

TXRF for Trace Elemental Analysis of Air, Land, and Water



Bruker AXS Inc., Madison, WI, USA
November 2012

A blue-themed graphic illustrating TXRF technology. It features a periodic table of elements with various elements highlighted in white text on dark blue blocks. A central X-ray fluorescence spectrum shows peaks for elements like V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, and Kr. The text "XFlash® Technology" is prominently displayed. The acronym "TXRF" is written in large, white, sans-serif letters on the right. At the bottom, a schematic shows an X-ray source, a sample, and a detector, with a beam of light representing the X-ray path.

XFlash® Technology

TXRF

Ca Sc Ti
Sr Y Zr
Ba La Hf
Ra Ac

V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

0.8
0.6
0.4
0.2
0.0

6 8 10 12 -keV-

Cr Fe Ni Cu Zn Ga Ge As Se Br Kr

Mo Mn Cd In Sn Sb Te I Xe

V Nb Ta

Al Si P S Cl Ar

K α K β
L α L β
M α M β

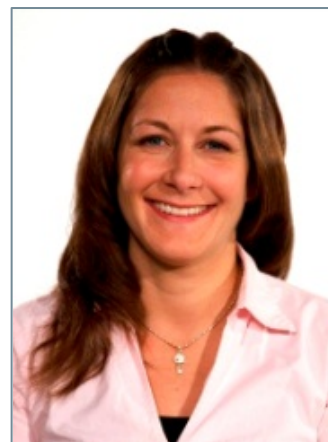
Welcome



Today's Topics

- Introduction to TXRF and principles of X-ray fluorescence spectroscopy
- Sample preparation of liquids, solids, and filters
- Examples of Environmental applications
- Comparison with atomic spectroscopy methods
- Question and Answer

Speakers



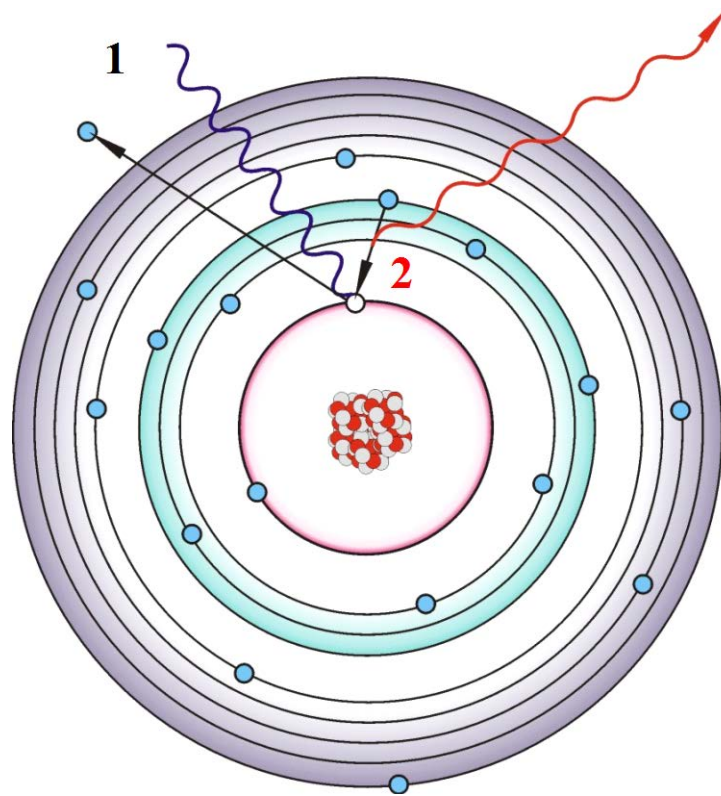
Kristin Odegaard
XRF Technician
Madison, WI, USA



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Product Manager TXRF
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

