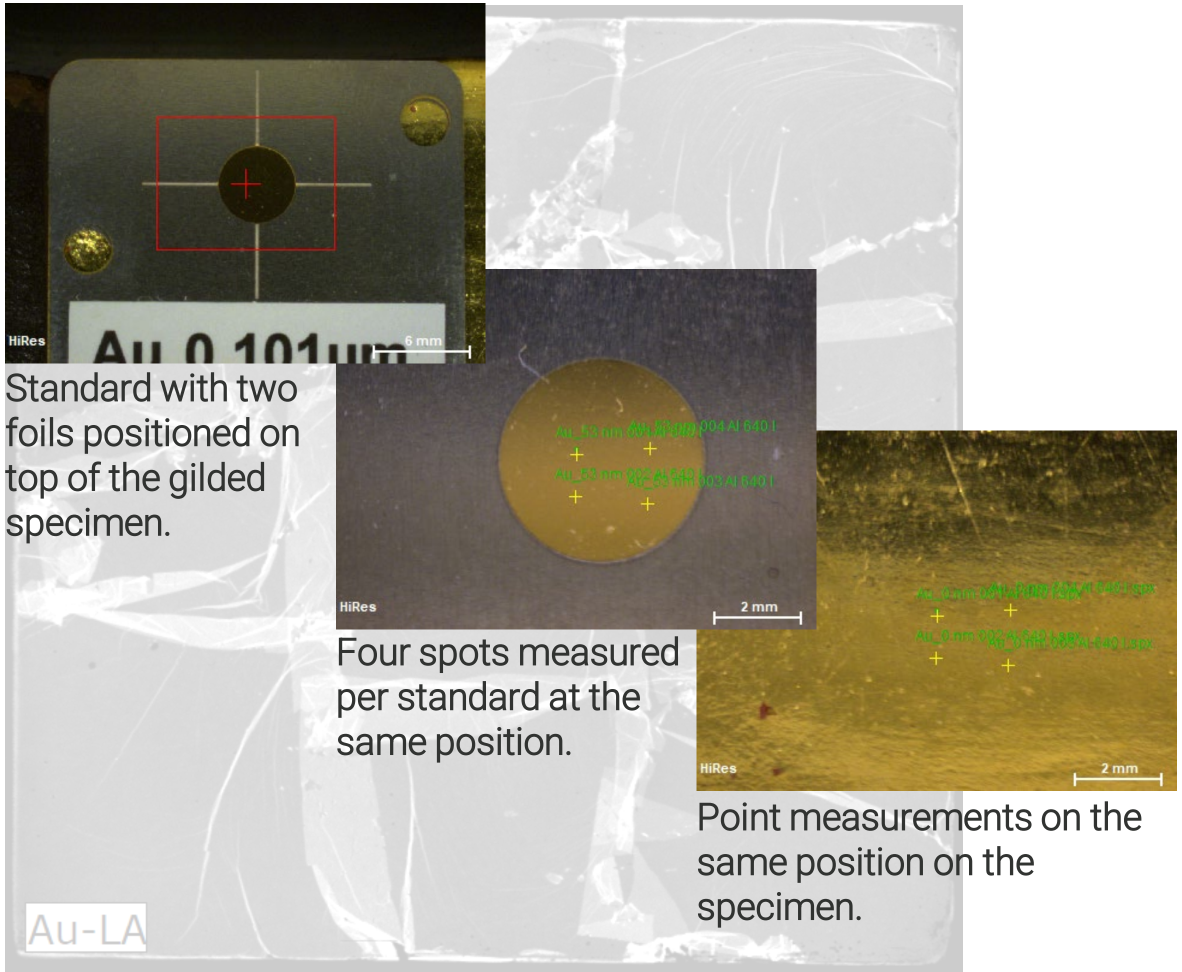
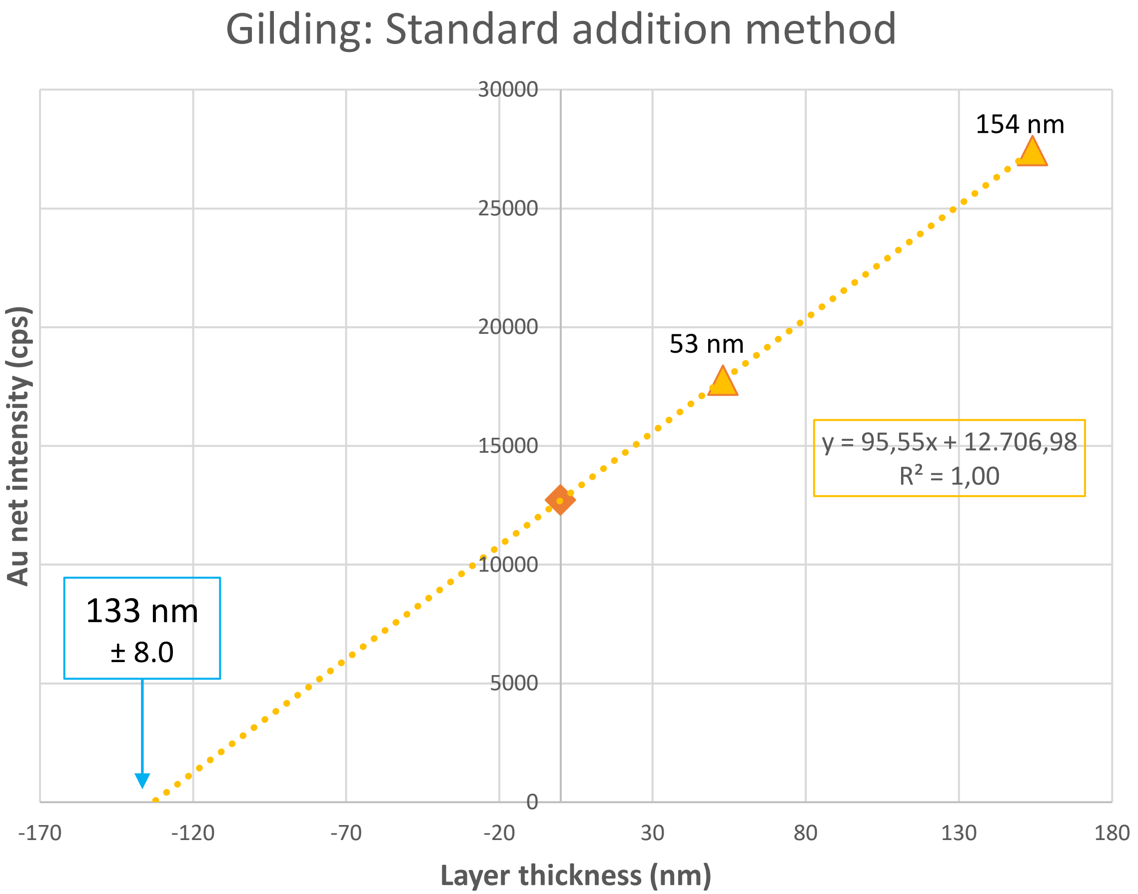


Standard with two foils positioned on top of the gilded specimen.

Four spots measured per standard at the same position.

Point measurements on the same position on the specimen.



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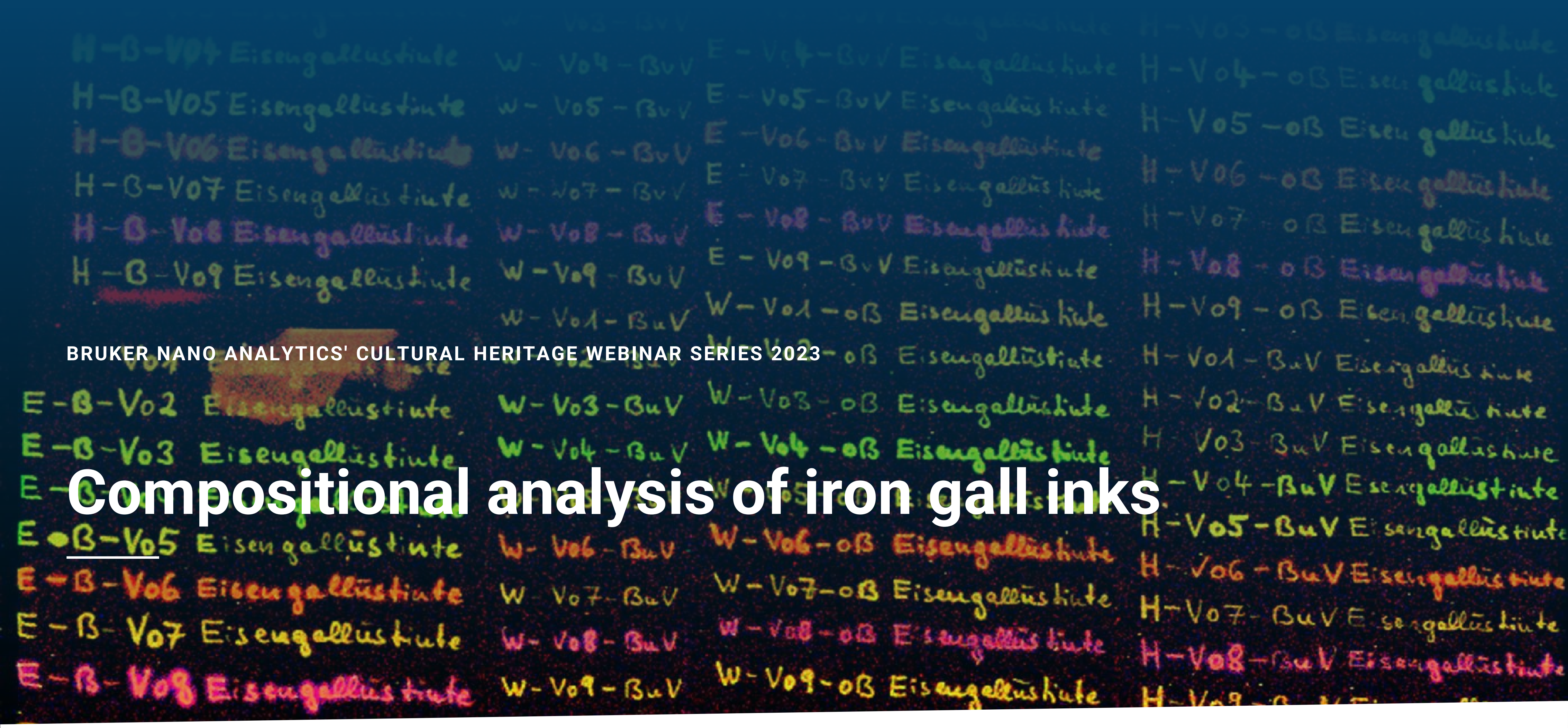
Compositional analysis of iron gall inks



