Forensics Analysis with X-Ray Diffraction and X-Ray Fluorescence

Bruker AXS Inc., Madison, WI, USA
April 16, 2013

Welcome

Today's Topics

- Introduction to XRD
- Examples of forensic applications with XRD
- Introduction to TXRF, learn about X-ray fluorescence analysis
- Trace elemental analysis with TXRF
- Introduction to µXRF for forensics
- Application examples of µXRF
- Question & Answer

Speakers

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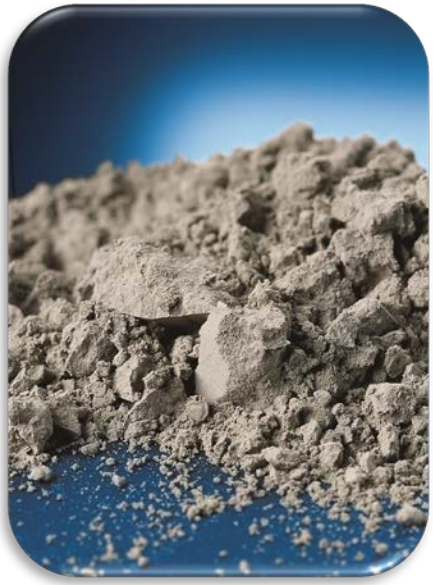
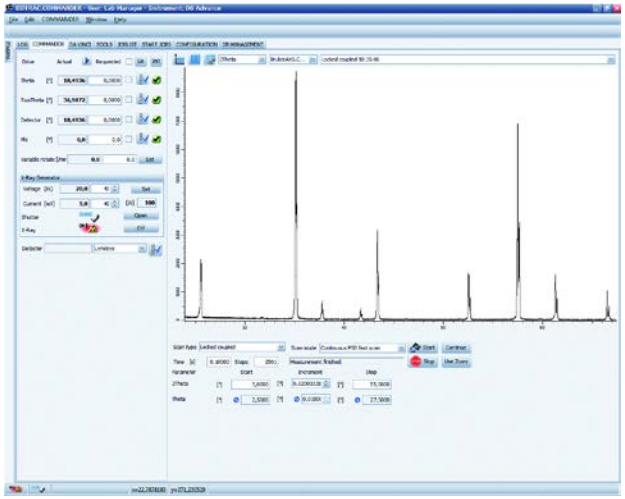
Forensics Analysis with X-ray Diffraction

Forensics Analysis with X-ray Diffraction

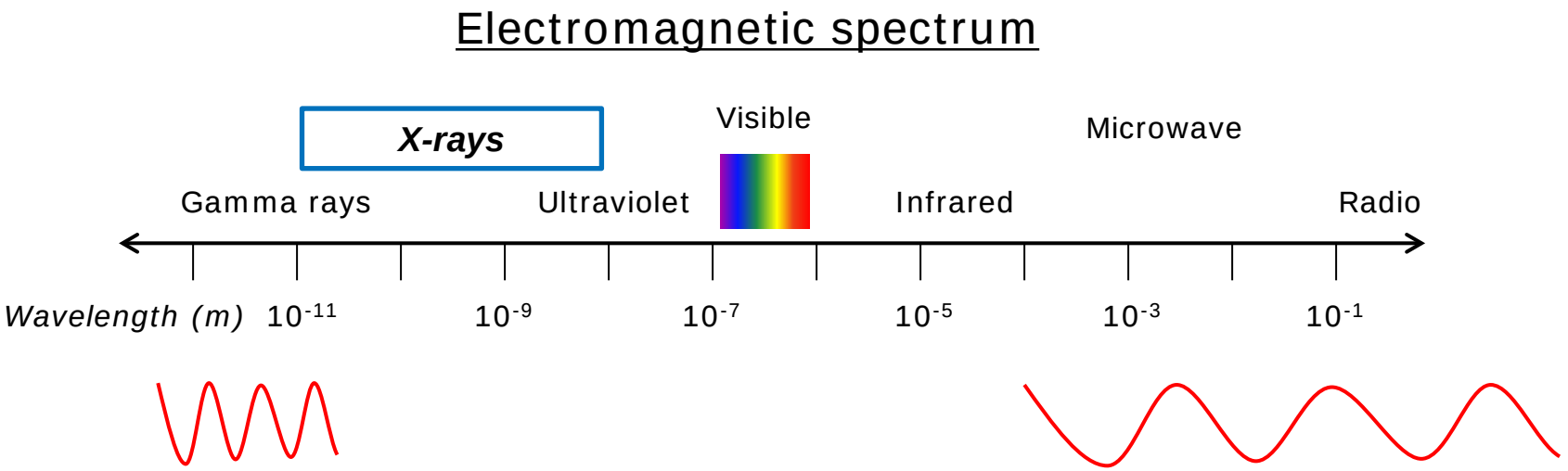
- Basic Principles of X-Ray Diffraction
- Typical Applications
- Benchtop Diffraction with the D2 PHASER
- Selected Forensics Applications
  - Pigment Analysis
  - Pharmaceuticals
  - Explosives

A Typical Powder Diffraction Experiment





What are X-rays?
...and why do we use them?

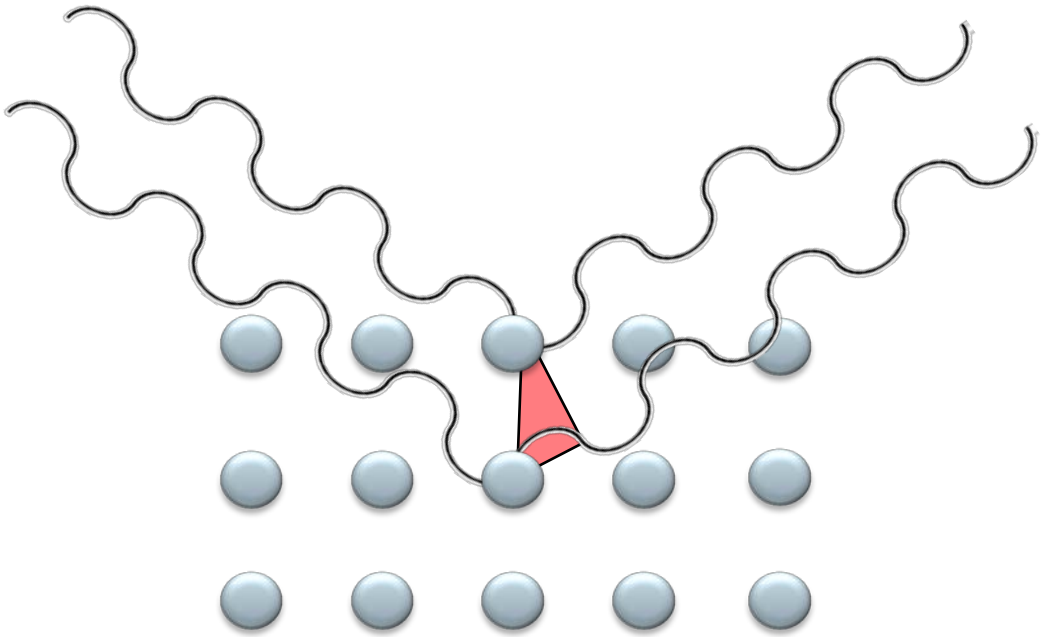


Wavelength of X-rays on same magnitude as atomic spacing
Probe to determine atomic order and crystal structure

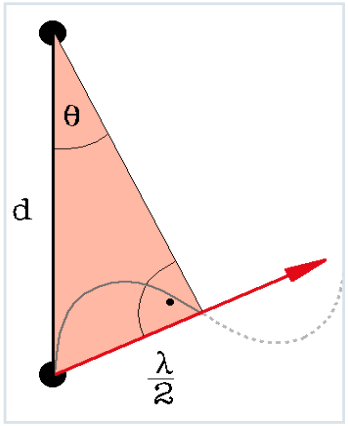
The Interaction of X-rays and Matter
Scattering from Multiple Atoms

Constructive Interference (peak!)

Deconstructive Interference (background)



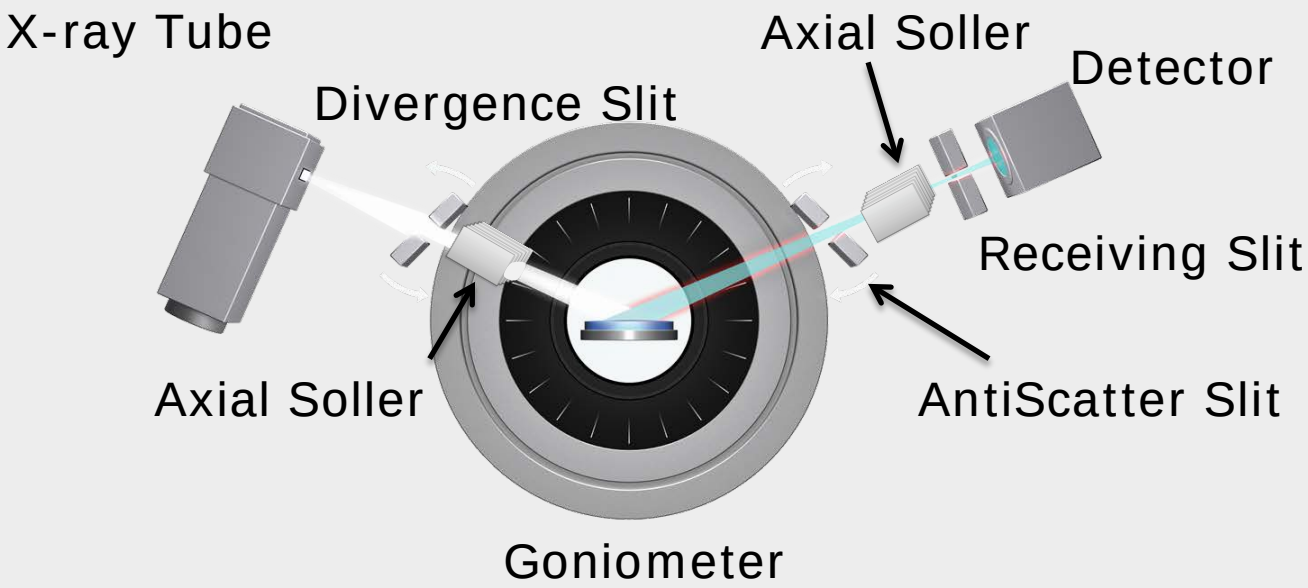
Bragg's Law



$$\sin\theta = \frac{\lambda/2}{d} = \frac{\lambda}{2d}$$

$$2d\sin\theta = \lambda$$

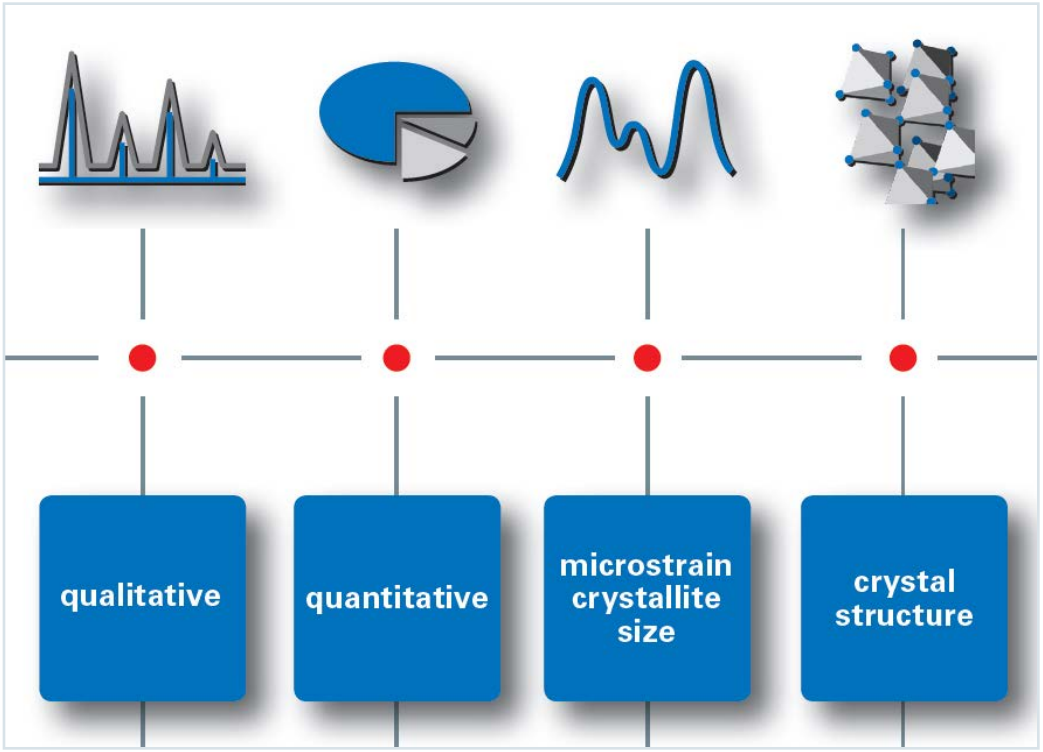
Bragg Brentano Geometry



Sample Holders

- Various cavity dimensions
- Low-background holders
- Back-loading holders
- Clay slides
- Air-sensitive holders

