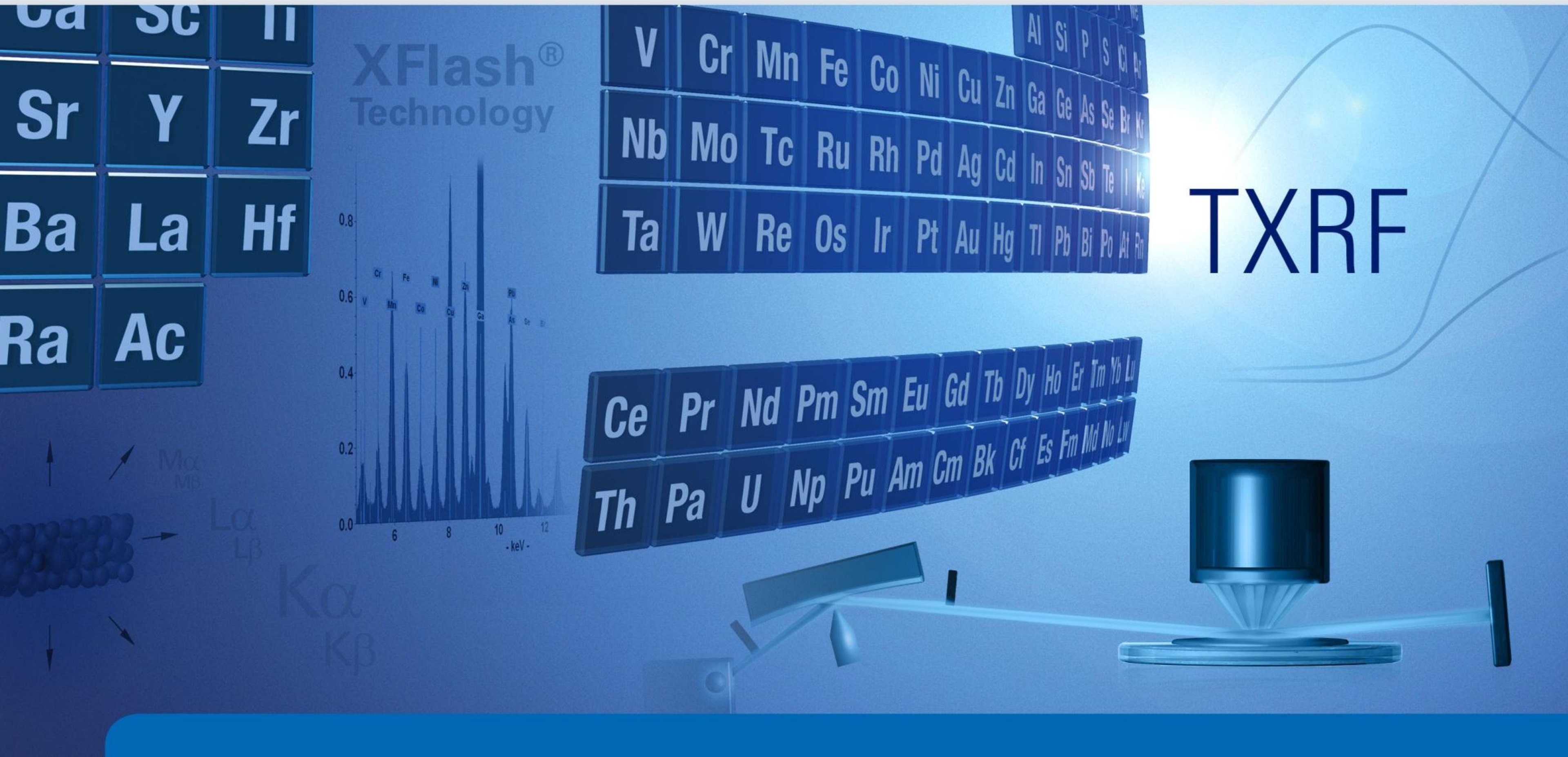
Why Teach TXRF: Trace Elemental Analysis in the University Laboratory

Bruker AXS Inc., Madison, WI, USA
March 7, 2013



Welcome

Today's Topics

- Introduction to TXRF, learn about X-ray fluorescence analysis
- Analysis of a rum sample
- Straightforward data evaluation
- Sample preparation
- Examples of research applications
- Comparison with atomic spectroscopy methods

Speakers

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XRF Technician
Madison, WI, USA

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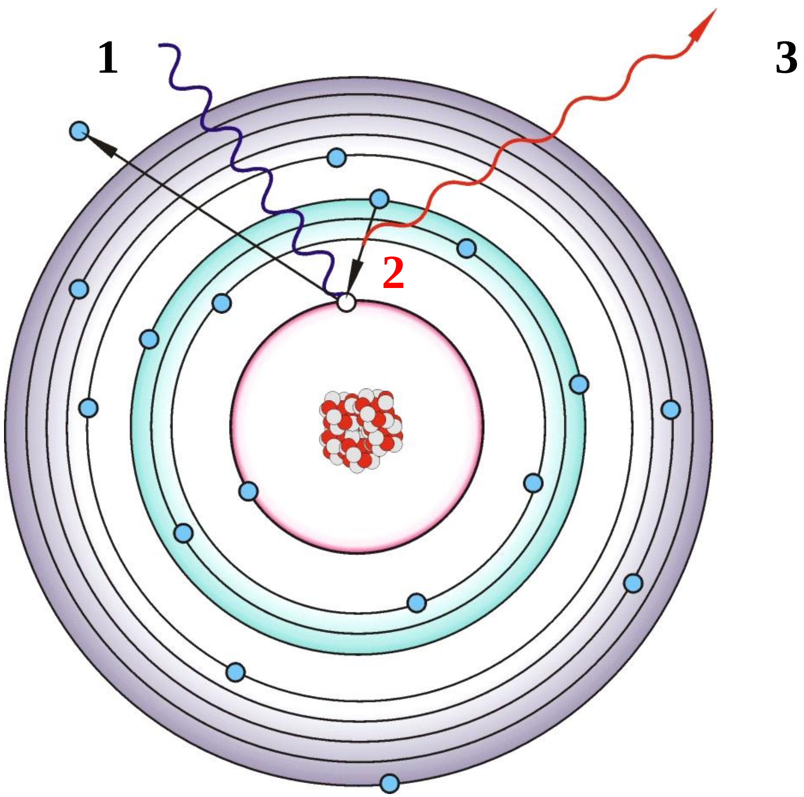
Business Development Manager
Americas - XRFi
Madison, WI, USA

TXRF – How does it work?

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)

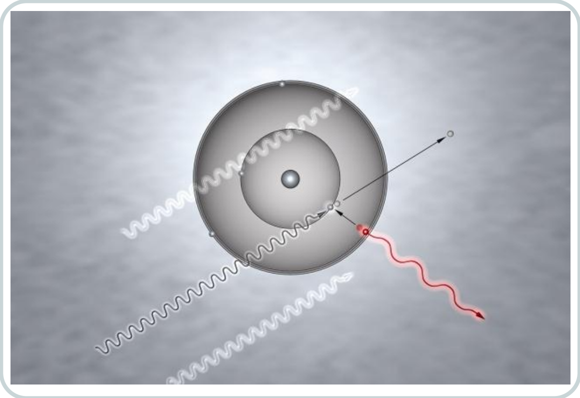
Principles X-ray Fluorescence (XRF) Spectroscopy

- The energy, and therefore the wavelength, of the X-ray fluorescence radiation is characteristic for the different chemical elements.

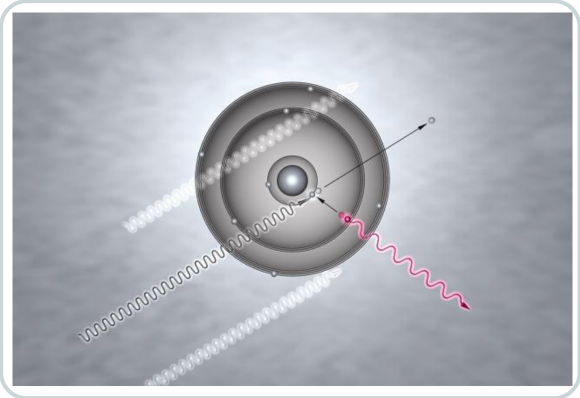
  QUALITATIVE ANALYSIS

- The intensity of the X-ray fluorescence radiation is, in first approximation, proportional to the element concentration.