Studying iron gall inks
An introduction to… the art-technology and ongoing research

- Iron gall inks have been used already in the antique and until late 20th century. It is one of, if not THE most important writing material in history.
- Iron gall ink is created using oak galls or any other tannin-rich plant material and vitriol, a $FeSO_4$ mineral, that is often accompanied by $ZnSO_4$, $MnSO_4$ and $CuSO_4$.
- The ratios of the different sulfates may vary between different region and centuries and can be used to distinguish different writing phases from each other, as e.g.

X-RAY SPECTROMETRY

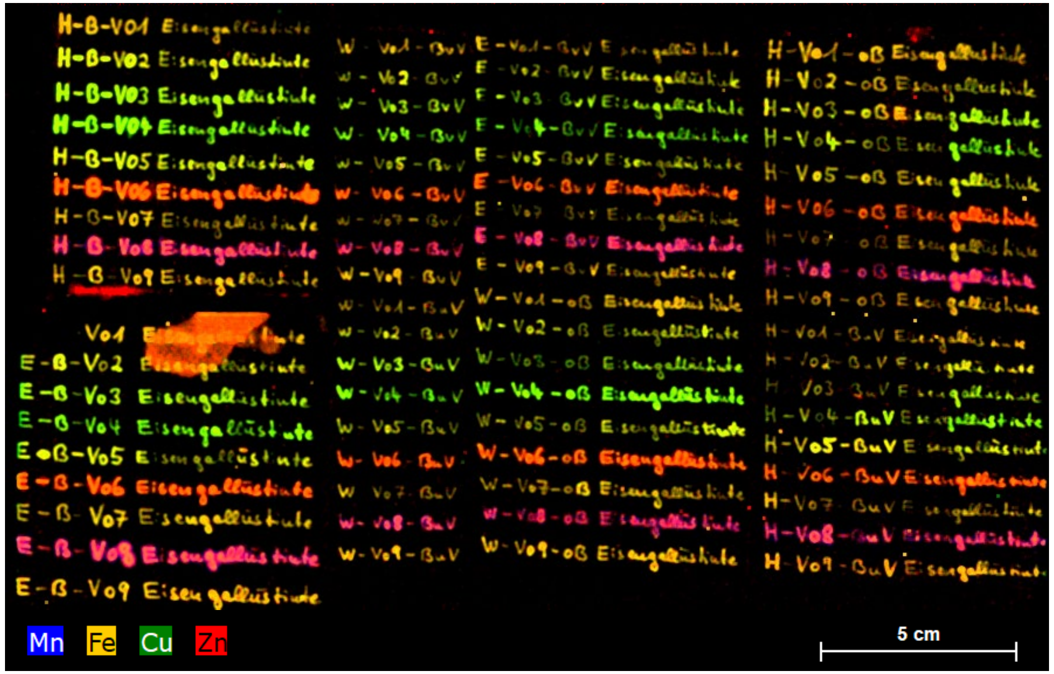
Research Article

Characterization of iron-gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry†

O. Hahn, W. Malzer, B. Kanngiesser, B. Beckhoff

First published: 10 February 2004 | https://doi.org/10.1002/xrs.677 | Citations: 88

† Presented at the European Conference on EDXRS, Berlin, Germany, 16–21 June 2002



Micro-XRF mapping with a M6 JETSTREAM (at 35 kV, 800 µA, 100 µm spot size, 300 µm pixel size and 75 ms dwell time per pixel) of iron gall ink mock-ups with varying content of Fe, Mn, Zn and Cu created by Prof. Dr. rer. nat. habil. Oliver Hahn, BAM, Berlin, Germany.

The need for reference materials
An introduction to the methodological approach

Why do we need reference materials and what do they offer?

Studying non-infinitely thick samples, the direct approach of FP quantification requires full-instrument modelling as well as the consideration of the object in all its complexity.

Wolff, Timo (2009): “Referenzprobenfreie quantitative Mikro-Röntgenfluoreszenzanalyse.”, Dissertation, BAM-Dissertation series no. 50, Berlin.

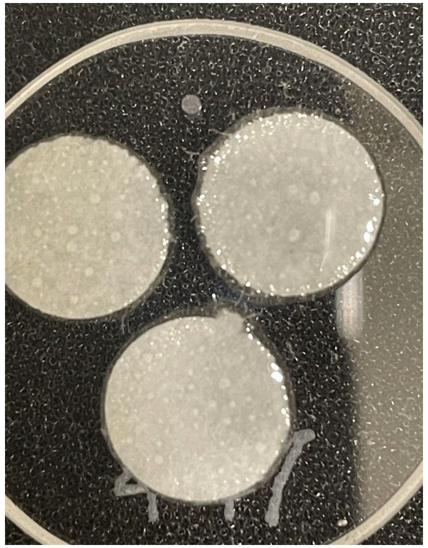
Reference materials allows to simplify the quantification!

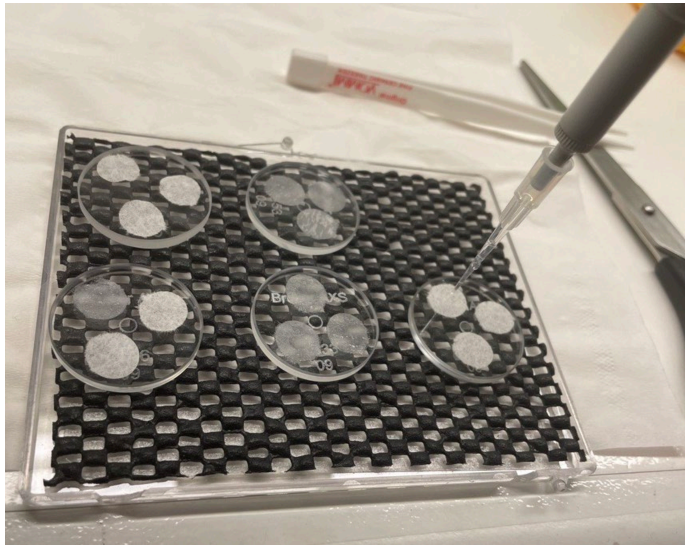
- Reference materials are commercially available for different thicknesses or mass depositions, usually recognized by the units used for description such as µm, nm, or µg/cm^2.
- However, there is a limitation due to the fact that specific reference samples may not be available.
- We would like to show, how this can be self-made using a micro-XRF scanning device.
- In addition, It will help to illustrate how the whole procedure of mass deposition can work, making it possible to quantify a large variety of non-infinitely thick samples.

Creating reference materials for inks
Counting atoms: The Methodology

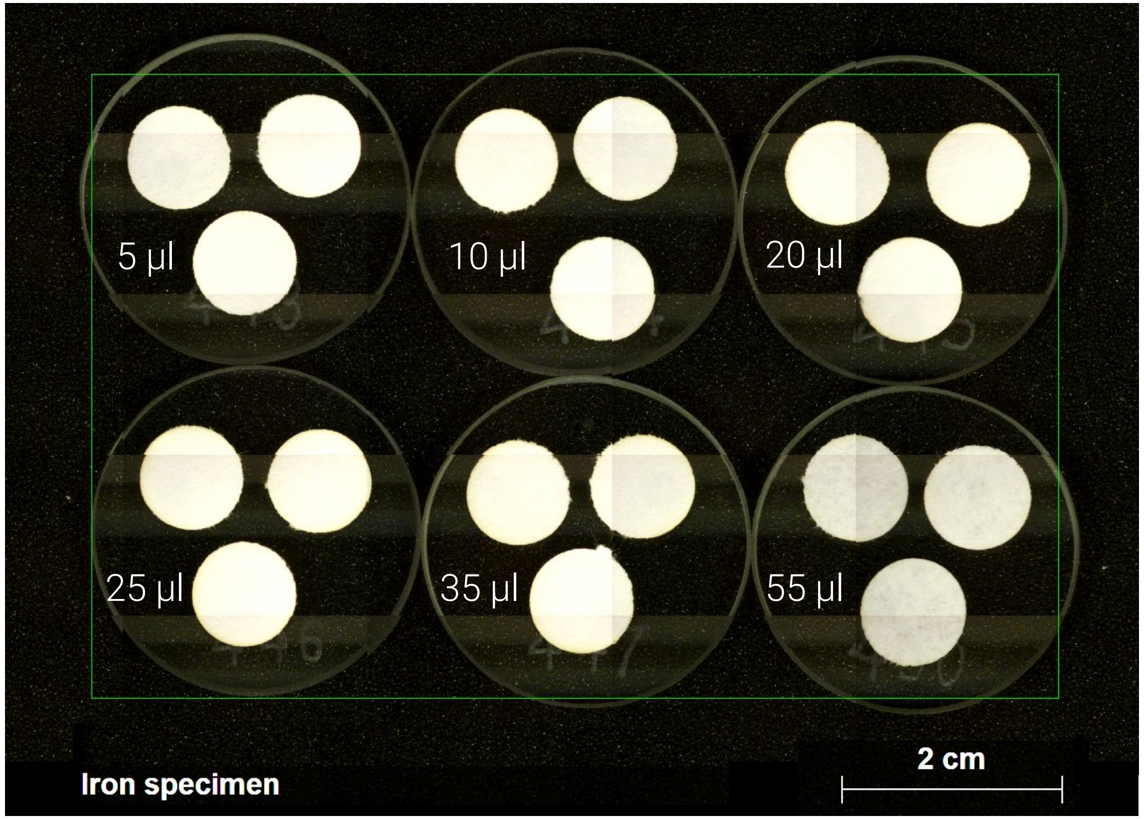
Production process

- A defined amount of different chemical elements solved in an acid (µg)
- Different quantities are titrated onto paper (µl)