Powder X-ray Diffraction Applications



- Qualitative Phase Analysis (Phase ID)
- Quantitative Phase Analysis
- Crystallite Size & Microstrain Analysis
- Structure Determination and Refinement

Powder diffraction *CAN* tell you: Structure, Crystallinity, Phase Composition

Powder diffraction is *NOT* an elemental analysis technique

D2 PHASER
XRD in a Benchtop Design

Smart Design

- Small footprint
- Innovative goniometer
- Bragg-Brentano geometry
- Sample rotation (up to 80 rpm)
- Choice of X-ray tubes and detectors

System Mobility

- No pre-installation
- Standard wall sockets supported
- Integrated monitor
- Internal cooling system

Pigment Analysis

Red Pigments

-Iron(III) oxide, Fe_2O_3

-Lead(II,IV) tetroxide, Pb_3O_4

-Mercuric sulfide, HgS

Orange Pigments

-Lead(II) chromate/Lead(II) oxide, $PbCrO_4/PbO$

Yellow Pigments

-Lead(II) chromate, $PbCrO_4$

-Cadmium sulfide, CdS

Green Pigments

-Chromium(III) oxide hydrate, $Cr_2O_3 \cdot 1.5\ H_2O$

Blue Pigments

-Cobalt(II) stannate, $CoSnO_3$

-Iron(II,III) hexacyanoferrate(II,III), $Fe_7(CN)_{18}$

Violet Pigments

-Cobalt(II) phosphate hydrate, $Co_3(PO_4)_2 \cdot 8H_2O$

Black Pigments

-Iron(II,III) oxide, Fe_3O_4

-Lead sulfide, PbS

-Carbon black, C

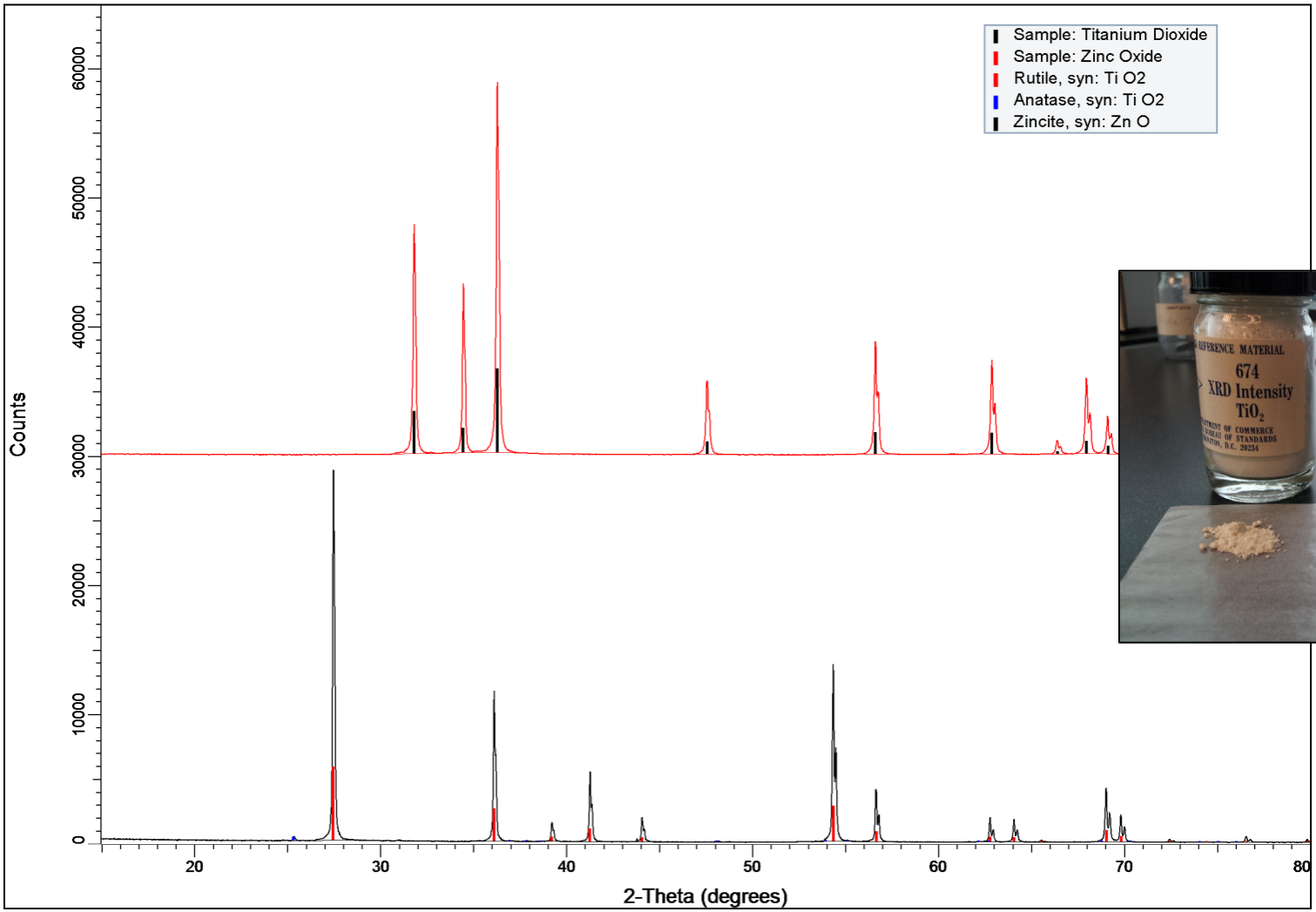
White Pigments

-Titanium dioxide, TiO_2

-Zinc oxide, ZnO

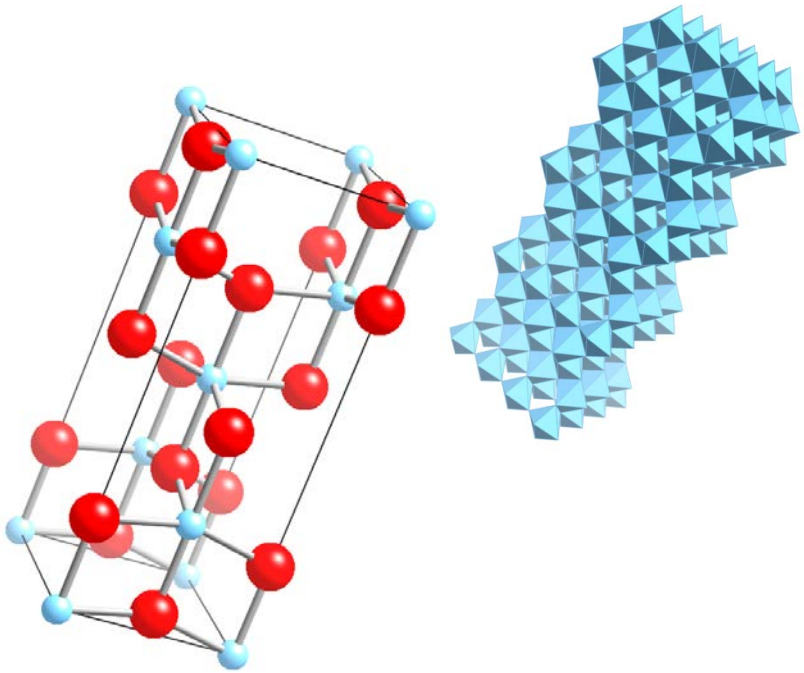
-Lead carbonate hydroxide, $2PbCO_3/Pb(OH)_2$

Pigment Analysis
Discrimination between TiO_2 and ZnO

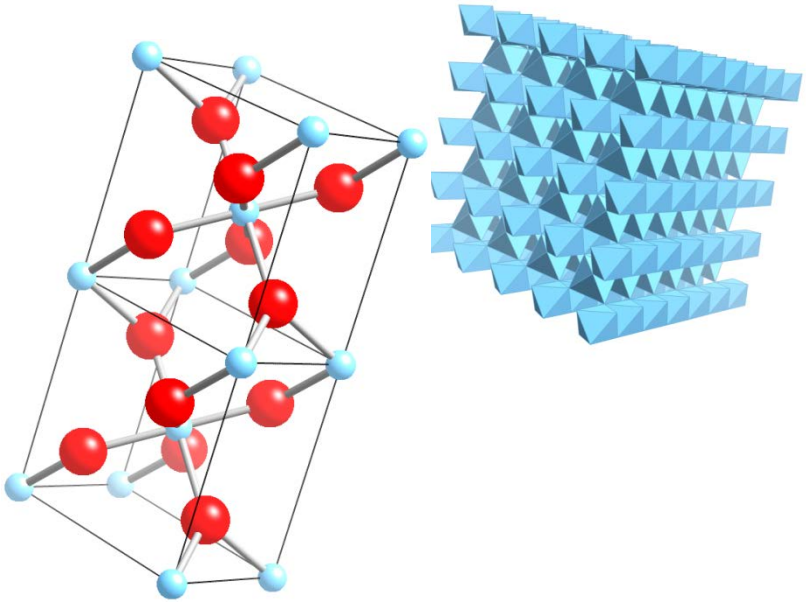


Pigment Analysis
Various Forms of TiO_2

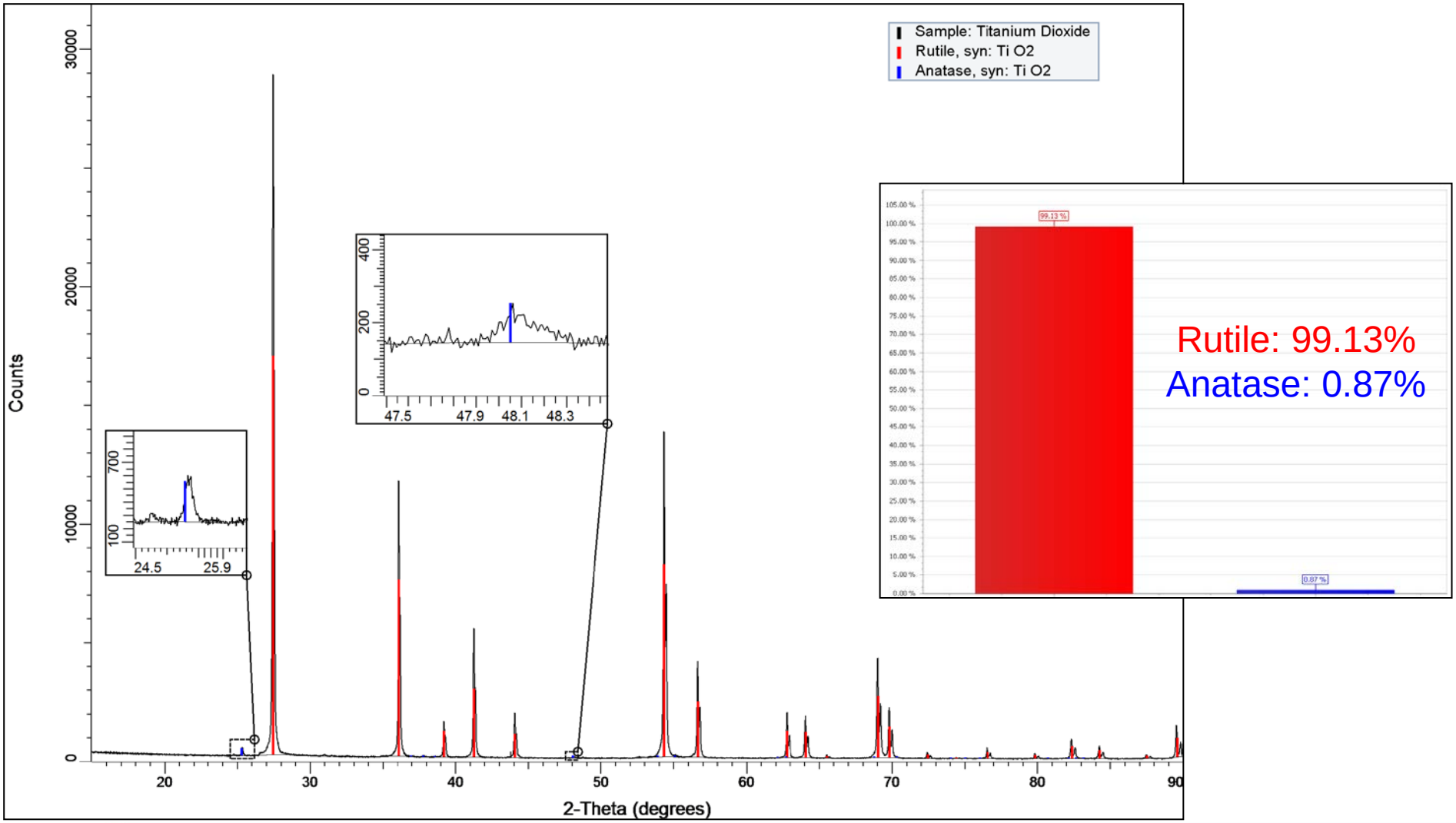
Anatase
Tetragonal
Spacegroup: I 41/a m d (141)



