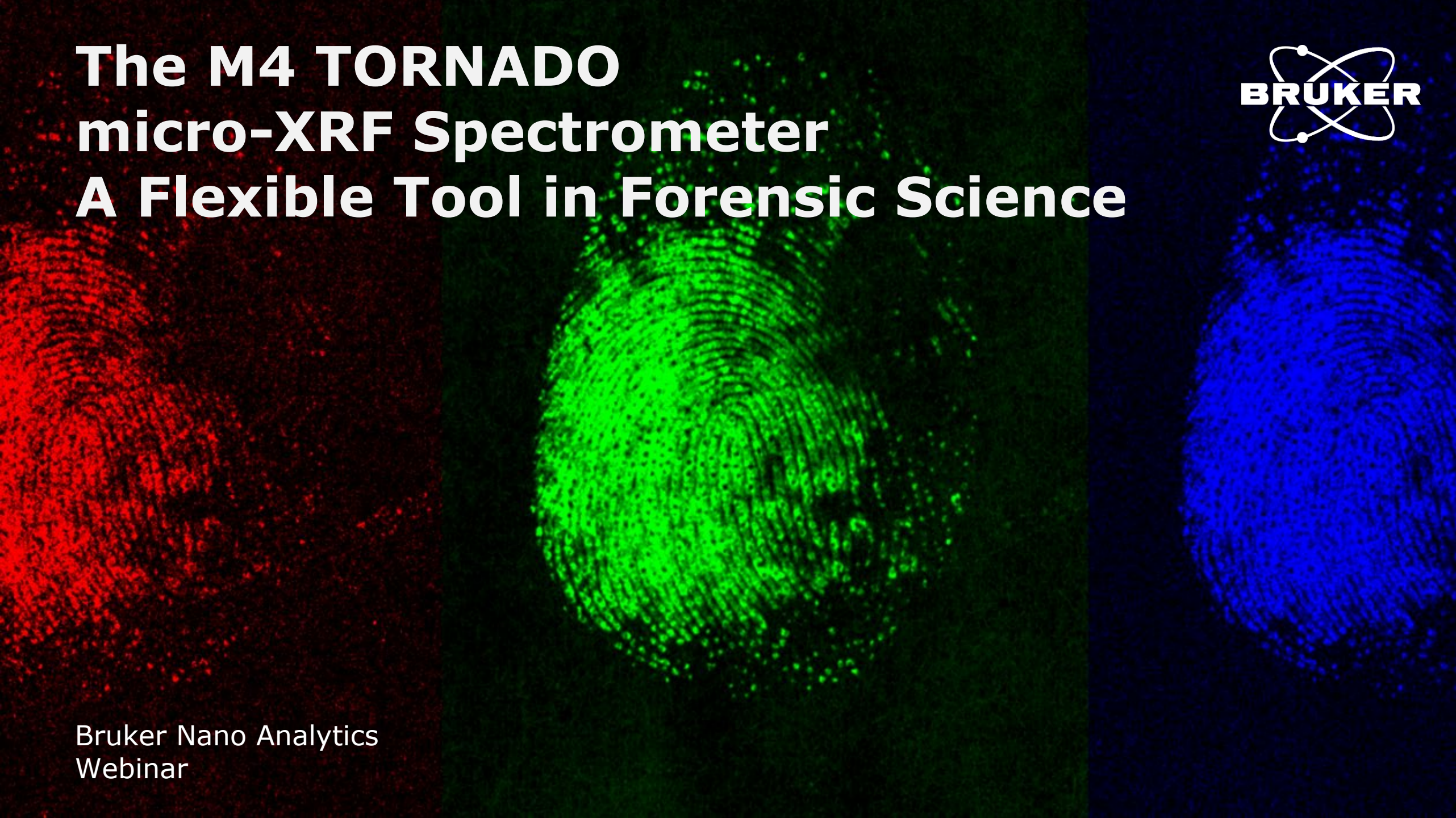
The M4 TORNADO micro-XRF Spectrometer A Flexible Tool in Forensic Science



Bruker Nano Analytics
Webinar

Today's Presenters
Micro-XRF Application Scientists

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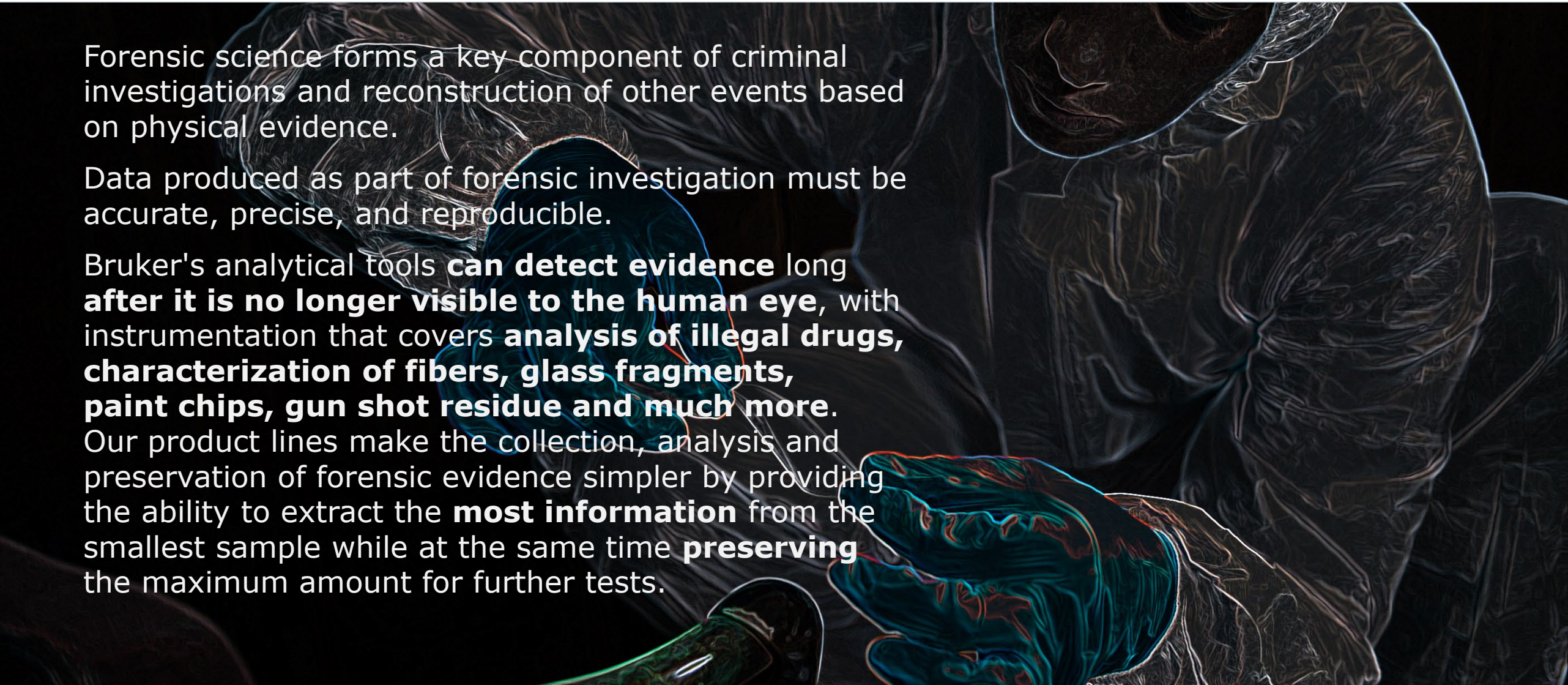


Forensic science forms a key component of criminal investigations and reconstruction of other events based on physical evidence.

Data produced as part of forensic investigation must be accurate, precise, and reproducible.

Bruker's analytical tools **can detect evidence** long **after it is no longer visible to the human eye**, with instrumentation that covers **analysis of illegal drugs, characterization of fibers, glass fragments, paint chips, gun shot residue and much more**. Our product lines make the collection, analysis and preservation of forensic evidence simpler by providing the ability to extract the **most information** from the smallest sample while at the same time **preserving** the maximum amount for further tests.

Commitment and Areas
Bruker in Forensics

Bruker is constantly seeking to develop products capable to elevate Forensic Scientist's work.

We have designed a team to assist customers in this field.

We clearly see our engagement in all the activities where one of our instruments is used to prevent or to investigate a criminal event against nature, people or property.

Criminal forensics

Forensic drug analysis

Gun shot residue analysis and shooting distance determination

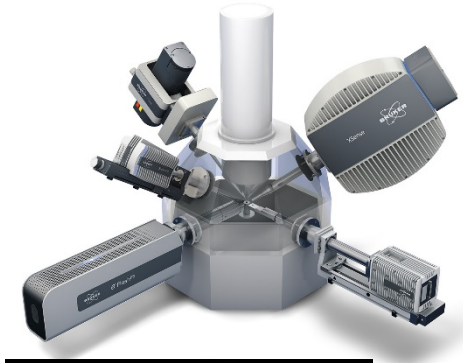
Glass analysis

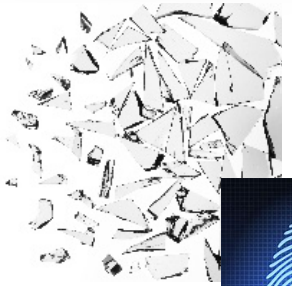
Environmental forensics

Art and document forgery

Addressing a Range of Needs
From the Field to the Lab

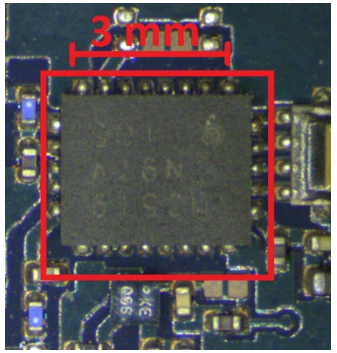
Handheld & Portable XRF TITAN, TRACER CTX	**Micro-XRF** M4 TORNADO, M6 JETSTREAM, ELIO	**Electron Microscope Analyzers** QUANTAX systems, range of detectors	**Total-reflection XRF (TXRF)** S2 PICOFOX S4 T-STAR

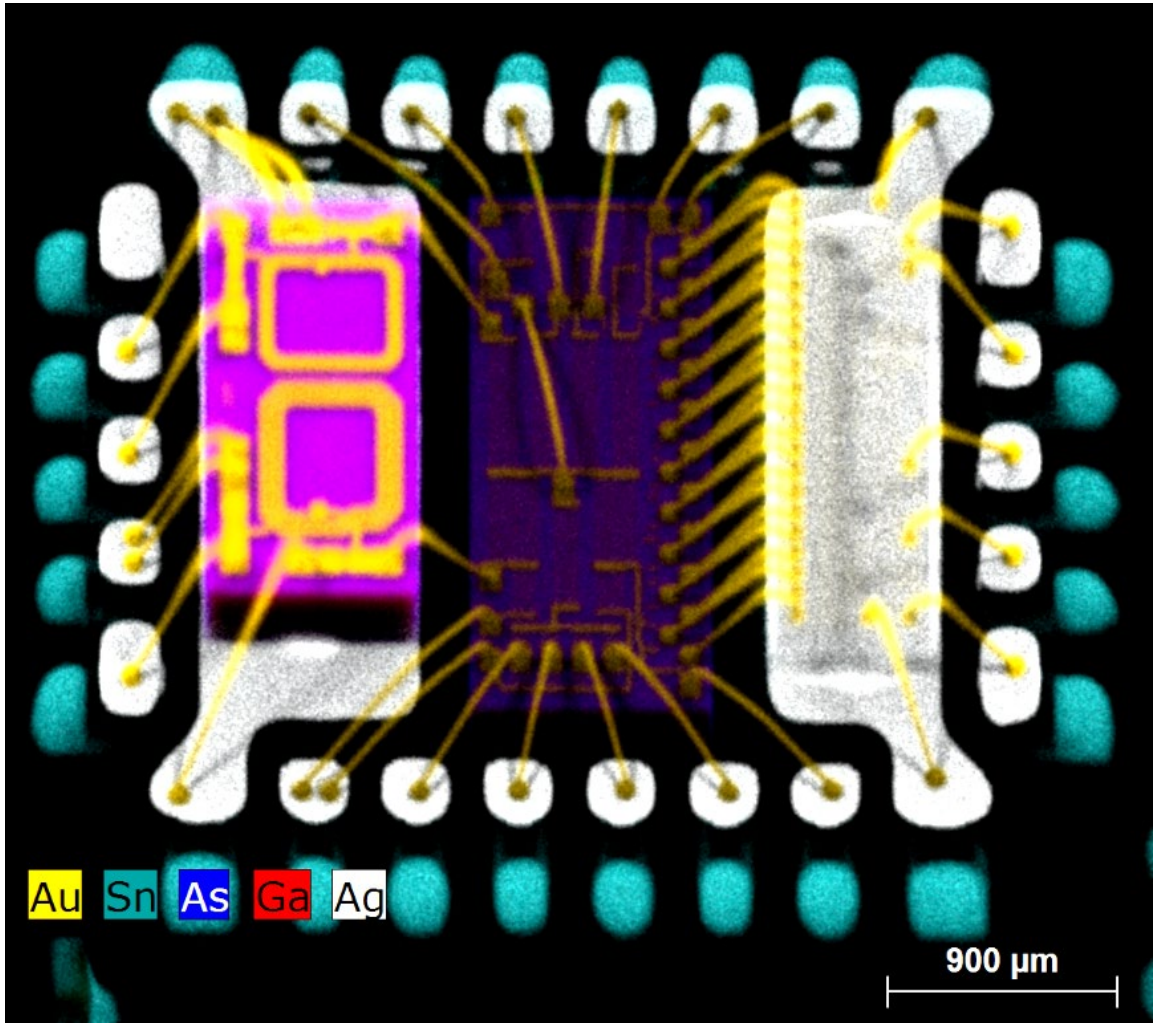




Micro-XRF
Rapid, non-invasive Compositional Analysis

- Little to no sample preparation
- Non-destructive
- Multi-element information
- Small-spot analysis
- Information from within the sample
- Large samples
- Quantitative analysis
- Low maintenance and low consumable costs