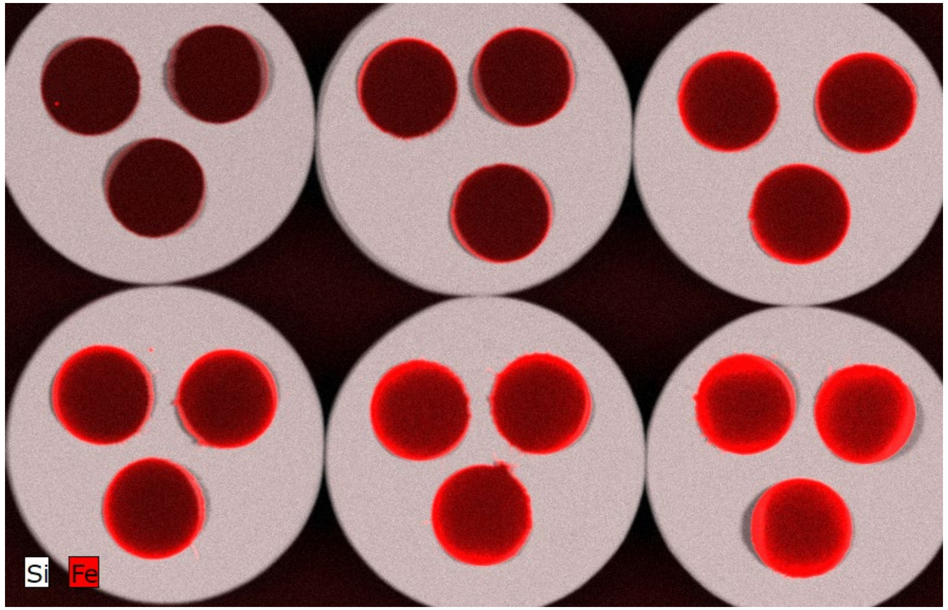


Final specimen test single element (for iron on glass substrate and filter paper)

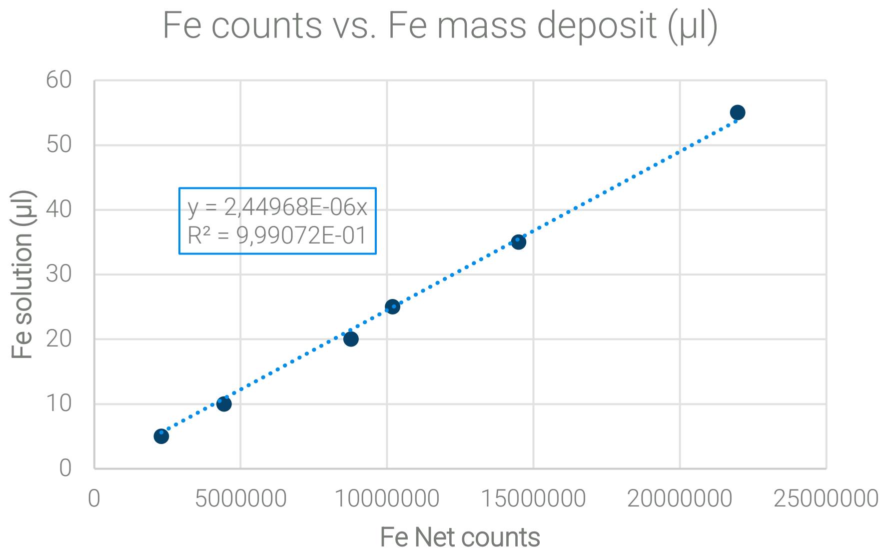


Creating reference materials for inks
Counting atoms: The specimen

- The micro-XRF elemental distribution of Fe clearly indicates that the intensity increases with the amount of material present. However, also inhomogeneities are visible, as the solution accumulated close to the edges of the specimen.
- Net count rate of the single specimen is extracted and correlated to the mass deposit on the filter paper.



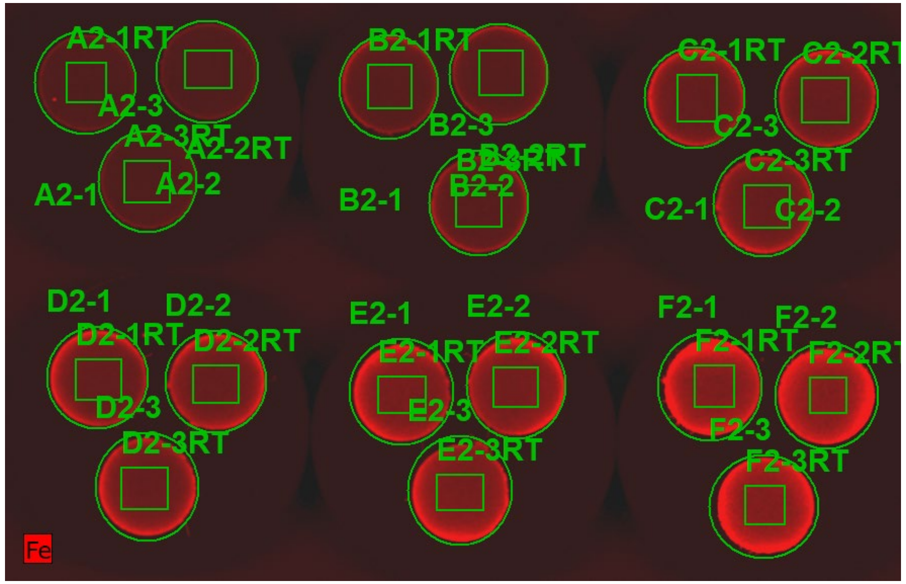
Micro-XRF mapping with a M6 JETSTREAM 35 kV 800 µA, 100 µm spot size, 100 µm pixel size, 80 ms dwell time per pixel.



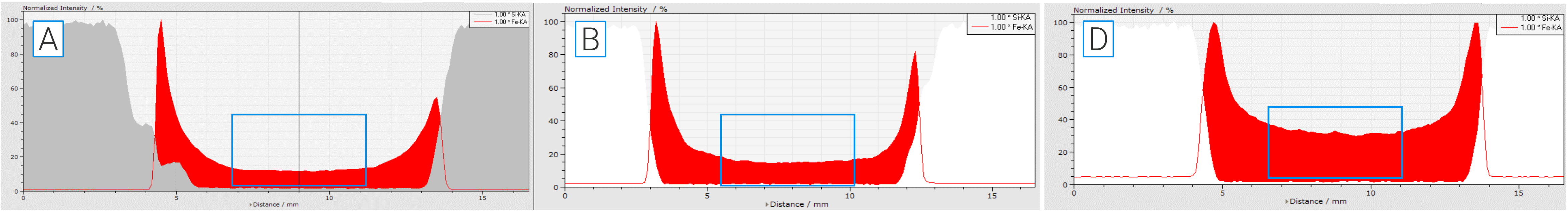
The plot of Fe net count rate against the mass deposit (µl) shows a nice linear correlation (Fe solution 1g/l).

Creating reference materials for inks
Counting atoms: Ensuring accuracy

- The variation of material deposit over the specimen can be studied using line scans, that show the Fe accumulation on the edges of the paper. The more material (µl), the stronger the accumulation in the edge.
- Yet, there is a homogeneous area in the center of each specimen (< 4.5 mm).
- Using an **object** from this homogeneous center, we can determine its area and link the net counts to the correlation we saw before with known values of net counts vs. mass deposit (µg).



Objects used for evaluation and calculation.



Line profile.

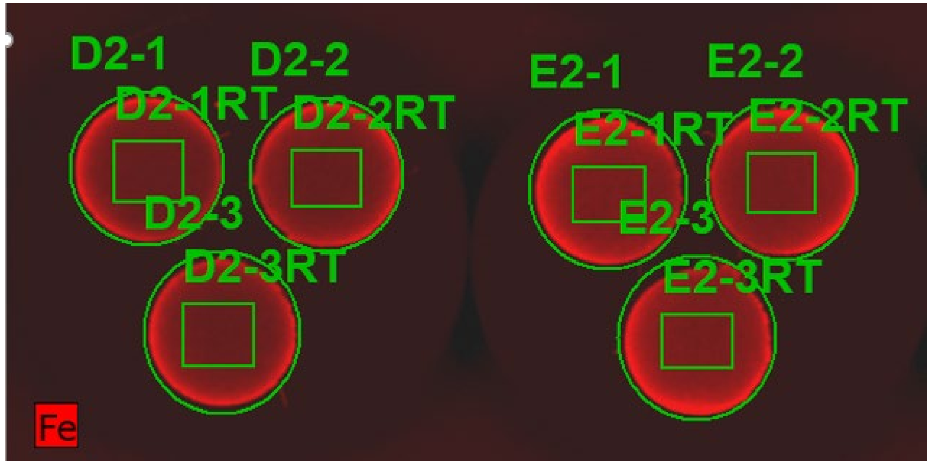
Creating reference materials for inks
Counting atoms: Calculating the mass deposit

- Again, now the net counts of Fe are extracted but now only from the homogeneous center of the references.
- These net counts are used afterwards to determine the mass deposited in the homogeneous center.