  QUANTITATIVE ANALYSIS



Low Z

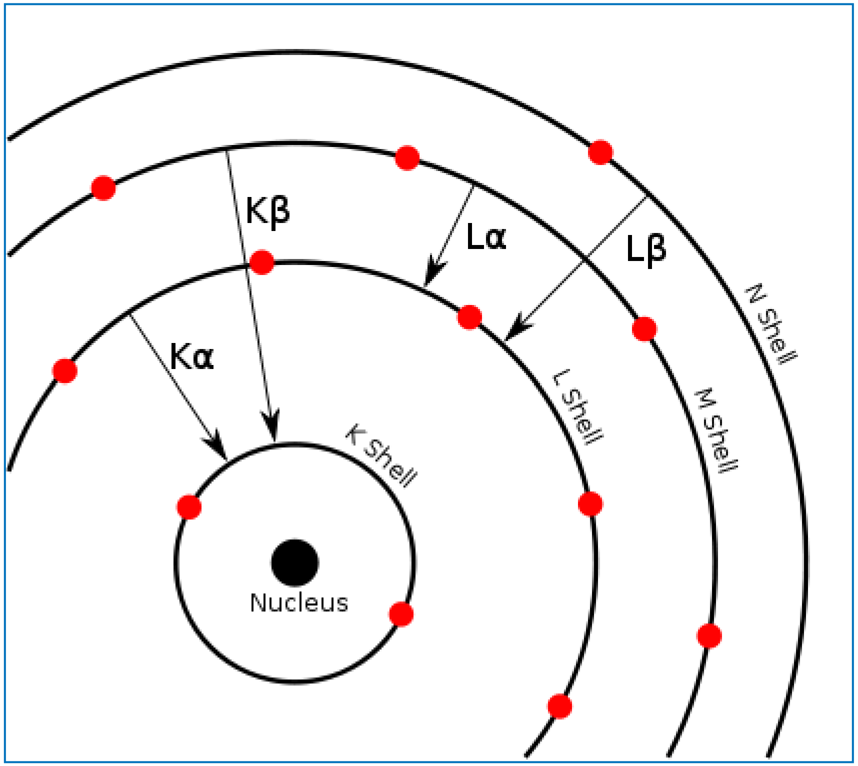


High Z

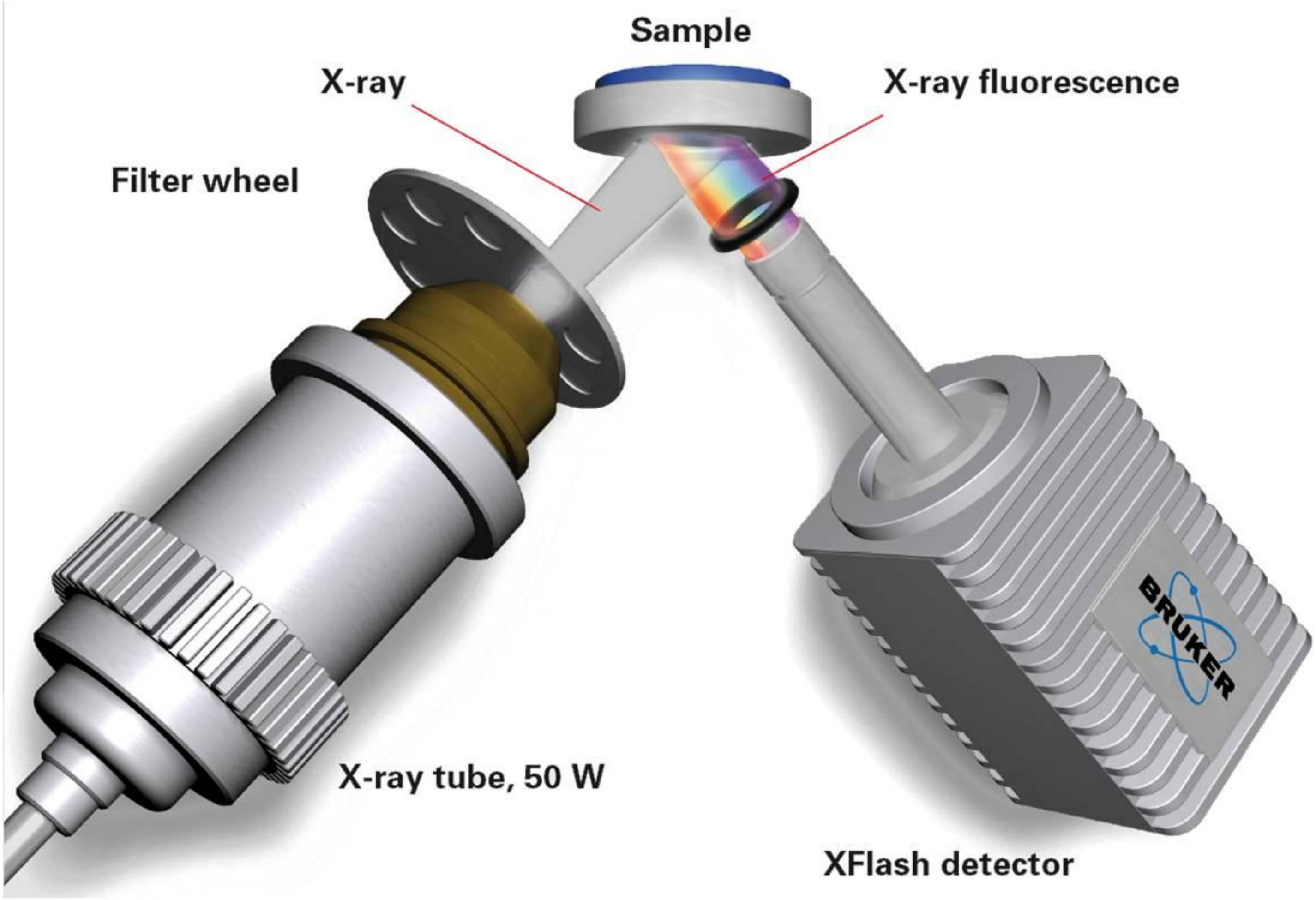
Principles of X-ray Fluorescence (XRF) Spectroscopy

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

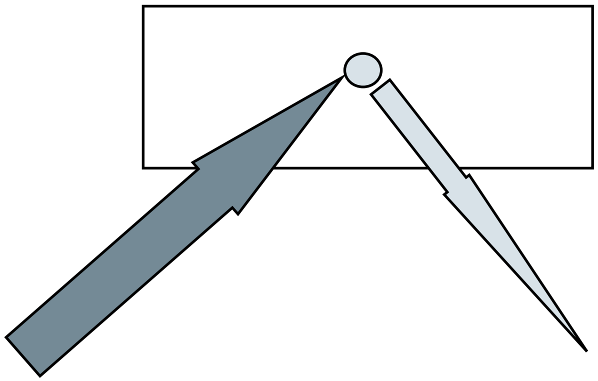
- L→K transition = Kα line
- M→K transition = Kβ line
- M→L transition = Lα line
- N→L transition = Lβ line



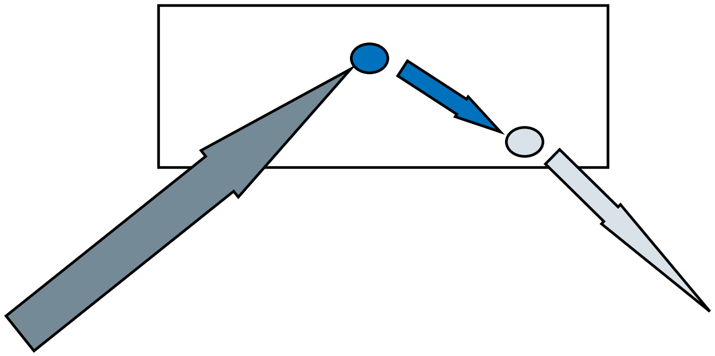
Traditional EDXRF



Traditional EDXRF Quantification



absorption of primary beam and fluorescence radiation



secondary fluorescence enhancement

$I_i = f(c_i, c_j)$ and $c_i = f(I_i, c_j)$

Concentration needs to be determined with matrix matched standards

DO YOU HAVE STANDARDS?

Traditional EDXRF

Samples for common XRF spectrometry (ED and WDXRF)

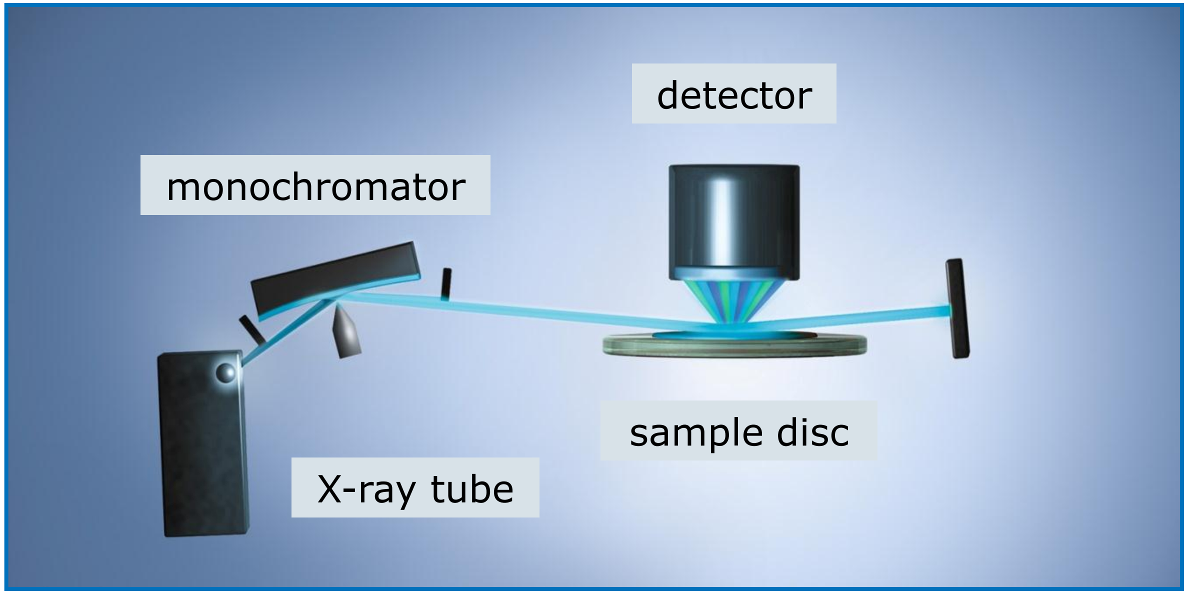
- Solids (cut, polished and put into suitable shape)
- Powders (as pressed pellets, fused beads
  or loose powders in liquid cups)
- Liquids (in liquid cups)

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

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

BRUKER

Total reflection X-ray fluorescence spectroscopy

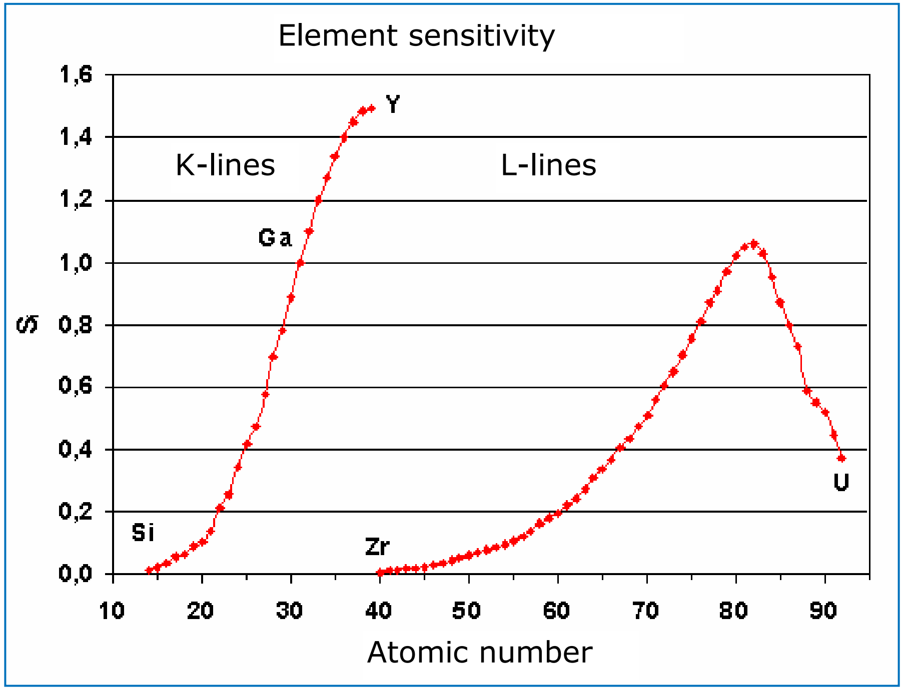


Beam angle: 1° / 90°

- 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

Principles of TXRF Quantification

$$C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i}$$



C_i: Element concentration

C_{IS}: Internal standard concentration

N_i: Element net count rate

N_{IS}: Internal standard net count rate

S_i: Element sensitivity factor

S_{IS}: Internal standard sensitivity factor

Principles of TXRF Quantification

Add internal standard to all blanks and samples

- Can compensate for (systematic and random) errors
- Standard should be similar to analyte in terms of instrumental response and concentration
- Standard should not be present in sample
- Good quantification and widely used

