Forensic Applications for Micro-XRF

Bruker Nano Analytics, Berlin, Germany
Webinar, September 20, 2017

M4 TORNADO Webinar
Outline

- Introduction
  - Presenters
  - The M4 instrument
  - Micro-XRF
  - Information depth
- Gun Shot Residue (GSR)
  - Qualitative GSR
  - Semi quantitative GSR
- Glass fragments
  - Qualitative differentiation of glass fragments
  - Quantitative analysis
  - Semi-quantitative, as per ASTM E2926 (“finger printing”)
- Live part – data extraction and evaluation
- Summary

M4 TORNADO Webinar
Presenters

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Bruker Nano Analytics, Berlin, Germany

Dr. Roald Tagle

Sr. Application Scientist,
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M4 Tornado micro-XRF spectrometer
Standard configuration

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)
Option: other target materials and second X-ray tube (collimated) for extended excitation conditions

30 mm² silicon drift detector (SDD)
with energy resolution < 145 eV (for Mn-Kα)
Option: second detector with second independent SPU for double pulse throughput
Option: 60 mm² detector(s)

Sealed sample chamber
with adjustable pressure between 1 mbar (for detecting light elements down to Na) and ambient pressure

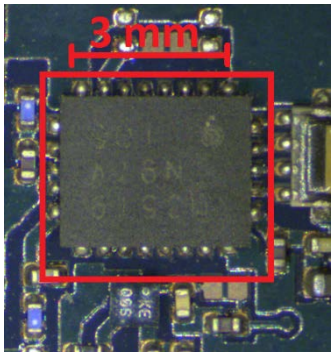
Sample stage with measureable area of 190 mm x 160 mm

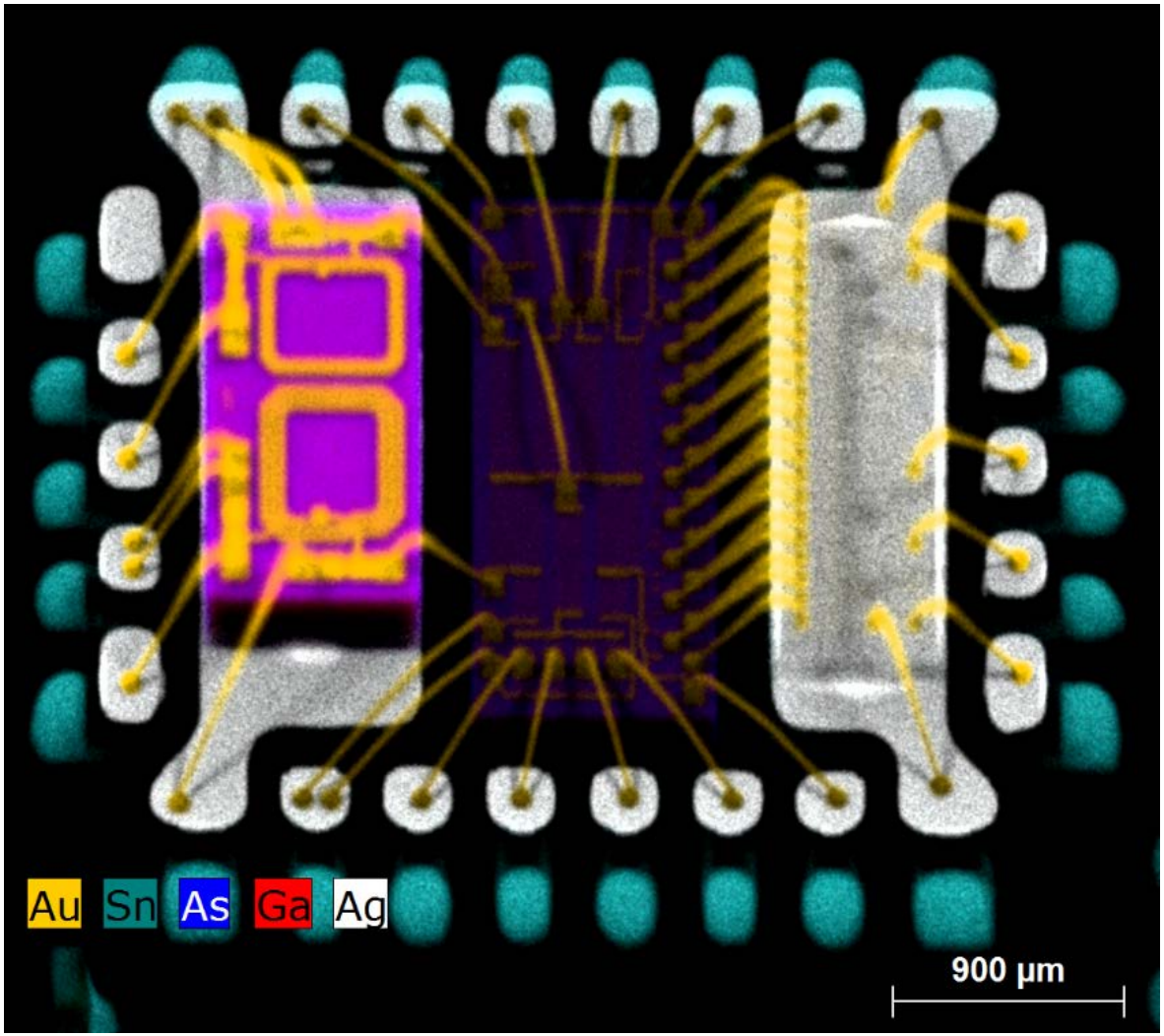
Maximum sample height 120 mm, maximum sample weight 5 kg

Sample stage speed up to 100 mm/s, minimum step size 4 µm

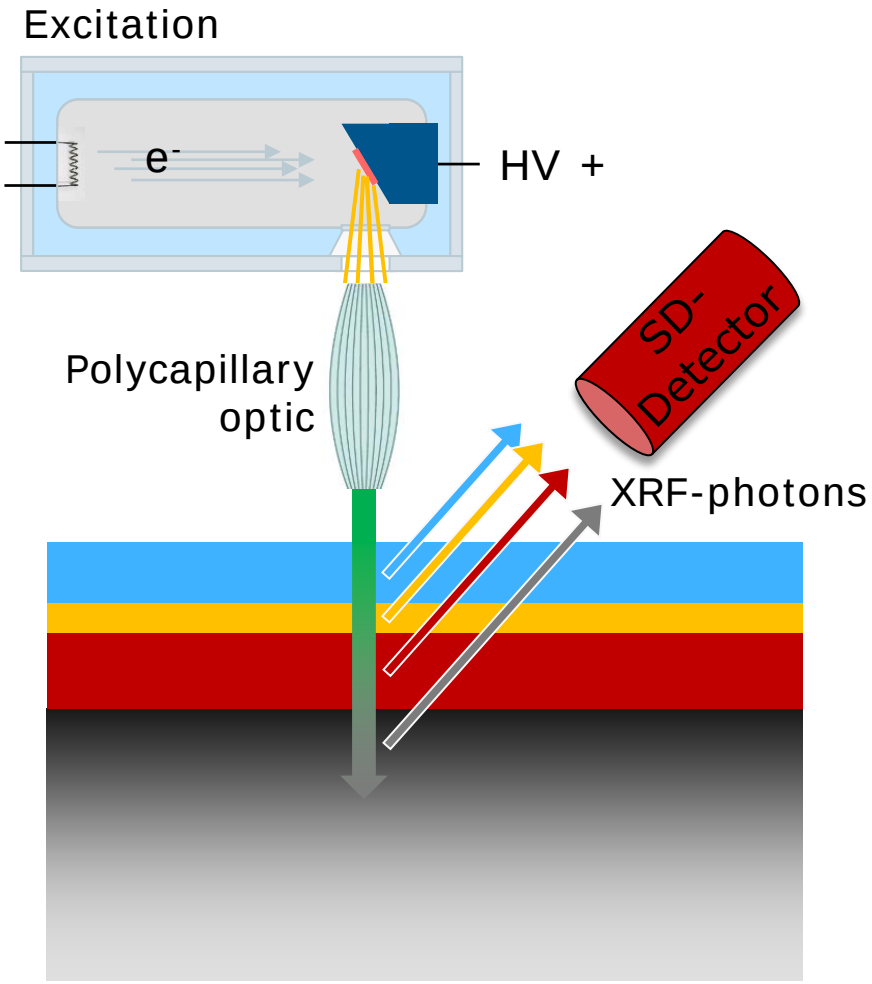
Micro-XRF features and benefits
At a glance