Rutile
Tetragonal
Spacegroup: P 42/m n m (136)



Pigment Analysis
Quantification of Minor Phases

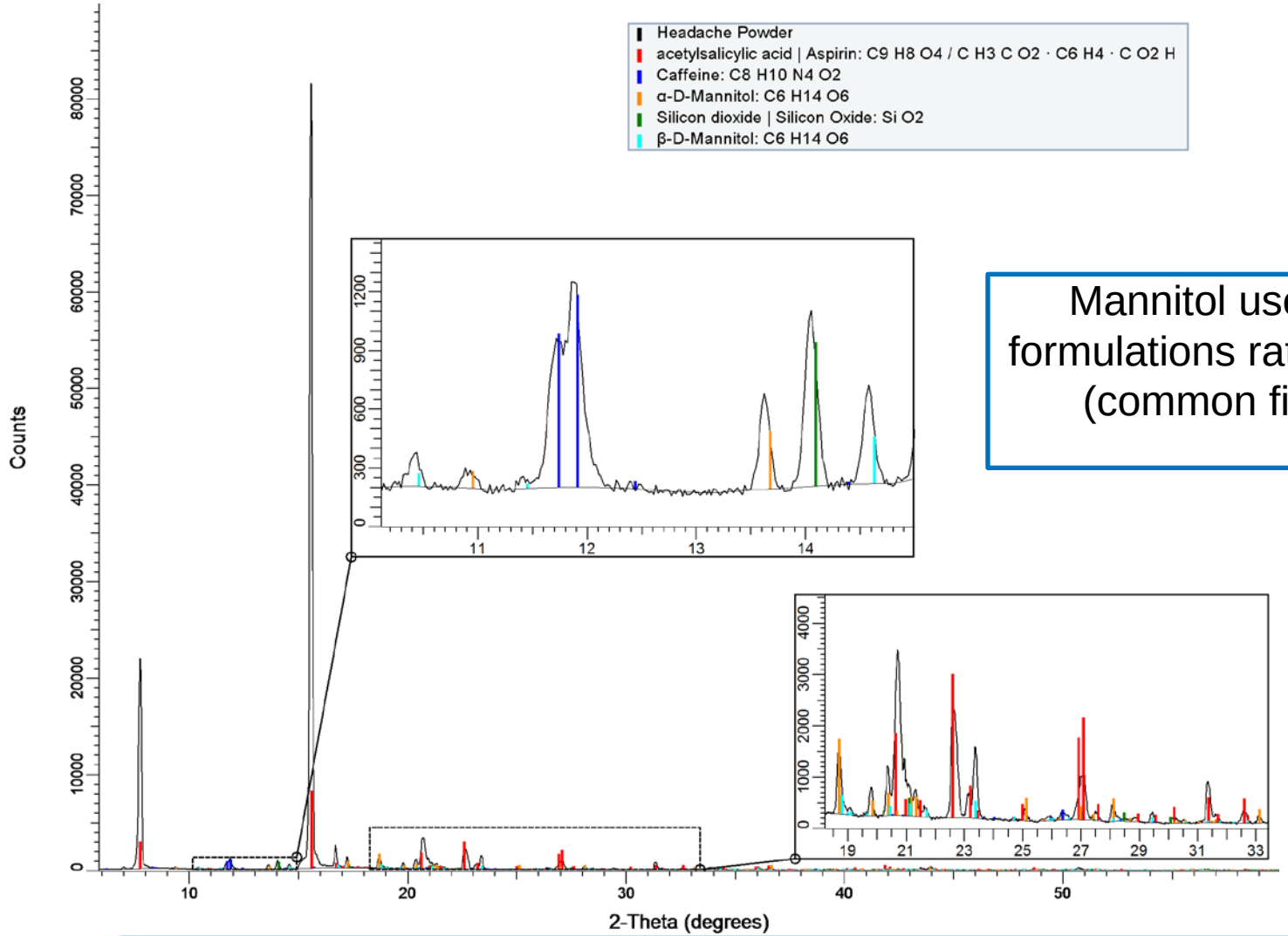


Pharmaceuticals

- Identification of active pharmaceutical ingredients (API), excipients, adulterants, fillers, and binders
- Common Adulterants
  - Sugars
    - Sucrose
    - Lactose
    - Dextrose
    - Mannitol
  - Caffeine
  - Acetaminophen
  - Methylsulfonylmethane (MSM)
  - Dextromethorphan
  - Corn starch
  - Sodium bicarbonate

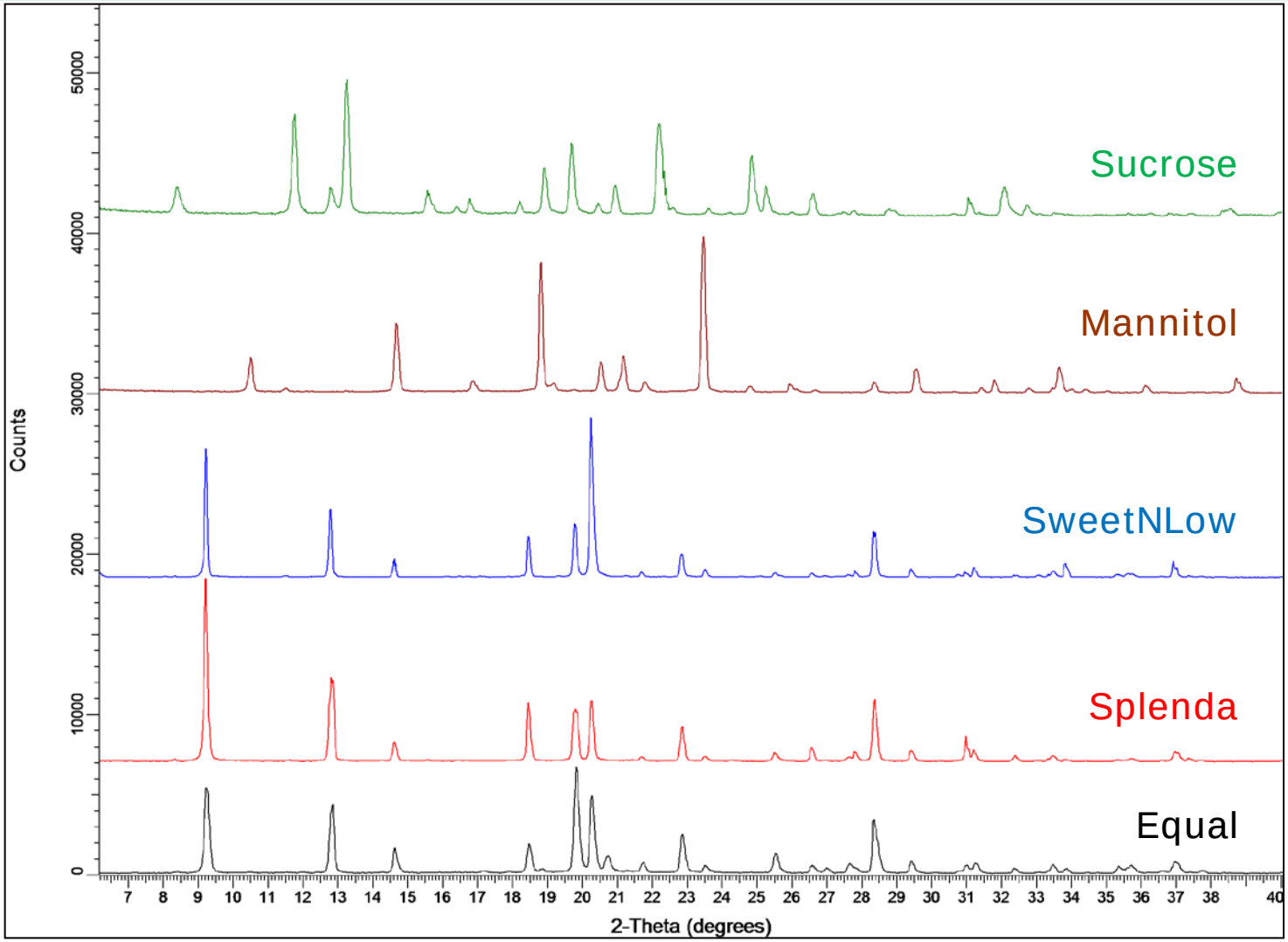
Cole, C.; Jones, L.; McVeigh, J.; Kicman, A.; Syed, Q.; Bellis, M.A. “A Guide to Adulterants, Bulking Agents, and Other Contaminants Found in Illicit Drugs” Centre for Public Health, Liverpool John Moores University, **2010**.

Pharmaceuticals
Headache Powder (Aspirin and Caffeine)



Mannitol used in flavored formulations rather than lactose (common filler material)

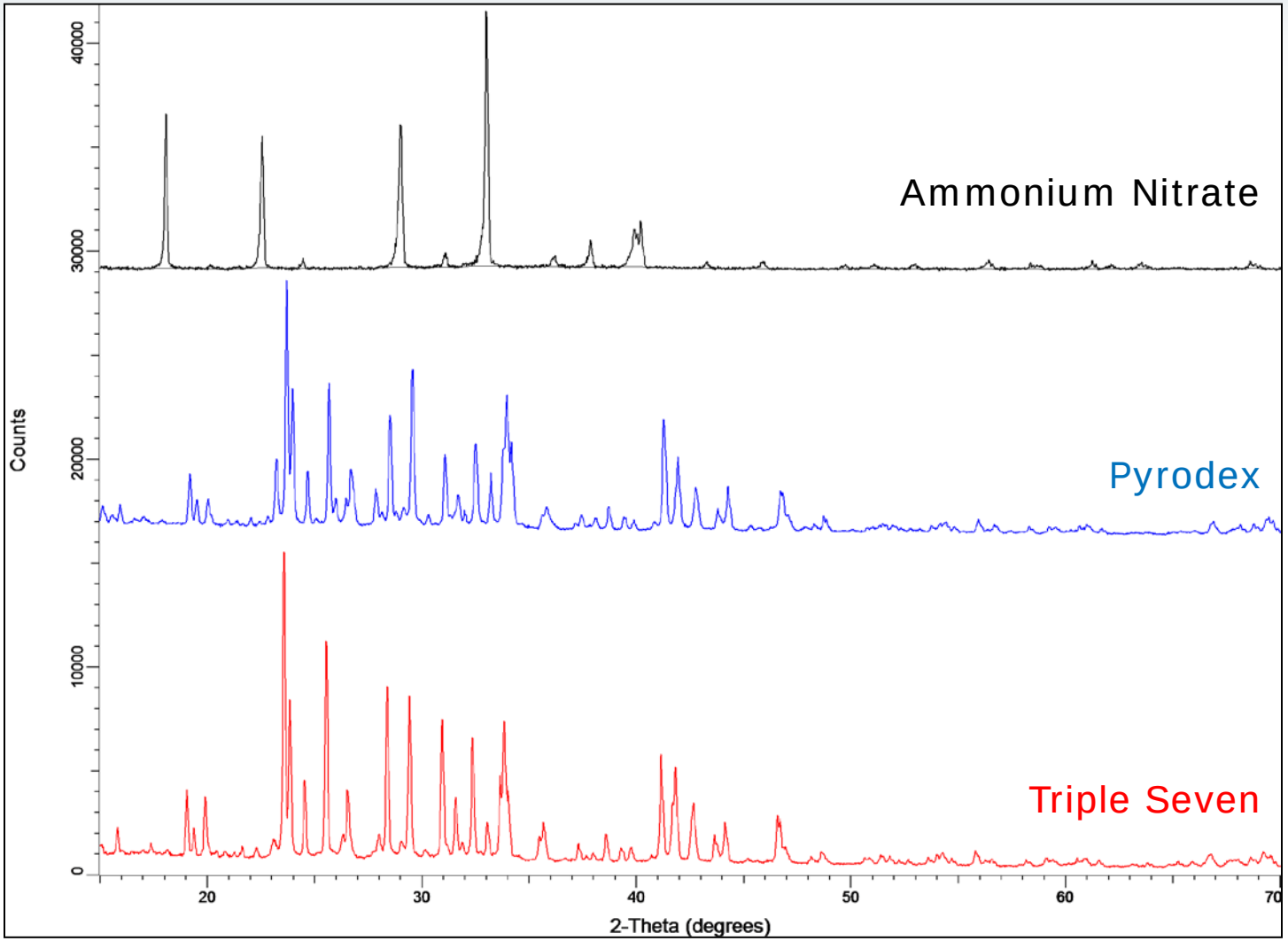
Pharmaceuticals
Various Sweeteners (Adulterants)