Principles of Total Reflection X-ray Fluorescence Spectroscopy

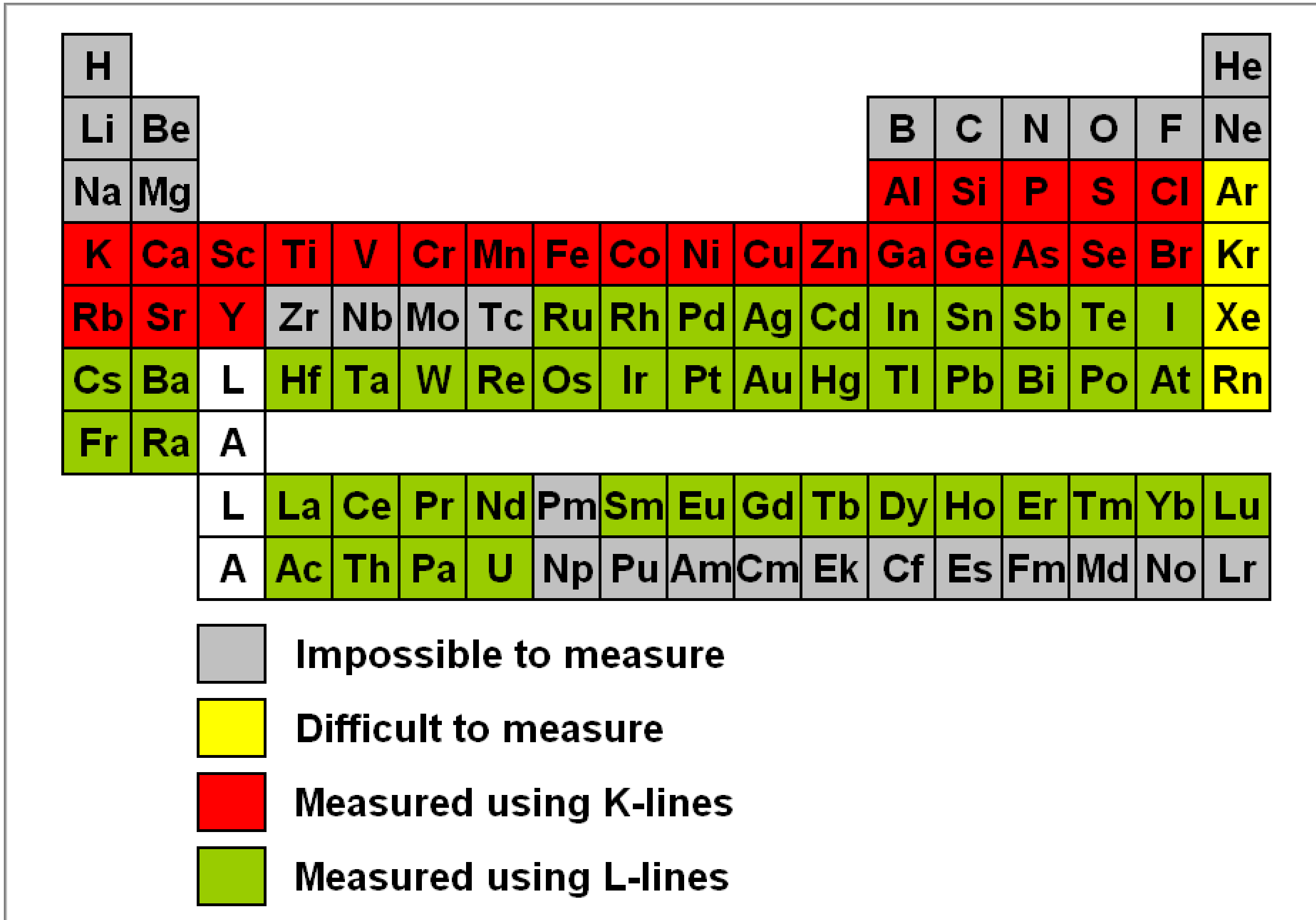
Samples for TXRF

- Powders: Direct preparation or as suspension
- Liquids: Direct preparation
- Always as a thin film, micro fragment or suspension of a powder
- Necessary sample amount: Low µg respectively µl range

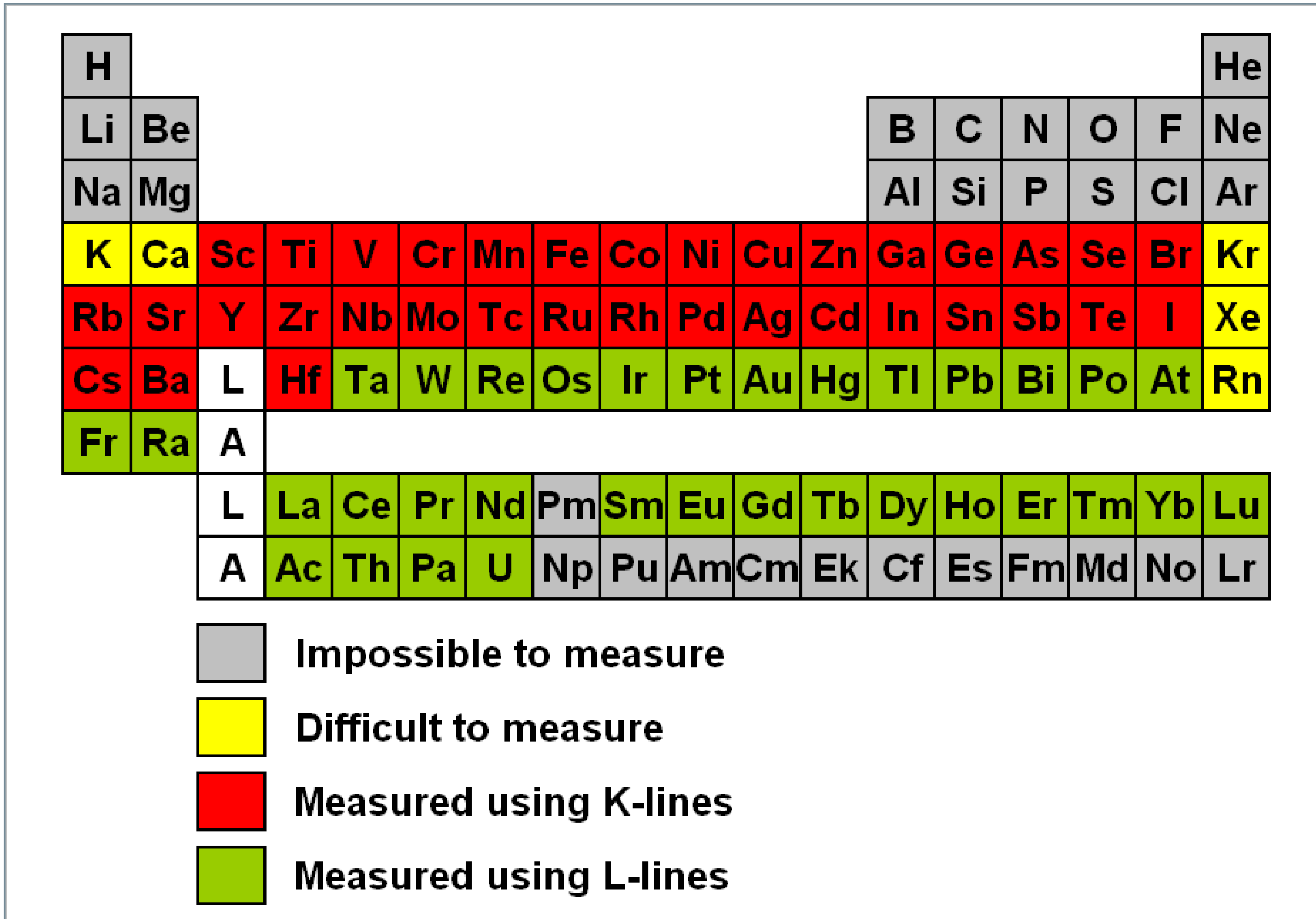
Simple quantification

- Matrix effects are negligible due to thin layer
- Quantification is possible by internal standardization

Elements Measured by the Mo PICOFOX



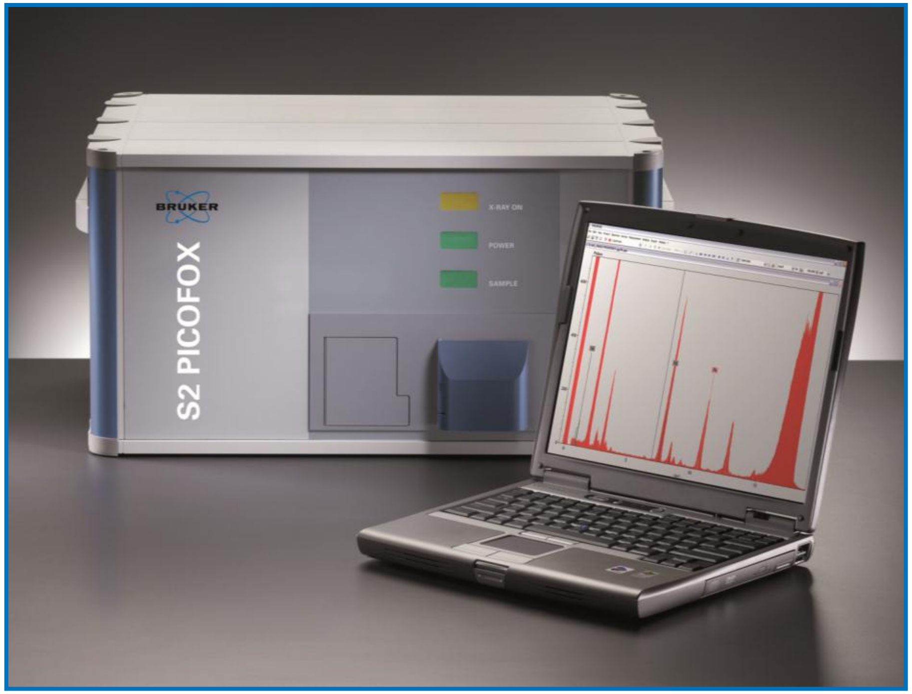
Elements Measured by the W PICOFOX



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



Analysis of 18-Year-Old Rum

Analyzing Rum

Sample

- Rum, 18 years old
- Analyzing for Pb and other heavy metals

Current method of analysis

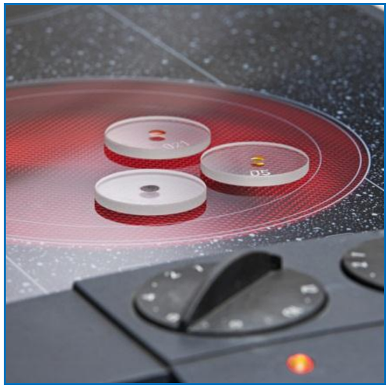
Flow-injection hydride-generation atomic absorption spectrometer with flame-quartz atomizer (FI-HG-AAS)