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

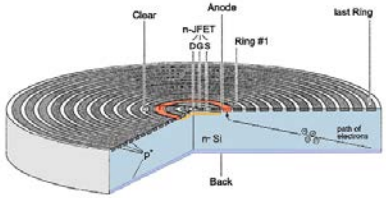




X-Ray Fluorescence
...information from beneath



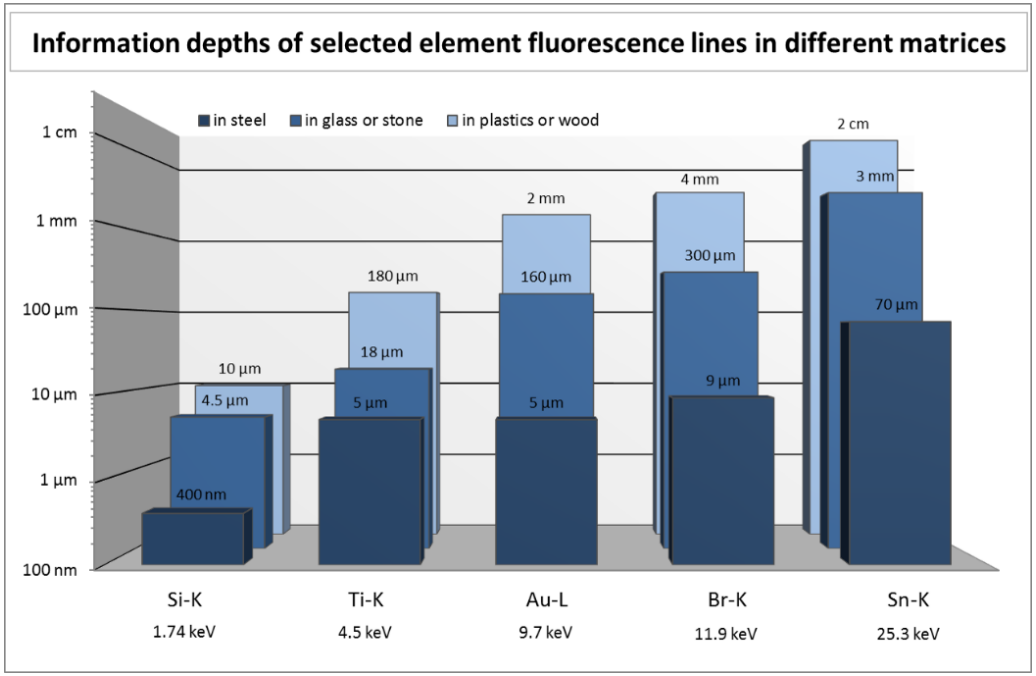
XRF Detection

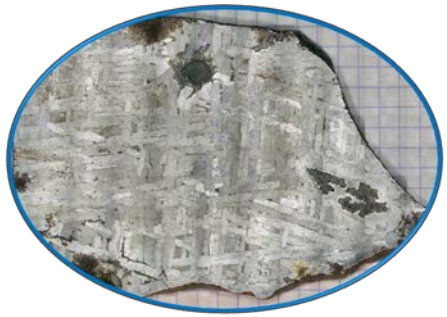


Silicon **D**rift **D**etector
with XFlash® Technology

- X-rays can penetrate and excite matter
- Signal from base material and covered layers can still be detected
- X-rays are attenuated in characteristic ways on their path through matter
- Intensity ratios of observed elemental lines

X-Ray Fluorescence
...understanding information depth

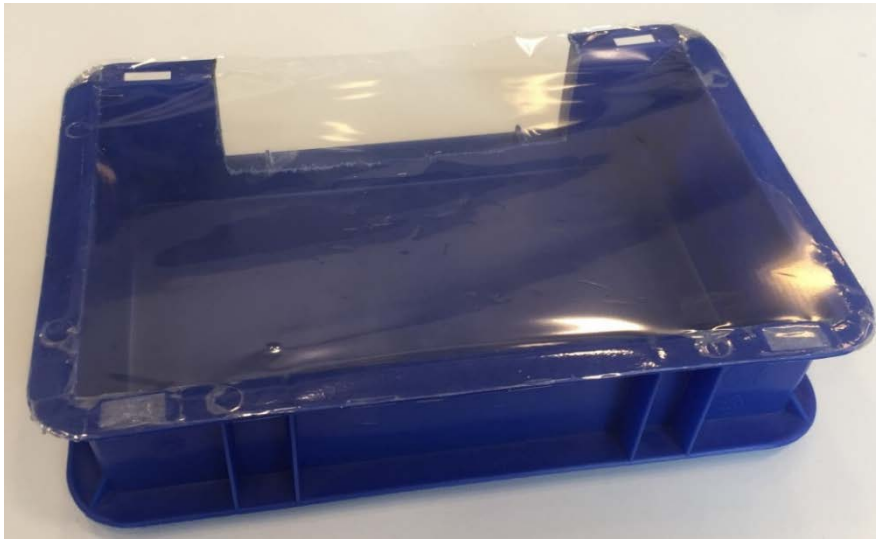


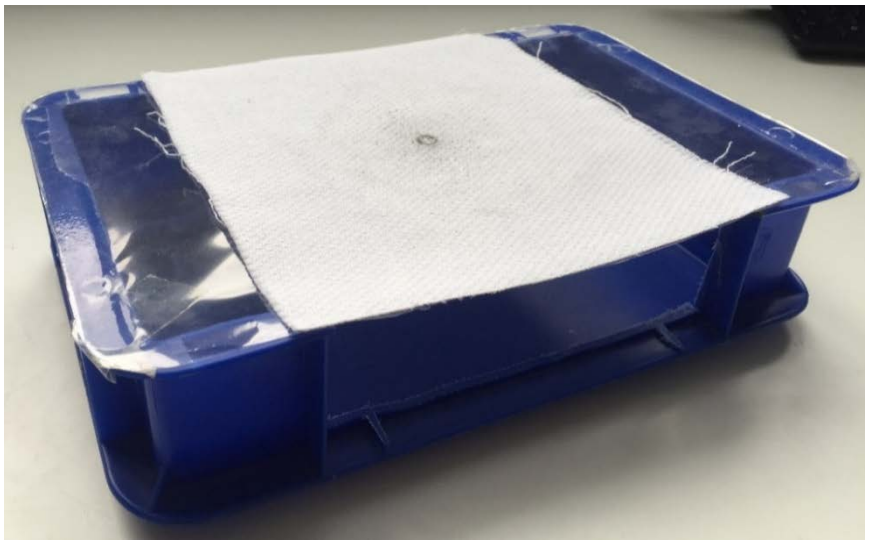


- Information depth depends on the energy of the photon and the density of the material
- Information on different elements can originate from different sample positions

Optimizing Results
Sample Mounting for Minimal Background

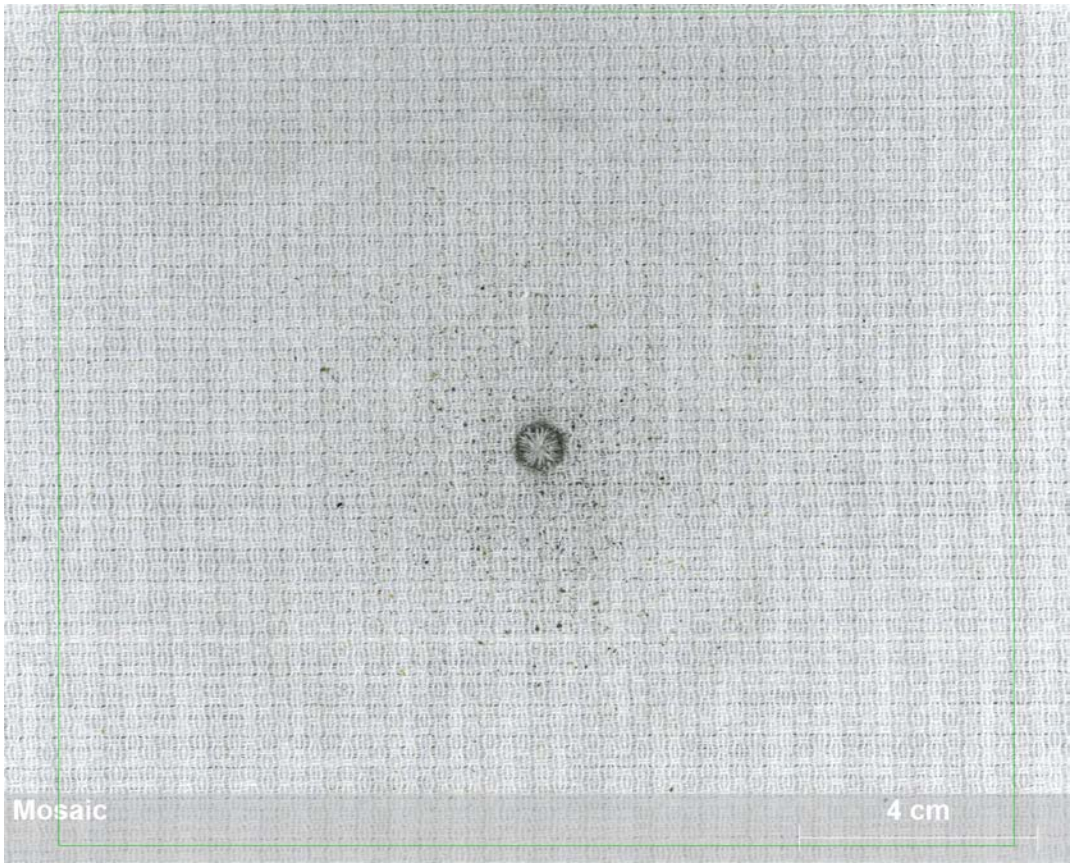
- Small signals are easily overwhelmed by background due to scattering of primary radiation (excitation), reducing the signal-to-noise ratio (SNR)
- For optimal limit of detection (LOD) background should be minimal
- Sample suspended on Mylar foil to minimize the scattering background
- Mylar can be spanned over a storage box, rear wall cut out to avoid changes in scattering at the rear edge of sample support