Explosives and Blast Residue

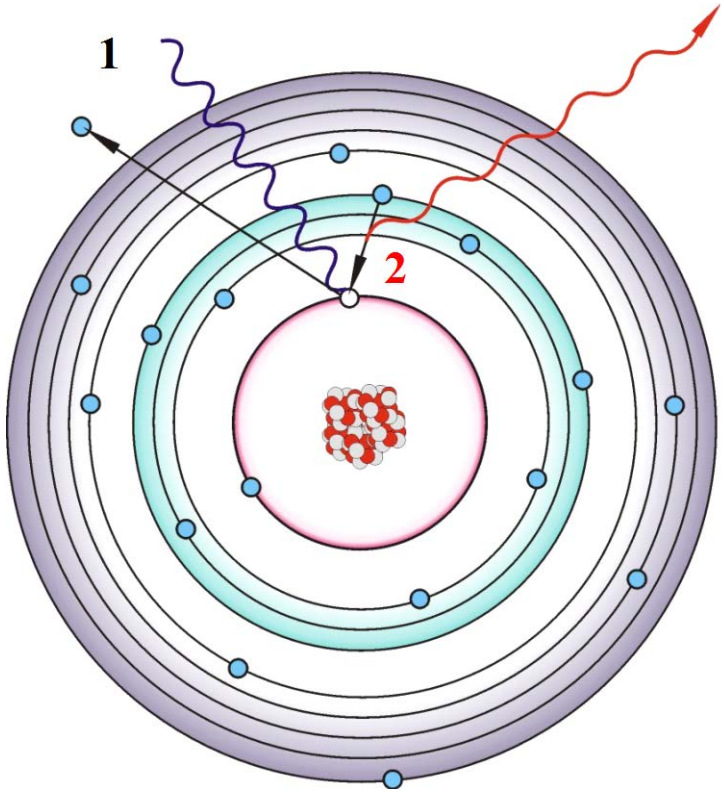
- Raw Explosives
  - Positive identification of explosive materials
  - Discrimination between types of explosives
    - Pyrodex
    - Triple Seven
    - Ammonium Nitrate
- Blast Residues
  - Indication of type of explosive used
  - Oxide and halide residues
    - Aluminum chloride hexahydrate

Explosives


Ammonium Nitrate
Pyrodex
Triple Seven
Counts
40000
30000
20000
10000
0
20
30
40
50
60
70
2-Theta (degrees)

Introduction to TXRF

Principles X-ray Fluorescence (XRF) Spectroscopy

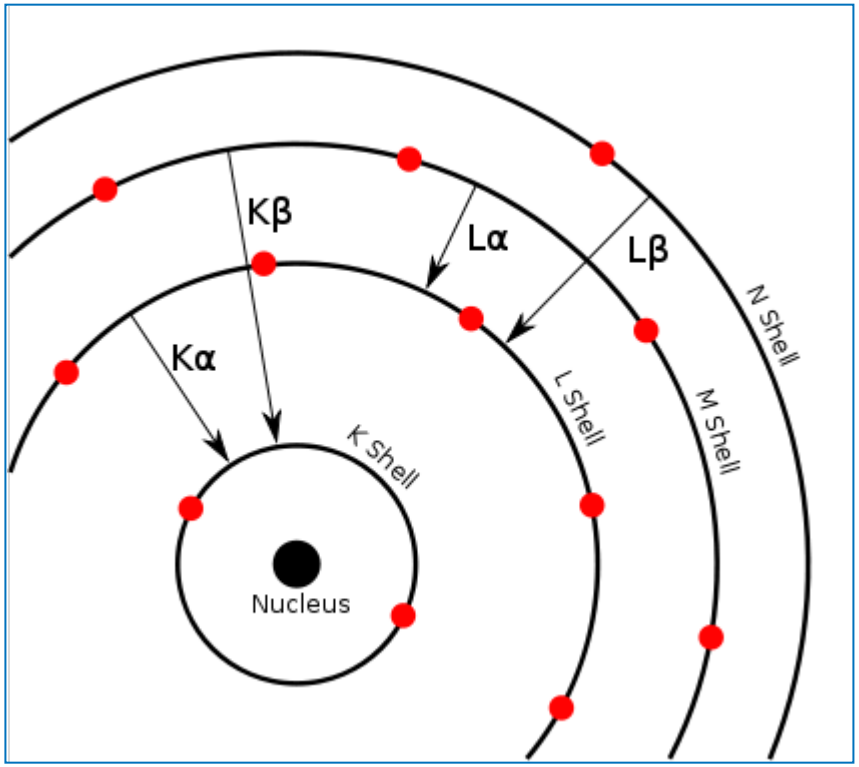


1. An X-ray quantum hits an inner shell electron in a (sample) atom. The electron is removed leaving the atom in an excited state
2. The missing inner shell electron is replaced by an electron from an outer shell
3. The energy difference between the inner and outer shell is balanced by the emission of a photon (fluorescence radiation)

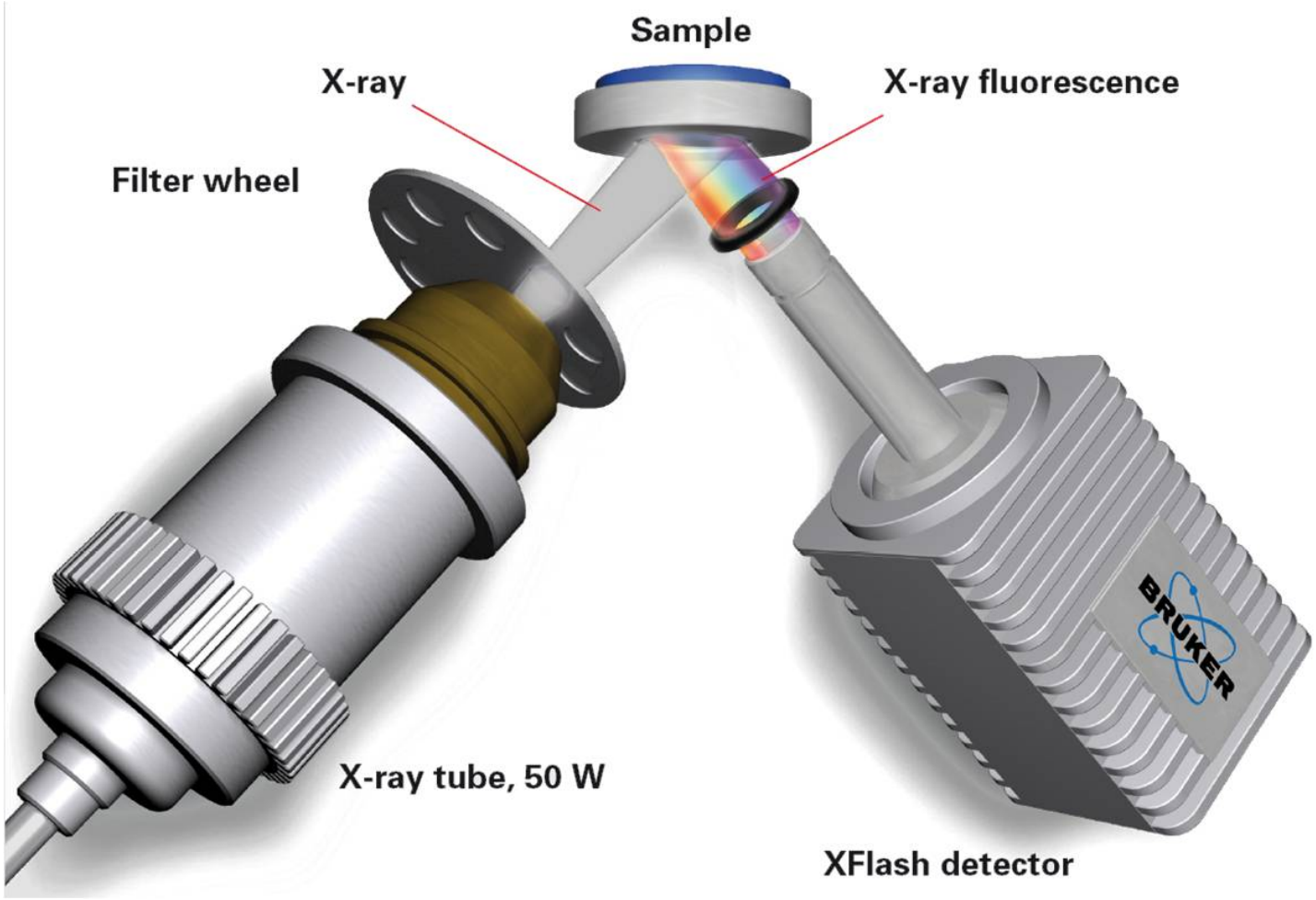
Principles of X-ray Fluorescence (XRF) Spectroscopy

Each element shows a specific line pattern in a spectrum depending on the orbitals involved

- L→K transition = Kα line
- M→K transition = Kβ line
- M→L transition = Lα line
- N→L transition = Lβ line



Traditional EDXRF



Traditional EDXRF

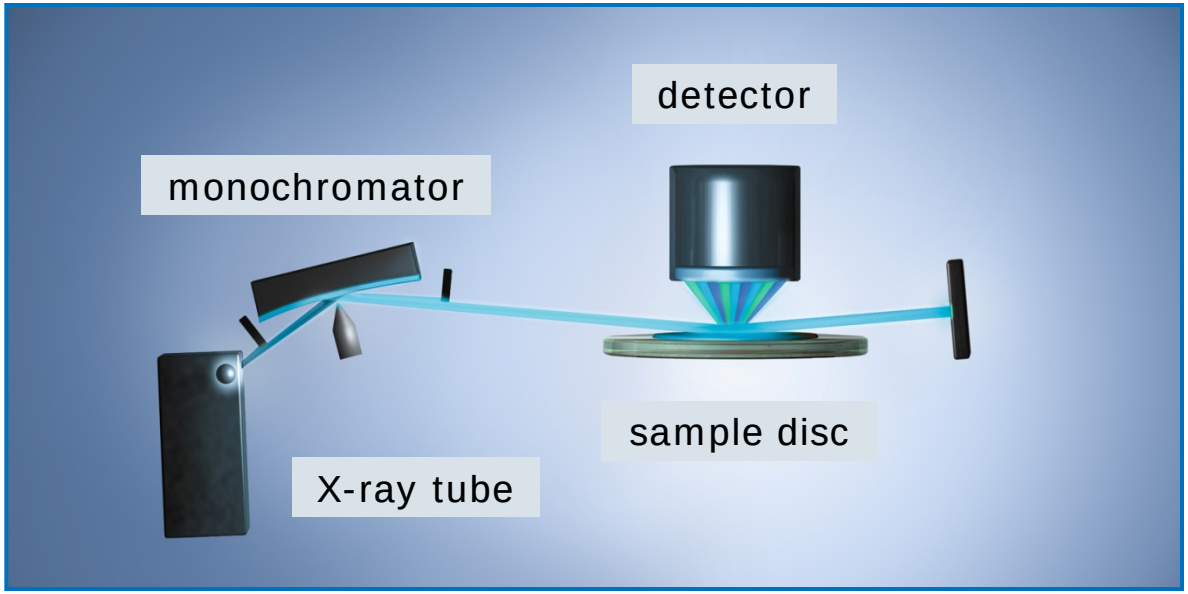
Samples for common XRF spectrometry (ED and WDXRF)

- Solids (cut, polished and put into suitable shape)
- Powders (as pressed pellets, fused beads or loose powders in liquid cups)
- Liquids (in liquid cups)

Necessary sample amount: from 1 g to 10 g!!