Spectrum	area mm^2	Fe counts	µg	µg/mm^2	ng/mm^2
A2-1RT	16.01	407580	1.0	0.1	62
A2-2RT	17.87	467965	1.1	0.1	64
A2-3RT	19.33	483900	1.2	0.1	61
B2-1RT	19.37	695327	1.7	0.1	88
B2-2RT	19.81	698016	1.7	0.1	86
B2-3RT	19.33	719333	1.8	0.1	91
C2-1RT	18.81	1094939	2.7	0.1	143
C2-2RT	21.16	1326324	3.2	0.2	154
C2-3RT	19.79	1264479	3.1	0.2	156
D2-1RT	18.87	1101810	2.7	0.1	143
D2-2RT	17.49	1094838	2.7	0.2	153
D2-3RT	19.75	1258052	3.1	0.2	156
E2-1RT	17.77	1730027	4.2	0.2	238
E2-2RT	18.01	1666634	4.1	0.2	227
E2-3RT	16.93	1694134	4.2	0.2	245
F2-1RT	16.81	2090765	5.1	0.3	305
F2-2RT	13.33	1812951	4.4	0.3	333
F2-3RT	15.61	2035670	5.0	0.3	319

Specimen	ng/mm^2	±	s%
A2	63	1.4	2.3
B2	88	2.5	2.8
C2	151	7.3	4.9
D2	151	6.9	4.6
E2	237	9.3	3.9
F2	319	14.3	4.5

Calculated mass deposit (ng/mm^2).



Specimen D and E with 151 ng/mm^2 and 237 ng/mm^2, respectively.

Creating reference materials for inks
Counting atoms and improving the method

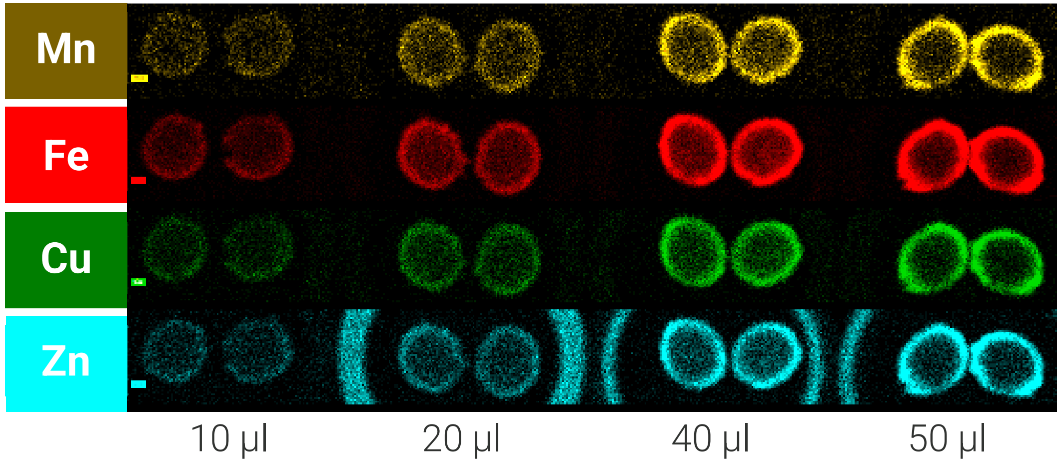
- The reference material is in principle similar to the one used for the gold leaves thickness determination.
- The references material can be used directly
  - ✓ to determine the sensitivity of the instrument
  - ✓ and then applied these values to the unknown sample.

➢ **Pitfalls**: Secondary effects might be different between the filter paper/reference sample and the unknown sample (~ 10 %).

Alternatively, can we use again the previously describe standard addition method?

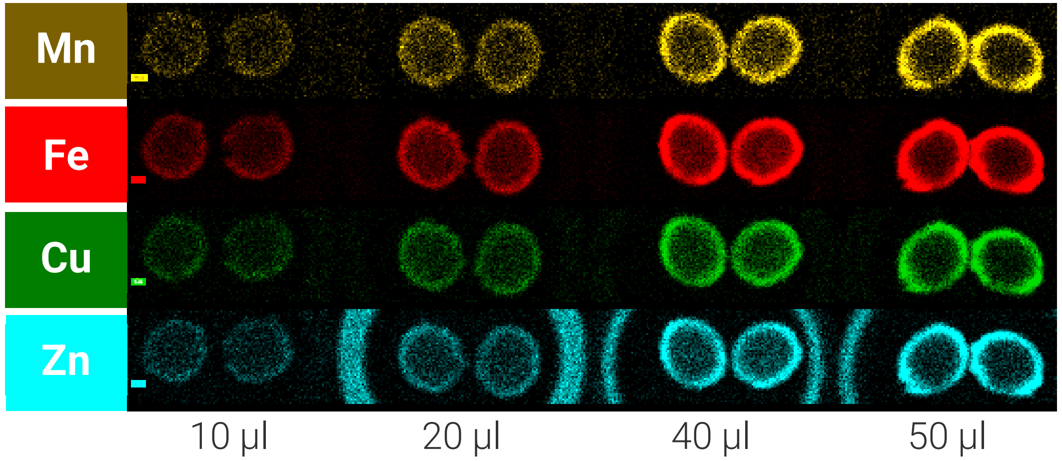
✓ Yes, to minimize absorption effects a very thin paper was used.

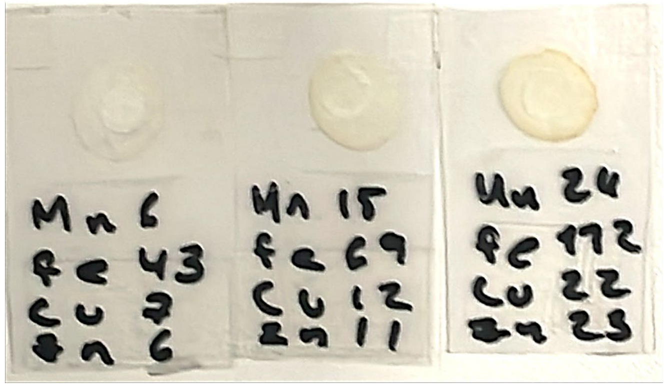
- A multi-element reference sample set was created with more elements relevant for iron gall ink quantification (Mn, Fe, Cu and Zn).



Creating reference materials for inks
Counting atoms and improving the method

- The samples were analyzed following the same procedure, **but** this time located on a **PE cap resting on a mylar foil** to reduce scattering.
- In addition, samples were measured with an **Al 640 µm filter** to reduce secondary excitation from backscatter signal from the strong bremsstrahlung.
- After determination of the mass deposit (ng/mm²) of each element in the center of the sample, the papers were placed on a transparent holder leaving the central area uncovered for analysis.
- Again, the reference samples can be placed on the homogenous part of the material in question.

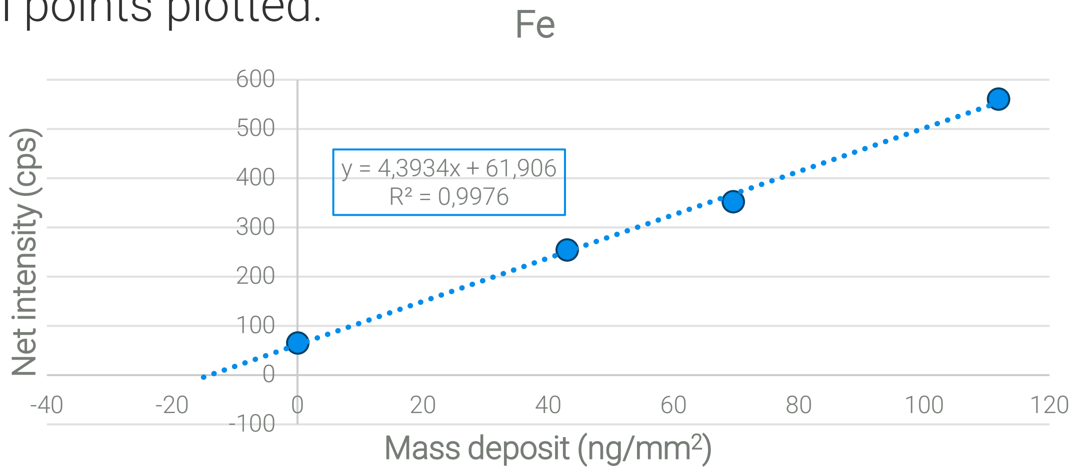


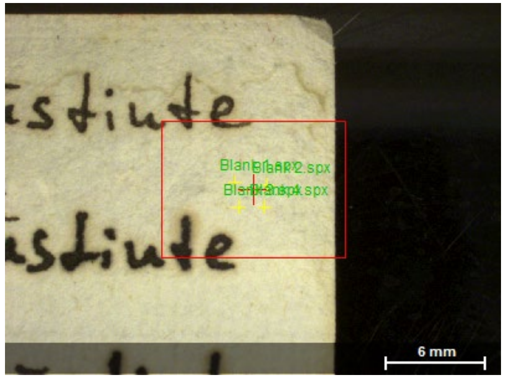


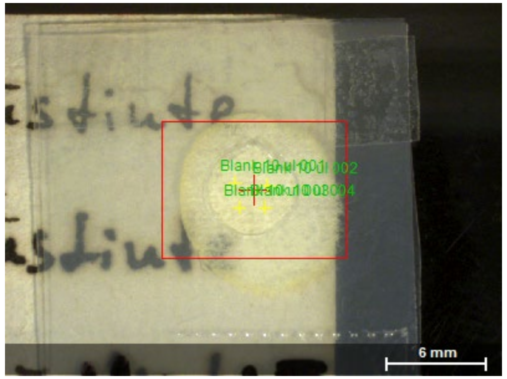
Final set of reference materials used for the standard addition method.