Gun Shot Residue
Overview Scan Settings

Overview scan of 16 cm x 14 cm with 150 µm pixel size in 1:40 h



Optical overview image based on stitched tiles

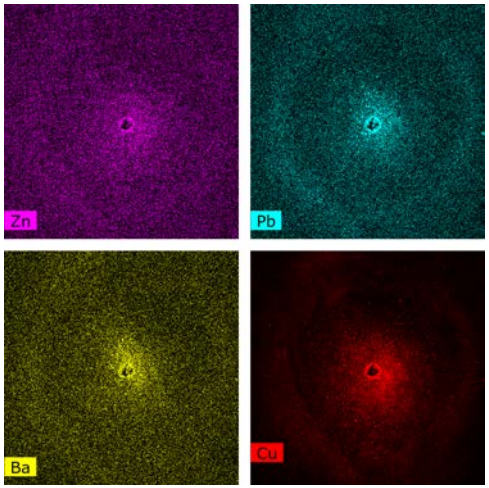
Map information

Mapping parameters		
Width:	1067	pixel
	160	mm
Height:	933	pixel
	140	mm
Pixel Size:	150	µm
Total number of pixel:	995511	pixel
Acquisition parameters		
Frame count:	1/1	
Pixel time:	5	ms/pixel
Measure time:	1:19 h	
Overall time:	1:39 h	
Stage speed:	30,0	mm/s
Tube parameter		
High voltage:	50	kV
Anode current:	600	µA
Filter:	Empty	
Optic:	Lens	
SpotSize:	14	
Chamber at:	Vacuum 20,1	mbar
Anode:	Rh	
Detector parameters		
Selected detectors:	1,2	
Max. pulse throughput:	130000	cps

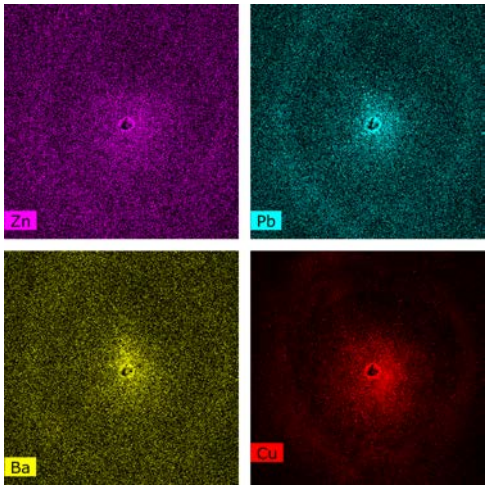
Close

Gun Shot Residue
Comparison of measurement settings

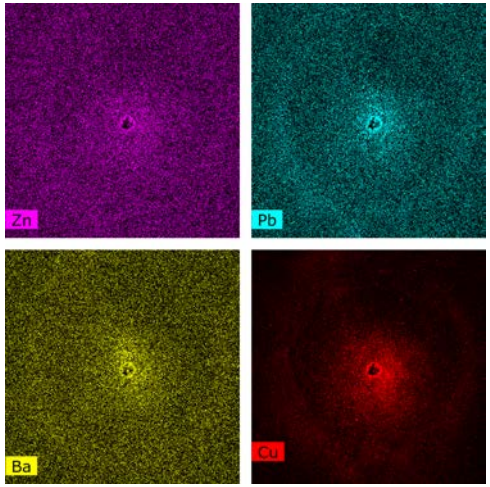
Scanned area: 13 cm x 13 cm, 20 mbar chamber pressure, 50 kV / 600 µA



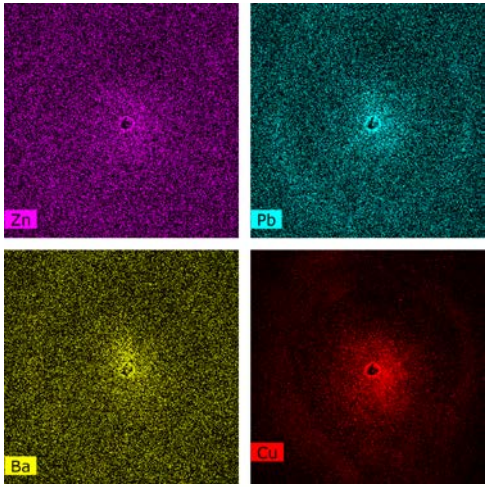
100 µm
5 ms/pixel
1 x 30 mm² SDD
3:35 h (2:14 h)



100 µm
2 ms/pixel
2 x 30 mm² SDD
1:38 h (53 min)



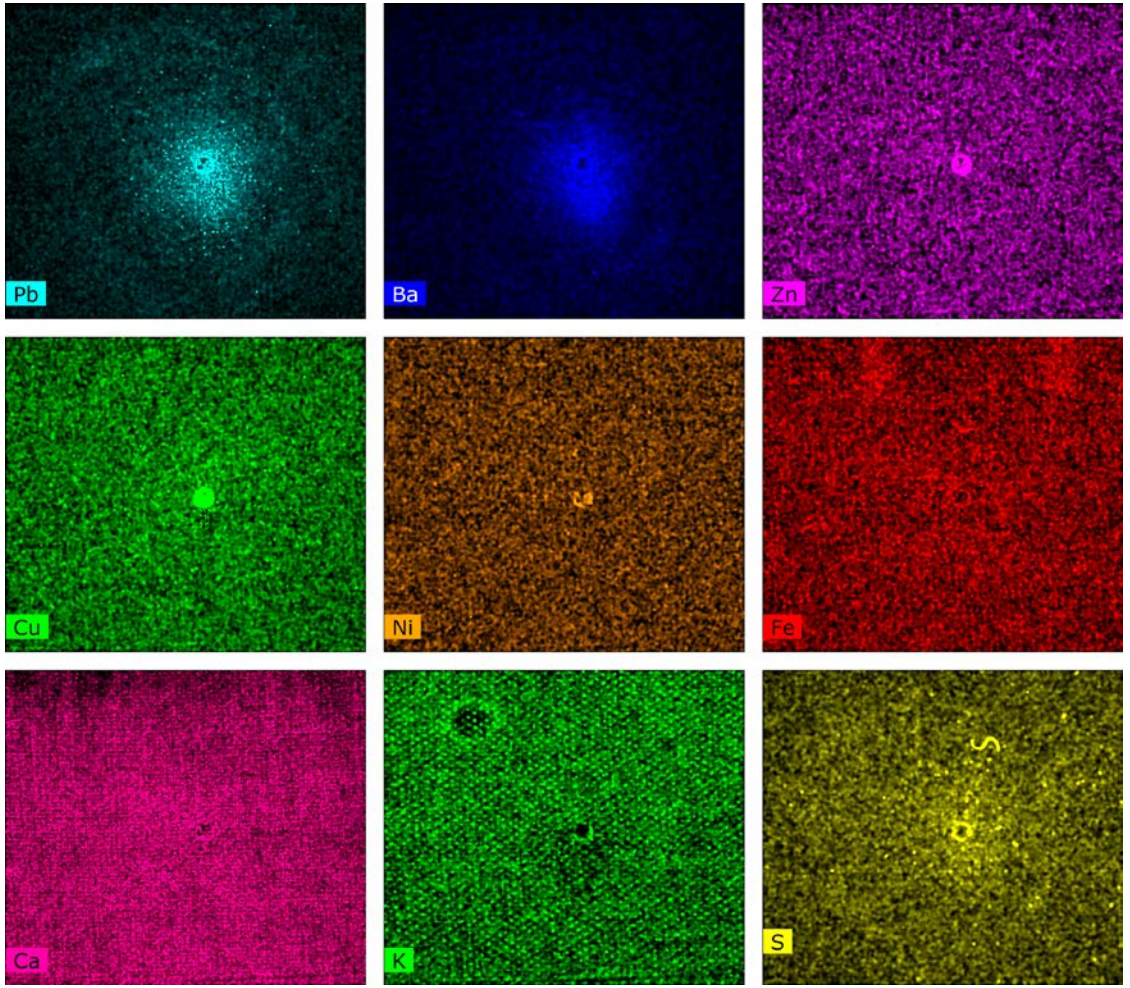
100 µm
1 ms/pixel
2 x 30 mm² SDDs
1:11 h (26 min)



130 µm
1 ms/pixel
2 x 30 mm² SDDs
54 min (20 min)

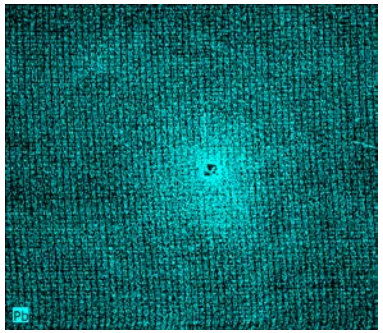
Gun Shot Residue
Element Distribution Maps

- Distribution maps for each element can be extracted easily
- Distribution of different elements allow for analysis of different aspects
- Pb, Ba, and S show cloud-like area around bullet hole
- K shows some contamination of the sample in top left part of specimen