Bruker's M4 TORNADO
A State-of-the-Art micro-XRF Spectrometer

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)
other anode materials available

Optional 40 W fine-focus tube with collimator
for excitation of 'heavy' elements, embedded in lighter matrices

Up to two Silicon drift detectors (SDD)
each having 30 or 60 mm² active area and an
energy resolution < 145 eV (for Mn-Kα @ 275 kcps throughput)
optional detectors configured for light element analysis

Sealed sample chamber with adjustable pressure between 1 mbar and atmospheric pressure for detecting elements down to Na (down to C with LEW detectors)

Motorized sample stage with measureable area of 200 mm x 160 mm, maximum sample height 120 mm, sample stage speed up to 100 mm/s, minimum step size 4 µm, maximum sample weight 7 kg

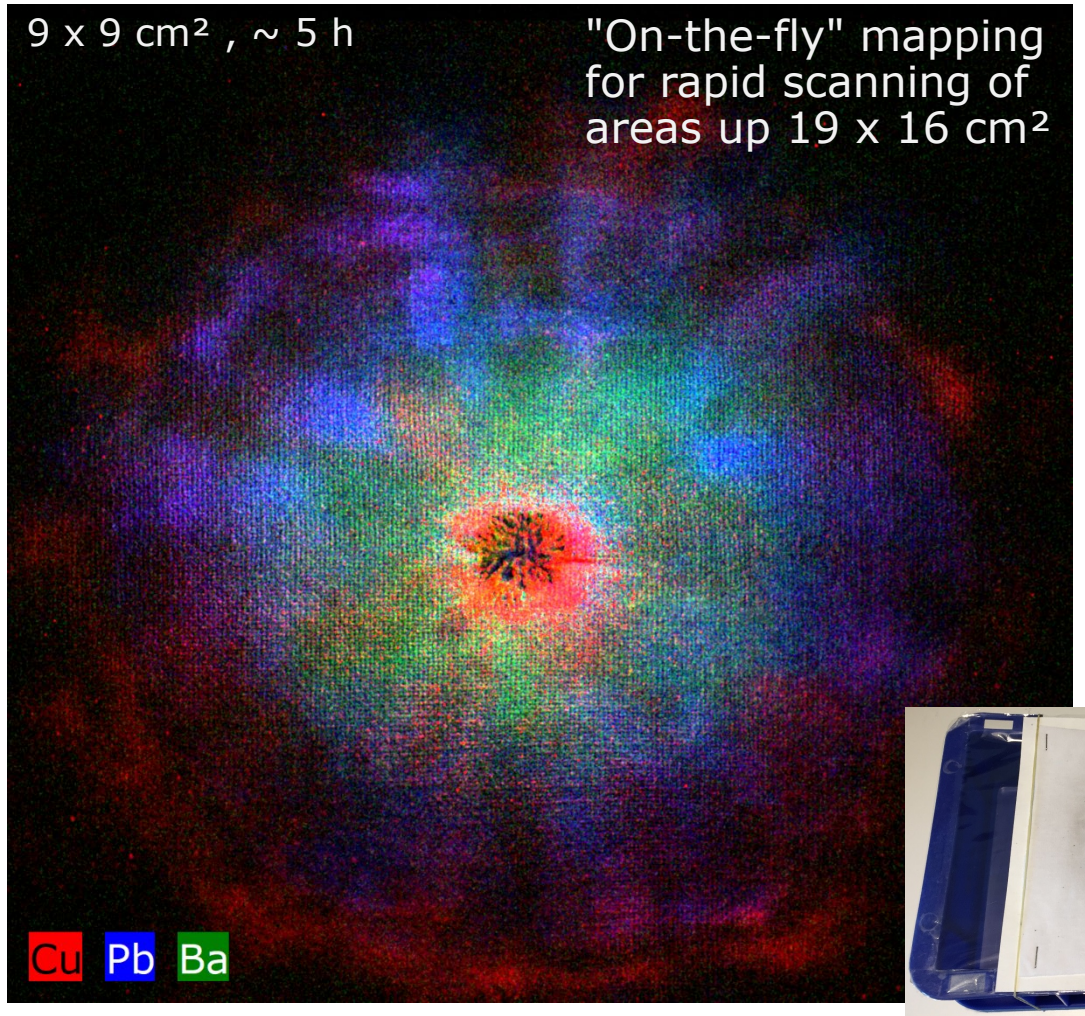
Introduction
micro-XRF Applications in Forensics

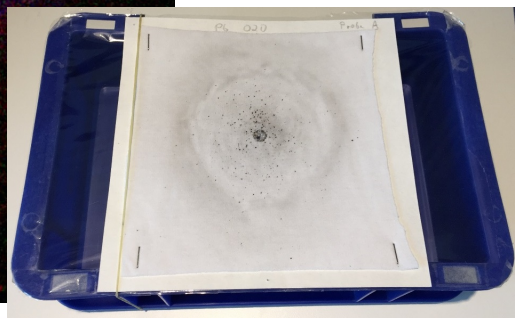
- Gun shot residue (GSR) analysis and shooting distance determination (SDD)
- Provenance analysis of soils
- Modern and historical document forgery
- Classification of glass shards
- **Residual fingerprint analysis**

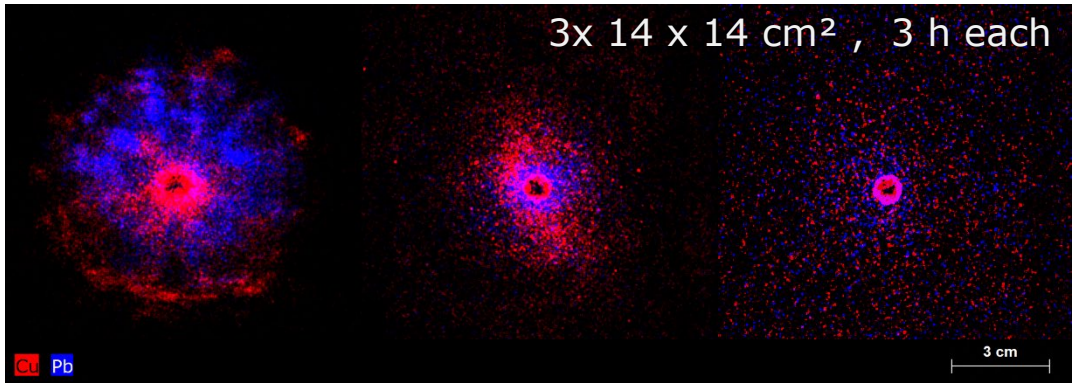
M4 TORNADO in Forensics

Gun Shot Residue Analysis

Gun Shot Residue Analysis
M4 TORNADO micro-XRF Spectrometer

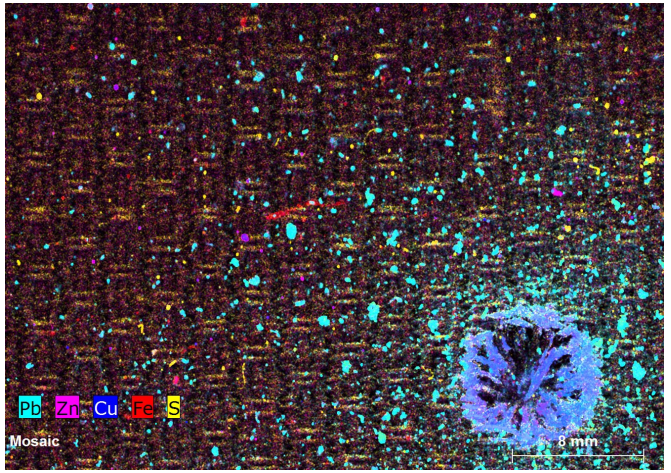






Gunshot distance determination through comparison mapping

Capture fine particle detail and chemistry



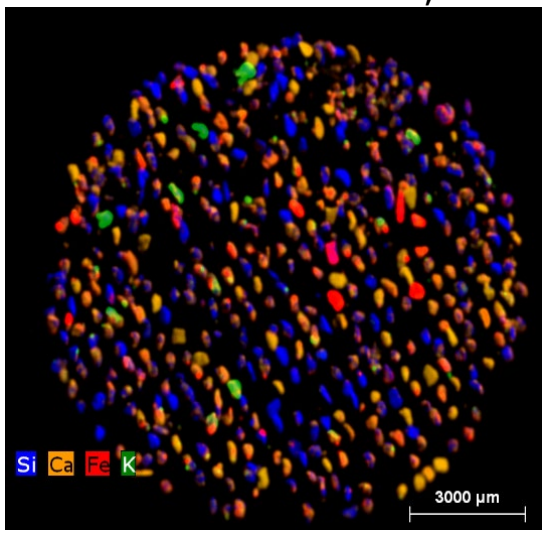
M4 TORNADO in Forensics

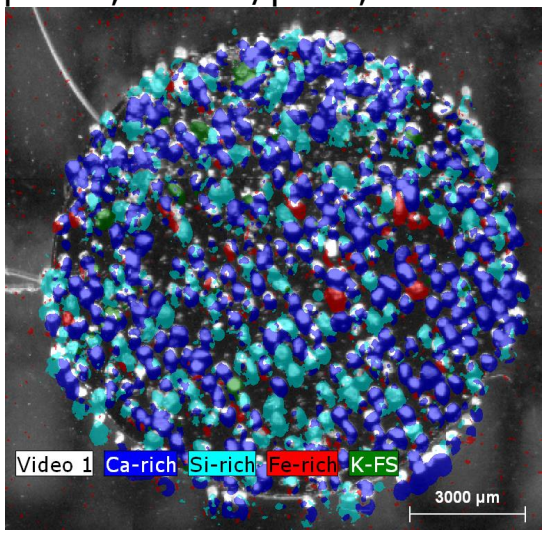
Environmental Forensics

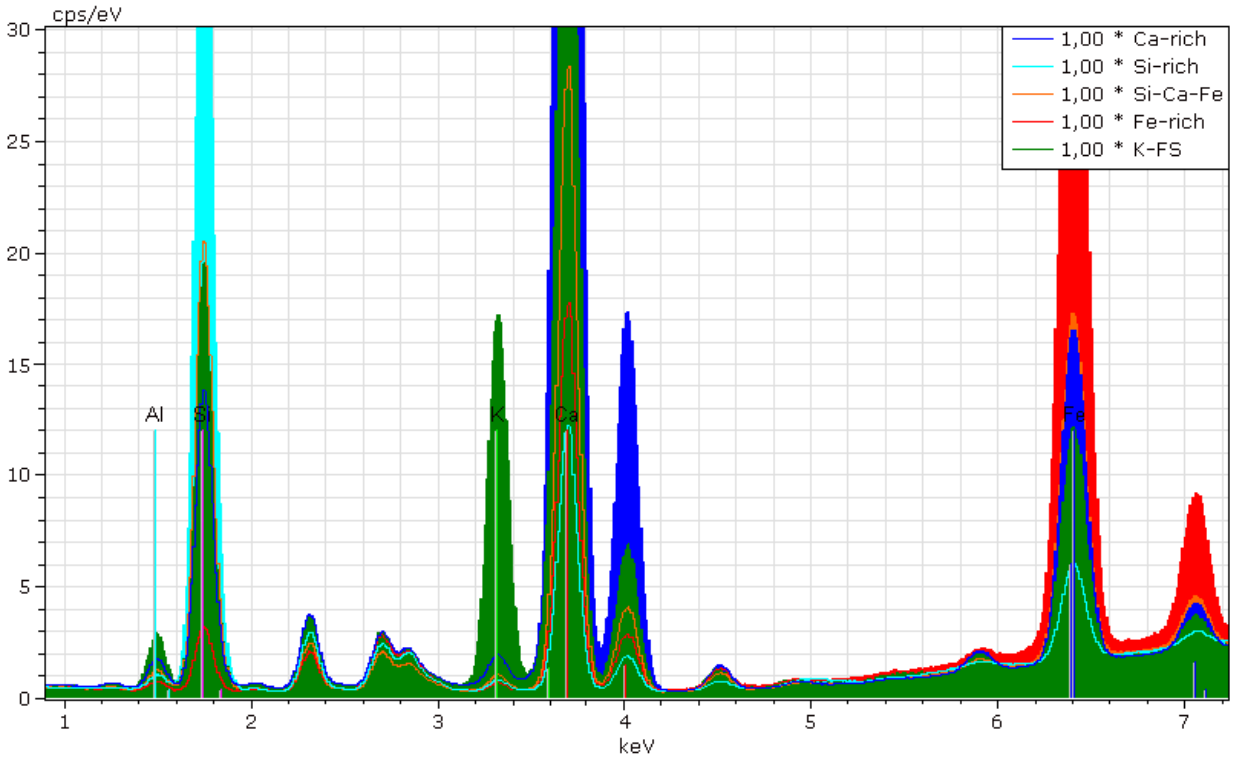
Environmental Forensics
M4 TORNADO micro-XRF Spectrometer

Fingerprint the source location (**provenance**) of soil, sand or other environmental detritus **through compositional analysis** of residues on boots or tires