Principles of Total Reflection X-ray Fluorescence (TXRF) Spectroscopy

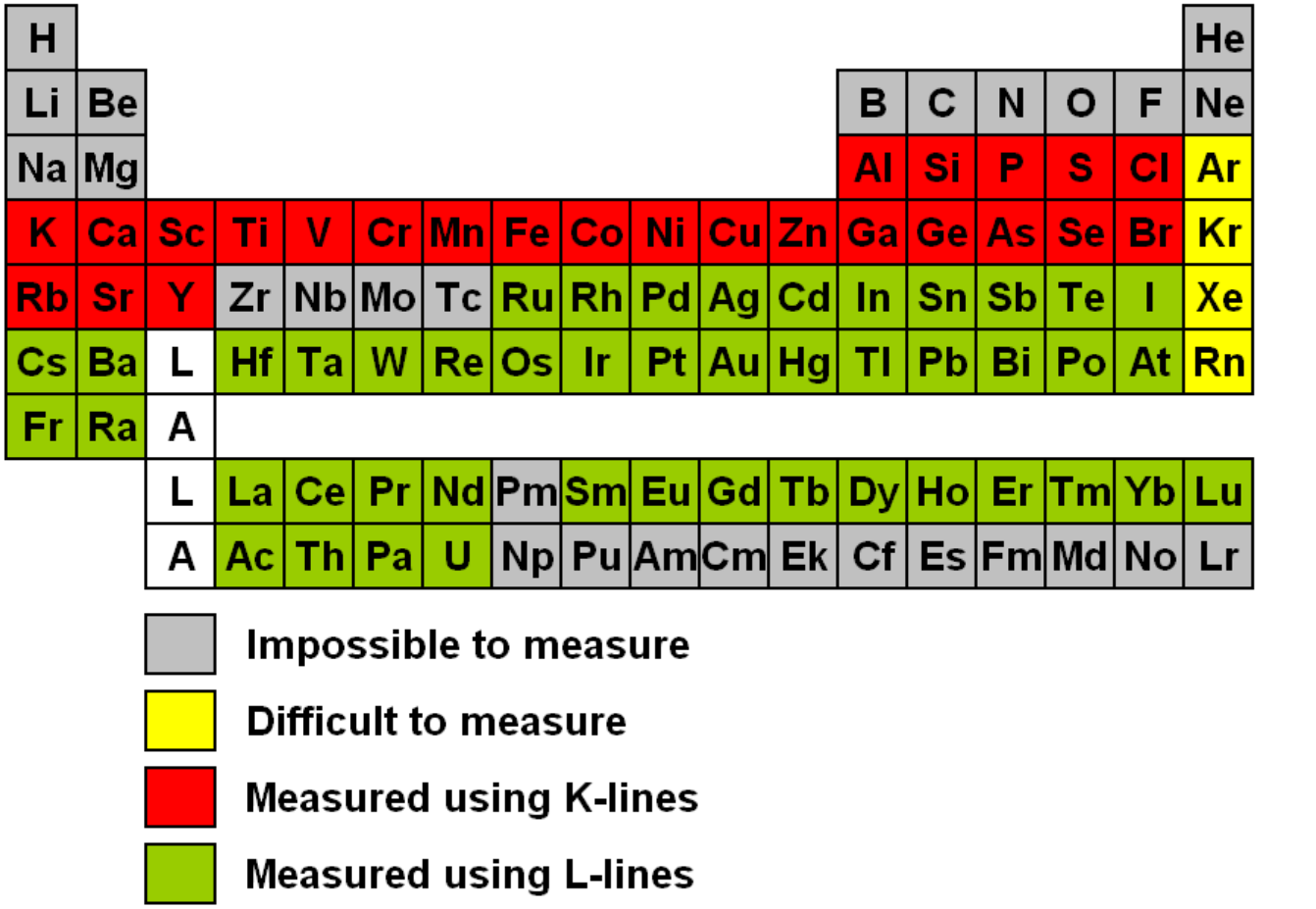
Total reflection X-ray fluorescence spectroscopy



Beam angle: 1° / 90°

- Samples must be prepared on a reflective media
- Polished quartz glass or polyacrylic glass disc
- Dried to a thin layer, or as a thin film or microparticle

Elements Measured by the Mo PICOFOX



The Instrument S2 PICOFOX

Benchtop TXRF spectrometer
S2 PICOFOX

- Metal-ceramic X-ray tube
  - Mo anode
  - Air-cooled
  - Other tubes available
- Multilayer monochromator
- XFlash® silicon drift detector
  - Electro-thermally cooled
  - ≤149 eV @ MnKα 100 kcps
- Automatic version
  - 25-sample cassette

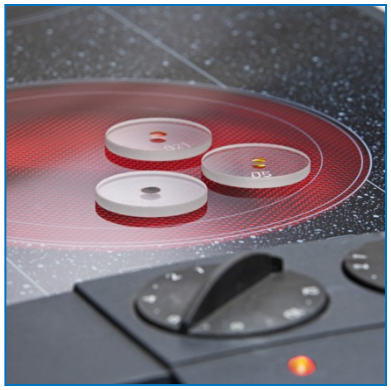
Application Examples

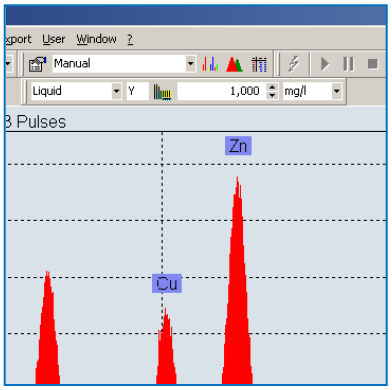
Sample Preparation
Liquid Samples - Toxicology




- fill sample in micro tube
- add internal standard
- homogenize
- pipette on carrier

Sample Preparation
Liquid Samples - Toxicology





- dry by heat / vacuum
- load the instrument
- start data aquisition

S2 PICOFOX
Trace Element Analysis - Toxicology

Introduction

- Analysis of nutrition-relevant elements (Cu, Fe, Zn, Se)
- Analysis of toxic elements (As, Pb, Hg)

Task

- Analysis of whole blood and blood serum standards

Sample preparation

- Serum
  - 1:10 dilution with water (p.a. grade)
  - Addition of Ga for internal standardization
- Whole blood
  - 1:1 dilution with water (p.a. grade)
  - Addition of Ga for internal standardization

S2 PICOFOX
Trace Element Analysis - Toxicology

- Toxicological analysis of heavy metals
- Precise results without sample digestion
- Accurate quantitation from Aluminum to Uranium
- Can analyze a variety of samples like hair, blood, urine, tissues

		Serum (ClinCheck L2)				Whole blood (Seronorm L2)			
Element	Unit	TXRF	Std. dev.	Reference [1]	Std. dev.	TXRF	Std. dev.	Reference [2]	Std. dev.
Fe	mg/l	440	7.4	435	12	2.9	0.09	1.964	0.20
Cu	µg/l	66	2.2	62	2.1	1685	43	1562	312
Zn	µg/l	501	4.9	504	6.9	2194	118	2225	334
Se	µg/l	12	0.29	12	1.0	97	18	102	26

[1]: Atomic Absorption Spectroscopy

[2]: Sector-Field Inductively-Coupled Plasma Mass Spectroscopy

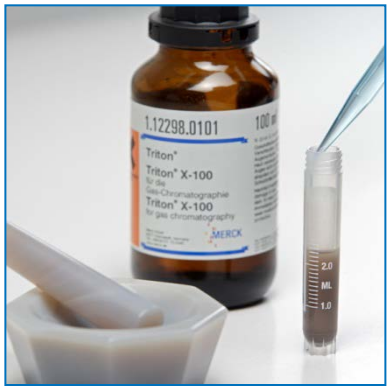
Sample Preparation
Solid and Powder Samples

Solids are ground to fine particle size and resuspended for direct analysis without digestion




- fill powder in mortar
- grind carefully (< 50 µm)
- weigh about 20-50 mg
- transfer to tube

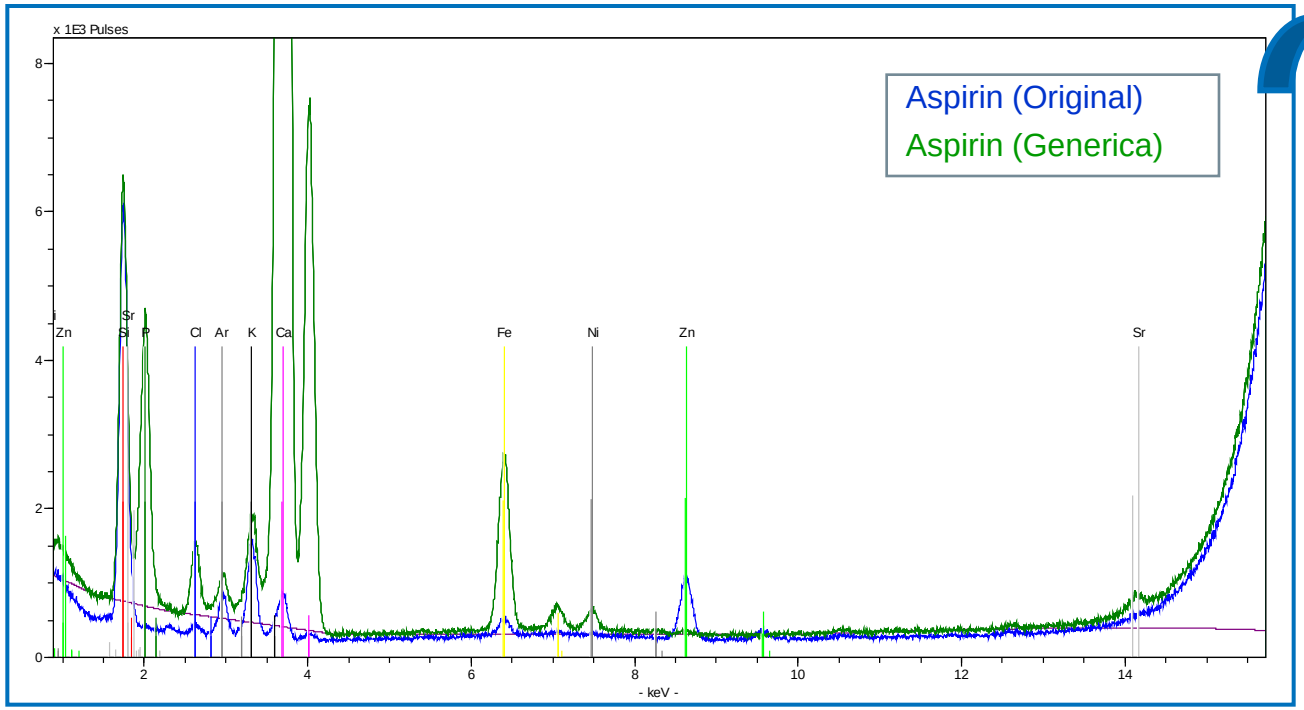
Sample Preparation
Solid and Powder Samples



- suspend in detergent solution
- add standard
- homogenize
- pipette on carrier

TXRF Applications
Authentication of Pharmaceuticals

Authentication and Purity Control of Pharmaceuticals



	Concentration (mg/kg)	
	Original	Generica
P	< LLD	25.8
Cl	2.8	16.7
K	35.2	28.9
Ca	10.5	243.8
Fe	0.85	5.4
Ni	< LLD	1.3
Zn	< LLD	1.9
Sr	0.06	0.74

- Spectra comparison after direct preparation
- Quantitative analysis after internal standardization

➔ **Fingerprint and authentication analysis**

Sample Preparation
Microparticles

Microparticles are measured semi-quantitatively and non-destructively

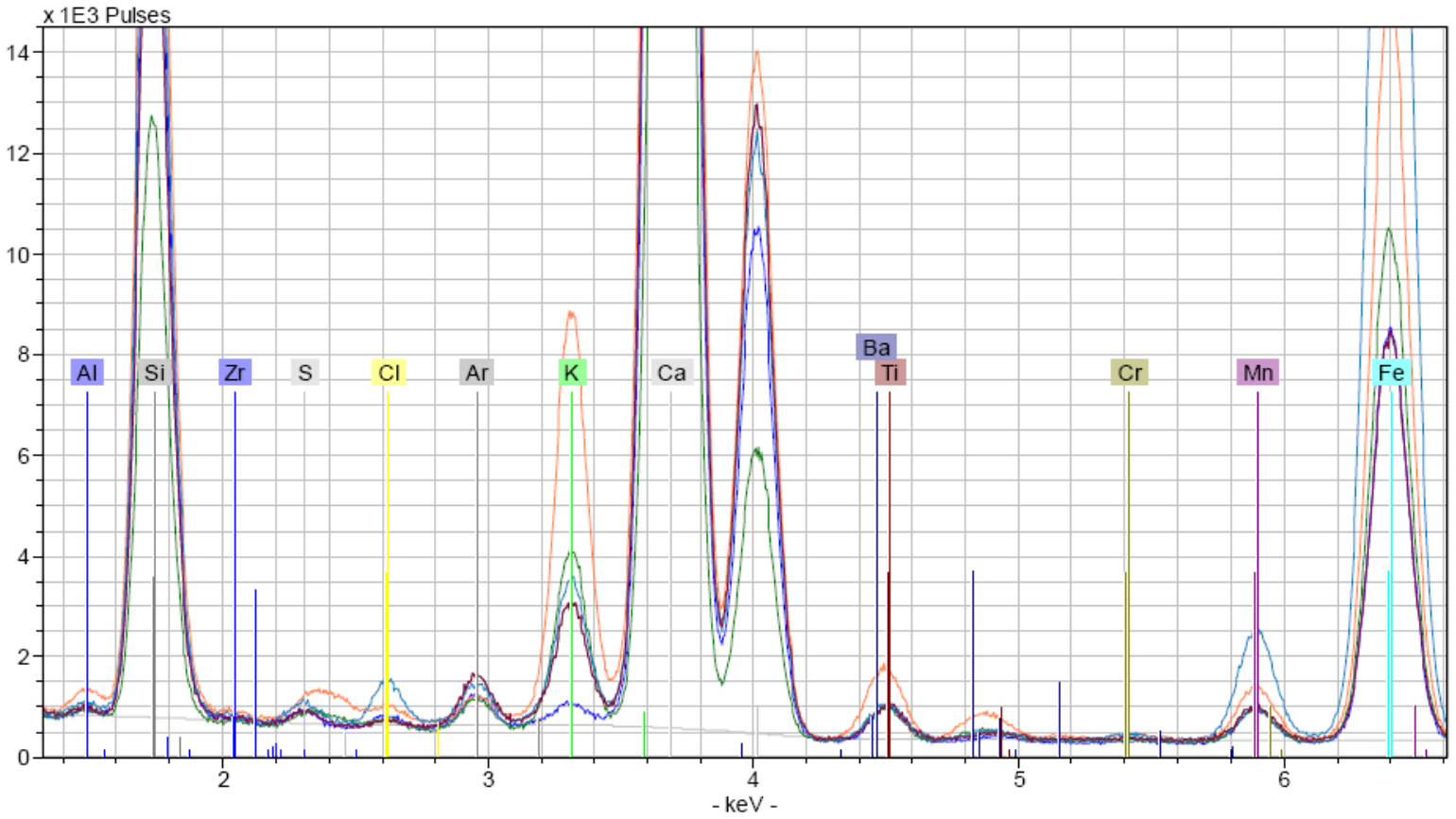
- dab vacuum grease on carrier
  - pick-up some particles with a (glass) rod
    - drop particles on grease