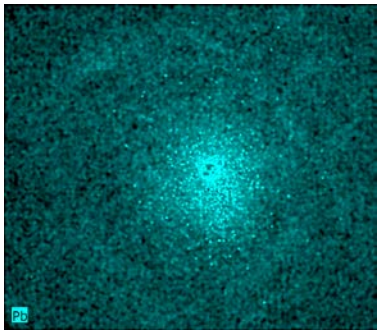


Gun Shot Residue
Element Distribution Maps

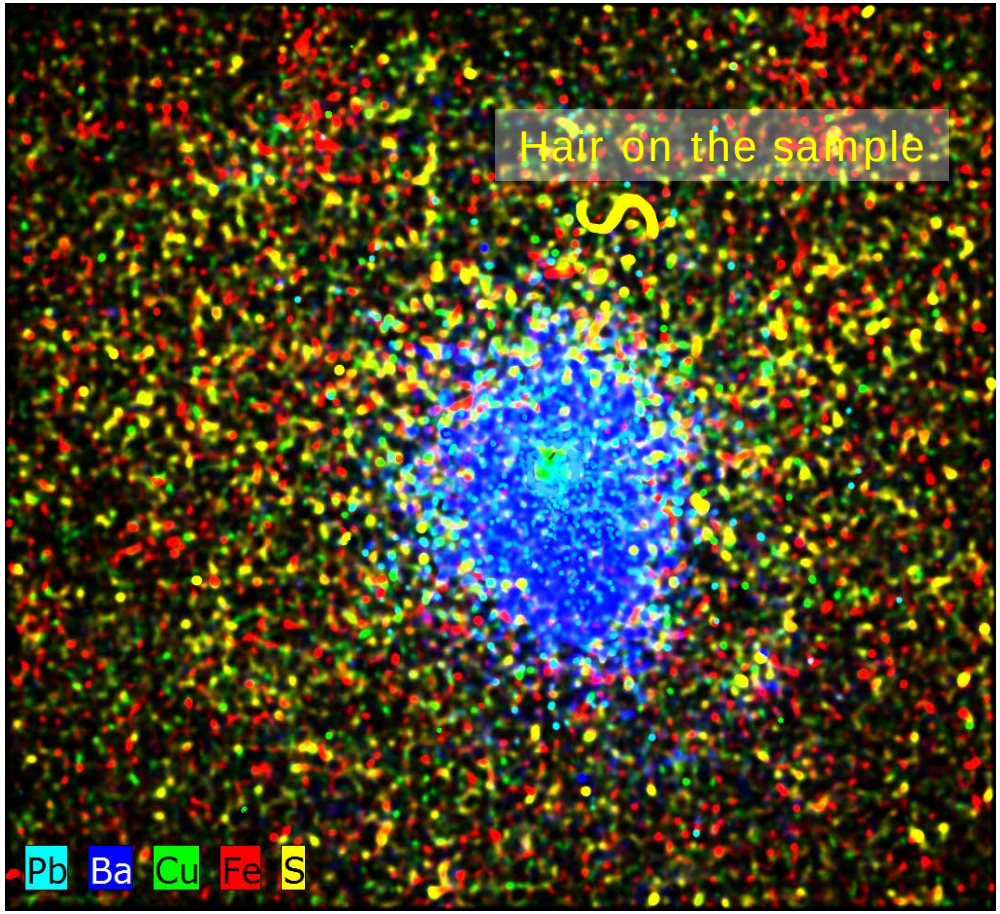
- Selection of fewer elements in a single plot allows for coordination of different signals
- Adjustment of threshold for intensity to display allows to suppress artefacts from scattering
- Fast deconvolution (FD) allows for efficient extraction of useful signal from background