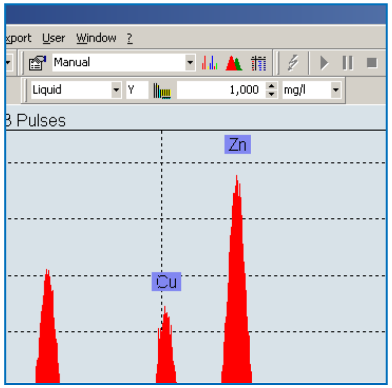
S2 PICOFOX TXRF spectrometer

Sample Preparation of Our Rum Sample

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

Sample Preparation
Final Steps

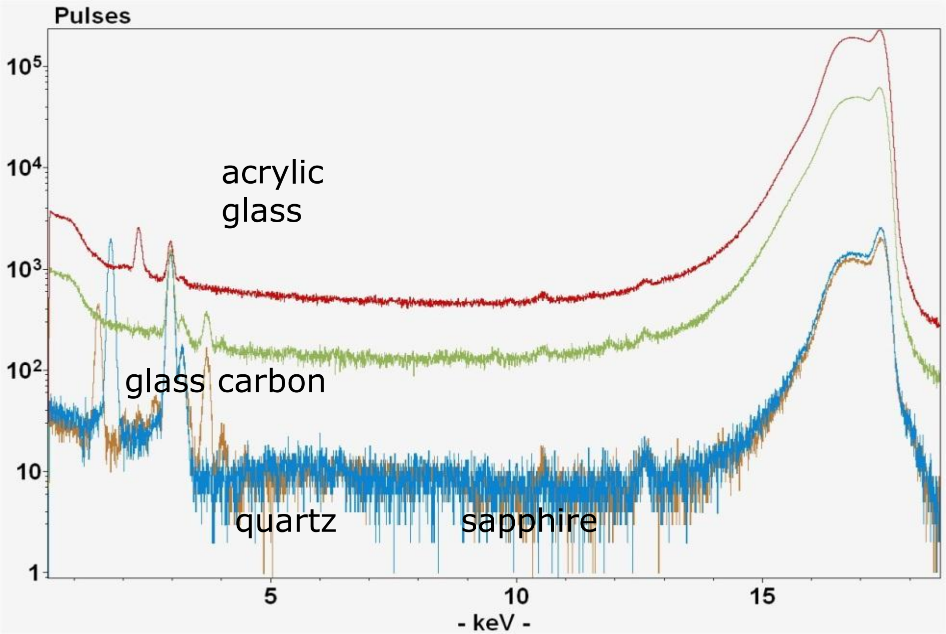




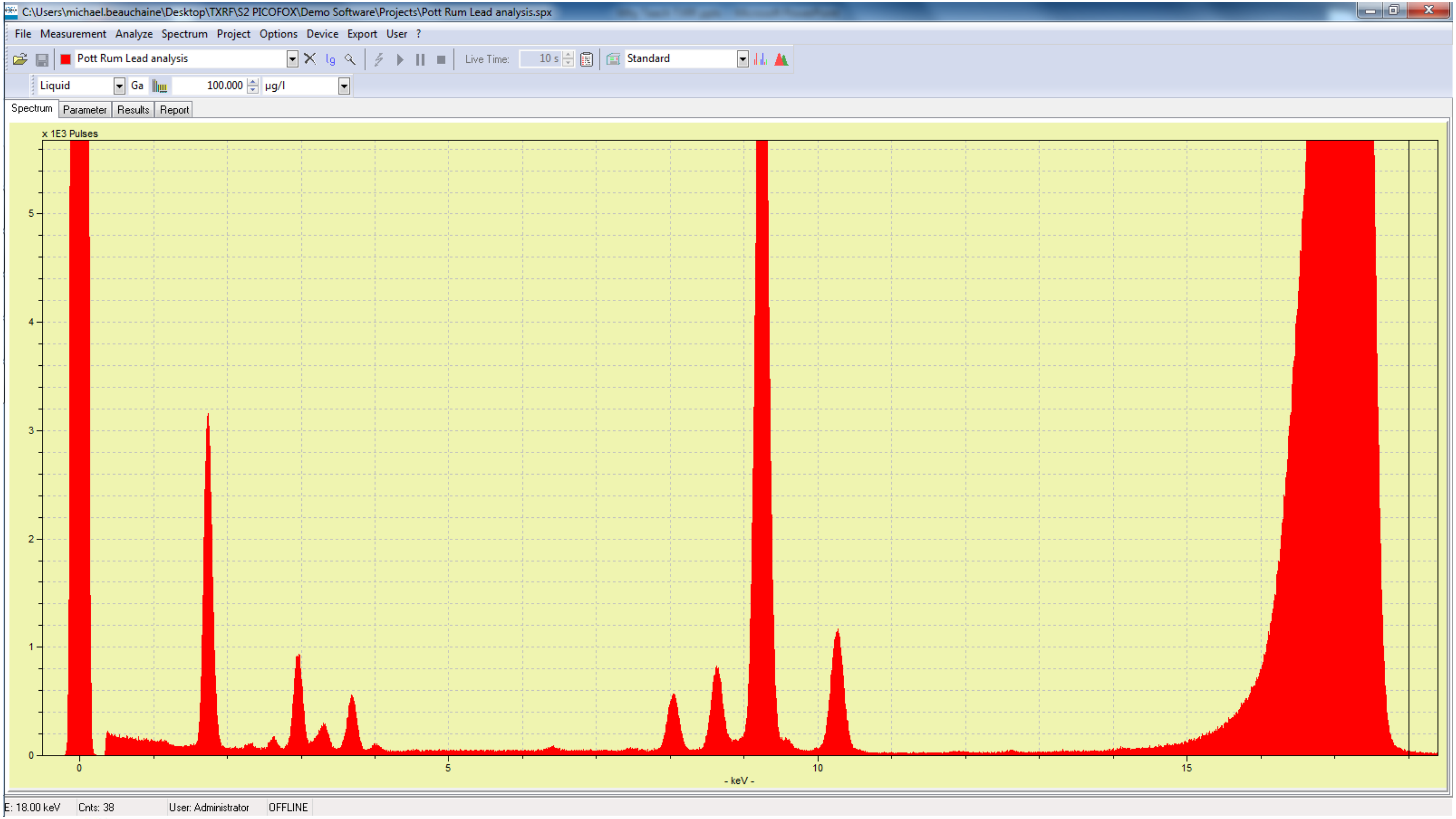
- dry by heat / vacuum
- load the instrument
- start data acquisition

Sample Carrier

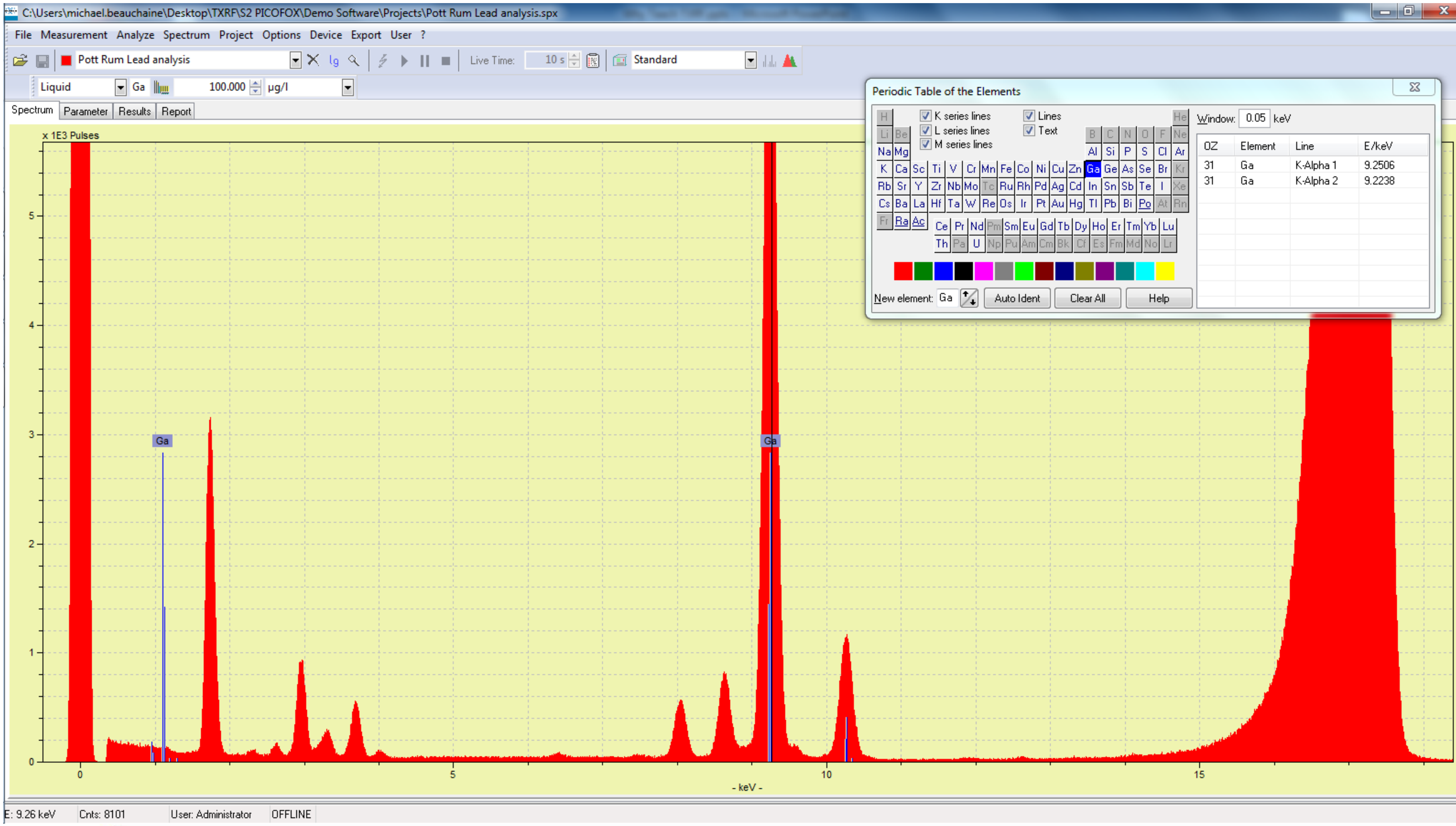
quartz glass | glass carbon | acrylic glass | sapphire