Scan: 14 x 13.5 mm² , 580k pixels, 10 ms/pixel, 2 h



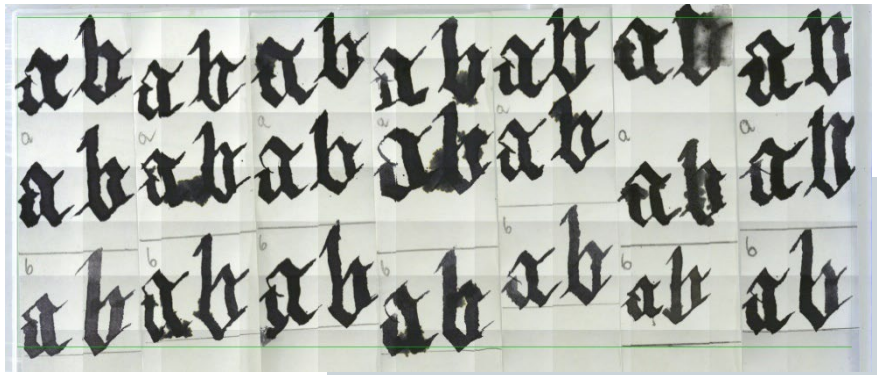




M4 TORNADO in Forensics

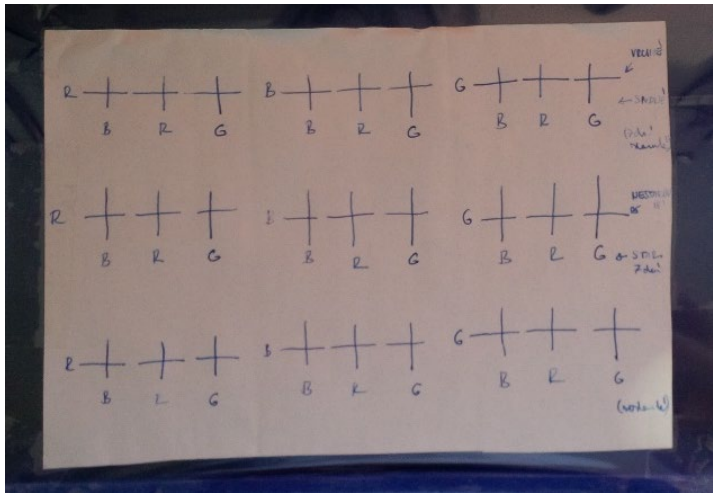
Modern and Historical Document Fraud

Modern and Historical Document Fraud
M4 TORNADO micro-XRF Spectrometer

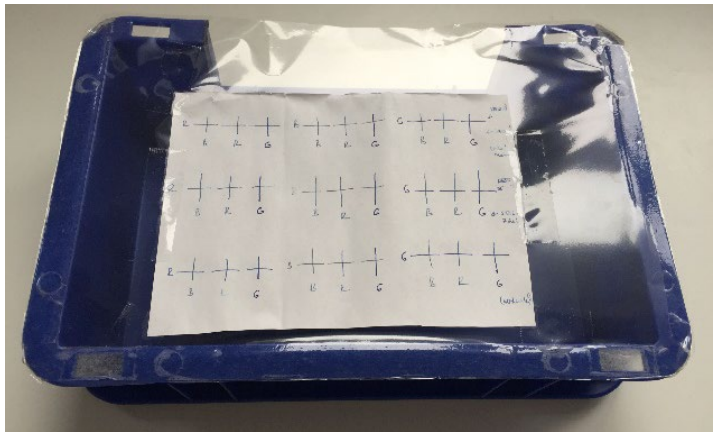


The M4 TORNADO allows for elemental scanning of materials used in the creation of modern and historic documents. For example, modern and historic inks have compositions unique to the manufacturer or time of production.

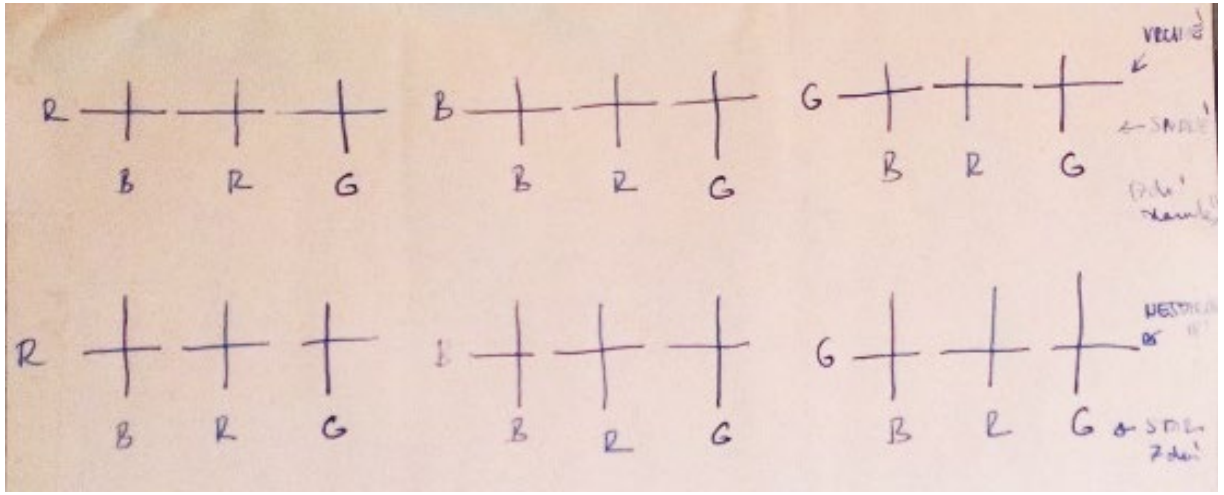
Sample and sample holder

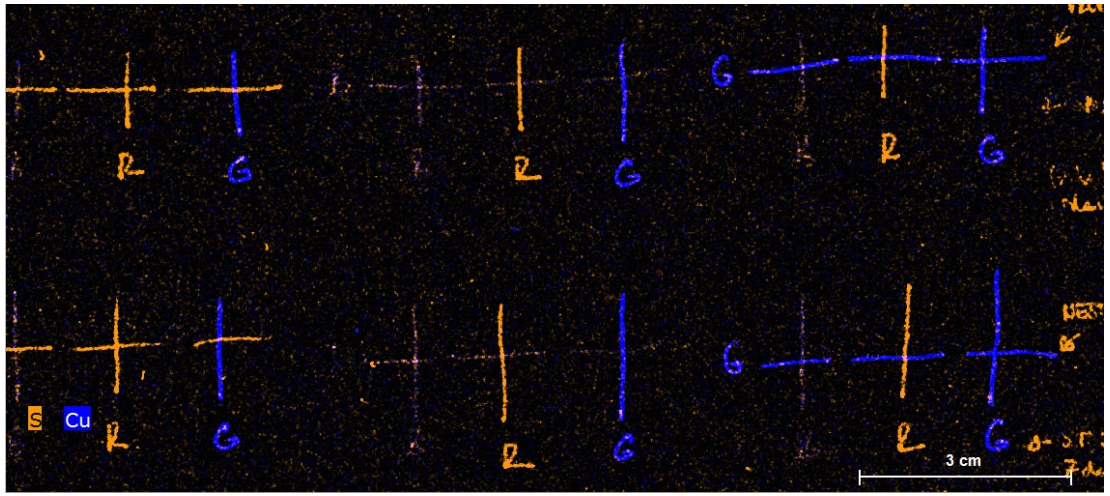


Comparison of the composition of 3 different blue pen types: Ball point (B), Roller ball (R), and gel ink (G) pen. The main pigments are typically copper phthalocyanine and iron oxides.
The sample was placed on a thin mylar foil, elevated above the sample holder surface by ~ 5 cm.
This greatly reduces the scattering background.



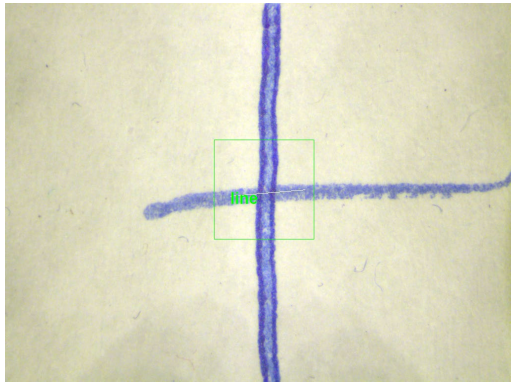
Modern and Historical Document Fraud
M4 TORNADO micro-XRF Spectrometer





156 x 69 mm², 50 µm pixel size, 5 ms time per pixel, 50 kV, 600 µA, 20 mbar 4.3M pixels, 7 h

Modern inks used in pens or printers commonly have **compositions unique to the manufacturer**. These differences may not be easily detected by visual means, in particular after fading.
Here 3 elements differ significantly: S, Cu, and Zn



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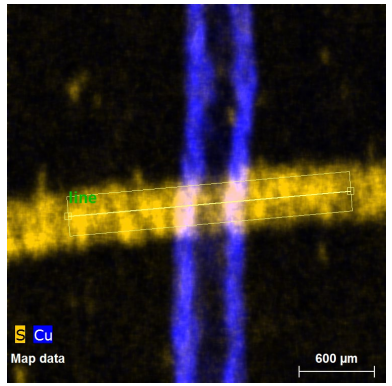
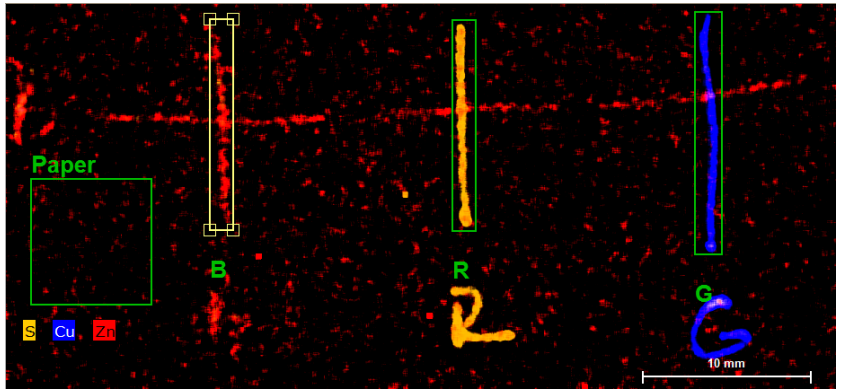


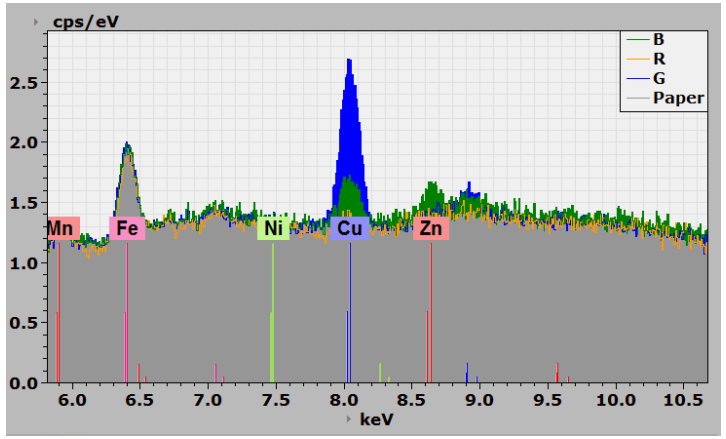
G

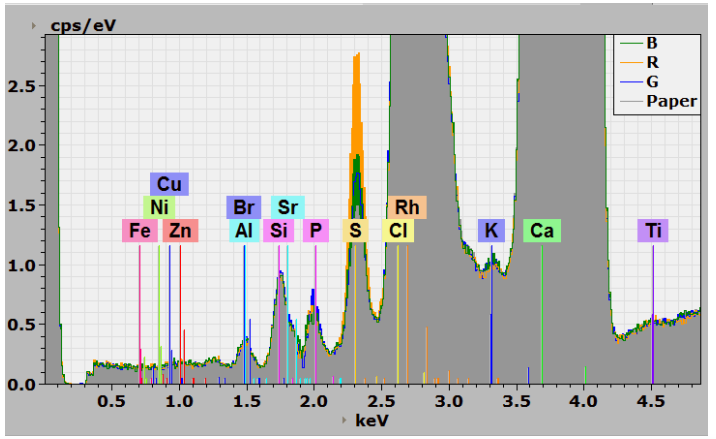
Modern and Historical Document Fraud
M4 TORNADO micro-XRF Spectrometer

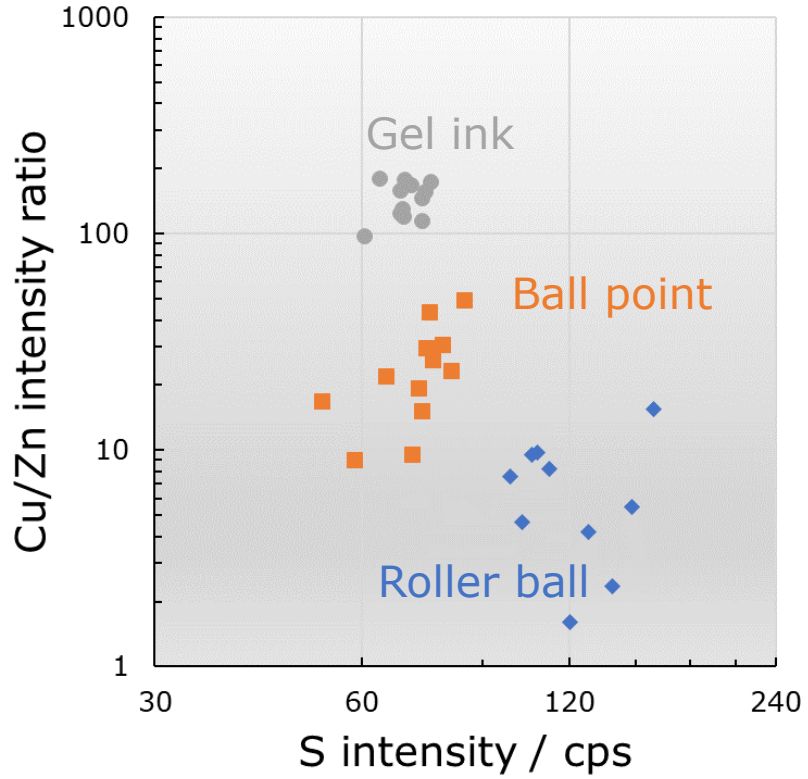


Roller ball and ball point pen inks are commonly similar. The main difference is the viscosity of the ink, which is lower for the roller pen.