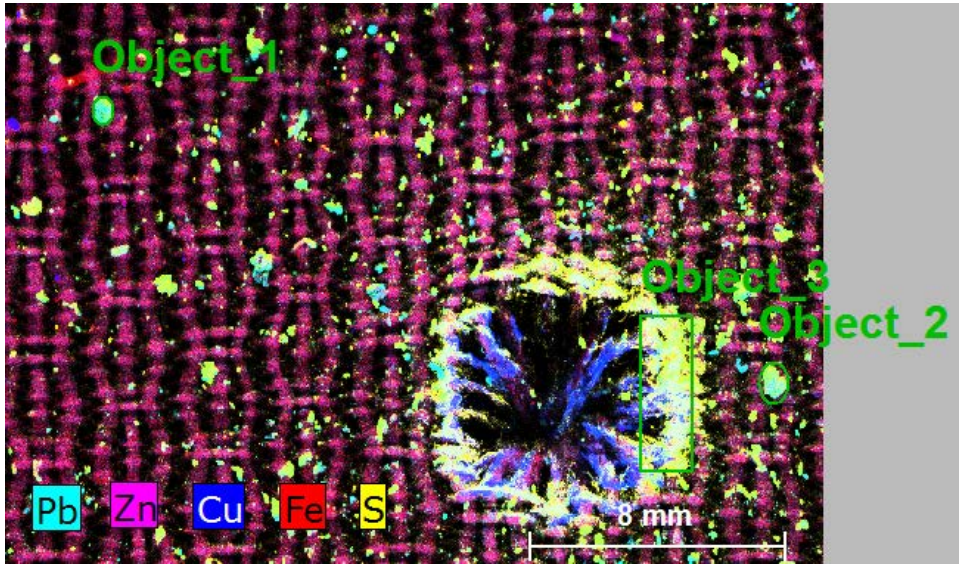
without FD

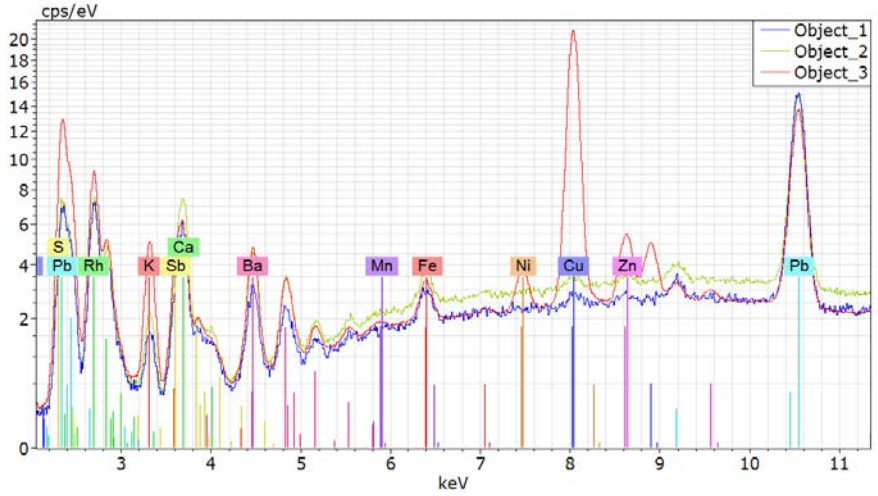


with FD



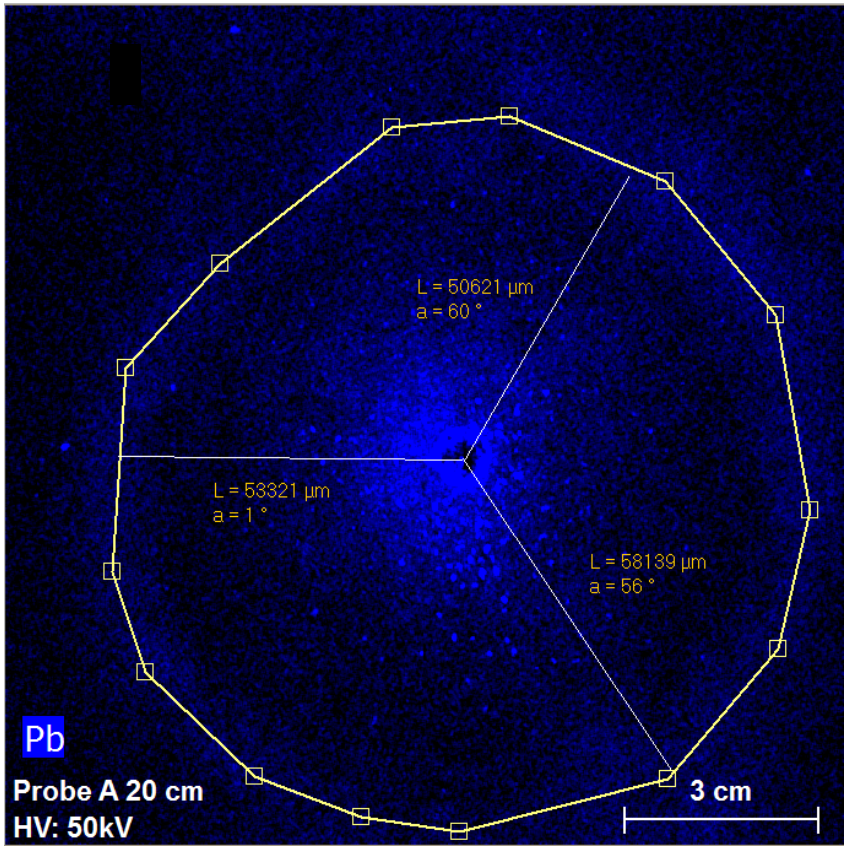
Gun Shot Residue
Details on Features

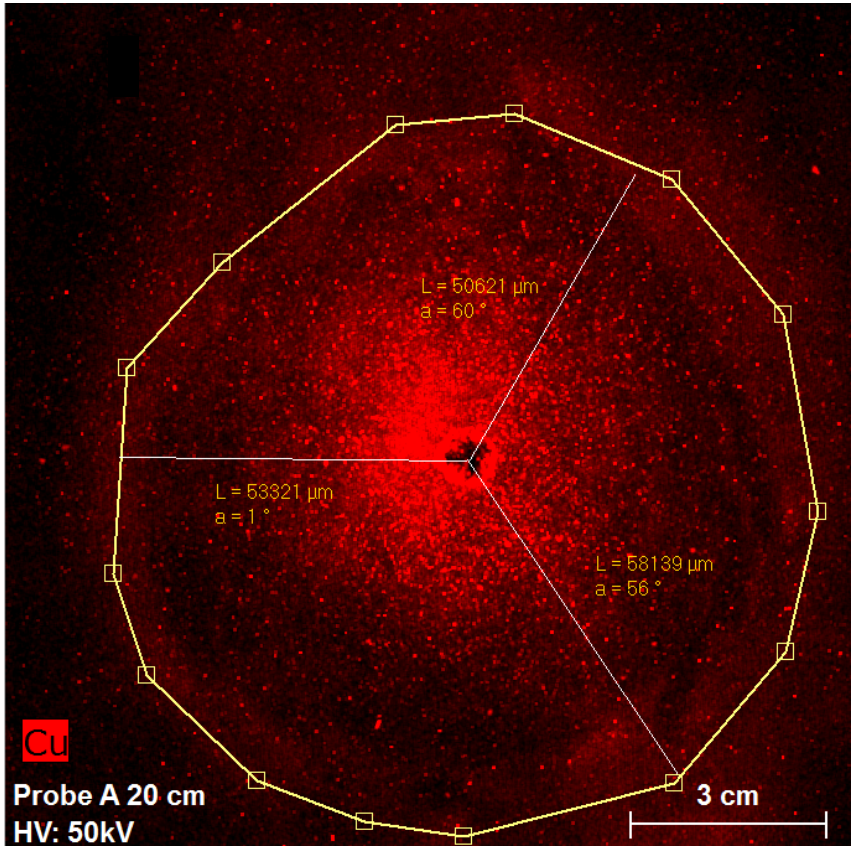




- By analyzing objects in the map, element composition can be qualitatively compared
- At the bullet hole K, Ni, Cu, and Zn are found as well as increased levels of Pb and Ba
- The sprinkles around only show Pb, S, and Ba

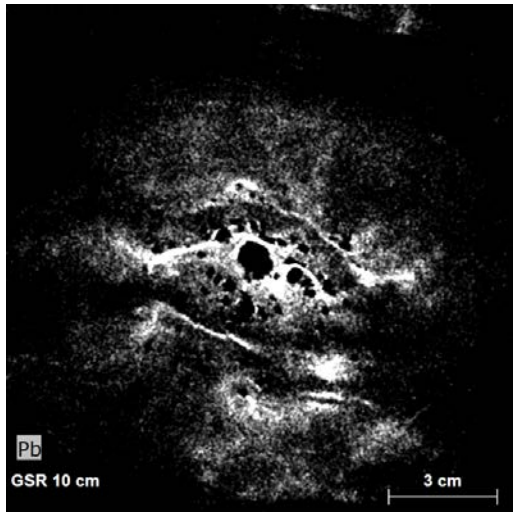
Geometrical Analysis
On 20 cm Sample on Cloth

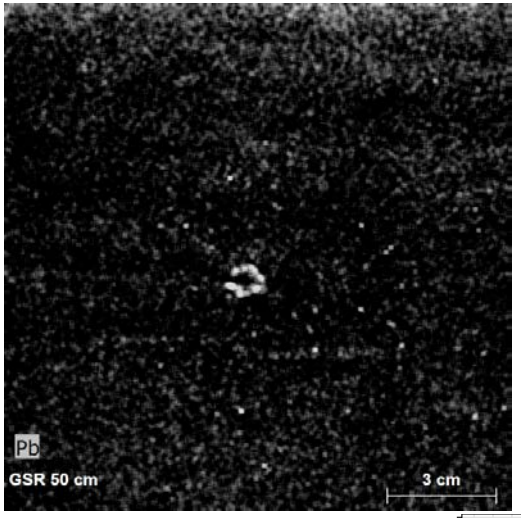


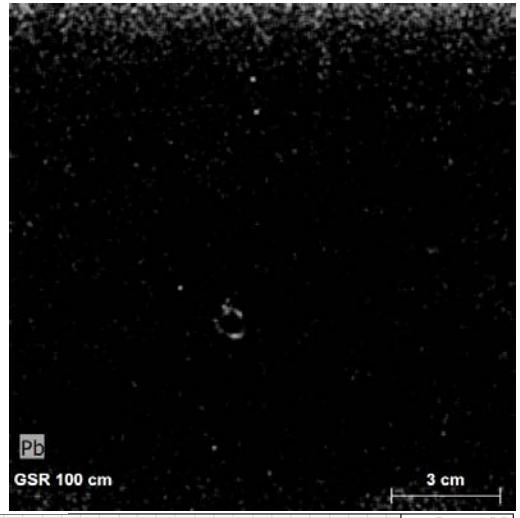


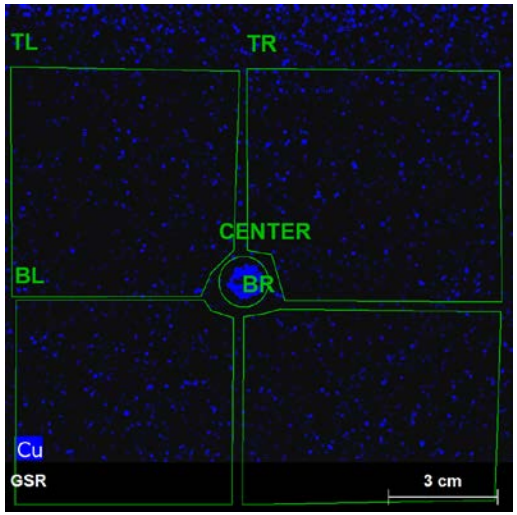
- Cloth appears to hold smoke residue and particles significantly better than paper
- Allows for analysis of significantly larger areas (due to better SNR)

Large Variation of Distance
Comparison 10, 50 and 100 cm on cloth

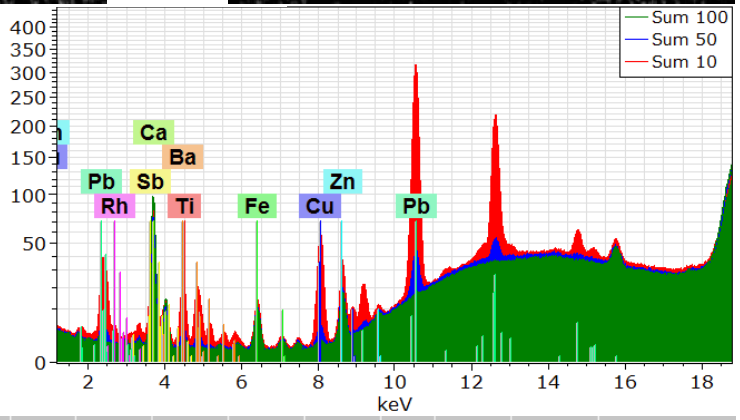








- Sum spectra over different samples (same size)
- With increasing distance the found amount of GSR decreases



	Ca	Ti	Fe	Cu	Zn	Rh	Sb	Ba	Pb	Sum
Sum 100	118411	2039	14004	1185	25710	57634	0	0	7874	**226857.00**
Sum 50	90313	2646	14529	5735	28024	61947	0	4143	86358	**293695.00**
Sum 10	101013	9347	20055	92851	53984	77105	157	59722	927696	**1341930.00**