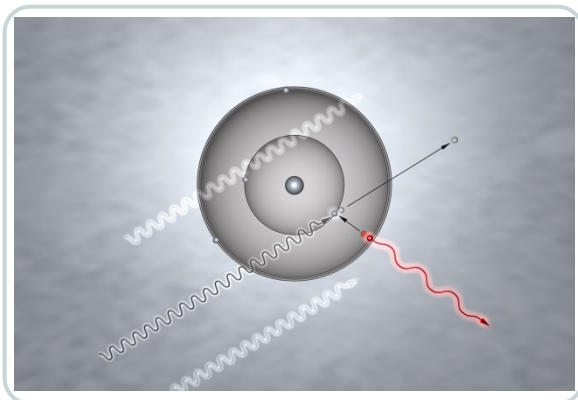


- The energy, and therefore the wavelength, of the X-ray fluorescence radiation is characteristic for the different chemical elements.

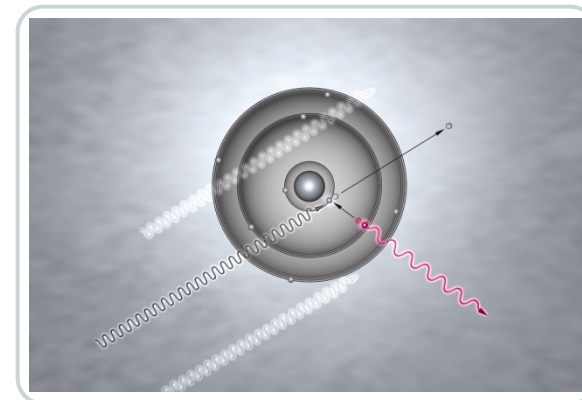
QUALITATIVE ANALYSIS

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