Integrated spectra show the **gel pen** is rich in Cu, the **roller pen** has no Cu or Zn but higher S content, and standard **ball pen** has almost as much Zn as it has Cu.







M4 TORNADO in Forensics

Forensic Glass Analysis

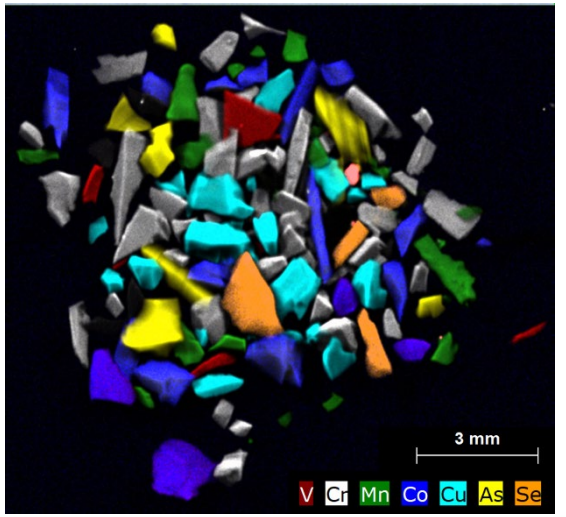
Forensic Particle Analysis
M4 TORNADO micro-XRF Spectrometer

Often particles that are interesting for forensic analysis **are small**.

- Usually it is no problem to hit the particles with the micro-focused X-ray beam
- The fluorescence spectra which are obtained from the samples can be quantified, usuallly using a fundamental parameter approach

X-rays can pass through material!

- Lighter matrices are more ‚transparent' than heavy ones
- If the samples are ‚too thin', the quantification, and even the fluorescence intensity ratios, will become unreliable, i.e. they are affected by the sample size



Forensic Particle Analysis
M4 TORNADO micro-XRF Spectrometer

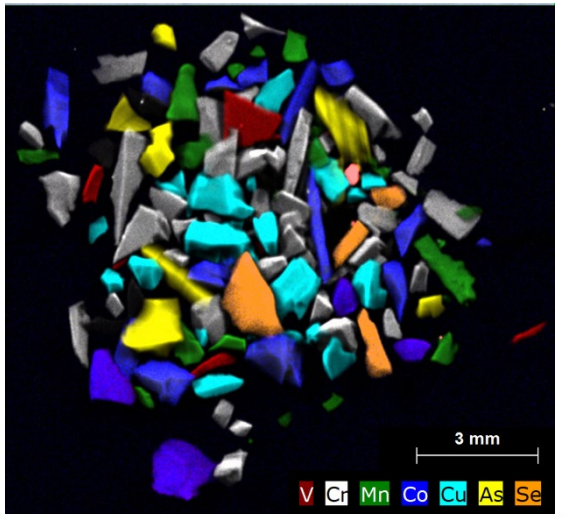
So how to find out, what particles can be quantified and what not?

1st step:
- validate the quantification on an ideal (thick, flat, homogeneous) sample system of known compostion

2nd step:
- transfer approach to a reference sample

3rd step:
- assess the size range for which the quantification can be trusted

Worst-case scenarios: Glass and aluminum. Both sample types are rather light matrix but the elements used for classification are in the higher energy range.



Forensic Particle Analysis
Quantification of Glass Particles

Stoich. conc. (norm.)

	Na2O	MgO	Al2O3	SiO2	SO3	K2O	CaO	TiO2	MnO	Fe2O3	Sum
Glass 1831_ 001	13.70	3.30	1.21	72.98	0.22	0.30	8.18	0.02	0.00	0.10	**100.00**
Glass 1831_ 002	13.10	3.34	1.21	73.48	0.21	0.30	8.24	0.02	0.00	0.10	**100.00**
Glass 1831_ 003	13.53	3.27	1.20	73.13	0.24	0.30	8.20	0.02	0.00	0.10	**100.00**
Glass 1831_ 004	13.16	3.35	1.20	73.43	0.21	0.30	8.22	0.02	0.00	0.10	**100.00**
Glass 1831_ 005	13.10	3.36	1.20	73.47	0.21	0.30	8.23	0.02	0.00	0.10	**100.00**
Mean value:	**13.32**	**3.33**	**1.20**	**73.30**	**0.22**	**0.30**	**8.21**	**0.02**	**0.00**	**0.10**	
Std dev.:	**0.28**	**0.04**	**0.00**	**0.23**	**0.01**	**0.00**	**0.02**	**0.00**	**0.00**	**0.00**	
Std dev. rel. [%]:	**2.08**	**1.10**	**0.37**	**0.31**	**5.76**	**0.54**	**0.30**	**4.41**	**22.74**	**0.35**	
Conf. interval:	**0.12**	**0.02**	**0.00**	**0.10**	**0.01**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	

with Type Calibration for MgO: factor 1.06

Stoich. conc. (norm.)

	Na2O	MgO	Al2O3	SiO2	SO3	K2O	CaO	TiO2	MnO	Fe2O3	Sum
Glass 1831_ 001	13.66	3.48	1.20	72.86	0.22	0.30	8.15	0.02	0.00	0.10	**100.00**
Glass 1831_ 002	13.06	3.53	1.21	73.36	0.21	0.30	8.22	0.02	0.00	0.10	**100.00**
Glass 1831_ 003	13.49	3.46	1.20	73.01	0.24	0.30	8.18	0.02	0.00	0.10	**100.00**
Glass 1831_ 004	13.12	3.54	1.20	73.31	0.21	0.30	8.20	0.02	0.00	0.10	**100.00**
Glass 1831_ 005	13.06	3.55	1.20	73.35	0.21	0.30	8.20	0.02	0.00	0.10	**100.00**
Mean value:	**13.28**	**3.51**	**1.20**	**73.18**	**0.22**	**0.30**	**8.19**	**0.02**	**0.00**	**0.10**	
Std dev.:	**0.28**	**0.04**	**0.00**	**0.23**	**0.01**	**0.00**	**0.02**	**0.00**	**0.00**	**0.00**	
Std dev. rel. [%]:	**2.09**	**1.10**	**0.37**	**0.31**	**5.77**	**0.54**	**0.30**	**4.41**	**22.74**	**0.34**	
Conf. interval:	**0.12**	**0.02**	**0.00**	**0.10**	**0.01**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1831

Soda-Lime Sheet Glass
(Nominal Mass Fraction 1.2 % Al_2O_3)

Table 1. Certified Mass Fractions

Constituent	Mass Fraction (%)		
SiO_2	$73.08^{(a,l)}$	±	0.08
Na_2O	$13.32^{(a,m,f,c)}$	±	0.05
CaO	$8.20^{(a,m,k,g)}$	±	0.05
MgO	$3.51^{(a,m,i,k)}$	±	0.05
Al_2O_3	$1.21^{(a,m,k,n,j,i,e)}$	±	0.04
K_2O	$0.33^{(a,c,m,e)}$	±	0.02
SO_3	$0.25^{(a,b)}$	±	0.01
Fe_2O_3 (total iron as)	$0.087^{(a,m,h)}$	±	0.003
FeO	$0.025^{(a)}$	±	0.007
TiO_2	$0.019^{(a,d,h)}$	±	0.002

Forensic Particle Analysis
Quantification of Glass Particles

Expected values

wt.-%	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
EC 1.1 Float glass	46.71	9.95	2.28	0.57	33.64	0.1	0.49	6.17	0.02	0.07

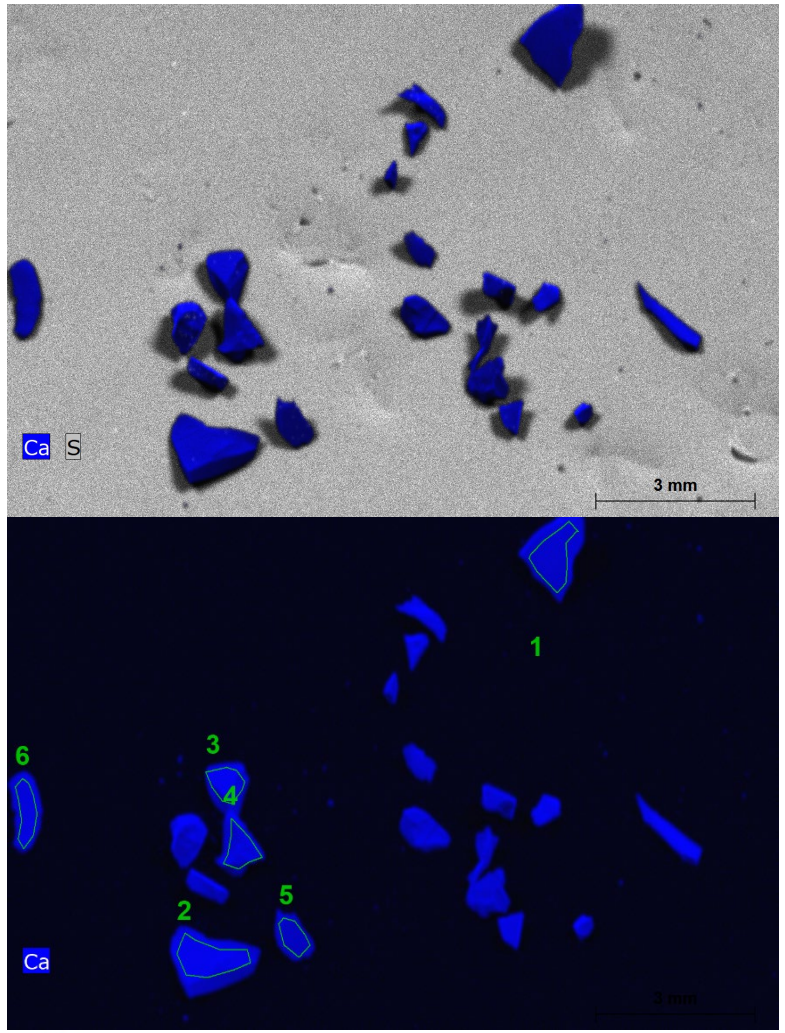
Measured values

Mass conc. (norm.)

	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Rh	Sum
Glass_ 001	46.53	10.21	2.27	0.57	33.57	0.08	0.52	6.14	0.03	0.08	0.00	**100.00**
Glass_ 002	46.53	10.19	2.29	0.56	33.58	0.07	0.53	6.14	0.03	0.08	0.00	**100.00**
Glass_ 003	46.54	10.19	2.26	0.57	33.59	0.08	0.52	6.15	0.03	0.08	0.00	**100.00**
Glass_ 004	46.56	10.14	2.25	0.57	33.63	0.07	0.52	6.15	0.03	0.08	0.00	**100.00**
Glass_ 005	46.56	10.11	2.29	0.57	33.63	0.08	0.52	6.14	0.03	0.08	0.00	**100.00**
Mean value:	**46.54**	**10.17**	**2.27**	**0.57**	**33.60**	**0.08**	**0.52**	**6.15**	**0.03**	**0.08**	**0.00**	
Std dev.:	**0.02**	**0.04**	**0.02**	**0.01**	**0.03**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	
Std dev. rel. [%]:	**0.03**	**0.42**	**0.68**	**0.92**	**0.08**	**1.29**	**0.42**	**0.05**	**2.29**	**0.08**	**0.00**	
Conf. interval:	**0.01**	**0.02**	**0.01**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	

All elements in the sample are in good agreement with the expected values for the reference glass.

Forensic Particle Analysis
Quantification of Glass Particles



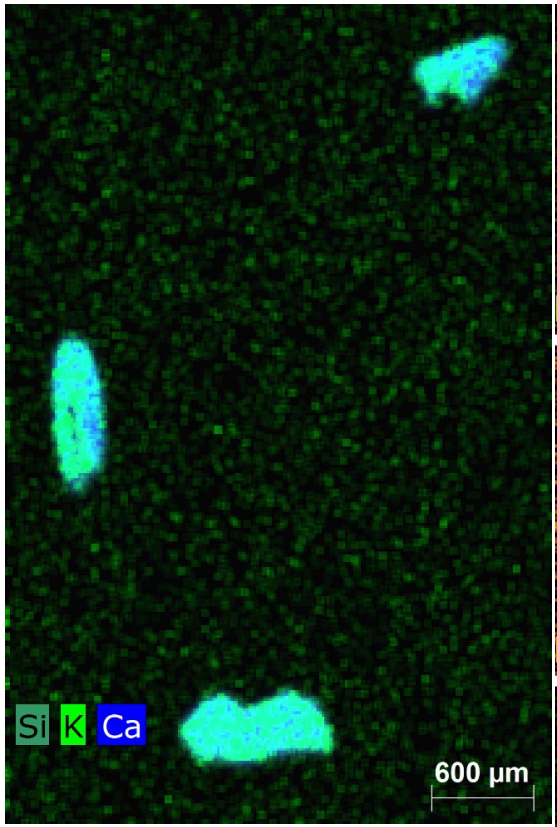
The composition of these glass fragments does not differ from the reference glass. The fragments are large enough for drawing objects and use the bulk quantification approach.