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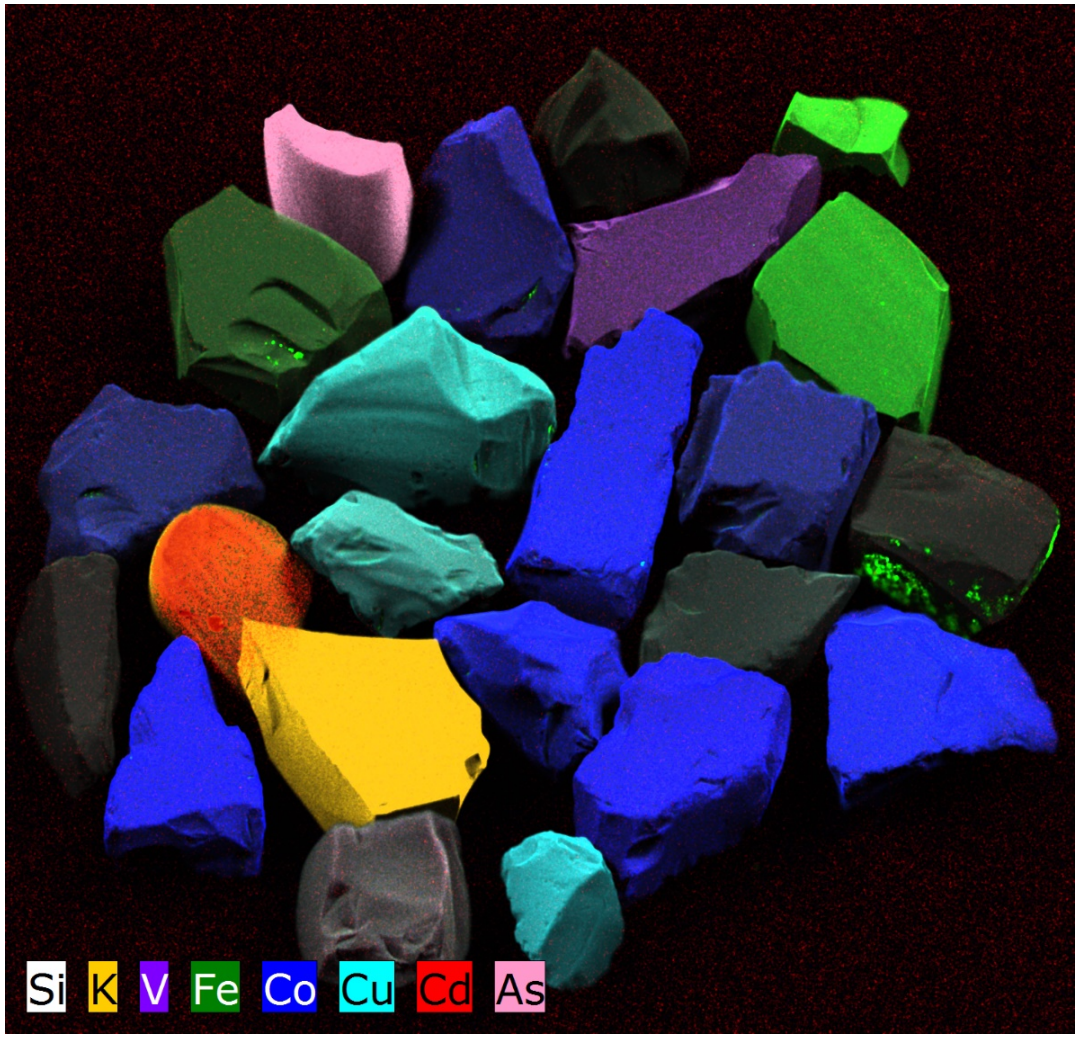
Glass Analysis
Qualitative: Color Mixing



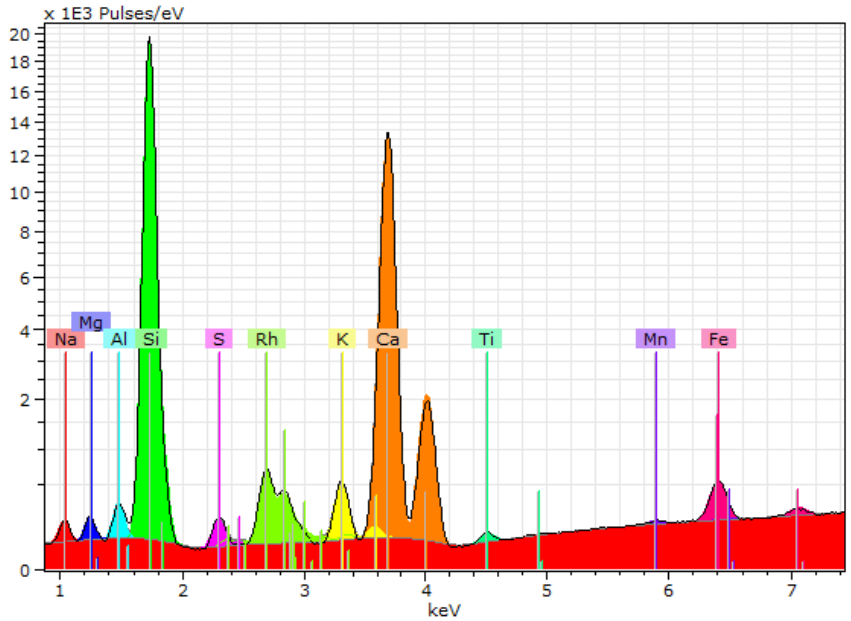
- At-a-glance classification by mixing the colors which represent selected marker elements
- Contaminations and float face can be easily be identified

Glass Analysis
Quantitative, using FP

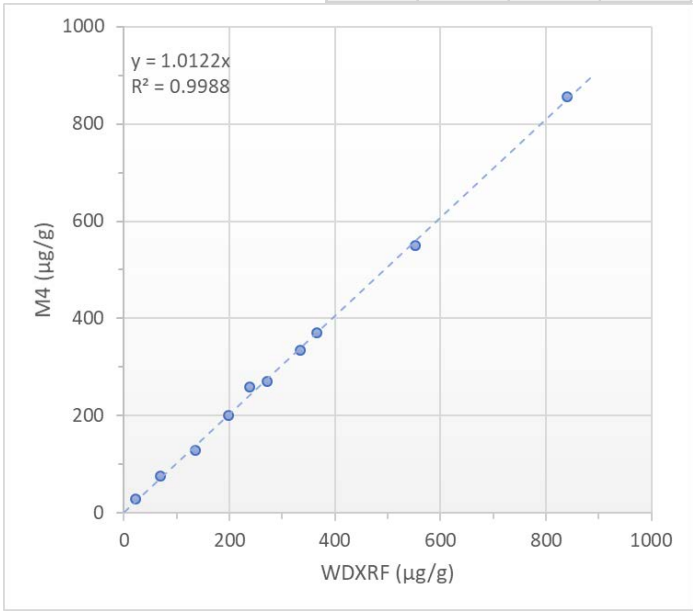
Powerful FP algorithm based on forward calculation of spectra

The quantitative results where shown to be very much in line with WDXRF measurements for steels
(LR 465, Webinar from 25.08.2016) and glasses
(here results from Stazione Sperimentale del Vetro, Murano)

	Pb concentration (µg/g)		
Sample	WDXRF	M4	Δ
A	22	29	-7
B	69	77	-8
C	135	128	7
D	198	200	-2
E	239	260	-21
F	271	271	0
G	335	334	1
H	365	371	-6
I	552	550	2
L	841	855	-14



Forward calculation of glass (NIST 620) spectrum



Data courtesy of Roberto Falcone, SSV

Glass Analysis
Semi-quantitative, as per ASTM E2926

ASTM E2926 – 13

Standard Test Method for

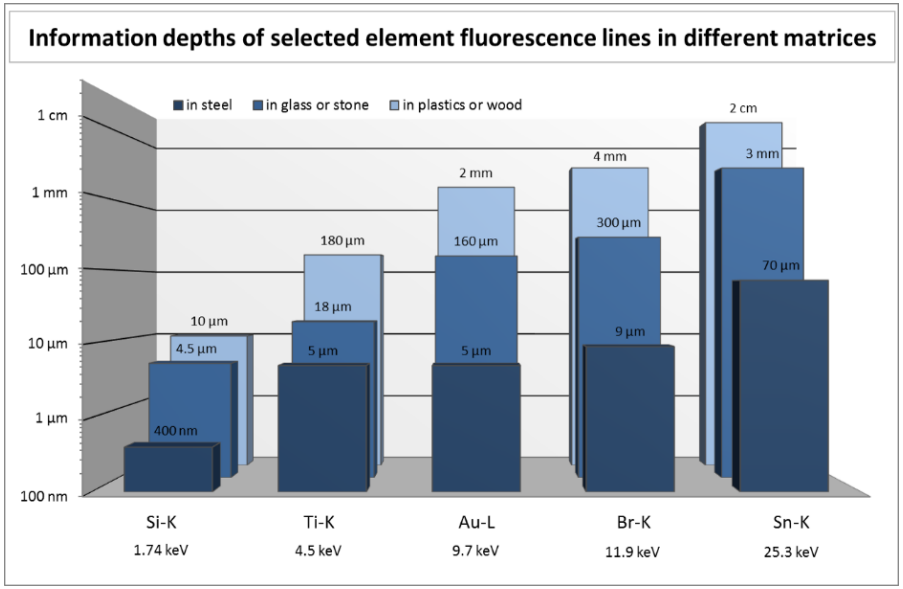
Forensic Comparison of Glass Using Micro X-ray Fluorescence Spectrometry