QUANTITATIVE ANALYSIS



Low Z



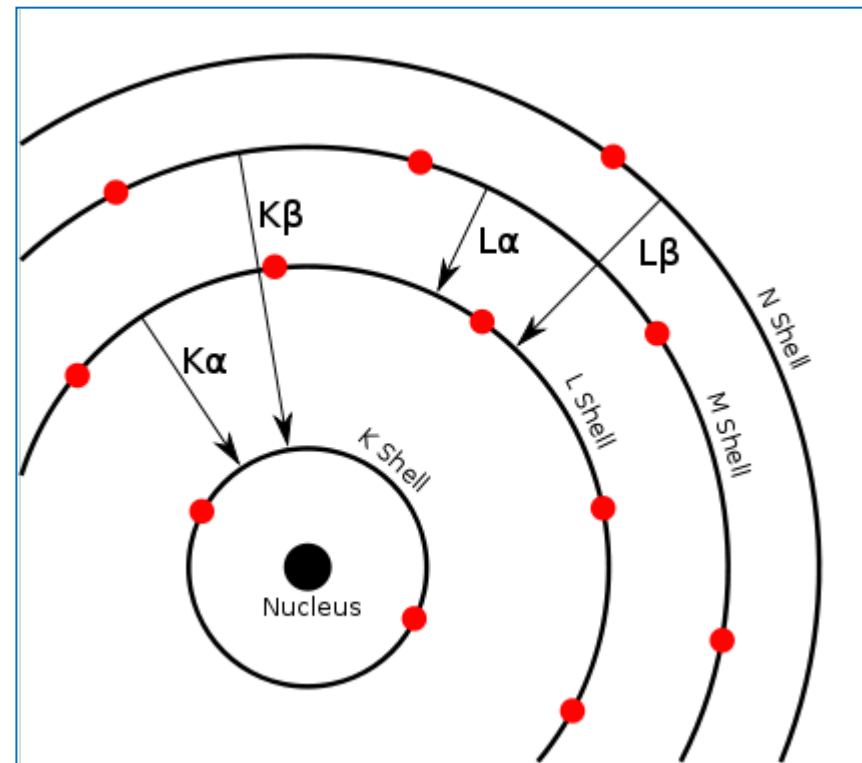
High Z

Principles of X-ray fluorescence (XRF) spectroscopy

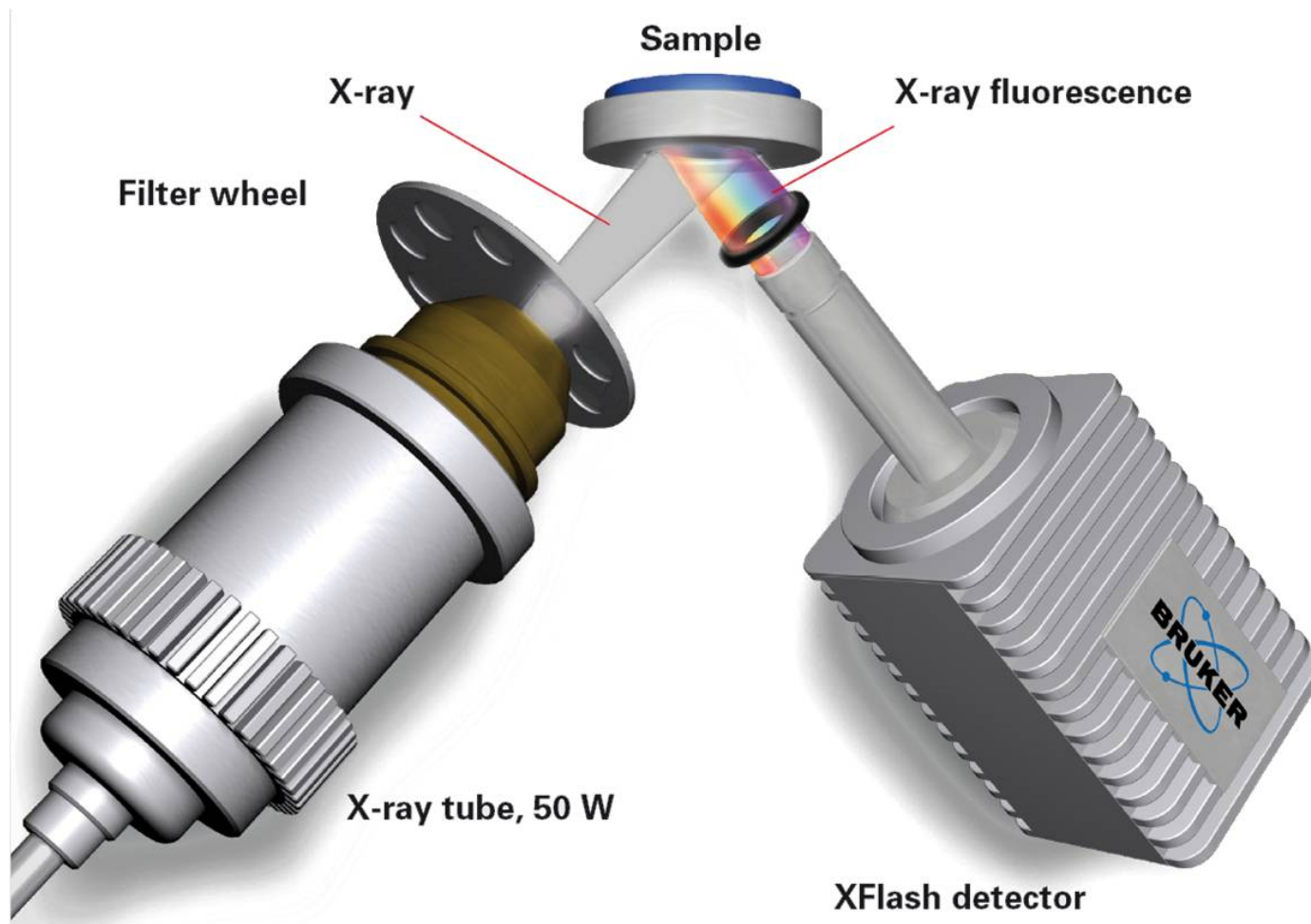


Each element shows a specific line pattern in a spectrum depending on the orbitals involved