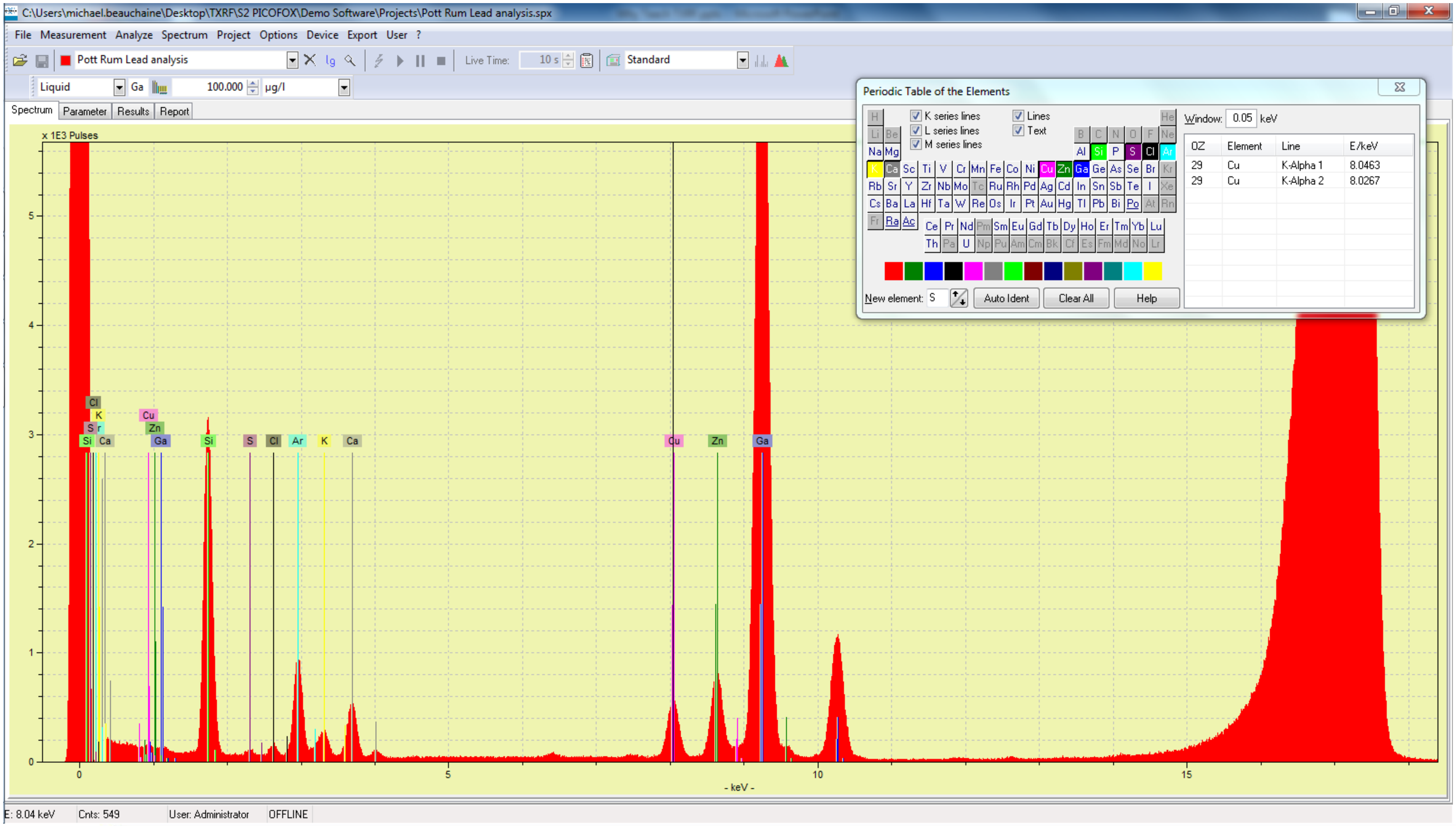
TXRF Rum Spectrum



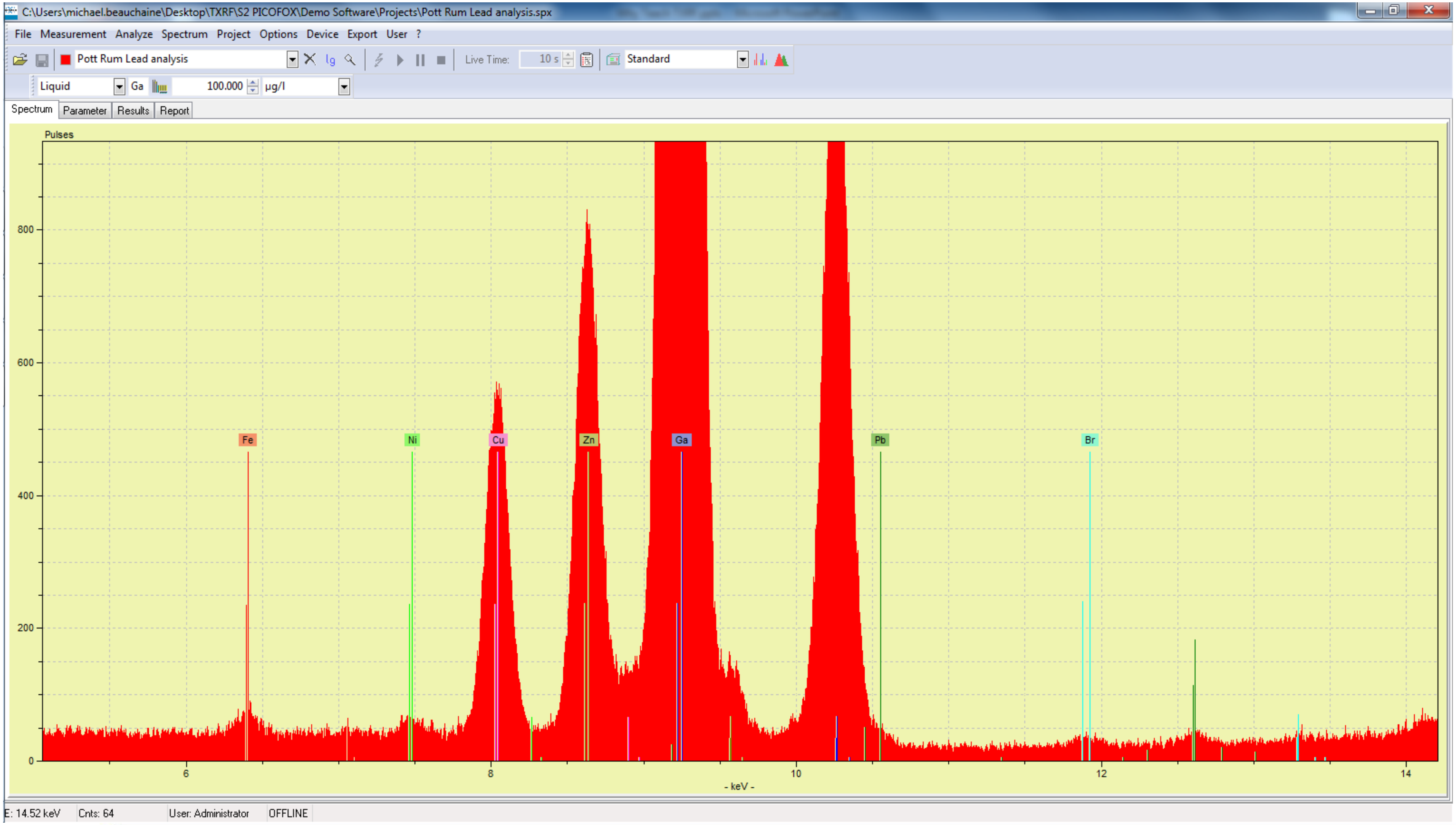
TXRF Rum Spectrum



TXRF Rum Spectrum



TXRF Rum Spectrum



TXRF Rum Results

C:\Users\michael.beauchaine\Desktop\TXRF\S2 PICOFOX\Demo Software\Projects\Pott Rum Lead analysis.spx

File Measurement Analyze Spectrum Project Options Device Export User ?

Pott Rum Lead analysis | Live Time: 10 s | Standard

Liquid | Ga | 100.000 | µg/l

Spectrum | Parameter | Results | Report

No.	Element	Line	Energy/keV	Cycl.	Net	Backgr.	Sigma	Chi	Conc./(µg/l)	SigmaC/(µg/l)	LLD/(µg/l)
1	Si	K12	1.740	51	78445	3439	292	0.90			
2	Cl	K12	2.622	251	3051	2323	88	0.95	30.774	0.889	1.459
3	Ar	K12	2.958	251	24841	2388	172	0.86			
4	K	K12	3.314	201	6393	2607	108	0.76	29.518	0.501	0.707
5	Ca	K12	3.692	301	14380	2268	138	1.22	33.620	0.326	0.334
6	Fe	K12	6.405	151	977	2902	82	1.45	0.654	0.055	0.108
7	Ni	K12	7.480	201	710	2988	82	1.20	0.327	0.038	0.076
8	Cu	K12	8.046	151	18976	3175	159	0.70	7.782	0.066	0.069
9	Zn	K12	8.637	251	28415	2804	184	0.95	10.026	0.066	0.056
10	Ga	K12	9.251	801	325234	2231	574	1.62	100.000	0.190	0.044
11	Ga	L1	1.098	1	1207	4797	104	5.63			
12	Br	K12	11.924	401	380	2247	70	0.76	0.084	0.015	0.031
13	Br	L1	1.481	51	464	3339	85	1.81			
14	Sr	K12	14.165	101	165	5479	105	1.08			0.045
15	Sr	L1	1.806	101	505	2868	79	1.07			
16	Mo	K12	17.480	1	985521	178077	1158	69.01			
17	Mo	L1	2.292	151	1688	2785	85	1.22			
18	Pb	L1	10.551	101	706	2089	70	1.37	0.249	0.025	0.048
19	Pb	M1	2.342	951	1	919	43	13.99			

TXRF Rum Results

Element	Energy/keV	Net	Backgr.	Sigma	Chi	Conc./(µg/l)	SigmaC/(µg/l)	LLD/(µg/l)
Si	1.74	78445	3439	292	0.9			
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Pb	10.551	706	2089	70	1.37	0.249	0.025	0.048

Principles of TXRF Quantification

$$C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i}$$

C_i: Element concentration

C_{IS}: Internal standard concentration

N_i: Element net count rate

N_{IS}: Internal standard net count rate

S_i: Element sensitivity factor

S_{IS}: Internal standard sensitivity factor

Other Sample Preparation Techniques

Sample Preparation
Suspensions

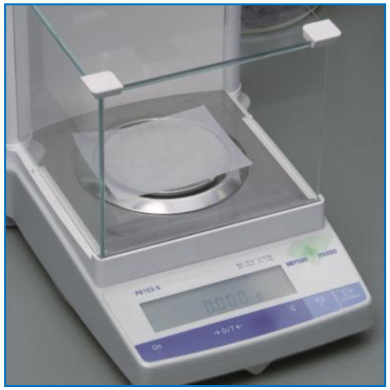
Suspensions can be analyzed just after dilution

- dilute sample with distilled water
- add internal standard
- homogenize
- pipette on carrier

Sample Preparation
Solid and Powder Samples I

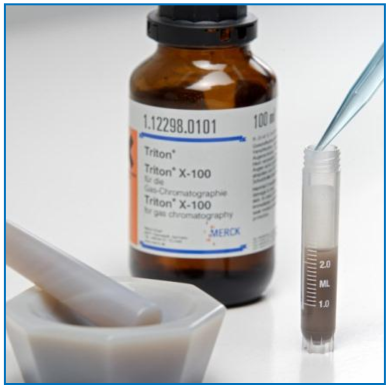
Solids are ground to fine particle size and resuspended for direct analysis without digestion






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

Sample Preparation
Solid and Powder Samples II




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

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

Application Examples

TXRF Applications
Blood, Serum and Urine Analysis

Introduction

- Analysis of nutrition-relevant elements (Cu, Fe, Zn, Se)
- Analysis of other toxic elements and Pt & Au (chemotherapy)

Task

- Analysis of whole blood and blood serum standards

Sample preparation

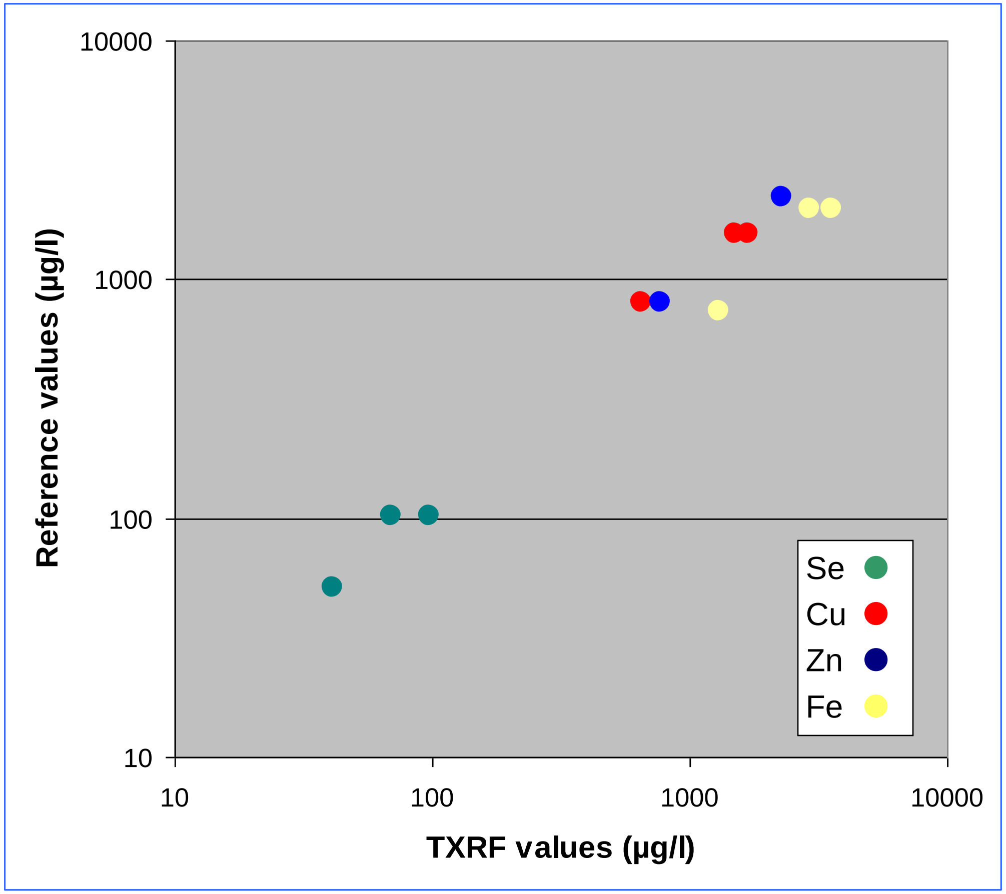
- Serum
    - 1:10 dilution with water (p.a. grade)
    - Addition of Ga for internal standardization
- Whole blood
    - 1:1 dilution with water (p.a. grade)
    - Addition of Ga for internal standardization