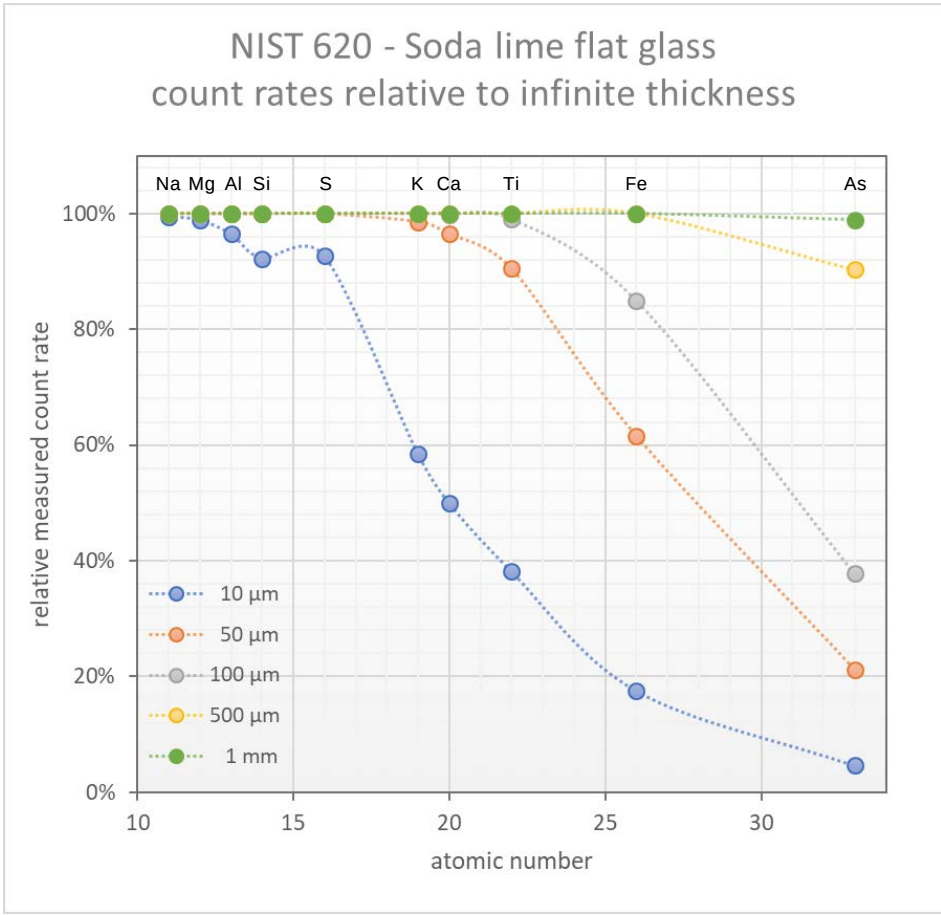
- No actual quantification of the sample required
- Based on peak intensity ratios
- Detailed and well-described workflow

> 1.3 This test method does not replace knowledge, skill, ability, experience, education, or training and should be used in conjunction with professional judgment.

Glass Analysis
Restrictions due to information depth

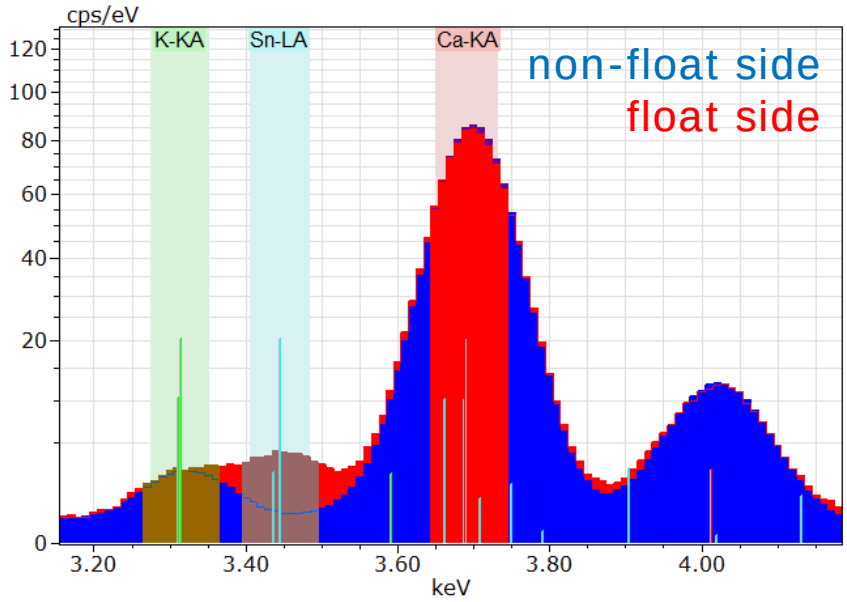
9.1.3.4 For comparisons, glass specimen should be of similar size, shape, and thickness to each other. For full thickness fragments of float glass, comparisons should be made between similar surface types (for example, non-float surface to non-float surface).

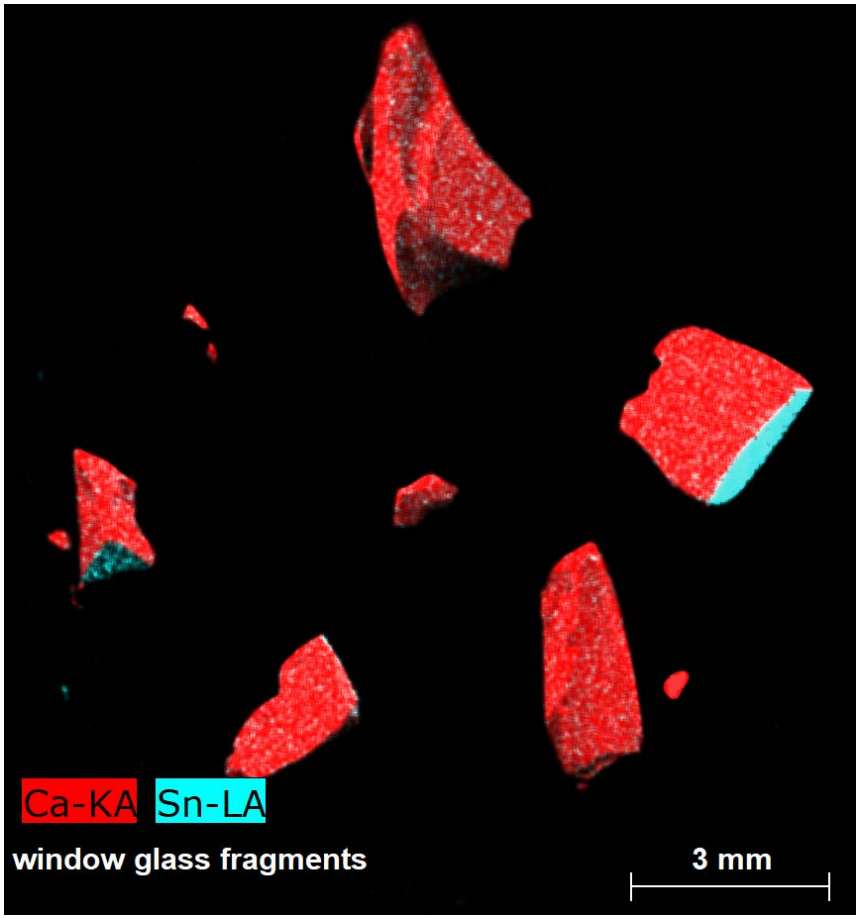




Glass Analysis
Identifying the non-float surface

9.1.3.4 For comparisons, glass specimen should be of similar size, shape, and thickness to each other. For full thickness fragments of float glass, comparisons should be made between similar surface types (for example, non-float surface to non-float surface).

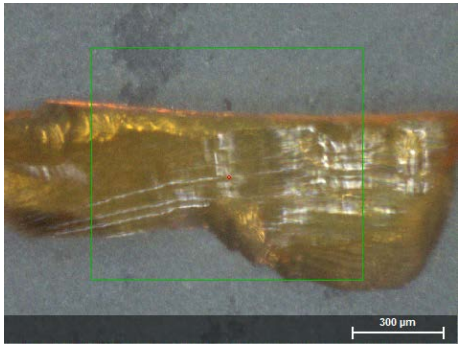




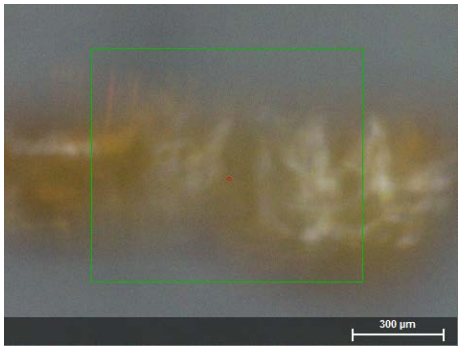
Glass Analysis
on the importance of accurate focusing

Defocusing of ~ 1 mm changes relative Na intensity (at 20 mbar) by ~ 8.5 ‰
(general intensity loss/gain by change in solid angle of detection is ~ 10 %)