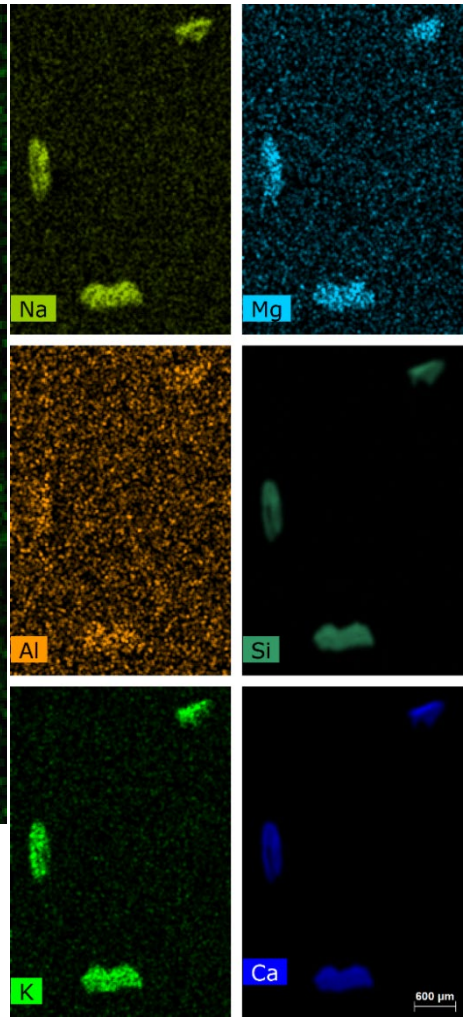
Mass conc. (norm.)

	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Rh	Sum
1.spx	46.65	9.97	2.20	0.57	33.79	0.09	0.52	6.10	0.03	0.08	0.00	**100.00**
2.spx	46.37	10.47	2.29	0.57	33.26	0.09	0.54	6.31	0.03	0.08	0.00	**100.00**
3.spx	46.27	10.62	2.27	0.56	33.05	0.12	0.55	6.45	0.03	0.09	0.00	**100.00**
4.spx	46.45	10.18	2.21	0.57	33.41	0.10	0.54	6.42	0.03	0.09	0.00	**100.00**
5.spx	46.73	9.82	2.12	0.54	33.86	0.17	0.51	6.13	0.03	0.09	0.00	**100.00**
6.spx	46.53	10.25	2.21	0.56	33.58	0.09	0.53	6.15	0.03	0.07	0.00	**100.00**
Sum reference glass	46.53	10.09	2.28	0.61	33.53	0.08	0.54	6.24	0.03	0.08	0.00	**100.00**
Mean value:	**46.50**	**10.20**	**2.22**	**0.57**	**33.50**	**0.10**	**0.53**	**6.26**	**0.03**	**0.09**	**0.00**	
Std dev.:	**0.16**	**0.28**	**0.06**	**0.02**	**0.29**	**0.03**	**0.01**	**0.14**	**0.00**	**0.01**	**0.00**	
Std dev. rel. [%]:	**0.34**	**2.72**	**2.67**	**3.65**	**0.85**	**29.78**	**2.58**	**2.22**	**4.18**	**7.46**	**0.00**	
Conf. interval:	**0.06**	**0.10**	**0.02**	**0.01**	**0.11**	**0.01**	**0.01**	**0.05**	**0.00**	**0.00**	**0.00**	

Forensic Particle Analysis
Quantification of Glass Particles

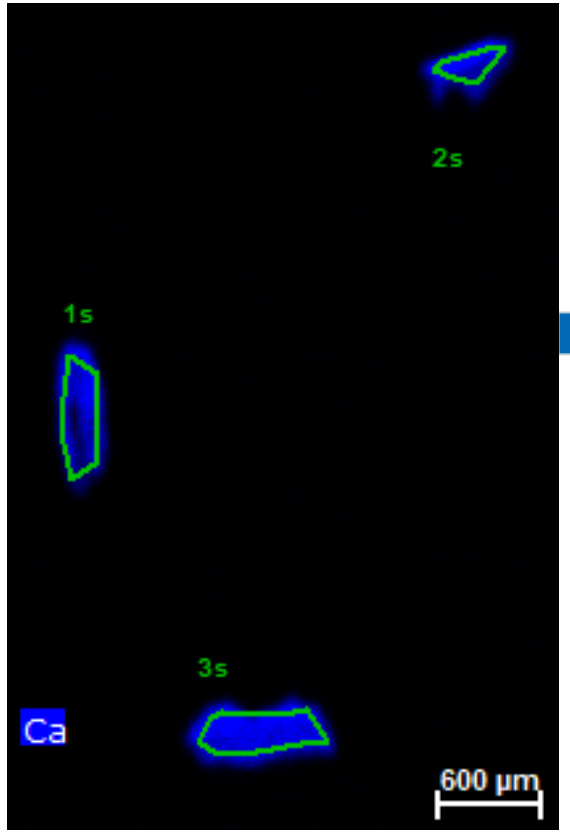
MAP INFORMATION		
Mapping parameters		
Width:	209	pixel
	3.14	mm
Height:	313	pixel
	4.69	mm
Pixel Size:	15	µm
Total number of pixel:	65417	pixel
Acquisition parameters		
Frame count:	1	
Pixel time:	10	ms/pixel
Measure time:	10 min	
Overall time:	25 min	
Stage speed:	1.5	mm/s
Stage position (X,Y,Z):	170.421;32.589;87.623	mm
Tube parameter		
High voltage:	50	kV
Anode current:	599	µA
Filter:	Empty	
Optic:	Lens	
Collimator diameter:	0	
SpotSize:	20	
Chamber at:	Air 10	mbar
Flow rate:	---	l/min
Anode:	Rh	
Detector parameters		
Selected detectors:	1,2	
Max. pulse throughput:	275000	cps





2nd set: the glass fragments are considerably smaller (~ 200 µm)

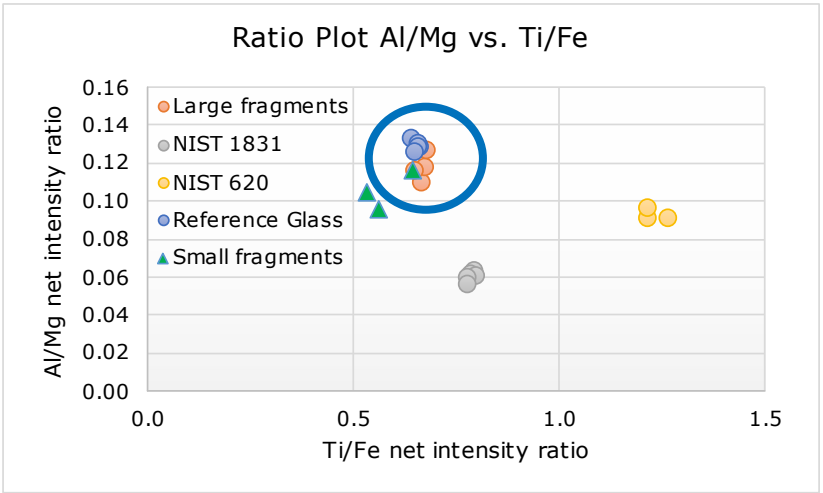
Forensic Particle Analysis
Quantification of Glass Particles

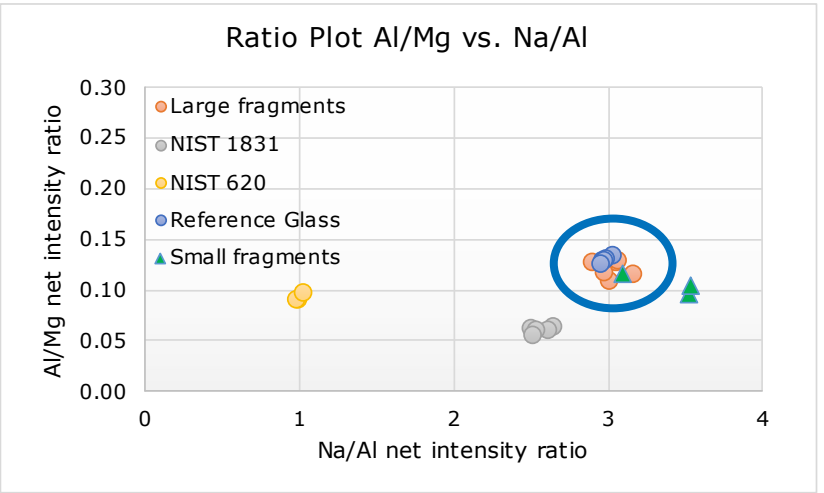


The measured composition of the glass fragments still does not differ from the reference glass. Some values are slightly lower – most likely caused by the relatively short measurement time over the small objects. Longer measurement time recommended for the recording the map.

All		cps/eV	Real	Live
3s		2.11	5.8 s	5.3 s
2s		3.20	1.9 s	1.7 s
1s		2.94	5.1 s	4.6 s

For the larger fragments the time was > 60 s





M4 TORNADO in Forensics

Residual Fingerprint Characterization

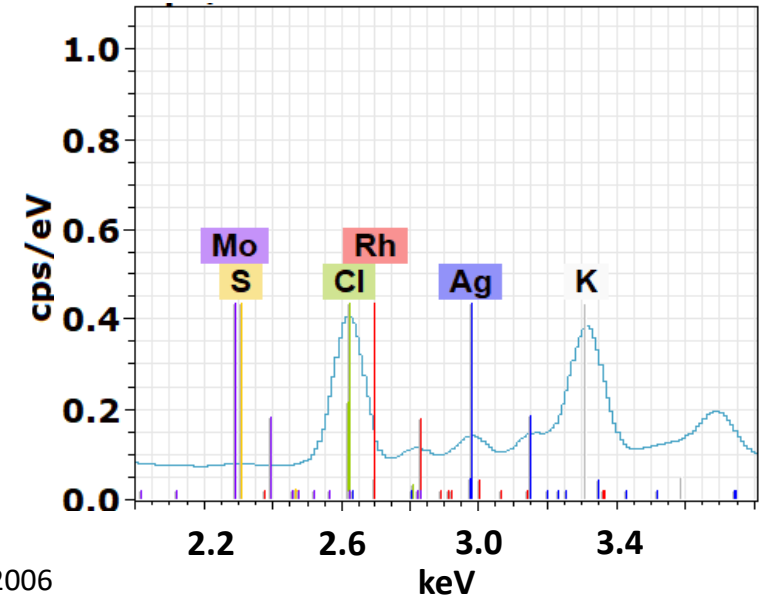
Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

The visualization of fingerprints by micro-XRF was first described in 2006 [1]

- The approach is based on detecting inorganic components like K, Ca, S
  - is not hampered by dark or multicolored backgrounds
  - does not rely on sebum or other organics
- With the technological advances in the 15 years since the first proof of principle, micro-XRF is now well-suited for the fingerprints visualization in circumstances where they are otherwise difficult to recover

Most common X-ray tube materials are Molybdenum and Rhodium

- Their characteristic lines either overlap with the Cl-fluorescence or cannot be used for Cl‘s excitation
- Ag tubes are best suited for the analytical task of detecting low amounts of Cl

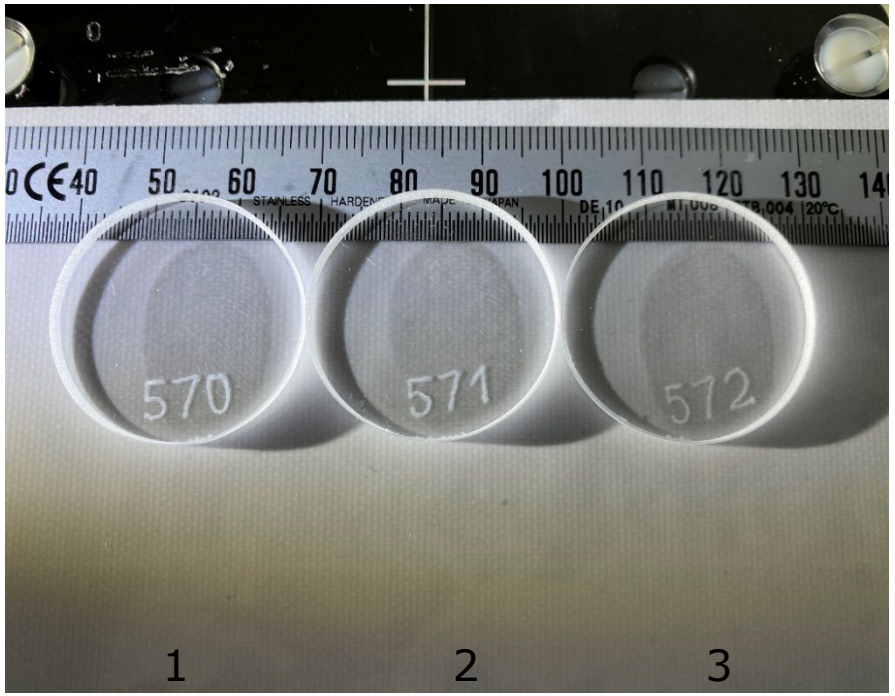


[1] Detection of visible and latent fingerprints by micro-X-ray fluorescence, Worley et al., Powder Diffraction **21** (2), 2006

Residual Fingerprint Analysis
Advantages of micro-XRF and our Experiment

- micro-XRF, in principle, is also a contrast enhancing method – the contrast needed here is an **elemental contrast**
- Substrates, which are challenging for conventional contrast enhancing methods – either because of their color(s) or because of their composition (leather, plastics, skin, or textiles) – could be straight-forward for micro-XRF measurements
- Since **micro-XRF detects the non-volatile inorganic components** of sweat it can be used to visualize fingerprints where the organic components are covered or have left the sample (after a fire?)