TXRF Applications
Analysis of Glass Fragments

- 5 glass fragments (1 – 2 mm and 0.5 – 1 mm thick) are embedded in a resin block
- Fragments were too large for direct analysis
- Ground samples with agate motor then transferred to disk
- Applied discriminate analysis to understand spectral differences
- Can be applied to other small samples like paint chips
- **Develop an Inorganic Spectral Library**

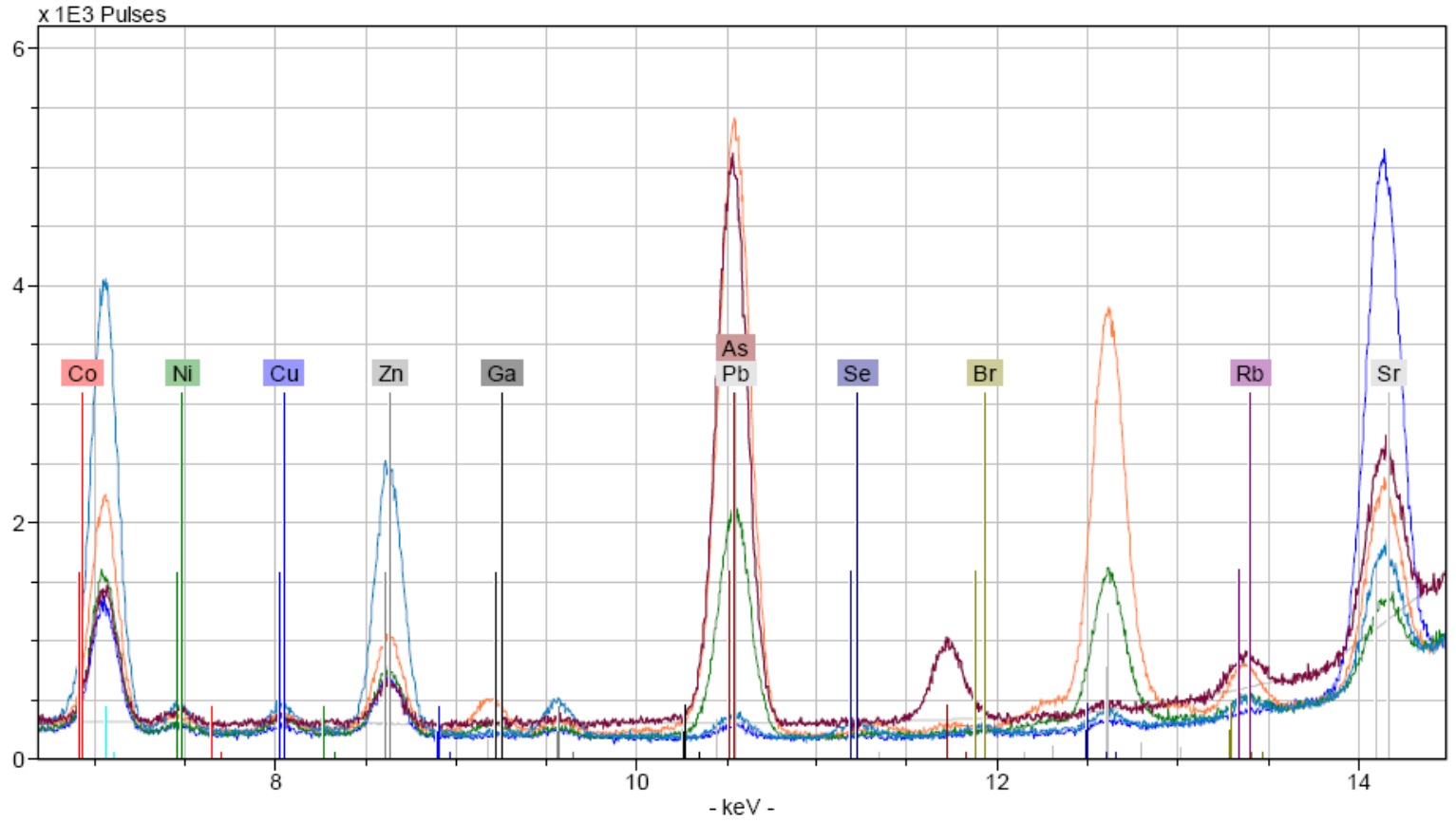
TXRF Applications
Analysis of Glass Fragments

Spectral Comparison



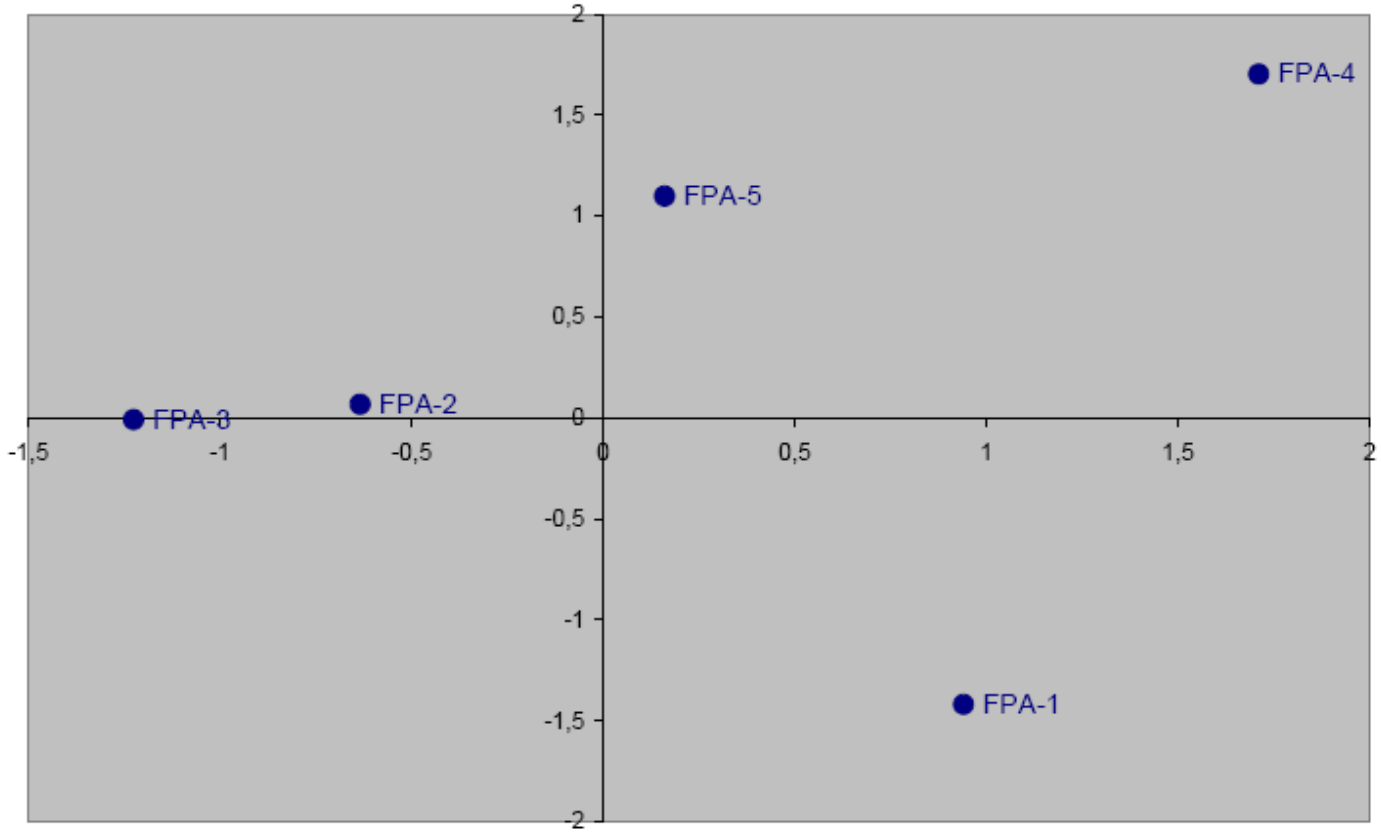
TXRF Applications
Analysis of Glass Fragments

Spectral Comparison



TXRF Applications
Analysis of Glass Fragments

Standardless Quant. – Discriminate analysis



Introduction to µXRF

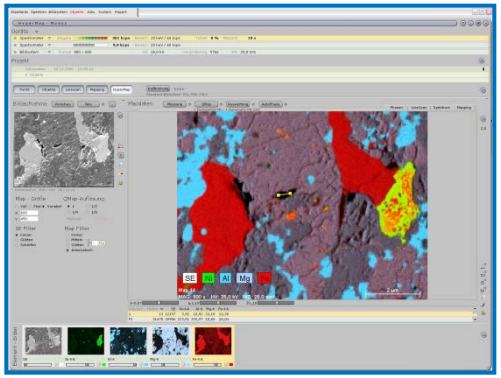
What is µXRF?

- Micro XRF focuses X-ray radiation to small concentrated areas of a samples by use of collimation
- This allows a position sensitive examination of:
  - Elemental distributions for non-homogenous samples of small particles, inclusions or non-regular shaped samples or
  - Thickness of composition of coatings
- Position sensitive analysis is required because a lot of materials are not homogenous and are not flat.
- µXRF is not a destructive technique so it does not require complicated sample preparation and preserves evidence.
- Distribution analysis gives information over a large area.
- Rapid X, Y, Z stage allows for fast mapping of samples.