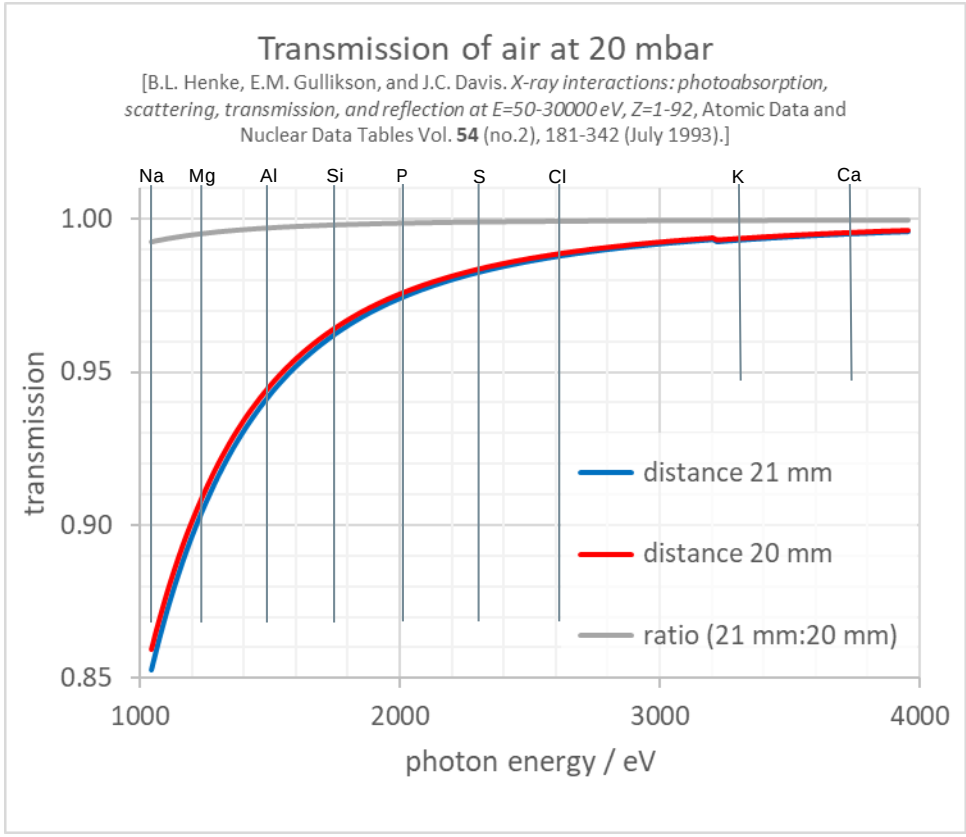
Note: At 10 mbar the difference ratio down to only 4 ‰



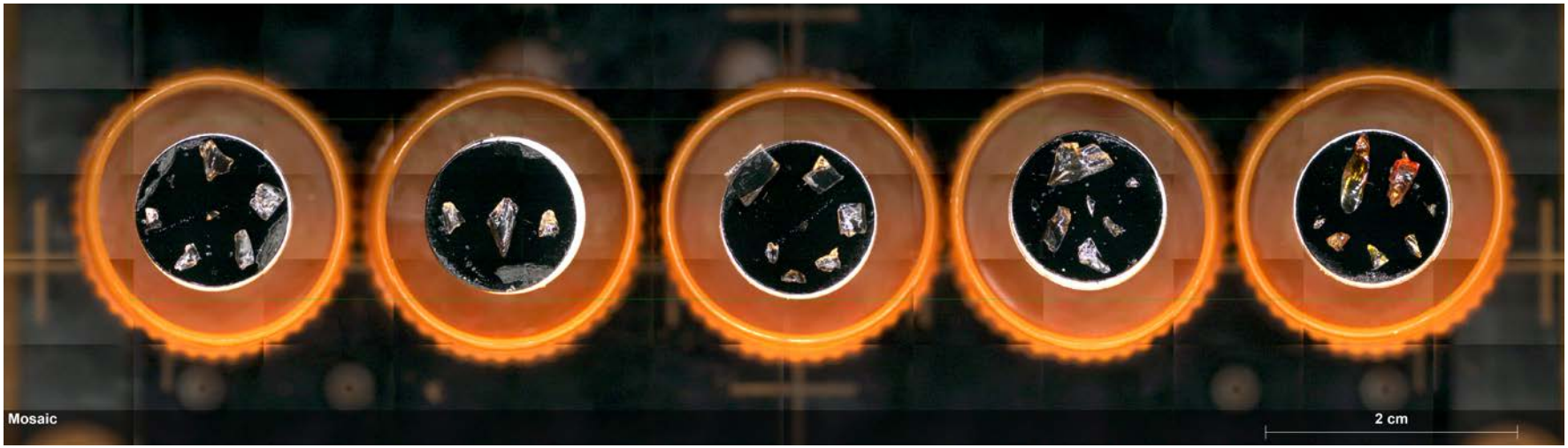
focused



defocused by 1 mm



Glass Analysis
Classification



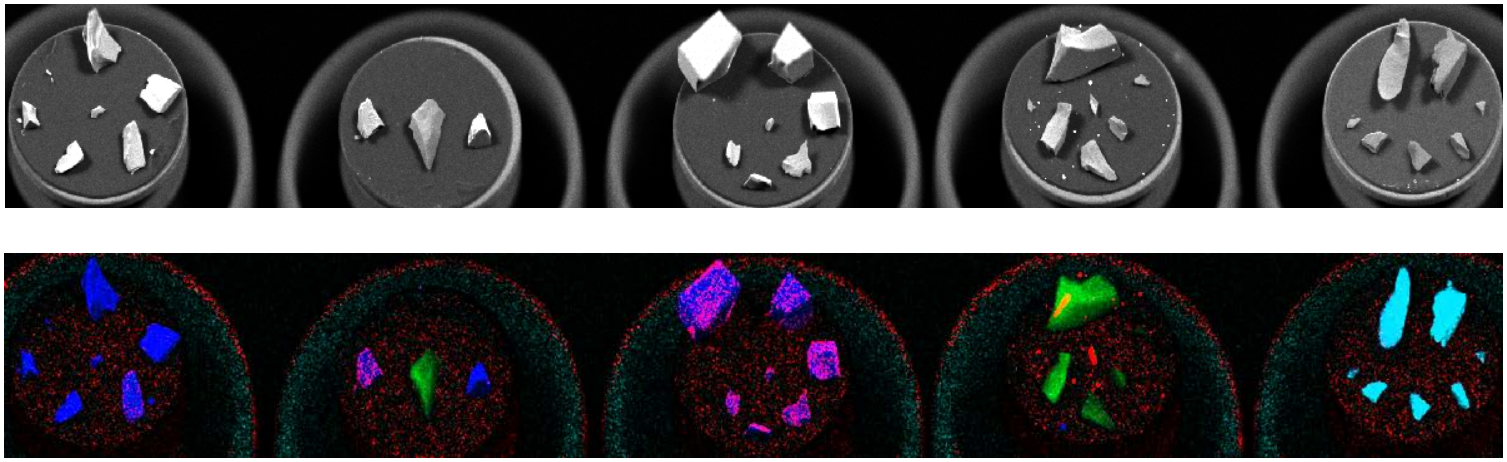
F1

Ca

Ti

Zr

Se



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Glass Analysis
Live

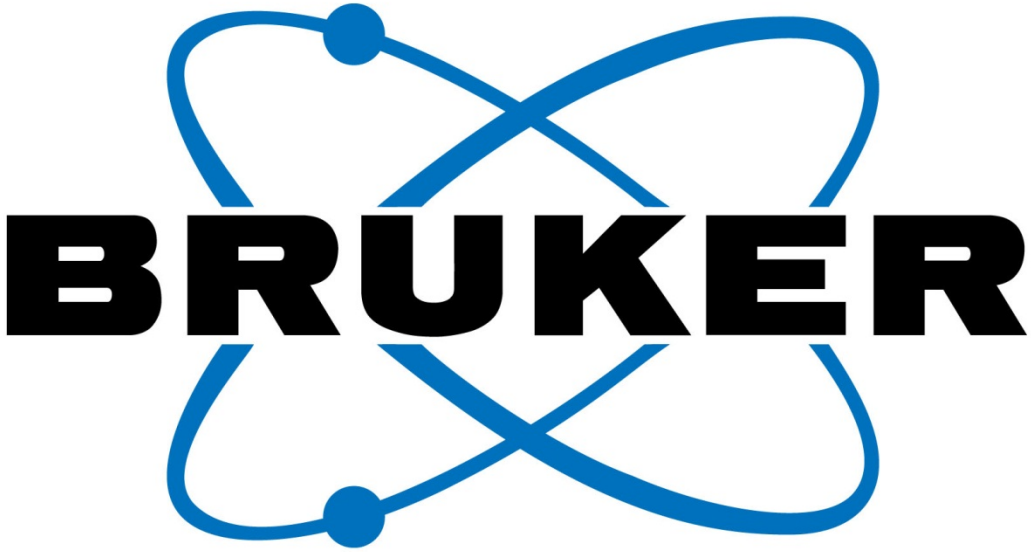
Summary

- Micro-XRF allows for fast, spatially resolved mapping of large sample areas
- It is non-destructive and requires almost no sample preparation
- Gunshot residues on cloth are best measured with a „spacing“ between sample and stage. Thus SNR is optimized
- Mutliple data mining tools allow for offline anaysis
- For glass shards analysis the information depth for the different elements has to be kept in mind
- Glass shards can be analyzed in different ways:
  - Qualitative, by simply looking at the color mixture in the map
  - quantitative, as the M4‘s FP algorithm yields stable and reliable results
  - Semi-quantitative, based on intensity ratios, according to ASTM E2926

Q&A

Are There Any Questions?

Please type in the questions you might have in the Q&A box and press *Send*.



Innovation with Integrity