Creating reference materials for inks
Counting atoms and improving the method

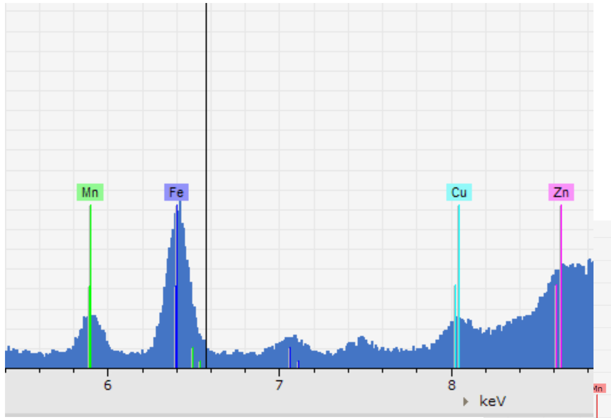
Reference location: Four points were measured on the object with and without the references and the sum of all points plotted.





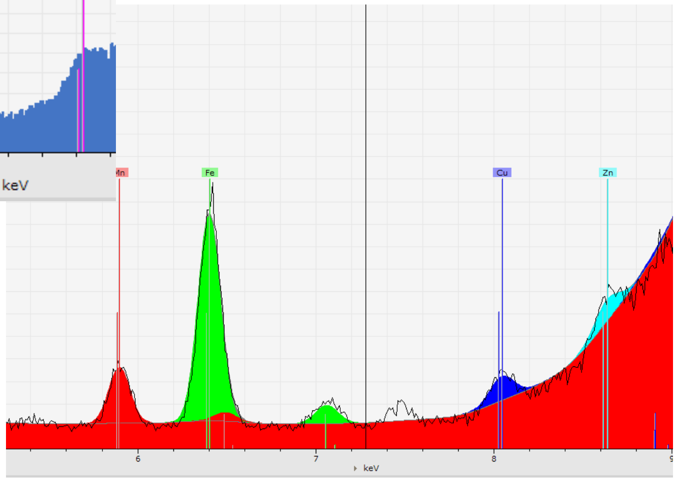


- The results allow to determine the mass of each element on the paper (ng/mm^2):
- Fe 14 ng/mm^2, Mn 7.6 ng/mm^2, Cu 2 ng/mm^2 and Zn 2.5 ng/mm^2.



Sum of all 4 spectra from the paper.

Net peak determination.



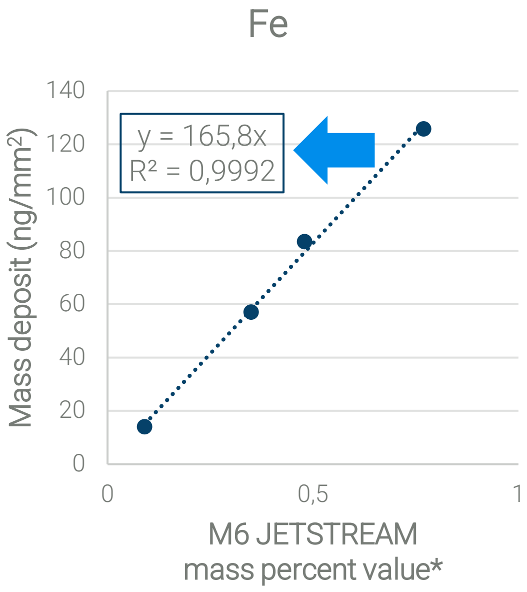
Creating reference materials for inks
Counting atoms and improving the method

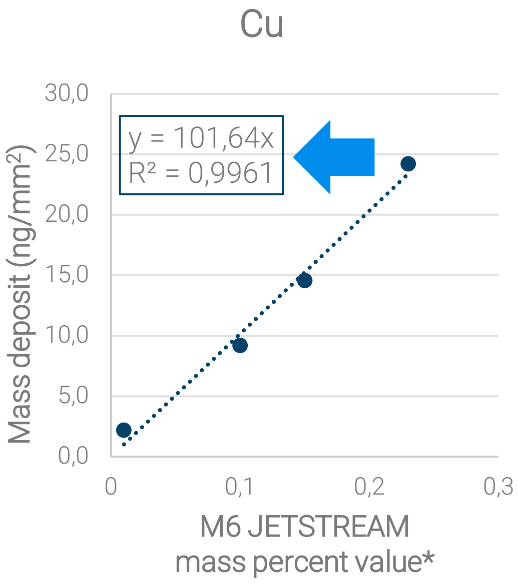
Using the results from the correlation and knowing that the Blank is not 0 ng/mm², we can determine the instruments sensitivity for the standards and measurement conditions.

Sample	Mn		Fe		Cu		Zn	
	*Unit	ng/mm²	*Unit	ng/mm²	*Unit	ng/mm²	*Unit	ng/mm²
0	0.04	7.65	0.09	14	0.01	2.2	0.01	2.5
10 µl	0.09	13.65	0.35	57	0.1	9.2	0.08	8.5
20 µl	0.12	22.61	0.48	83	0.15	14.6	0.11	13.7
40 µl	0.18	31.64	0.77	126	0.23	24.2	0.18	25.1

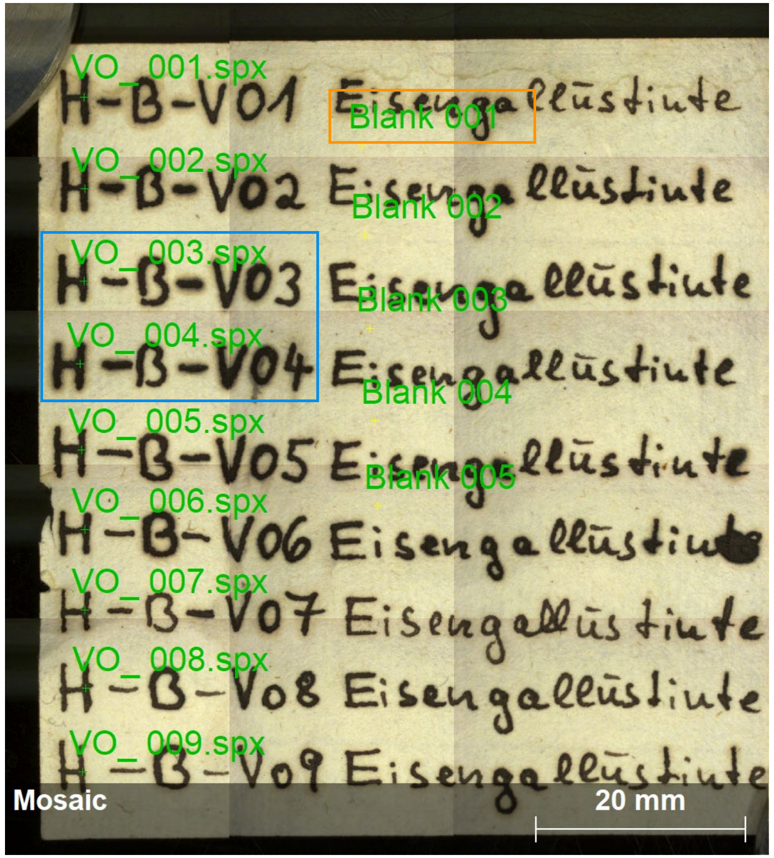
*Unit: Mass concentration values are here used for the correlation, as they provide a robust solution for this task. They can be converted as shown at the right.

Conversion factor from arbitrary units to ng/mm² for this setting and this sample:

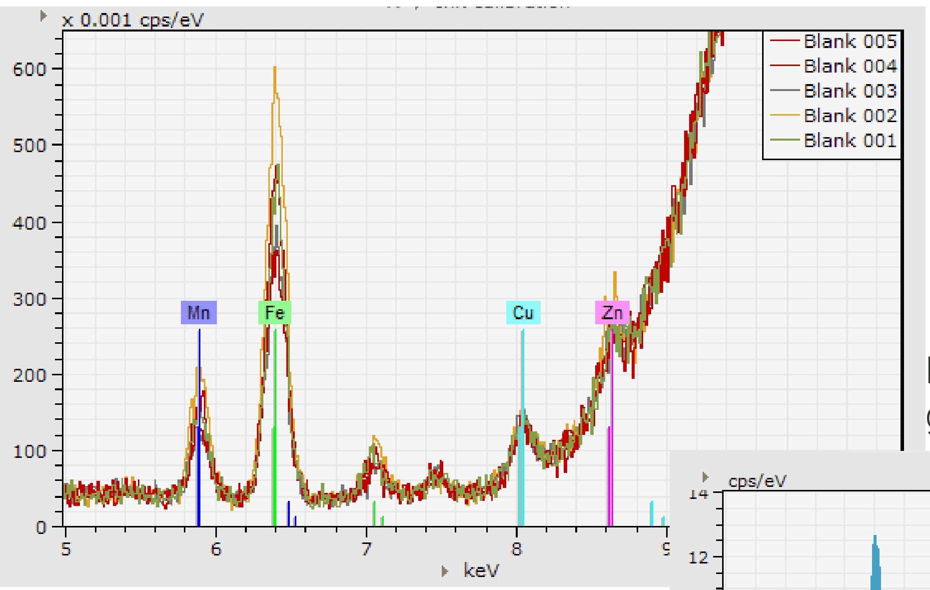




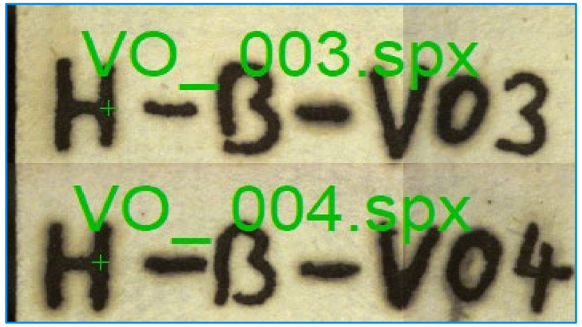
Finally, applying the method to a sample
From counting atoms to determining mass deposition on paper