TXRF Applications
Blood, Serum and Urine Analysis

Results I

- Serum reference standard (t = 600 s)
- good correlation for Cu, Zn & Se
- overestimation of Fe improved calibration curve required

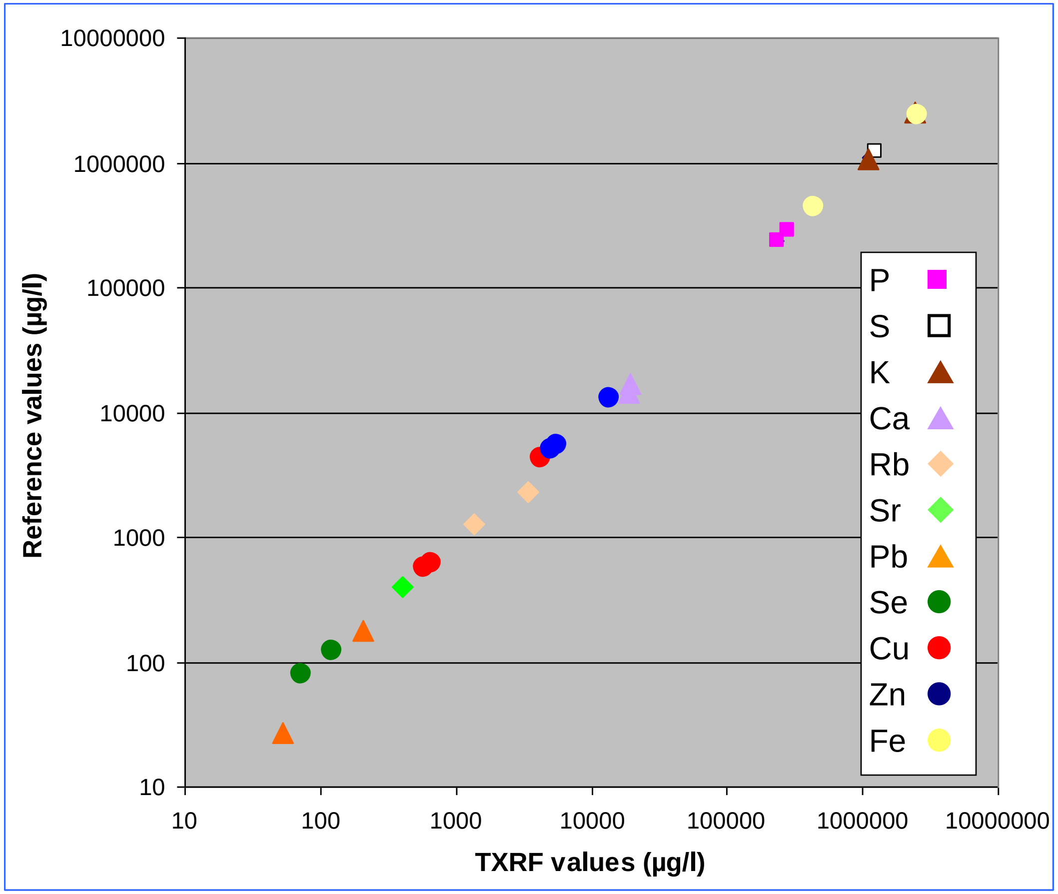
Note
Confidence level of reference values is up to 35 % (!)



TXRF Applications
Blood, Serum and Urine Analysis

Results II

- Whole blood reference standard (t = 600 s)
- application of optimized "blood calibration"
- excellent correlation for Fe, Cu, Zn, Se and others



TXRF Applications
Blood, Serum and Urine Analysis

Reproducibility

Precise TXRF results even without sample digestion

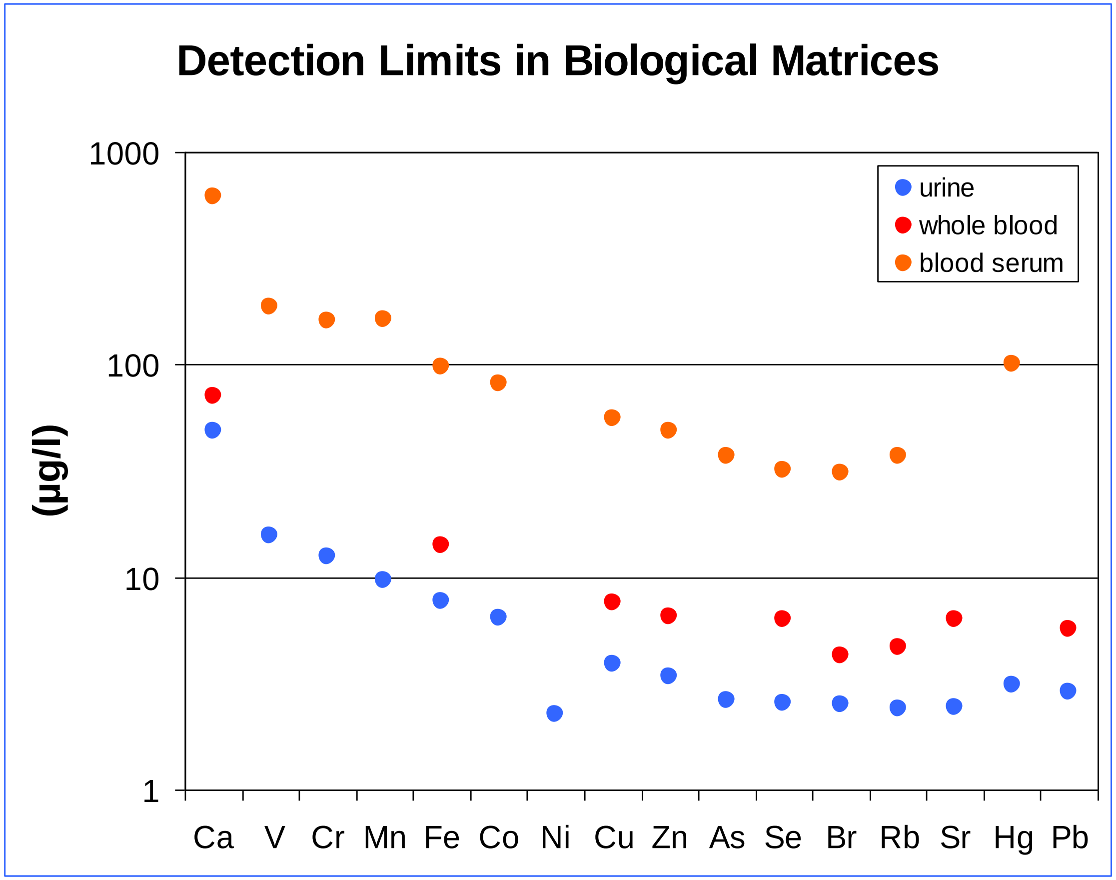
		Serum (ClinCheck L2)				Whole blood (Seronorm L2)			
Element	Unit	TXRF	Std. dev.	Reference [1)]	Std. dev.	TXRF	Std. dev.	Reference [2)]	Std. dev.
Fe	mg/l	440	7.4	435	12	2.9	0.09	1.964	0.20
Cu	µg/l	66	2.2	62	2.1	1685	43	1562	312
Zn	µg/l	501	4.9	504	6.9	2194	118	2225	334
Se	µg/l	12	0.29	12	1.0	97	18	102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

[1)]: Atomic Absorption Spectroscopy

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

TXRF Applications
Blood, Serum and Urine Analysis

Detection limits are in the low to middle ppb range



Water Monitoring with Bioindicators
Introduction

Bioindicators are biological species used to:

- Monitor the health and integrity of an environment or ecosystem
- Monitor for changes of metal pollutions in surface waters and sediments

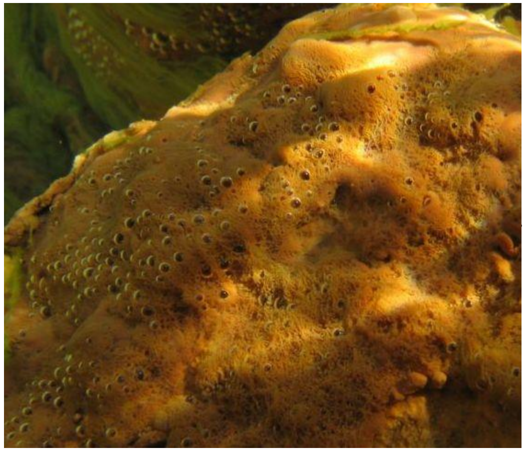
General questions

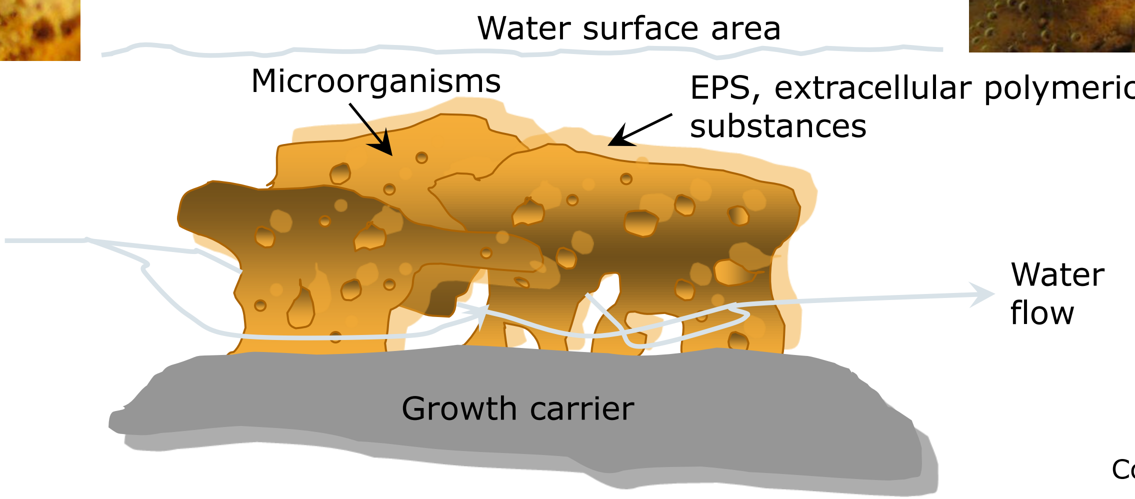
- Accumulation through the nutrition chain?
- Impact of sub-lethal metal concentrations?
- Methods for fast screening?

Water Monitoring with Bioindicators
What are Biofilms?