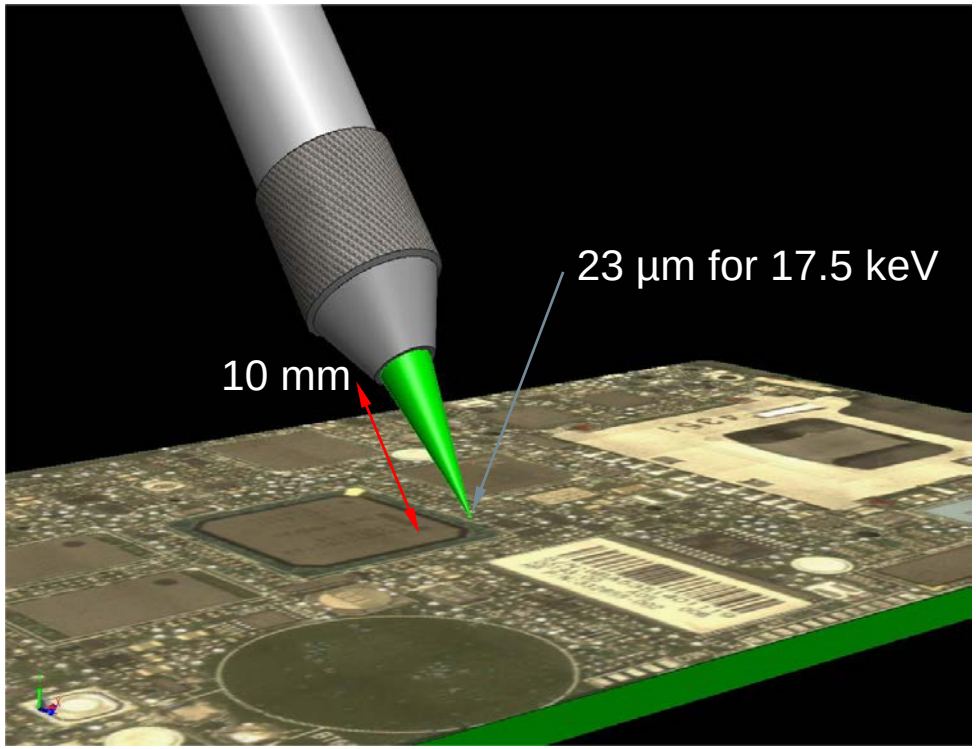
M4 TORNADO

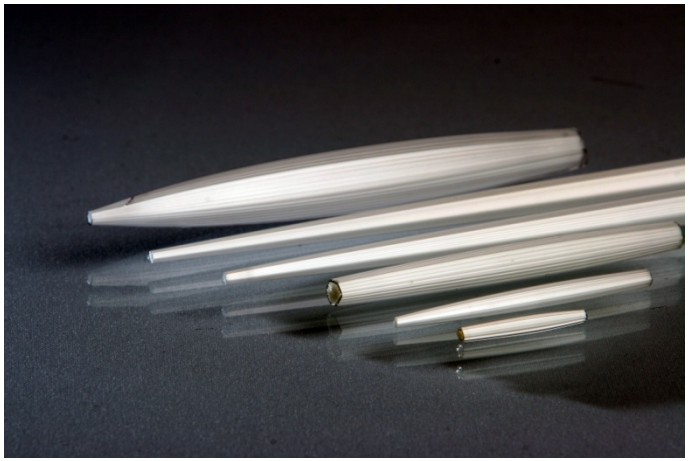
M4 TORNADO

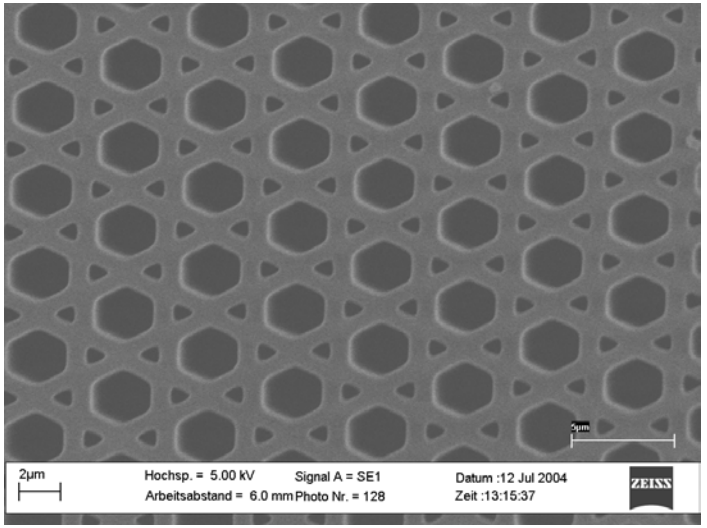
- High-end µXRF system for
  - composition analysis and
  - layer thickness measurements
- Vacuum chamber (light elements!)
- SDD detector (up to 3 simultaneously)
- 50 W fine focus X-ray tube (Rh, Mo, W, Ag)
- Spot size 25 µm – Polycapillary Optics
- High speed, motorized xyz-stage for fast line scan and mapping
- Operated with ESPRIT software with multiple analysis and display features
- Large chamber for various sized objects



M4 TORNADO
Focusing by poly-cap lens







Poly-cap lens collects large angle of tube radiation and concentrates this to the sample in small spots

Forensic Applications Where µXRF is Used

- Analysis of unknown and non-regular shaped samples:
  - Particles of glass and lacquer to identify cars involved in accidents
  - Particles of dust, soil, rocks, etc. found on clothing, shoes etc.
  - Different types of fibers
- Analysis of pigments on documents
  - Distinguish between different pigments
  - Detect covered or erased letters by trace analysis
- Analysis of Gun Shot Residue (GSR)
- Analysis of drugs for traces to identify their origin
- Identification of fraudulent money (paper) and of gems

Forensic Applications
Analysis of Paper Money

Bank notes are high tech-products, they contain a lot of features to protect against counterfeiting

many different analytical methods are required to verify all of them

µXRF can identify the different pigments and metal strips

Single element distributions for few elements.
they show:

- The watermark is a density variation of the TiO2-pigment
- The metallic wire is made from Fe

Forensic Applications

Examination of Paper Money

Paper money is a high-tech product with a series of safety issues such as the used pigments that can be analyzed with XRF.

Mosaic image

Multielement overview

Single element distributions of Cr

Fe and

Ti

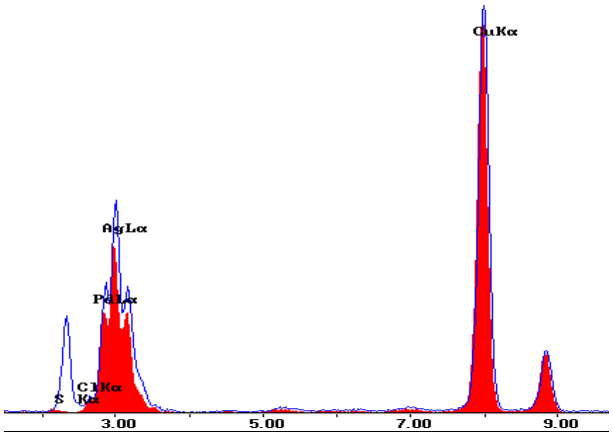
Measurement with
1225 x 606 pixel
25 ms/pixel

Forensic Applications
Identification of Fake Coins

The numismatic value of historic coins depends on the number of minted coins

Part of a coin of 2 Reichsmark, expected to be minted 1927, a year with low coin production

First tests are performed with sulfidic acid which generates AgSO4 (black color)

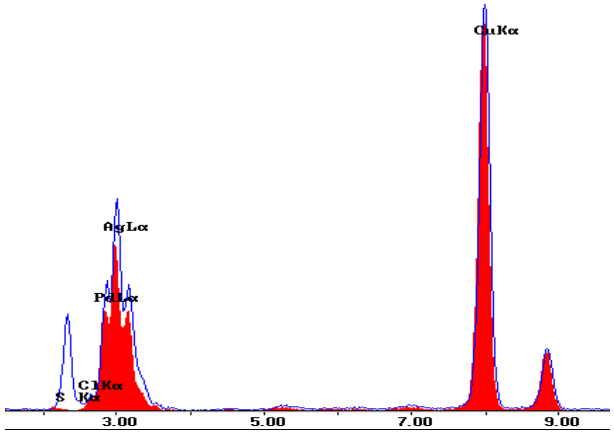


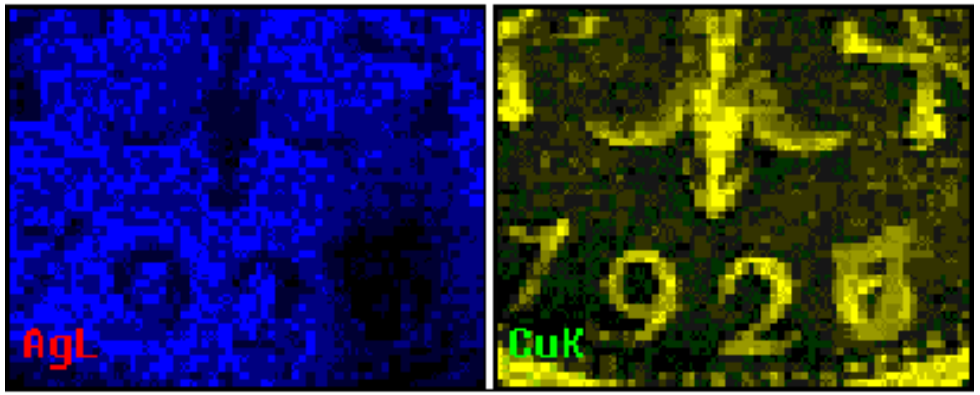
Measurement on the “2” (red spectrum) and “7” (blue spectrum) show the expected composition of Ag and Cu

The spectra show slight differences due to the AgSO4 layer

Forensic Applications
Identification of Fake Coins

The numismatic value of historic coins depends on the number of minted coins



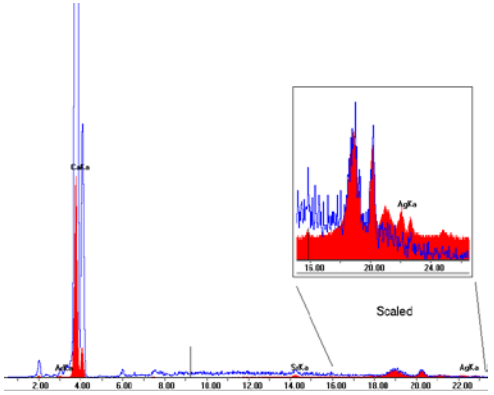


The mapping shows that the “7” is a fake. It was a “6”, was removed and replaced by a 7 which enhanced the value by approx. 2 orders of magnitude - seemingly!

Forensic Applications

Identifcation of Fake Gems

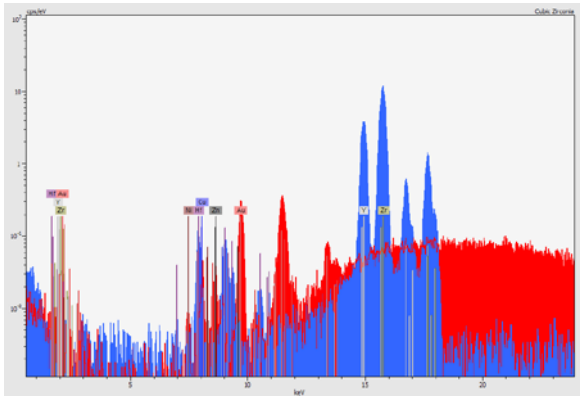
Fakes of pearls



These spectra of pearls shows Ca, Sr (from the seawater). But for the black pearl, there is also Ag.

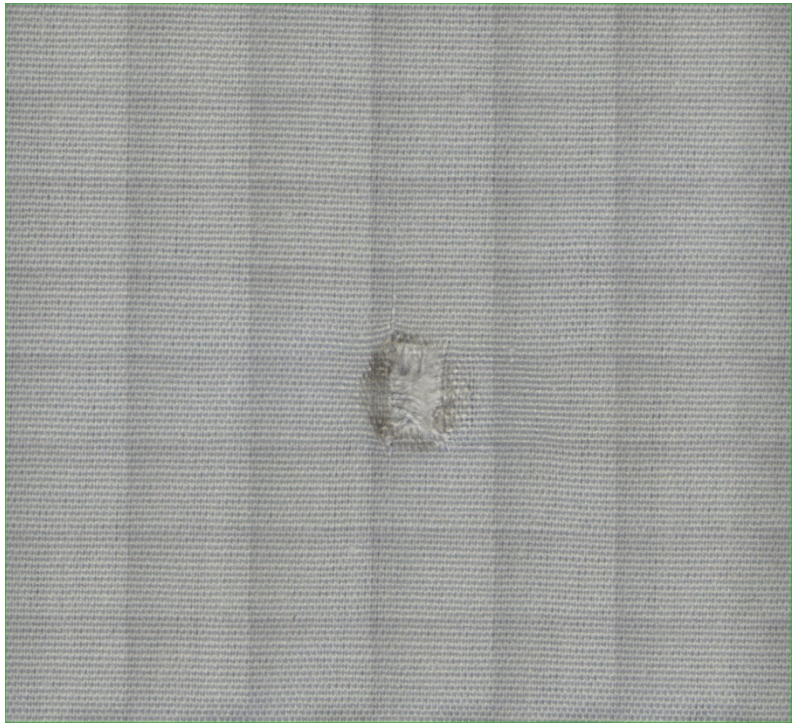
This can be only from a Ag-coating of the pearl to make it more valuable.

Fakes of diamonds

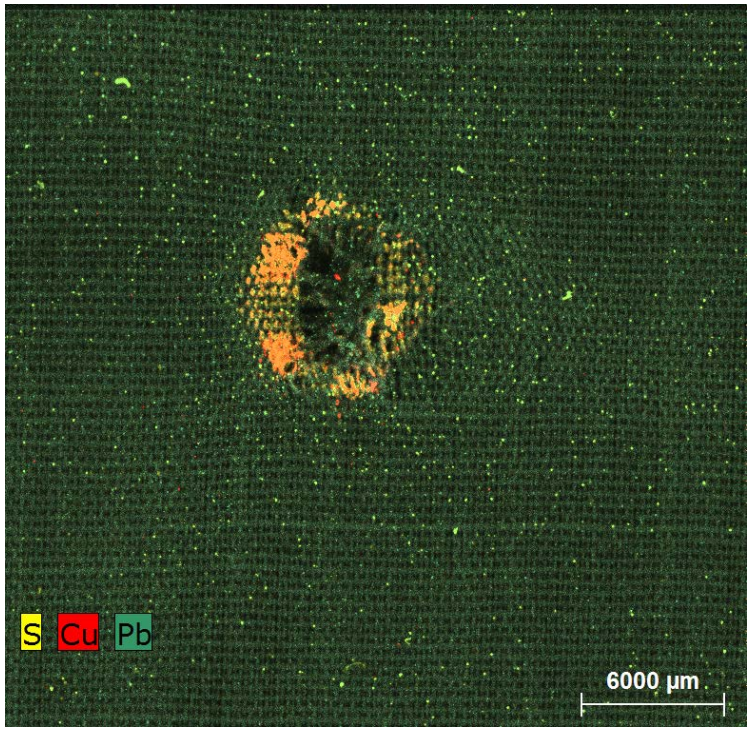


Zirconia can be easily mistaken for diamond. Diamond is from Carbon, it shows no XRF line, only a large background scatter.
The diamond spectrum (red) shows some Au-lines from the support of the gem.
The zirconia spectrum (blue) has significant lines of Zr, Y and also Hf.