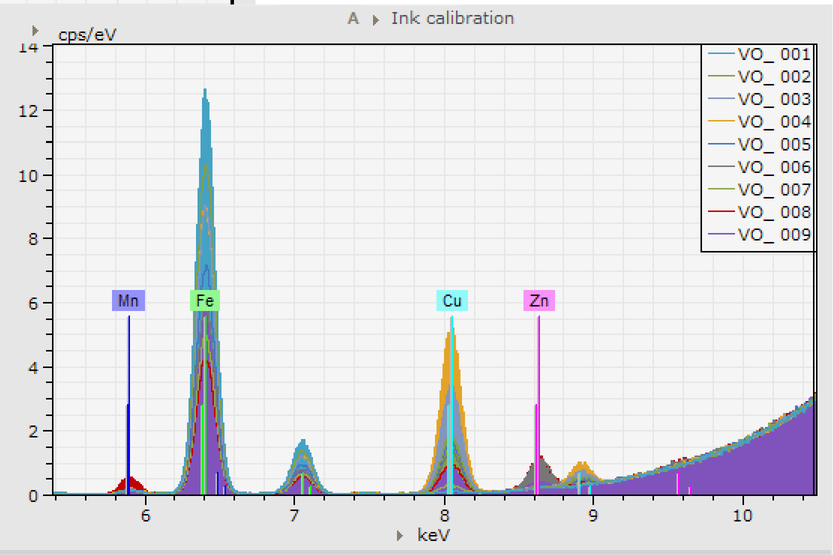
Iron gall ink mock-ups with varying content of Fe, Mn, Zn and Cu created by Prof. Dr. rer. nat. habil. Oliver Hahn, BAM, Berlin, Germany.



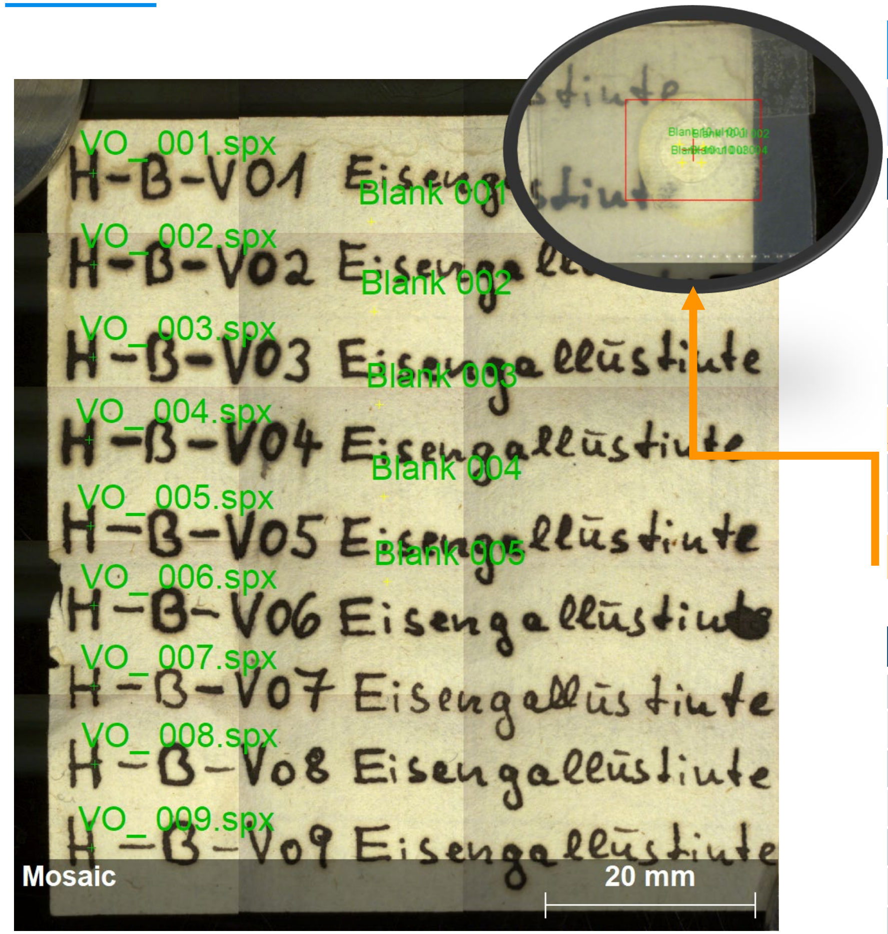
Point measurements of the blank paper.



Point measurements of the iron gall ink references.



Finally, applying the method to a sample
From counting atoms to determining mass deposition on paper



Iron gall ink mock-ups with varying content of Fe, Mn, Zn and Cu created by Prof. Dr. rer. nat. habil. Oliver Hahn, BAM, Berlin, Germany.

Chemical element	Mn	Fe	Cu	Zn
Conversion factors	**176**	**166**	**102**	**132**

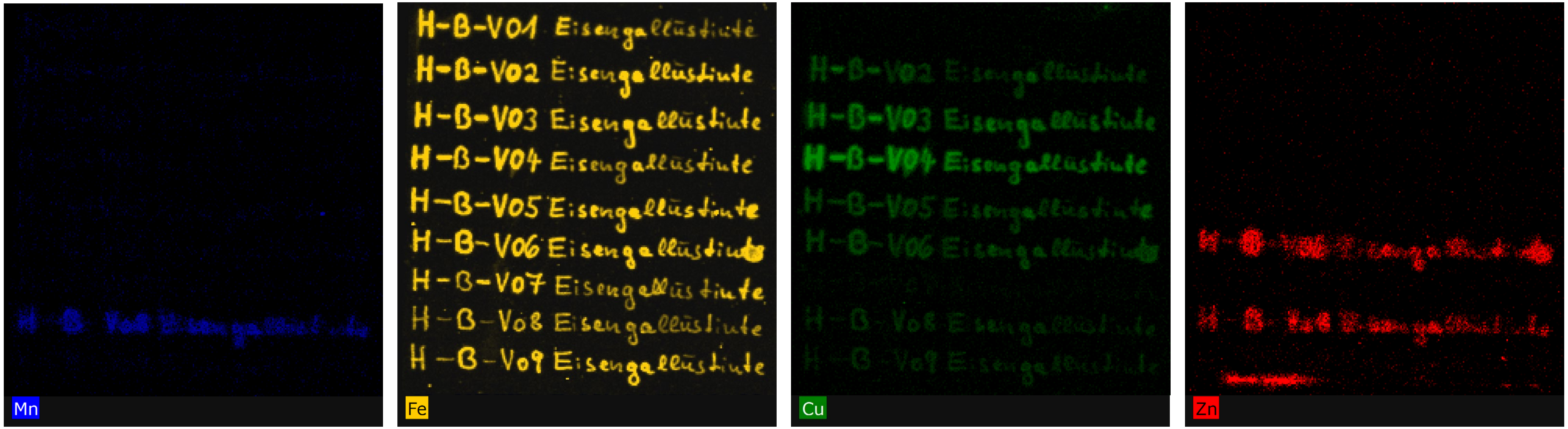
ng/mm^2	Mn	Fe	Cu	Zn
Blank_1	7.0	16.6	2.0	1.3
Blank_2	10.6	23.2	2.0	2.6
Blank_3	5.3	14.9	2.0	0.0
Blank_4	5.3	13.3	1.0	0.0
Blank_5	7.0	18.2	2.0	1.3
Ave.	7.0	17.2	1.8	1.1
s	2.16	3.82	0.45	1.10
s %	31	22	25	105
Reference location	7.6	14.0	2.2	2.5

Comparing the blank to the reference location

ng/mm^2	Mn	Fe	Cu	Zn
VO_1	0	517	0	0
VO_2	0	434	58	0
VO_3	0	371	102	0
VO_4	0	367	148	0
VO_5	0	293	50	0
VO_6	0	240	39	24
VO_7	0	193	6	0
VO_8	26	170	26	25
VO_9	0	235	25	4

Iron gall ink mock-ups: Final values

Finally, applying the method to a sample
From counting atoms to determining mass deposition on paper



ng/mm²	Mn	Fe	Cu	Zn
VO_1	0	517	0	0
VO_2	0	434	58	0
VO_3	0	371	102	0
VO_4	0	367	148	0
VO_5	0	293	50	0
VO_6	0	240	39	24
VO_7	0	193	6	0
VO_8	26	170	26	25
VO_9	0	235	25	4

Analysis of non-infinite samples in Cultural Heritage
Conclusion

Non-infinity does not prevent you from quantifying your sample!

- Standard-based XRF analysis offers a quick and reliable workflow to determine the coating thicknesses or mass deposit of your sample.
- The standard addition method can be performed by using both certified reference materials as well as lab-developed samples.
- Creating your own set of references allows you have full control of your results and calibrations.
- Yet, the standard support of liquid reference materials and the related scattering can affect your results and should be carefully considered during the methodological approach!