Dry sample
microscopy photo

Wet sample
underwater photo





Courtesy of UFZ Magdeburg

Significance of Biofilms

Negative impact of biofilms

- Bioaccumulation of harmful chemicals in aquatic systems
- Biogenic corrosion of metals, concrete etc.
- Biofouling in pipeline systems
- Germination of water pipelines
- Contamination with pathogens in hospitals

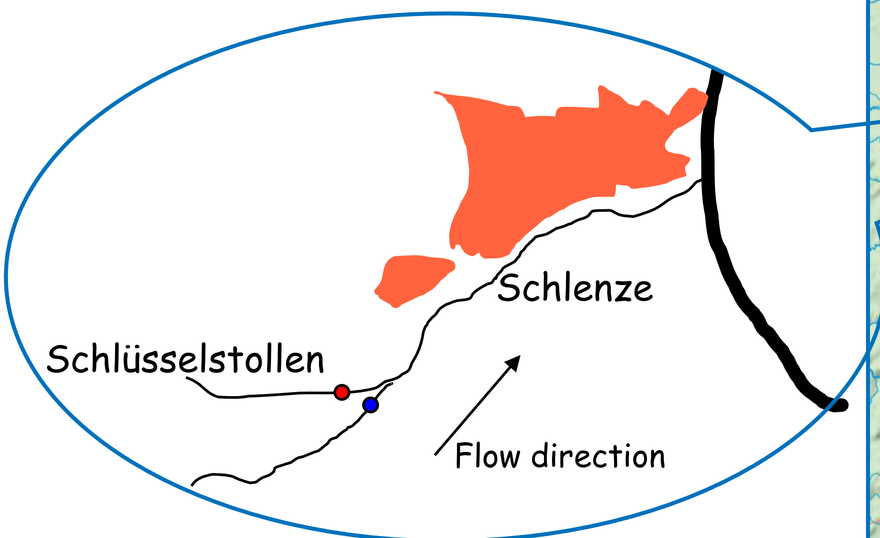
Application of biofilms

- Self-purification of waters
- Binding and removal of toxic materials
- Biotechnological use
- Removal of organics and N-compounds in wastewater treatment plants

Biofilms
Sampling Location

Elbe watershed

Harz mountain range mining area since bronze age



Courtesy of UFZ Magdeburg

Biofilms
Sampling Location

Upper Harz Water Regale

- System of dams, reservoirs, ditches
- Built from 16th to 19th centuries
- Drove water wheels of the mines
- In 2010 declared as a UNESCO World Heritage Site

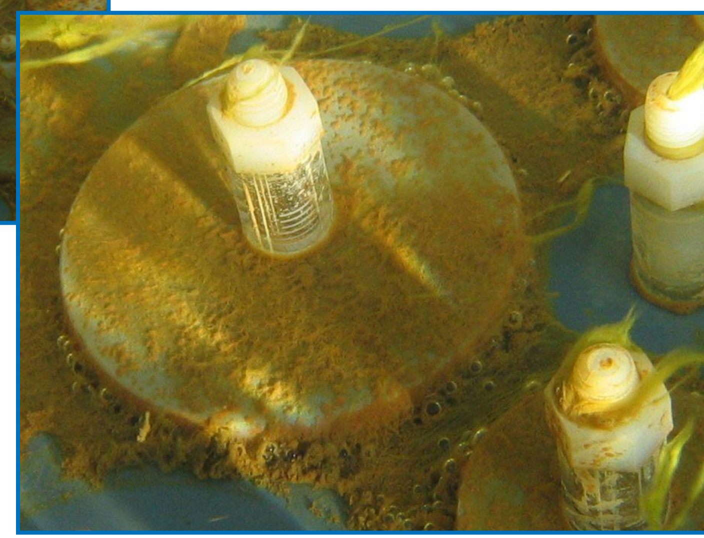
Sampling location “Schlüsselstollen”

- Gallery was built in 1879
- Drains the mining district at a length of 31 km

Courtesy of UFZ Magdeburg

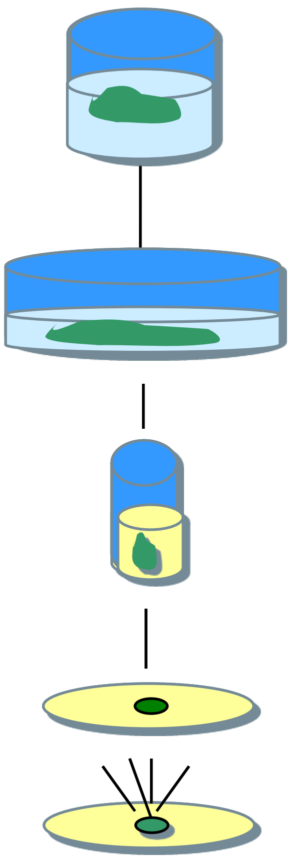
Biofilms
Sampling

Grown on round polycarbonate slide



Courtesy of UFZ Magdeburg

Biofilms
Sample Preparation for TXRF



- Sampling and transport (4°C)

- Rinse with clean water
- Freeze drying
- Homogenization

- Weighing ca. 500 µg at Ultrabalance
- Digestion with HNO_3/H_2O_2
- Internal standard Sc

- 10 µl sample aliquot

- Drying on a hot plate 80°C

Analysis with TXRF

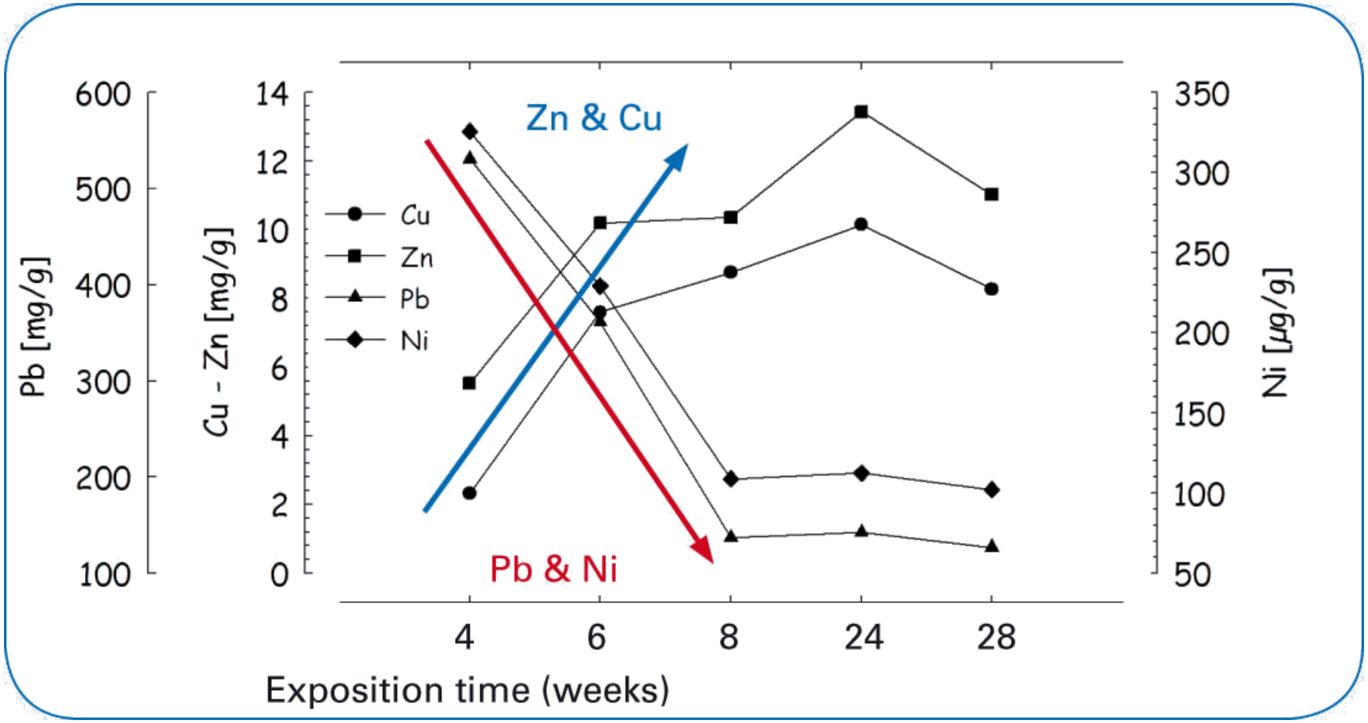
Accumulation Factors in Water and Biofilms

Element	Accumulation factor water*	Accumulation factor biofilm*
Pb	1400	2200
Zn	630	18
Cu	11	140
Ni	8	7

*) relation of gallery to creek water

Biofilms: Pb > Cu > Zn > Ni > Fe > Ca

Sorption Effects in Biofilms



- Immediate accumulation of Pb and Ni during growth
- Release during longer exposition
- Slow accumulation of Cu and Zn

Applications
Nanoparticle Characterization

Analytical question

- Element ratios in CdSe nanoparticles coated with ZnS

Analytical issues

- Extremely small sample amount (R&D)
- Non-destructive method preferred

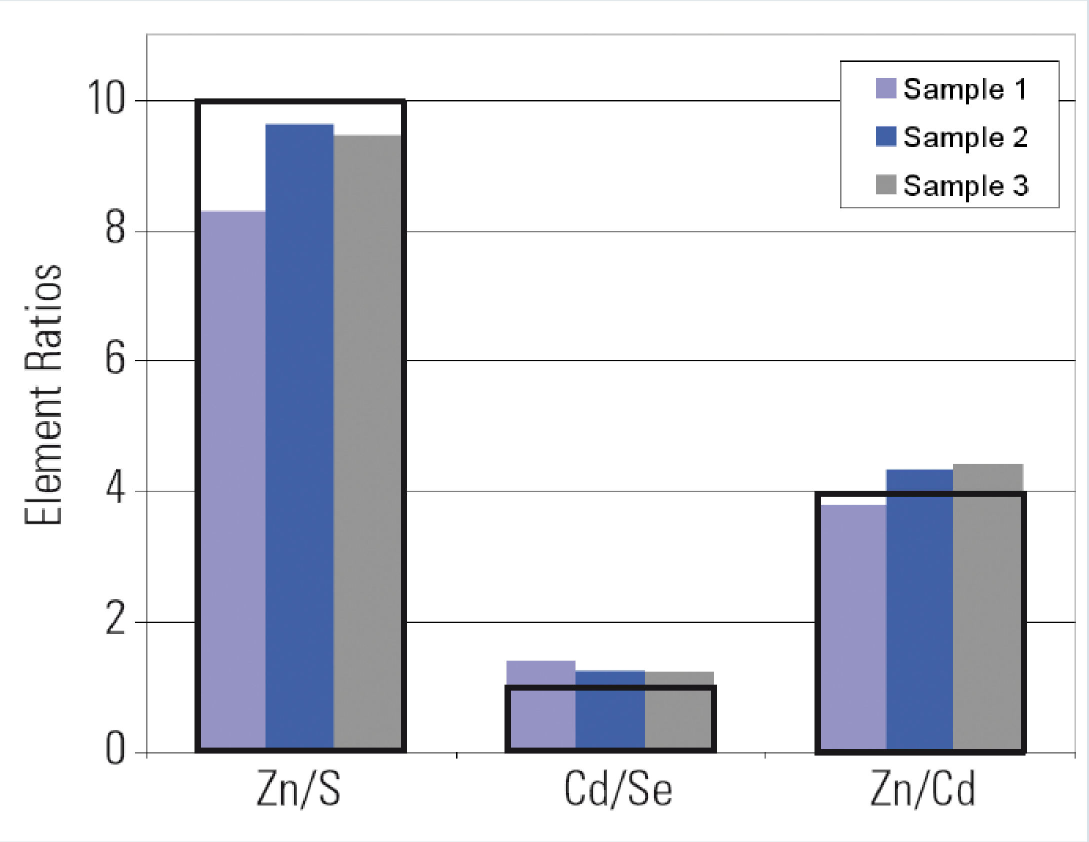
TXRF measurement

- Transfer of nanoparticles to quartz carrier by cotton bud
- Standardless quantification