Quartz discs with greasy fingerprints



Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

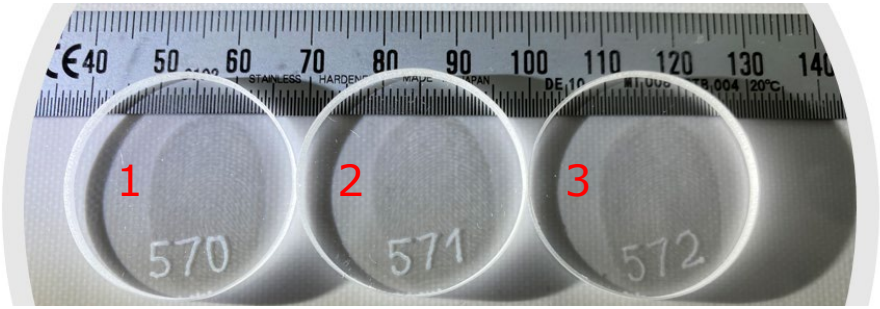
Experiment:

- Two sets of fingerprint were collected on 6 quartz glass discs
- One set was greasier the second was more sweaty
- Samples 1 were left untreated
- Samples 2 were heated to 500 °C
- Samples 3 were heated to 250 °C
- Using a conventional SEM carbon coater, the sweaty sample 3 was coated with carbon to simulate covering with soot

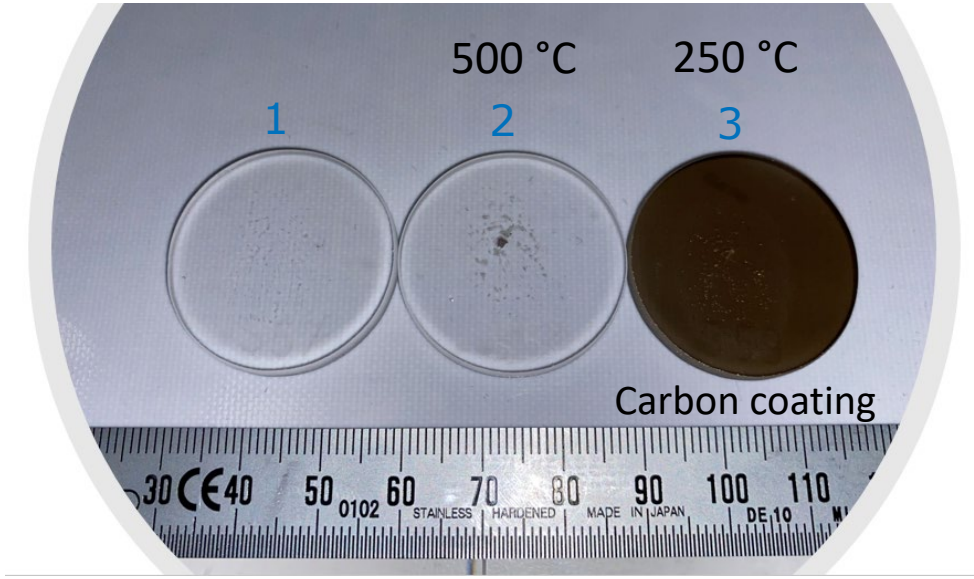
Conditions:

- M4 TORNADO Plus Ag-Tube; 30 kV, 600 µA, 2x 60 mm² SDD

Quartz discs with greasy fingerprints



Quartz discs of the sweaty group



Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

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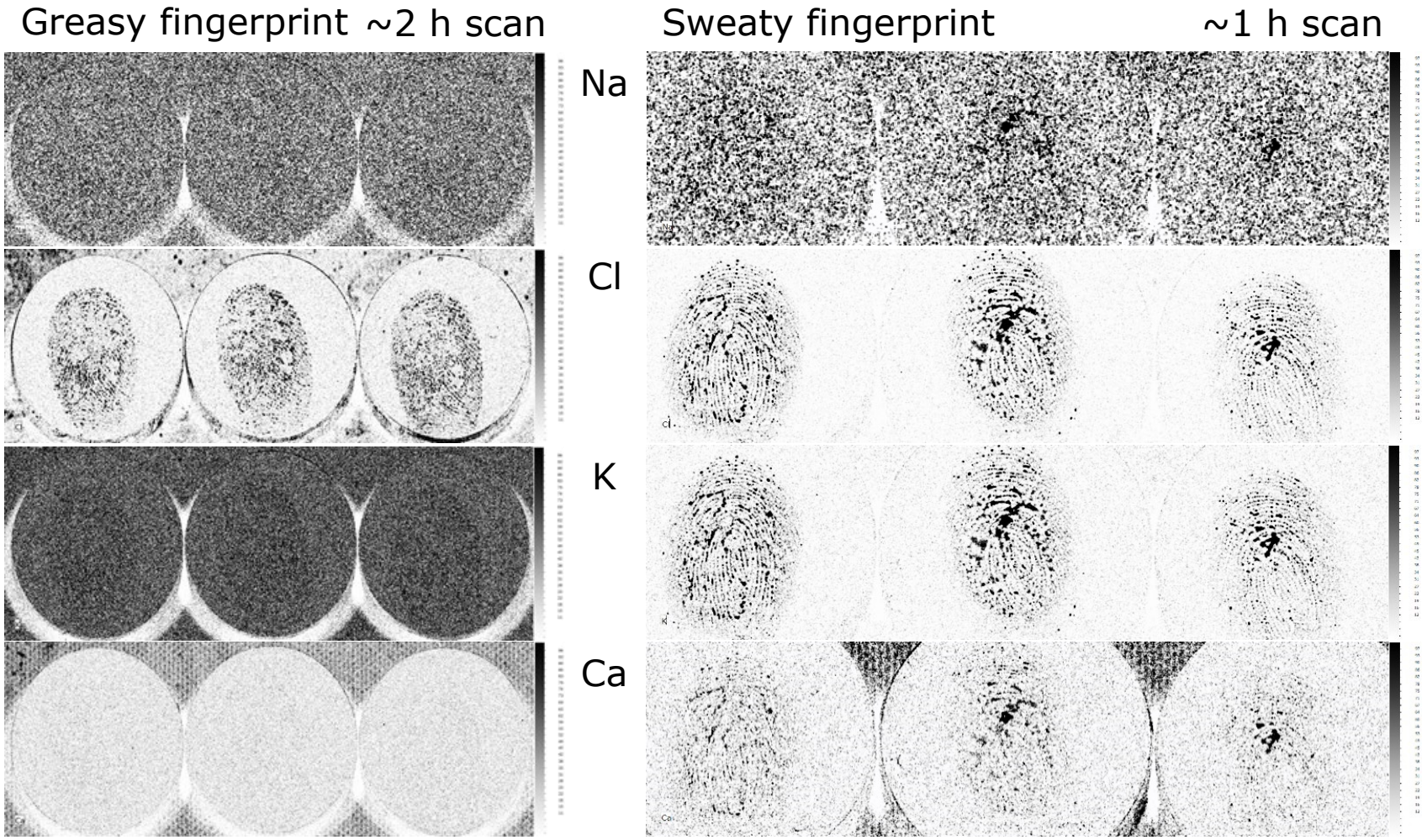
Quartz discs heating

Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Results:

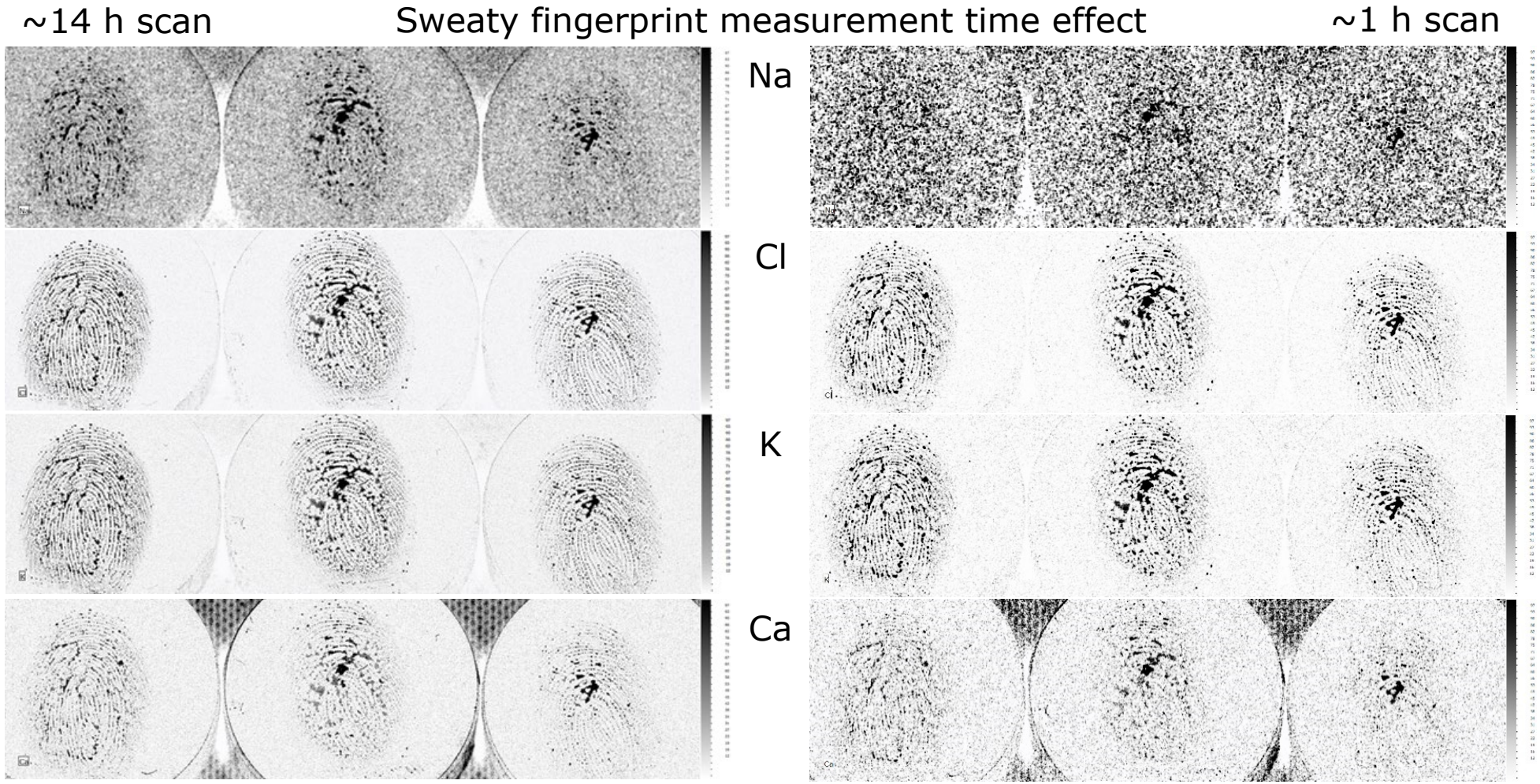
- On the sweaty fingerprint the signal of the print was detectable for all 4 shown elements
- On the greasy fingerprints only the element Cl gave a clear signal despite double measurement time



Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

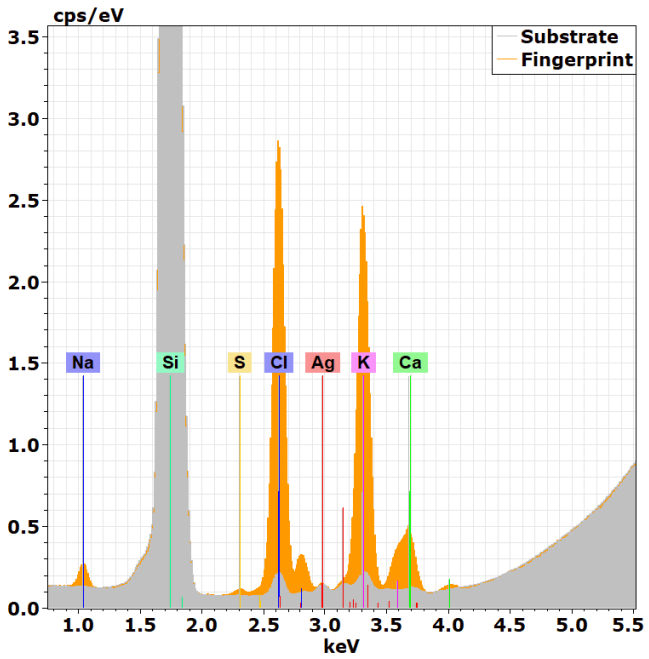
Results:

- Increasing the measurement time improves the quality of the element distribution significantly
- The best signal can be found for the elements Cl and K



Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Detail of disc 1

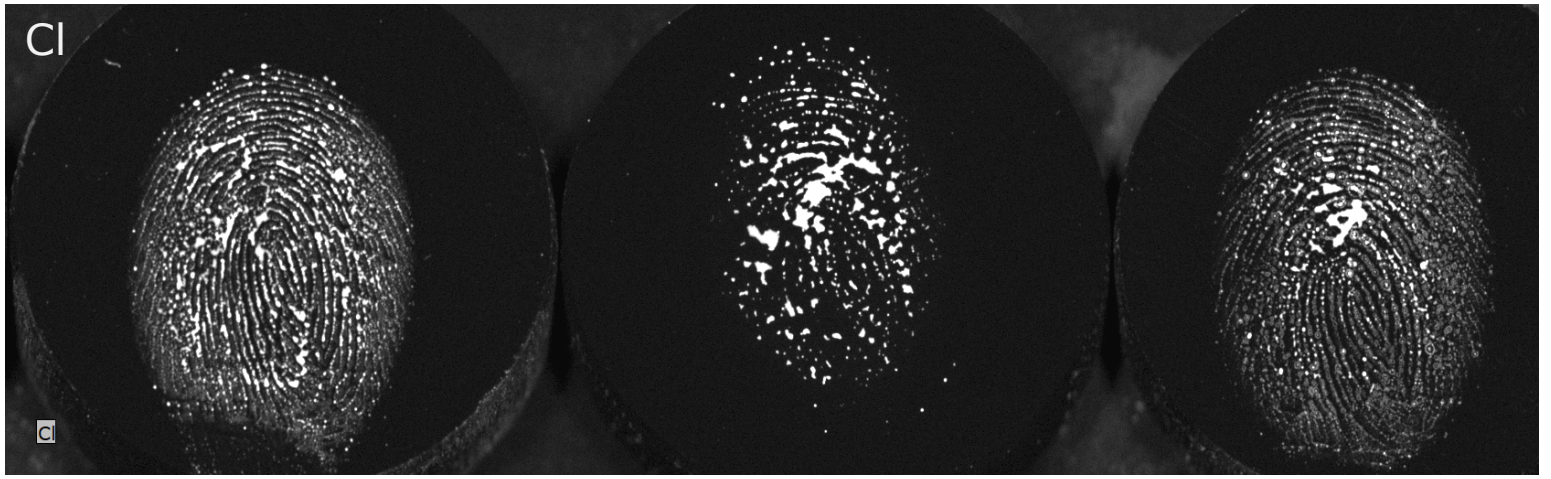


Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Results:

- The intensity distribution can be displayed in different ways, one is the multi-color scale (top) as white-to-black and the second is directly in gray scale with serval tools to adjust contrast and brightness

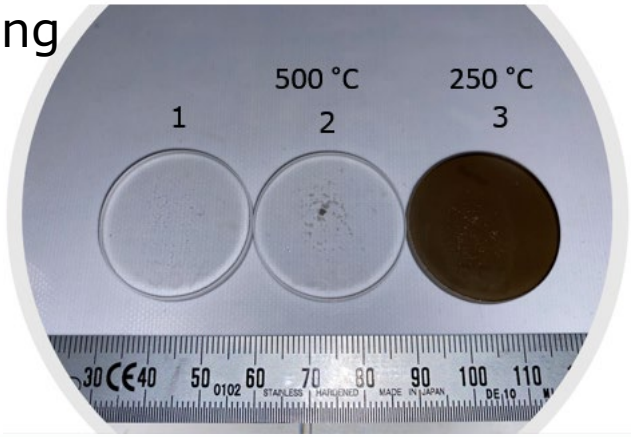
- The next results will be presented in grey scale

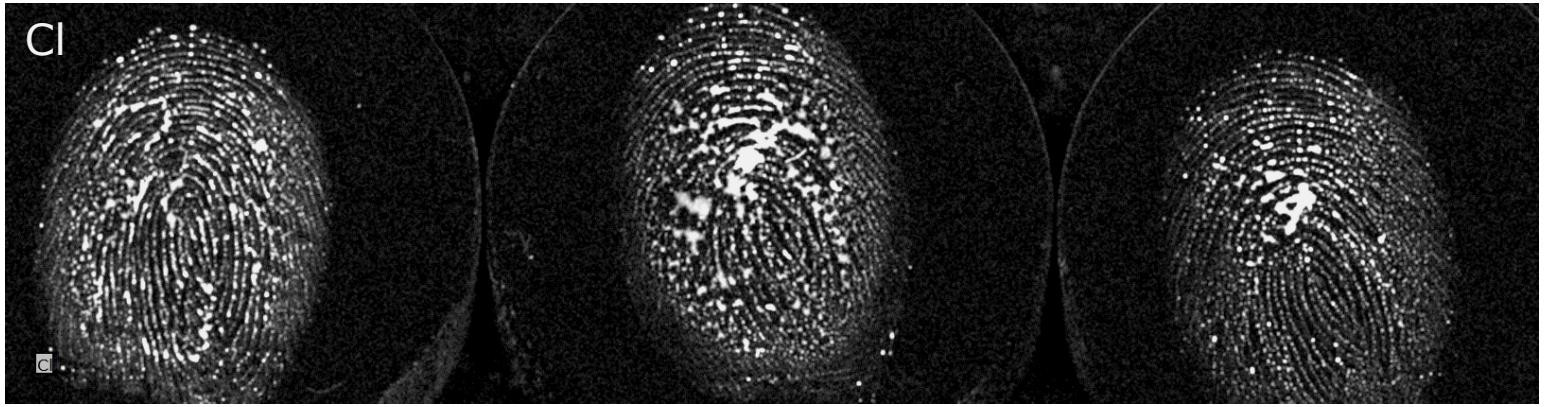


Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Results:

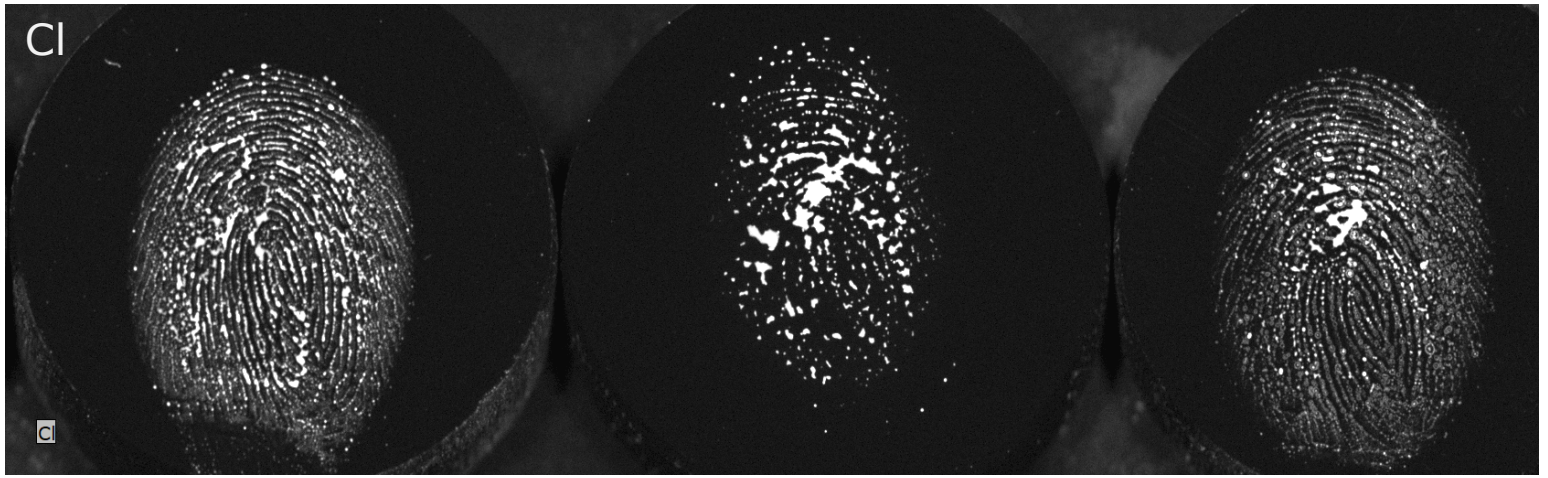
- The heating of the sample to 500 °C for 5 h, had strong effect of the quality of the fingerprints recorded
- A heating to 250 °C for 5 h had no significant effects on the fingerprint, the same appears valid for a carbon coating





~14 h, 70 ms per pixel

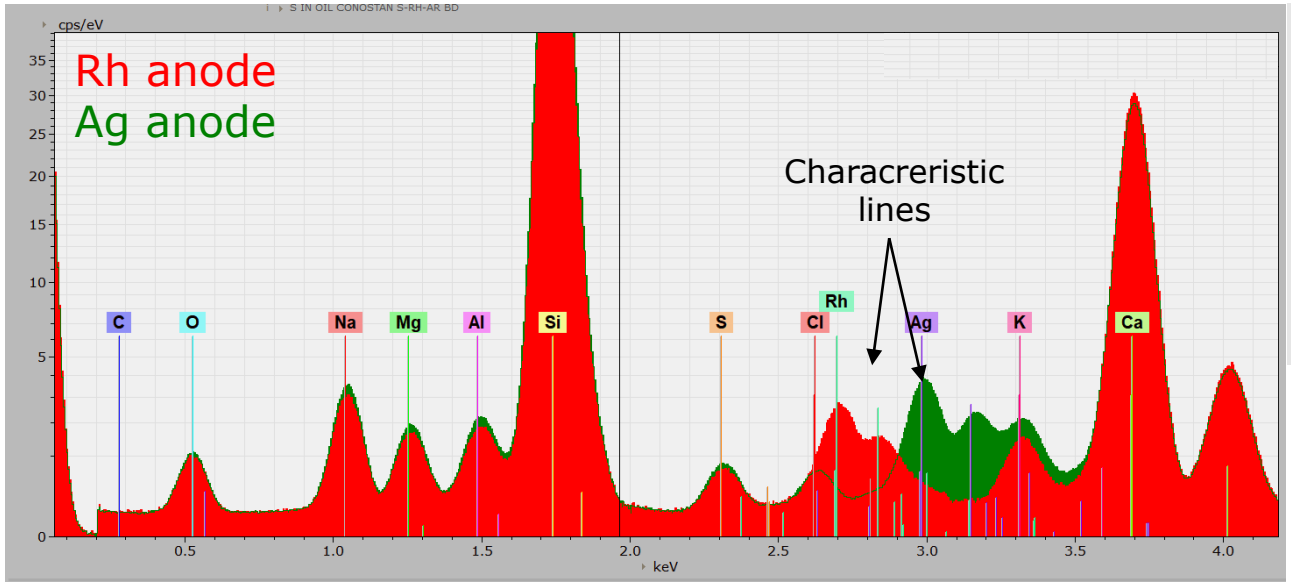
~17 h, 70 ms per pixel



Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Comparing Rh- and Ag-Anode

- Intensity comparison using NIST 620
- For the fingerprint detection the Cl apears to be one of the more indicative elements
- For a good detection of the Cl signal the Ag anode offers a significant improvement compared to a standard Rh anode



Excitation data:

High voltage [kV]	30
Current [µA]	199
Tube	ICT_A014B030_Rh
Filter	Empty
Optic	Lens
Pressure	2 mbar
Spot size	20 µm
Max. pulse throughput	130000 cps
Detector selected	2

Spectrum	O	Na	Mg	Al	Si	S	Cl
60 mm² SDD_Ag Anode_NIST620_30kV_200µA_2mbar	101	343	162	160	12867	89	37
60 mm² SDD_Rh Anode_NIST620_30kV_200µA_2mbar	89	297	136	126	10625	70	
Ag/Rh*100	**113**	**116**	**119**	**127**	**121**	**127**	

	K	Ca	Ti	Mn
60 mm² SDD_Ag Anode_NIST620_30kV_200µA_2mbar	151	4412	15	7
60 mm² SDD_Rh Anode_NIST620_30kV_200µA_2mbar	157	4654	13	5
Ag/Rh*100	96	95	113	120

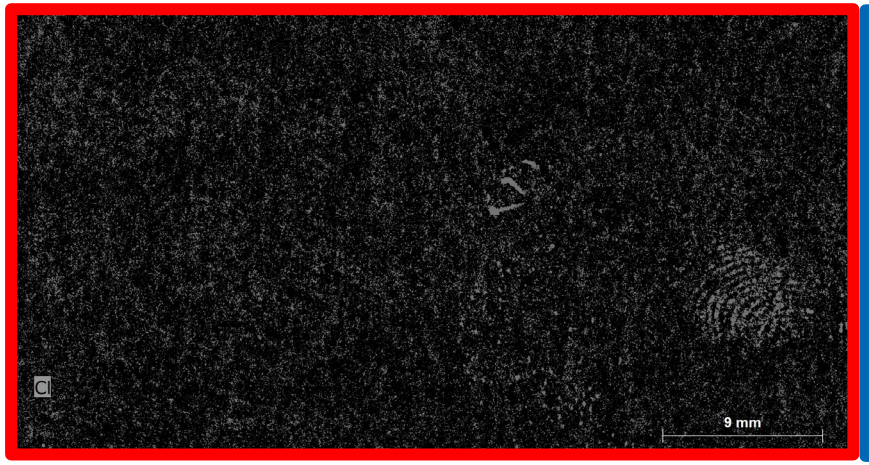
Not detectable

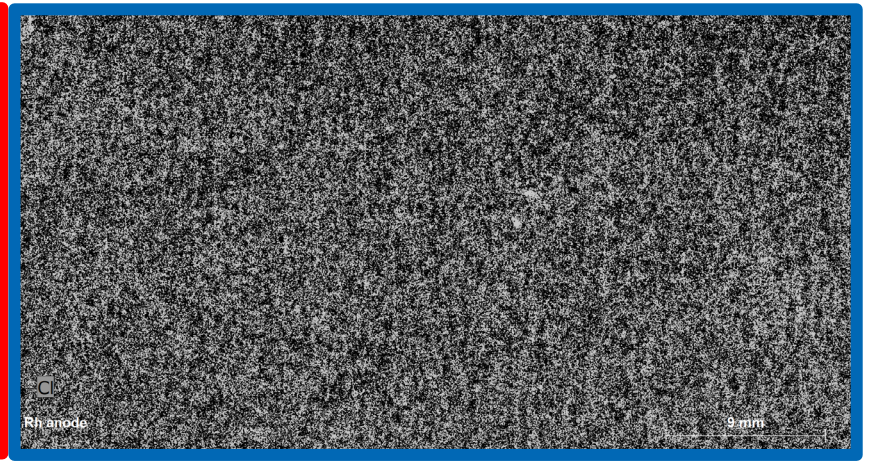
Comparison of counts per second live time