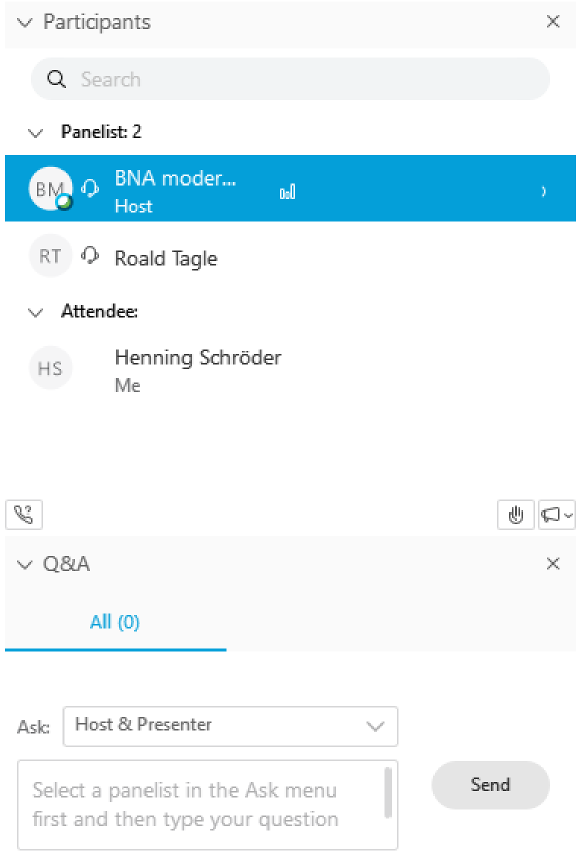
For more information on the quantification of Cultural Heritage objects see:

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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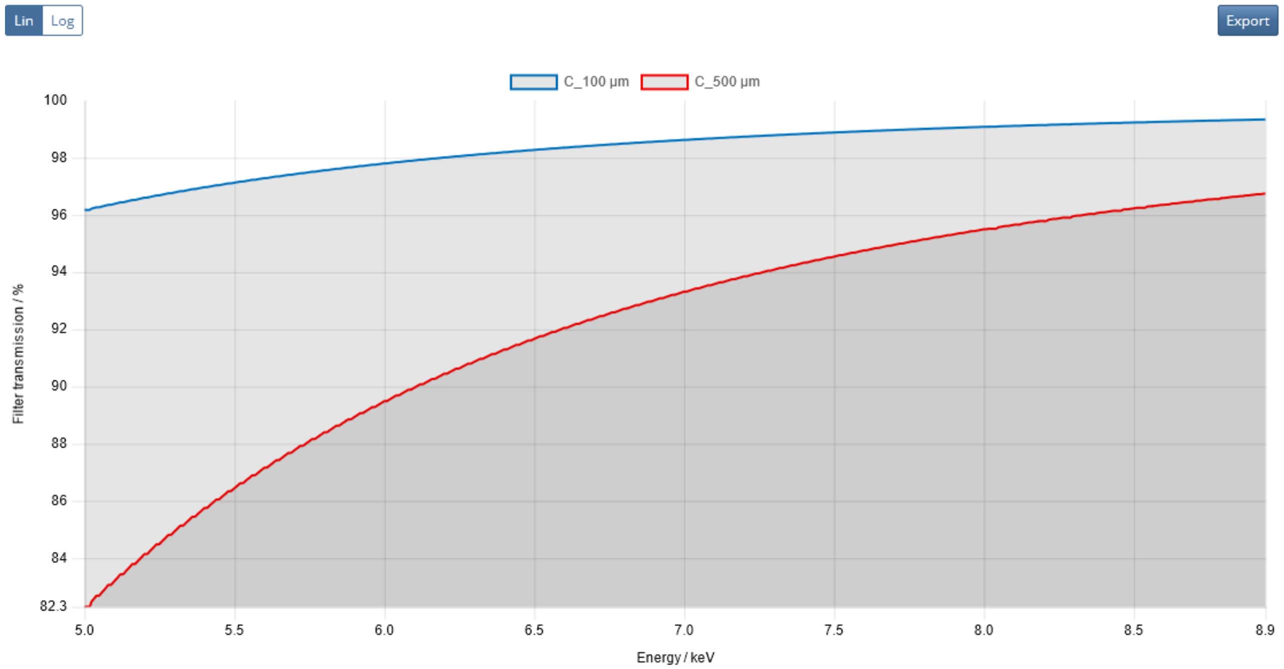
Paper transmission

Composition	Thickness	Density
100%C	100 µm	0.2 g/cm³

Add layer

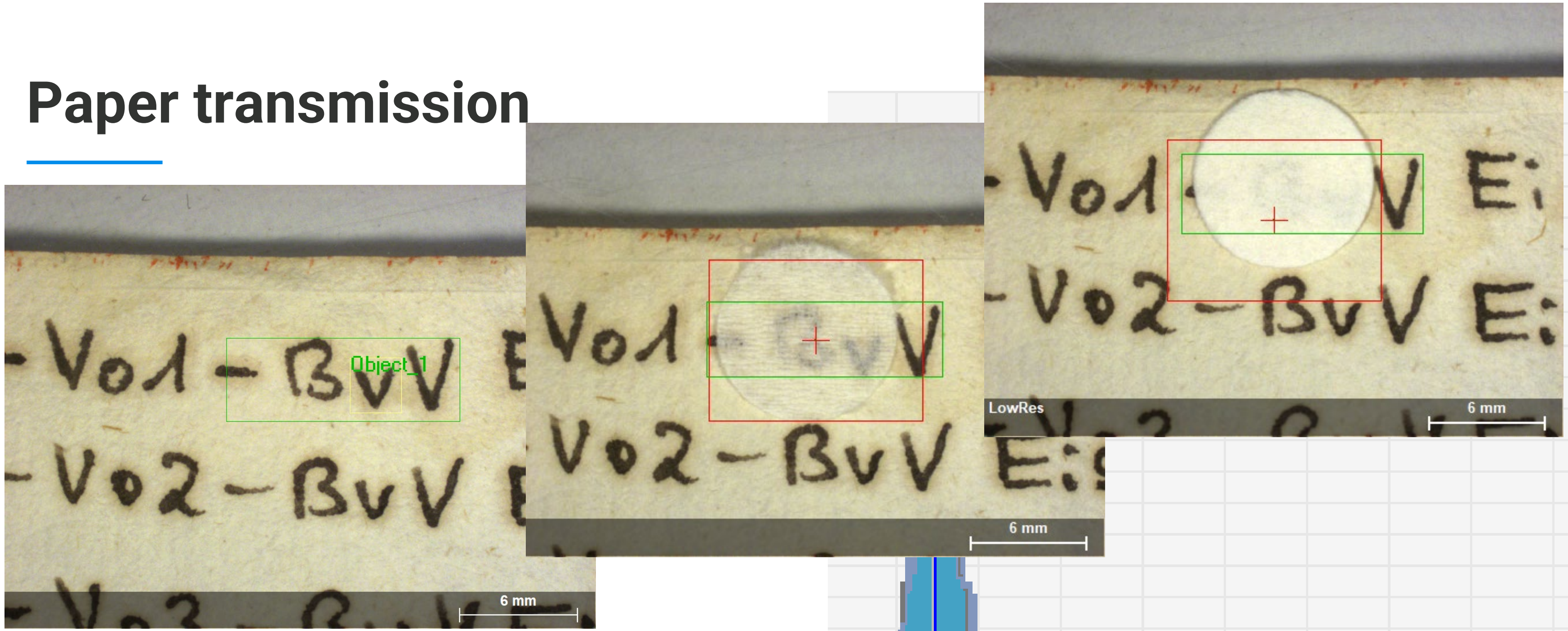
Composition	Thickness	Density
100%C	500 µm	0.2 g/cm³