Applications
Nanoparticle Characterization

Results

- Even smallest sample amounts allow the determination of element ratios in nanoparticles
- S2 PICOFOX "Standardless" analysis applied



Measured ratios of 3 samples versus target value (□)

Applications
Analysis of Nanoparticle Coating

Analytical task

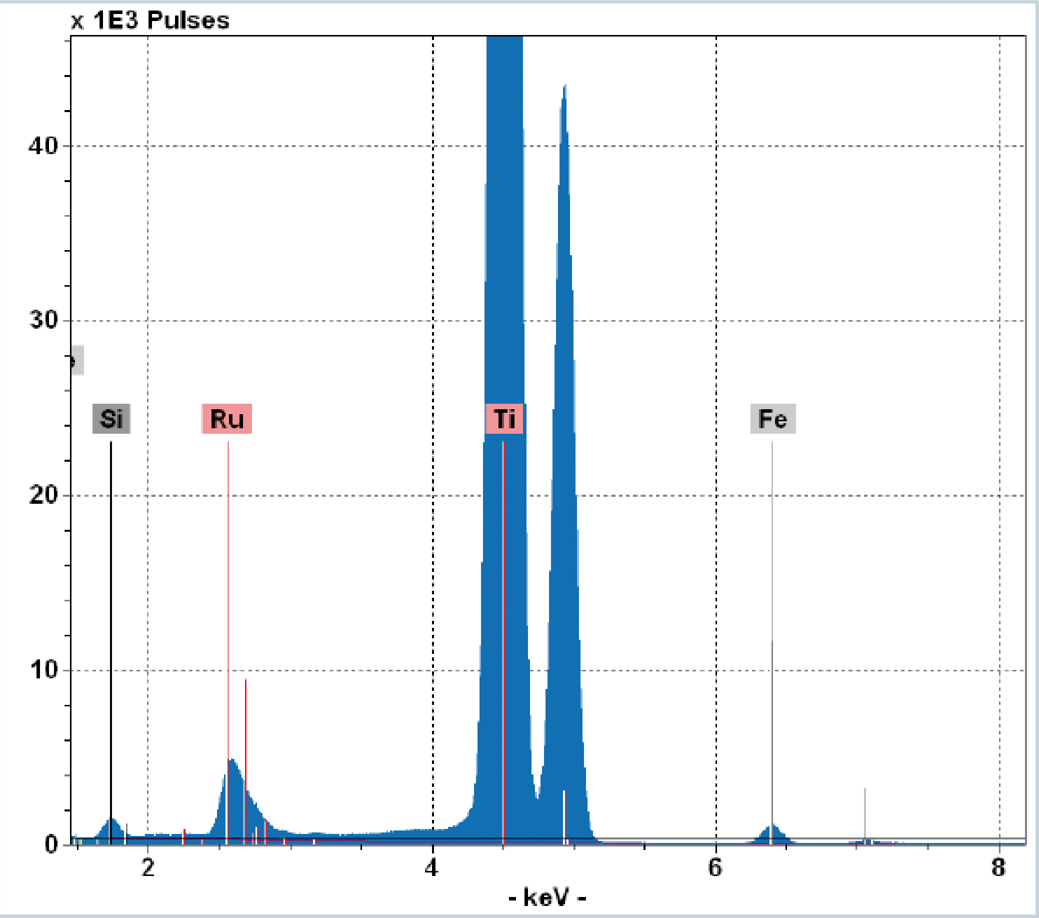
- Ru coating of TiO_2 nanoparticles

Sample preparation and measurement

- 40 mg resuspended in 2.5 ml Triton X-100
- Addition of Ga standard, homogenisation
- Transfer to quartz carrier, measuring time 120 s

Results

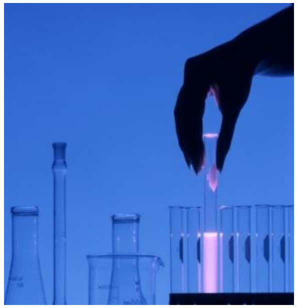
- The amount of Ru was calculated to 72 µg/l (ICP: 65 µg/l)



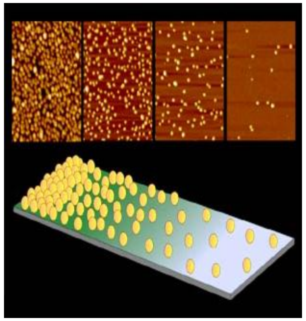
Studying Trace Elements

Studying Trace Elements

Courses where TXRF is used



Analytical Chemistry



Materials Research

Environmental Chemistry

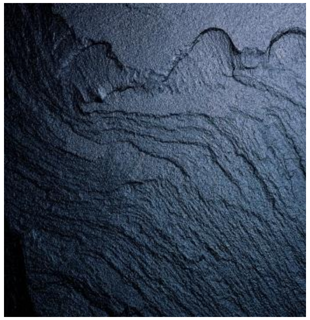
Forensics

Botany

Physics

Biology

Undergraduate & Graduate Research



Geology

Comparison
TXRF versus AAS & ICP-OES

Sample application

	TXRF	ICP-OES	AAS
Direct analysis of solids	Qualitative, quantitative with lower sensitivity	not possible	GF-AAS only
Sample amount	ng to µg range	mg range	mg range GF-AAS µg range

Comparison
TXRF versus AAS & ICP-OES

During operation

	TXRF	ICP-OES	AAS
Multielement analysis	Yes	Yes	Sequential only
Standardless	Yes (with restrictions)	Yes	No
Meas. time	300 – 1000 s	<10 s per element	<10 s per element
Calibration	Internal standardization	External, element-specific, to be updated	External, element-specific, to be updated

Comparison
TXRF versus AAS & ICP-OES

Cost of operation

	TXRF	ICP-OES	AAS
Consumables	(X-ray tube)	(Nebulizer parts)	Cathode lamps
Power consumption	Low (150 W)	High (HF generator 2.5 – 3.6 kW)	Low
Water consumption	none	> 0.5 l/min	~1.5 l/min (GF only)
Gas consumption	none	Carrier/burning gas (Ar, N_2), 15-20 l/min	FAAS: burning gas (C_2H_2), 1.5-8 l/min GF: Carrier gas (Ar, N_2)

Comparison
TXRF versus AAS & ICP-OES

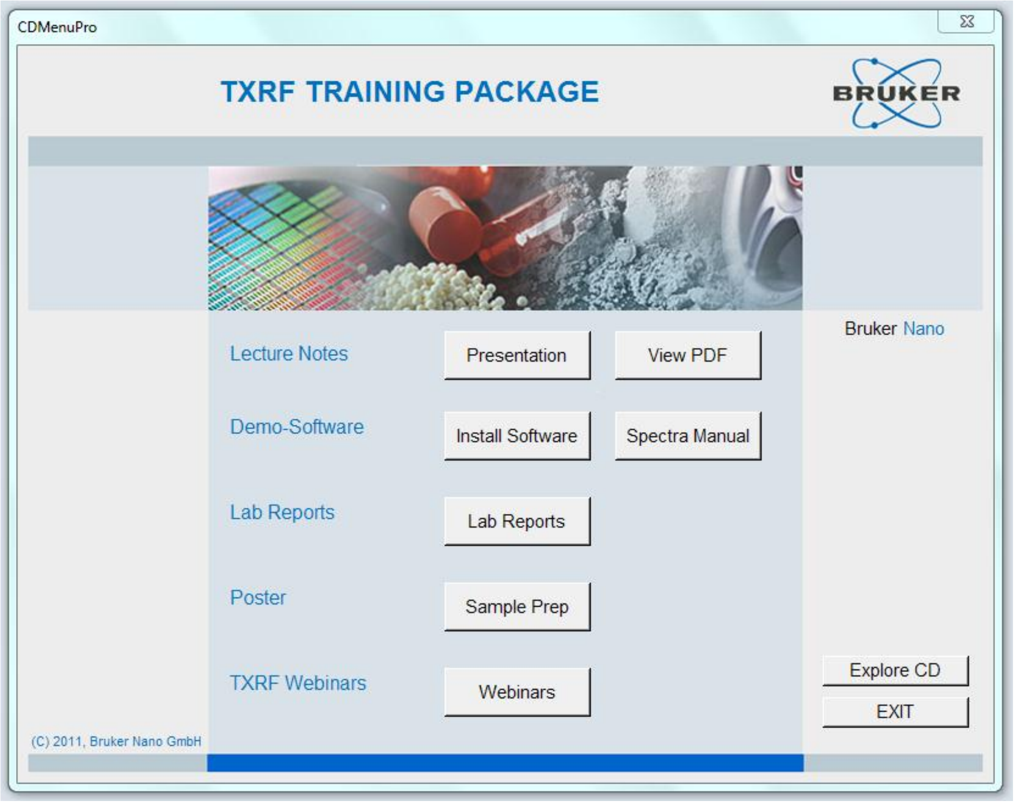
Other practical issues

	TXRF	ICP-OES	AAS
Method recognition	Low	High	High
Maintenance needs	Low	High	Medium
Instrument size and weight	Compact benchtop 37 kg	Large benchtop 190 – 290 kg	Benchtop 30 – 200 kg
Mobile use	Yes	Impossible	Hardly possible
Online (LC)	no	yes	

Benefits of TXRF for Education and Research

- Low cost-of-ownership
- Little to no maintenance
- Fast learning curve
- Wide range of applications
- Great publication opportunities
- Benefits of teaching XRF
  with trace element analysis capabilities
- Multiple references
- NO NEED FOR ACID DIGESTION!
- Comes with Bruker TXRF Training Package
  - Free software for students
  - Example data
  - XRF PowerPoint slides for Professors

TXRF Training Package



- TXRF training package includes
    - Free software
    - Example data
    - Lab Reports
    - Lecture slides
    - Sample prep poster
    - Webinars
- Free to university customers

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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Webinar	Content
Nov 20, 2012 **TXRF for Trace Element Analysis of Air, Land and Water**	This one-hour live webinar demonstrates the capabilities of TXRF for trace element analysis of air (aerosol and filters), land (soils and sediments), and water (fresh and effluents). Learn about level of detection, ease-of-use, regulated analysis, and advantages of TXRF in various, everyday environmental applications. Register now

Webinar	Content
Dec 13, 2010 **Trace Element Analysis of Industrial Wastewater and Sewage with TXRF and ICP-MS**	Join Mike Beauchaine and Andrew Toms as they present the capabilities of TXRF and ICP-MS for trace element analysis of wastewater. Learn about the combined advantages of the two techniques for routine, industrial and mobile lab testing. View recording Download slides

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Cast Expo – St. Louis, MO - Apr 6-9

ACS Spring – New Orleans, LA - Apr 7-11

ICDD XRF Clinic – Newtown Square, PA - Apr 29 - May 3

AISTech – Pittsburgh, PA – May 6-9

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