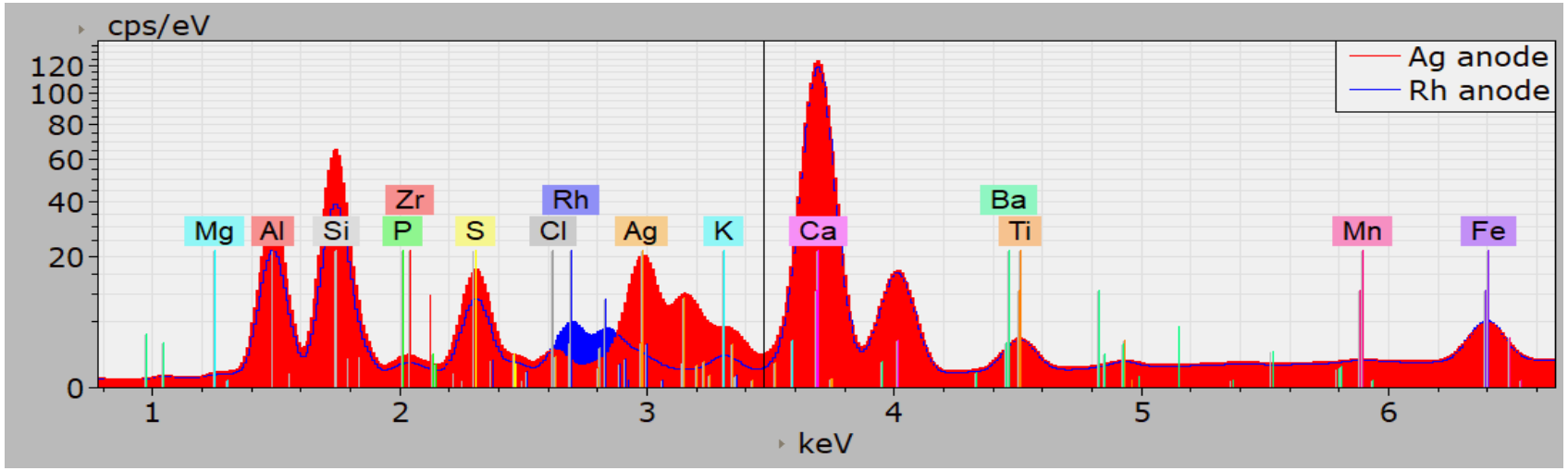
Residual Fingerprint Analysis
M4 TORNADO micro-XRF Spectrometer

Comparing Rh- and Ag-Anode

- Two measurements of the same **paper sample** show that the (**unintended**) fingerprint is clearly visible in the Cl signal measured with the Ag-anode (red)
- Both measurements were done under the same conditions

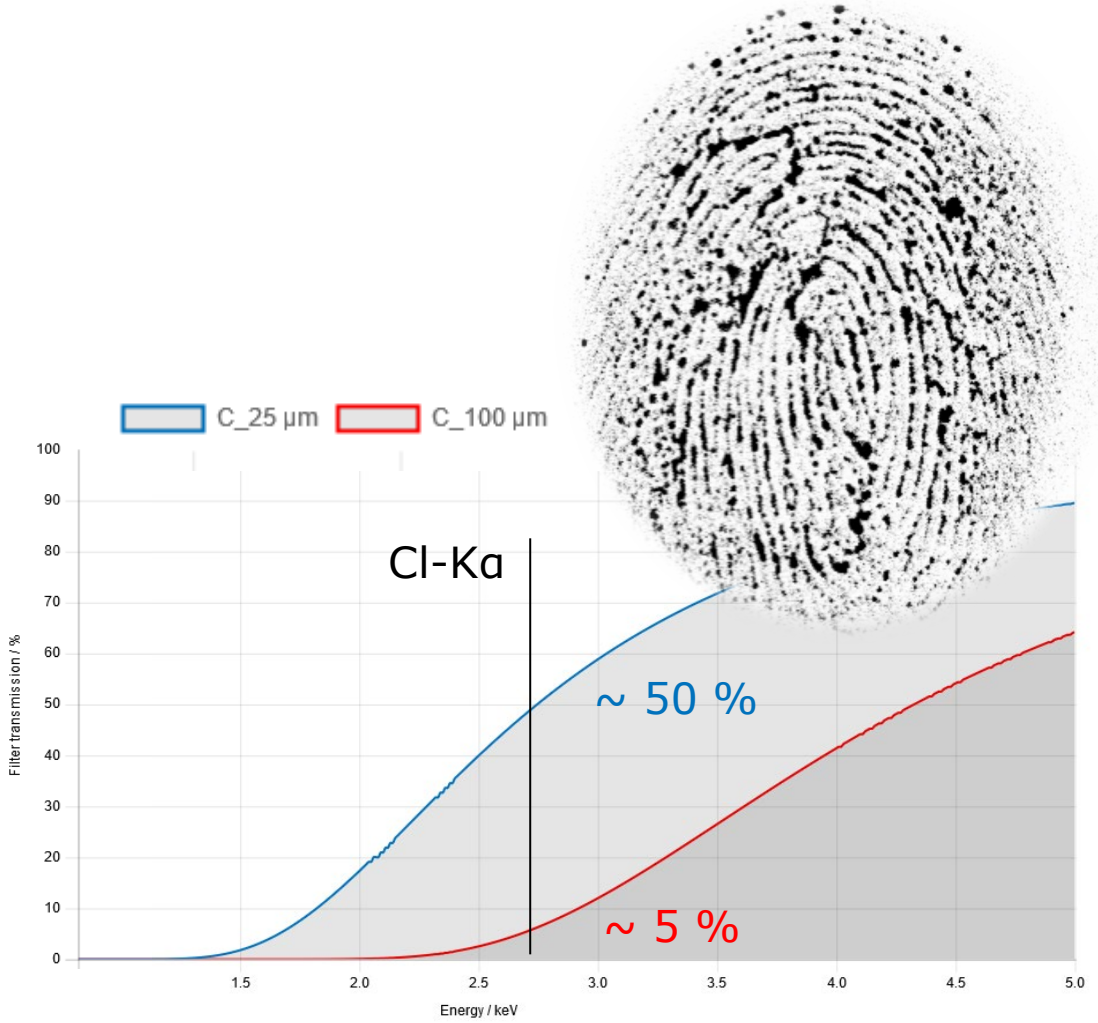






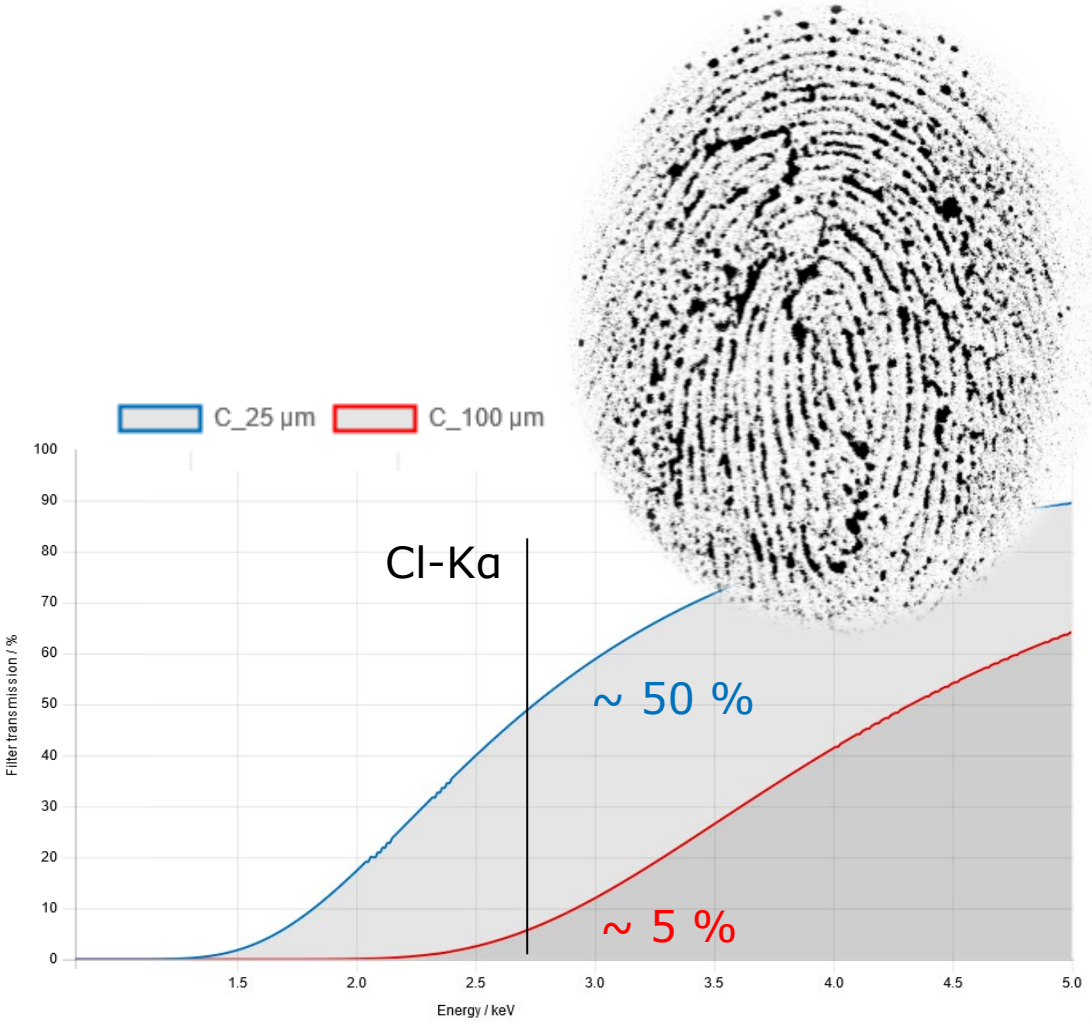
Residual Fingerprint Analysis
Summary

- In sebaceous, as well as in sweaty fingerprints, it was well possible to **visualize the friction ridges with micro-XRF**
- Only in the sweaty fingerprints all **4 main marker elements** (Na, K, Ca, Cl) could be detected
- In the sebaceous fingerprints the indicative element was Cl
- As Cl is a marker element in both kinds of fingerprints, the excitation by a **Ag-anode X-ray tube ensures best sensitivity**



Residual Fingerprint Analysis
Summary

- The small set of alteration experiments indicates that a **heating to 250 °C has no significant effect** on the visualization of the fingerprints
- The sweaty fingerprint heated to 500 °C suffered major alterations
- **No effect** on the quality of the recovered fingerprint was evident **when coating the sample** with a thin (< 100 nm) layer of carbon



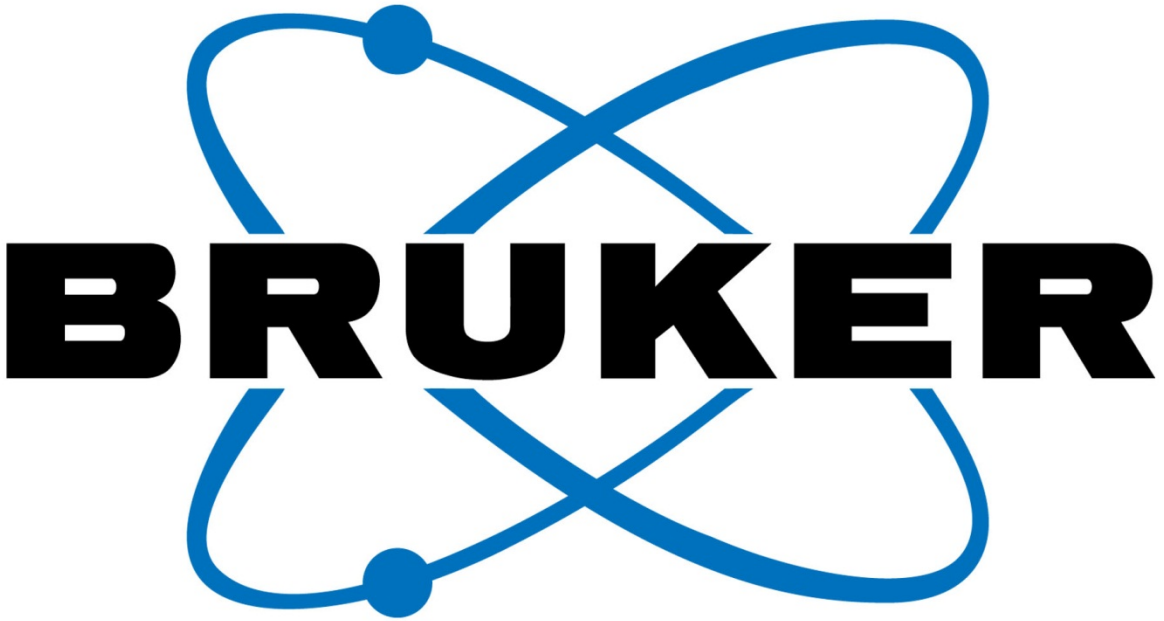
Micro-XRF Applications in Forensics
Outlook

- In this webinar, a short introduction to the main fields of application for micro-XRF in forensics was given
  - Gun shot residue (GSR) analysis and shooting distance determination (SDD)
  - Provenance analysis of soils
  - Ink analysis
  - Glass classification
  - Residual fingerprint analysis

- While we focused on fingerprints here, we will concentrate on the other topics in the oncoming webinars of the forensics series

- We are looking forward to your questions

- Please do not hesitate to include possible topics which could be discussed in a future webinar



Innovation with Integrity

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