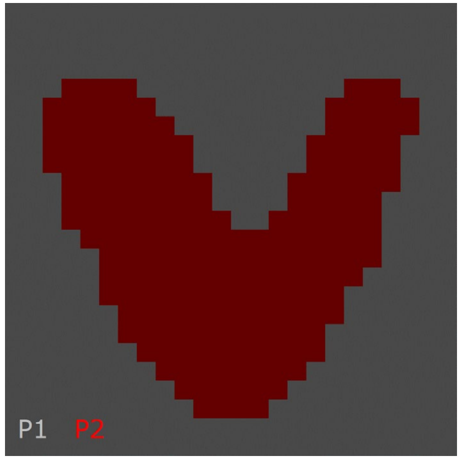
Add layer

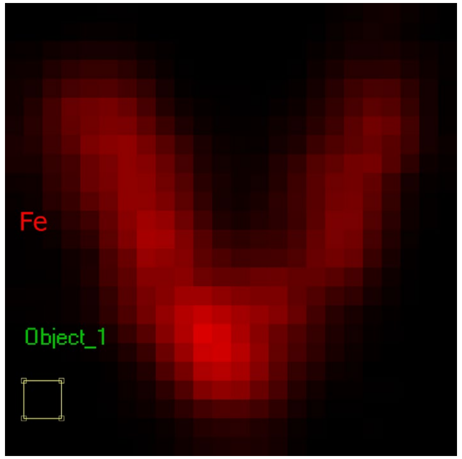


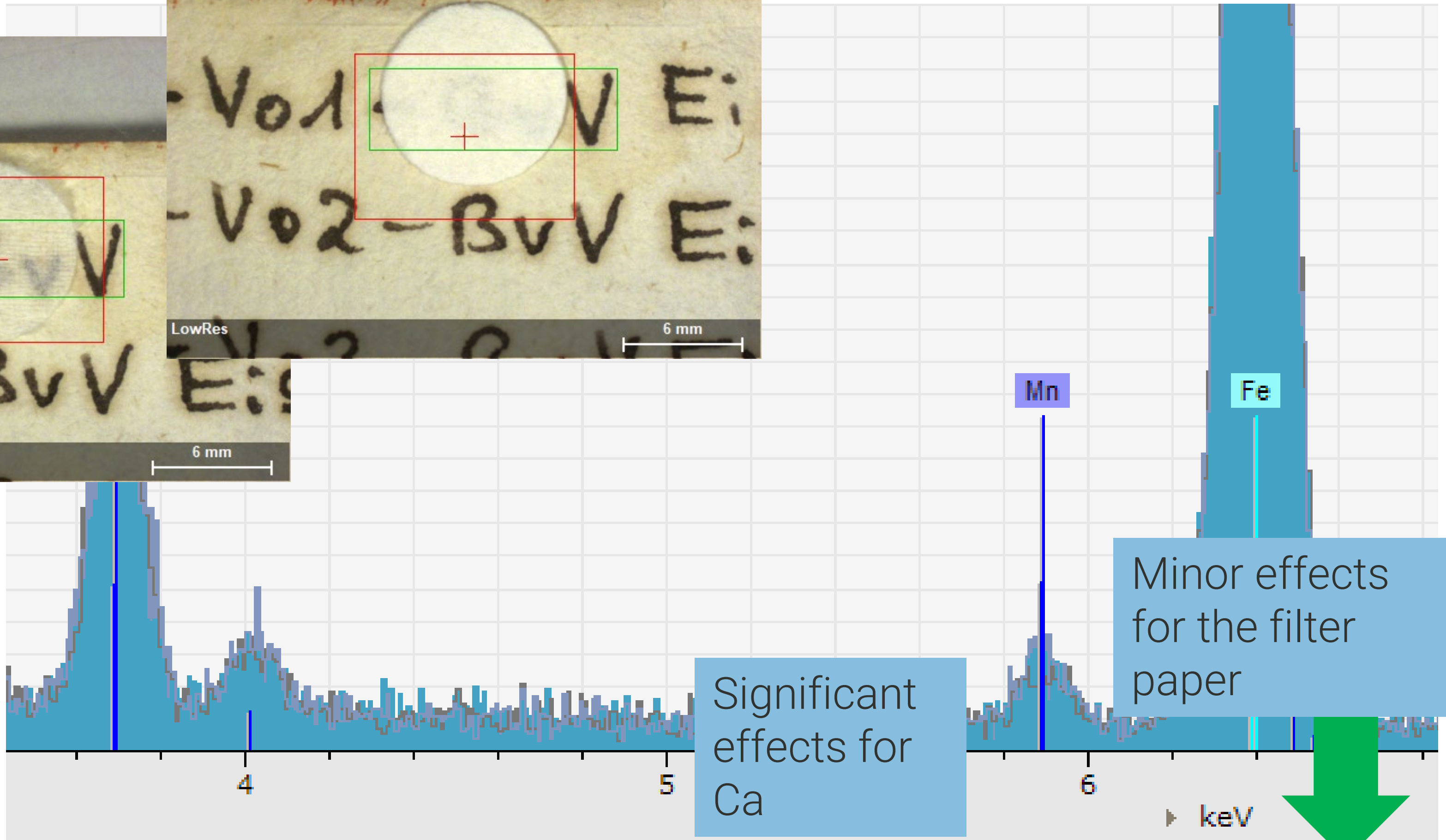
XRF Check - XRF Check (bruker.com)

Paper transmission



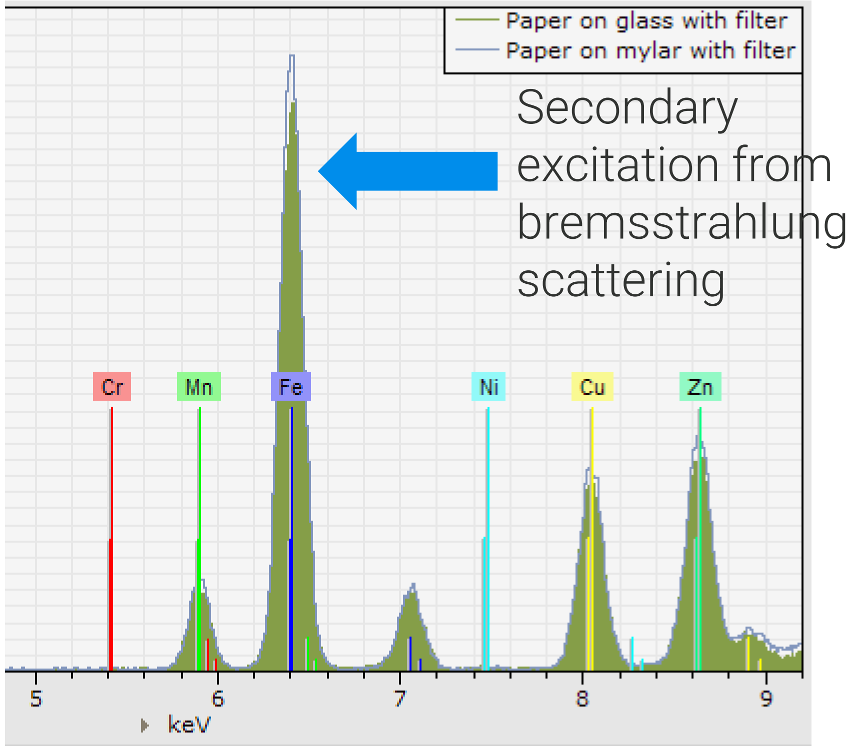




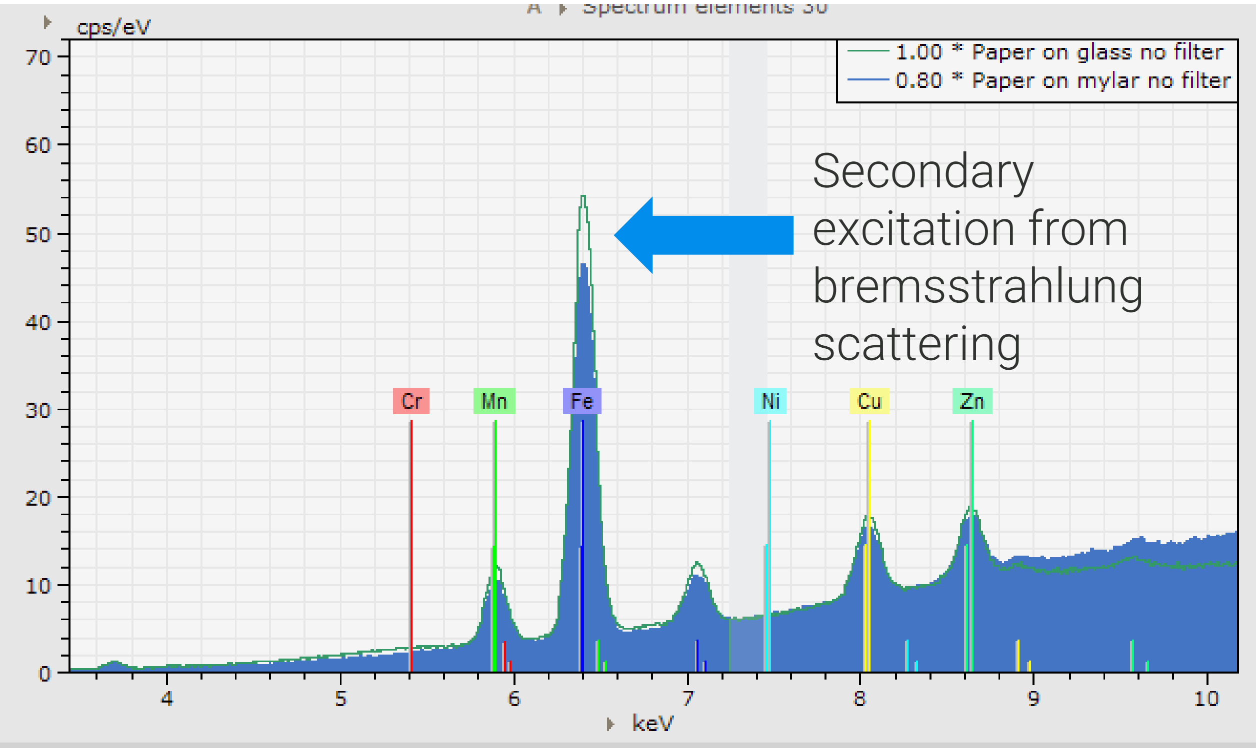


	cps/eV	Factor	Net intensity [s(LT)]	Sort: Element	
V manuscript	0.36	0.934	Ca 156.46	Mn 22.27	Fe 646.49
V manuscript thin paper	0.28	0.[illegible]	Ca 145.39	Mn 14.46	Fe 668.98
V manuscript filter paper	0.31	1.000	Ca 91.57	Mn 14.09	Fe 596.20

Filter Peak to background and secondary excitation from the glass



With filter



No filter

Secondary excitation from the glass

Net intensity [cps]	Mn	Fe	Cu	Zn
Spectrum	Mn	Fe	Cu	Zn
Paper on mylar no filter	1846.64	10908.62	2212.98	1908.02
Paper on glass no filter	1655.9	9873.29	2011.15	1789.18

live time	Mn	Fe	Cu	Zn
39	72019	425436	86306	74413
45	74516	444298	90502	80513
%	1.03	1.04	1.05	1.08

Net intensity [cps]	Mn	Fe	Cu	Zn
Spectrum	Mn	Fe	Cu	Zn
Paper on mylar with filter	91.68	654.63	228.16	256.64
Paper on glass with filter	82.64	593.84	214.19	240.35

live time	Mn	Fe	Cu	Zn
90	8251	58917	20534	23098
96	7933	57009	20562	23074
%	0.96	0.97	1.00	1.00

Better but still some matrix effects!