Forensic Applications
Gun Shot Residue – Detection of Elements of Interest



Textile with bullet hole

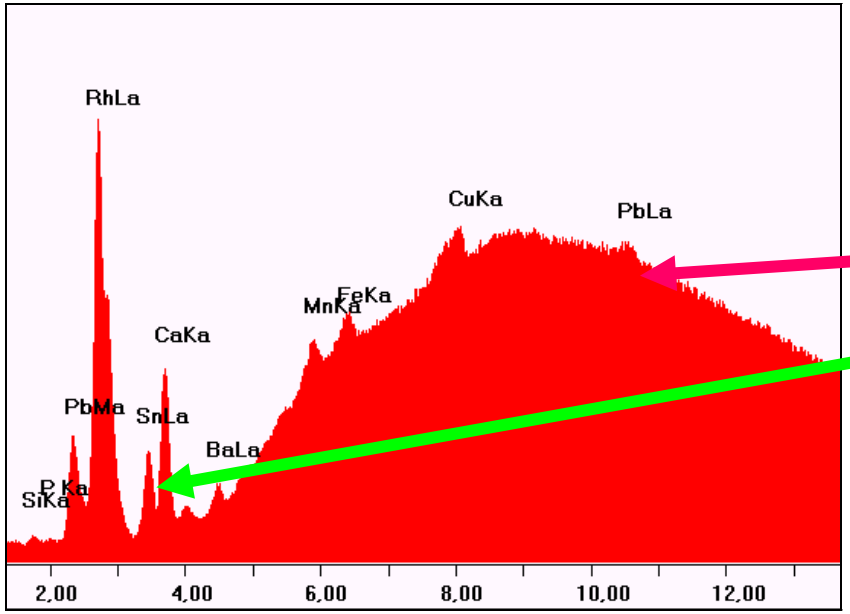


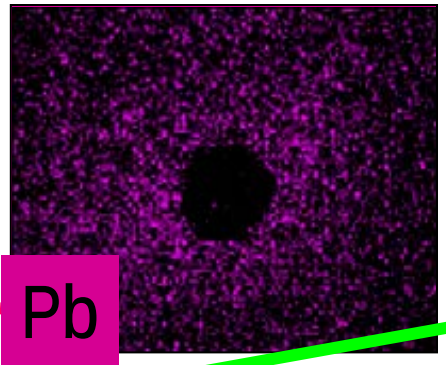
Distribution of S, Cu and Pb close to the bullet hole with high concentration on the hole and single particles around

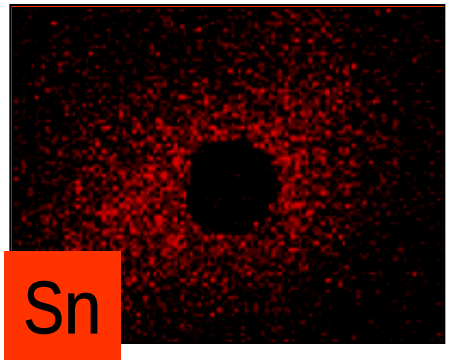
Pixel: 780 x 760, 40 µm step size, 5 ms per pixel or approx. 1 h total

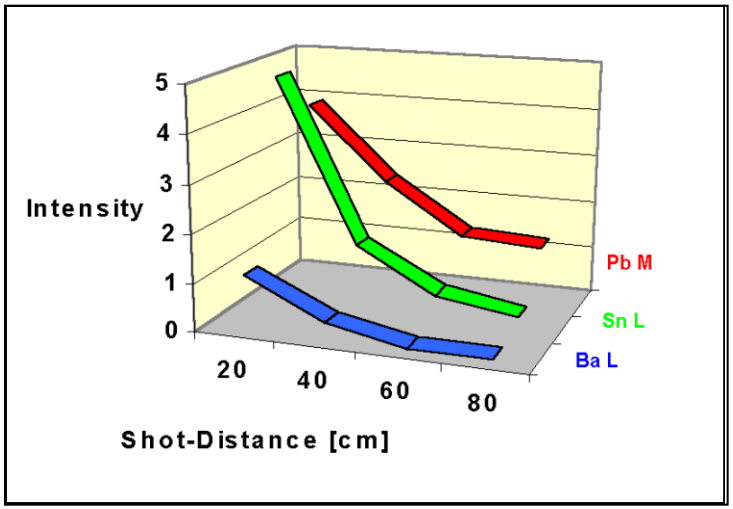
Forensic Applications
Gun Shot Residue – Shot Distance

Spectrum of a GSR contamination









Intensity of elements of explosives on the bullet hole depends on shot distance (drops down very fast).

This allows an estimation of shot distance.

Forensic Applications
Analysis of Pigments in an Art Object

Museum of
Fine Arts Leipzig
oil painting,
Max Klinger 1872
back side,
310 x 150 mm^2

The back side of this painting on wood was covered by a paper. It was assumed that this was a older painting by Klinger which was covered by paper and than the “back side” was used again to paint.

µXRF was able to measure through the paper to detect the distribution of pigments.

Forensic Applications
Analysis of Pigments in an Art Object

Museum of
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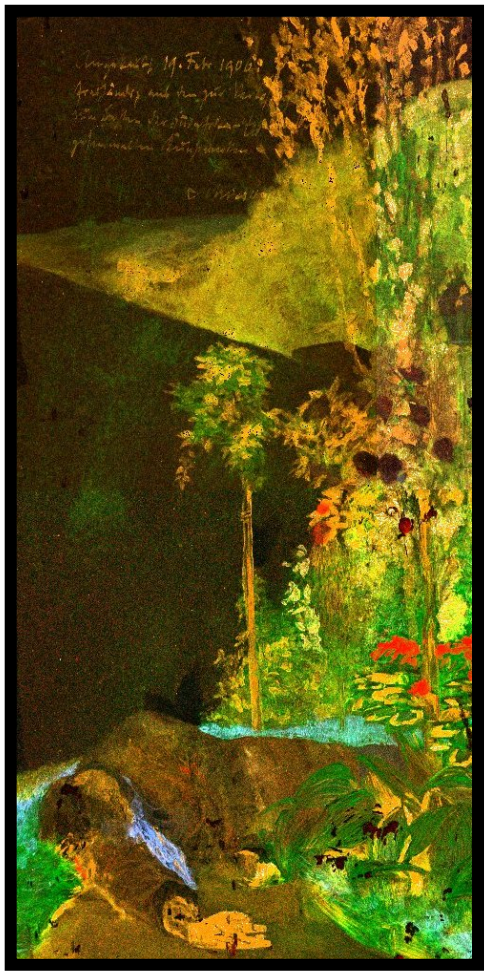
oil painting,
Max Klinger 1872
back side ,
310 x 150 mm^2



µXRF mapping,
1000 x 500 pixel,
Ca, Cr, Fe, Co,
Cu, Hg, Pb

This examination shows that there is another painting on the back side and it seems to be a natural scenery. This result forced the removal of the covering from the back side and restoration of the painting.

Q & A

Any questions?

Please type any questions you may have for our speakers in the Q&A panel and click Send.

How did we do?

When you exit the webinar, please fill out our evaluation survey to let us know. We appreciate your feedback.

Thank you!

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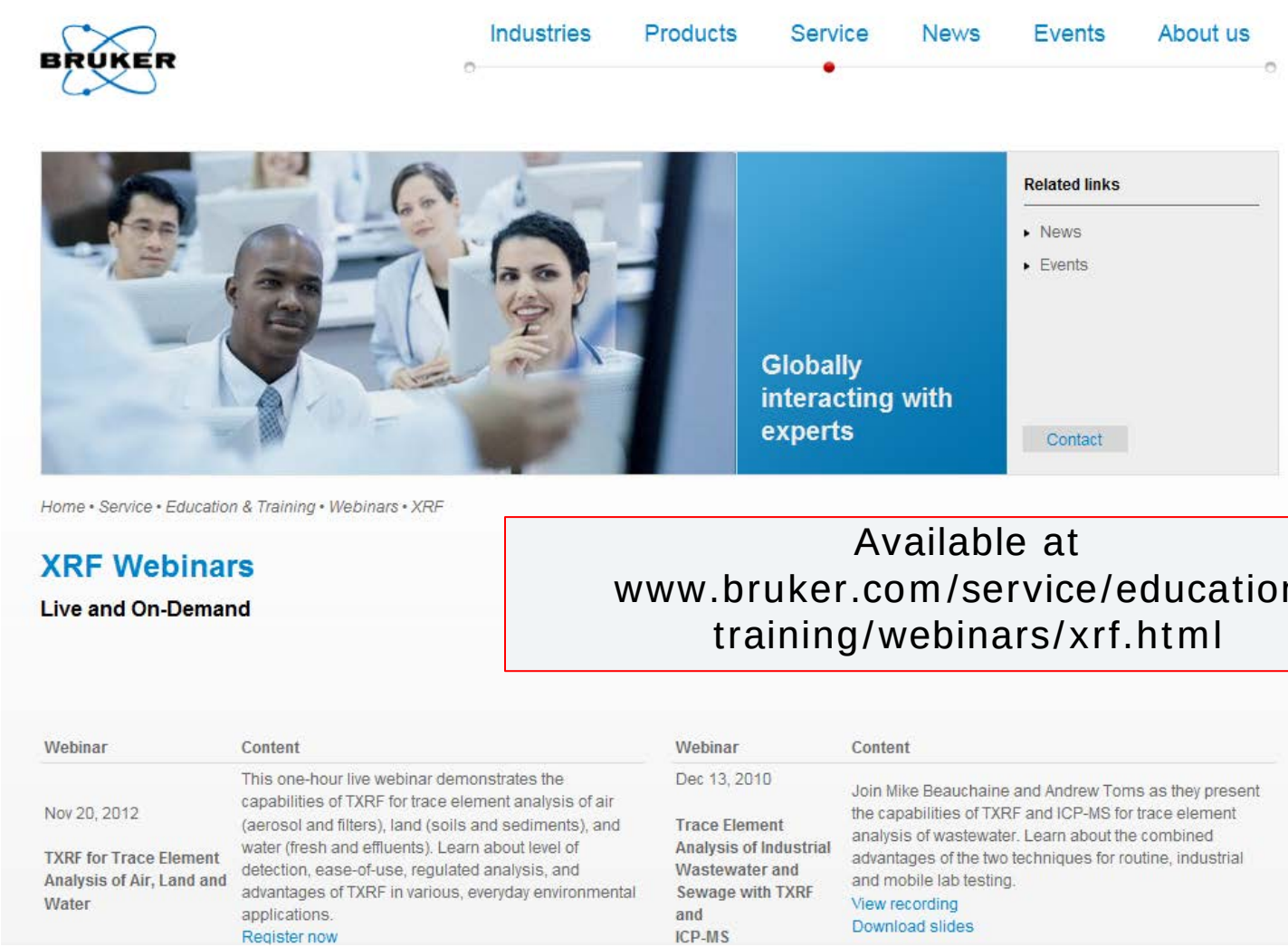

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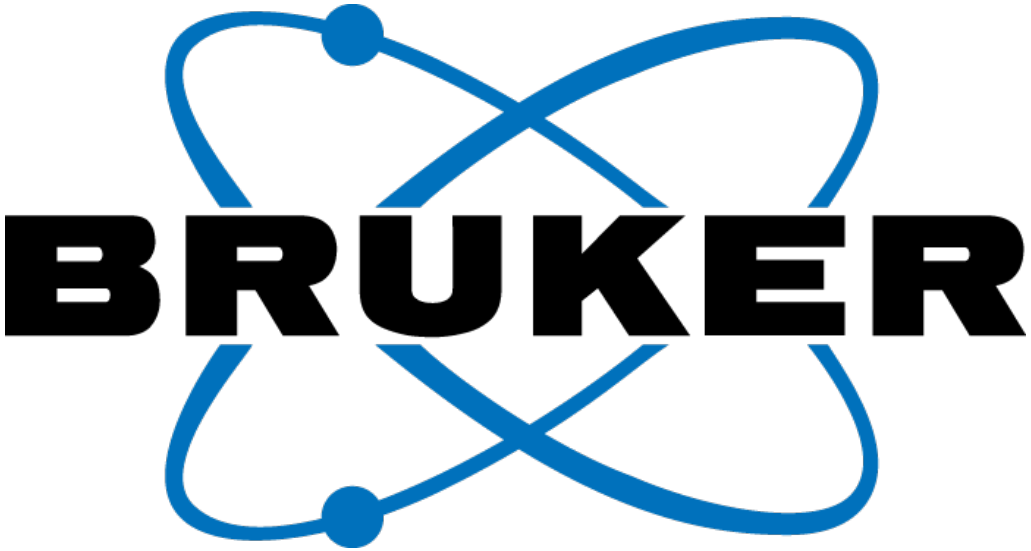

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