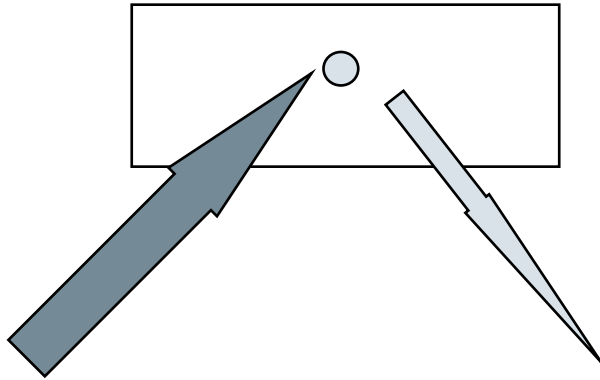
- L→K transition = $K\alpha$ line
- M→K transition = $K\beta$ line
- M→L transition = $L\alpha$ line
- N→L transition = $L\beta$ line



Traditional EDXRF



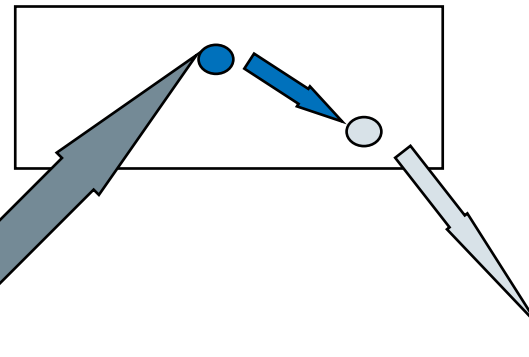
Traditional EDXRF Quantification



absorption of primary beam
and fluorescence radiation

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

and



secondary fluorescence
enhancement

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

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)

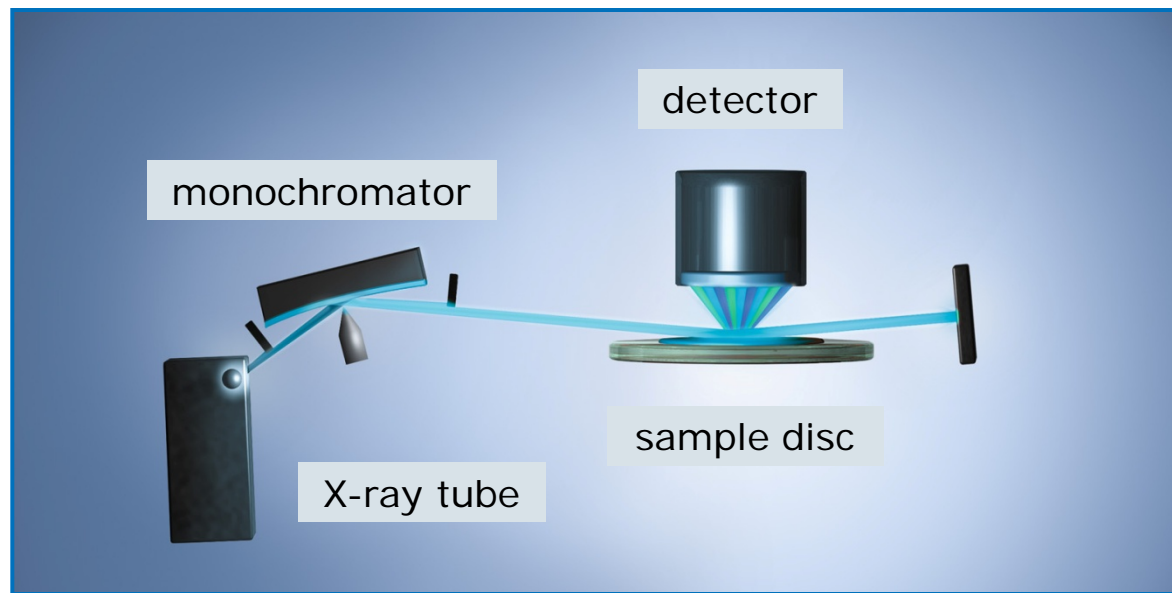
Necessary sample amount: from 1 g to 10 g!!



Principles of total reflection X-ray fluorescence (TXRF) spectroscopy



Total reflection X-ray fluorescence spectroscopy



Beam angle: $0.1^\circ / 90^\circ$

- 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

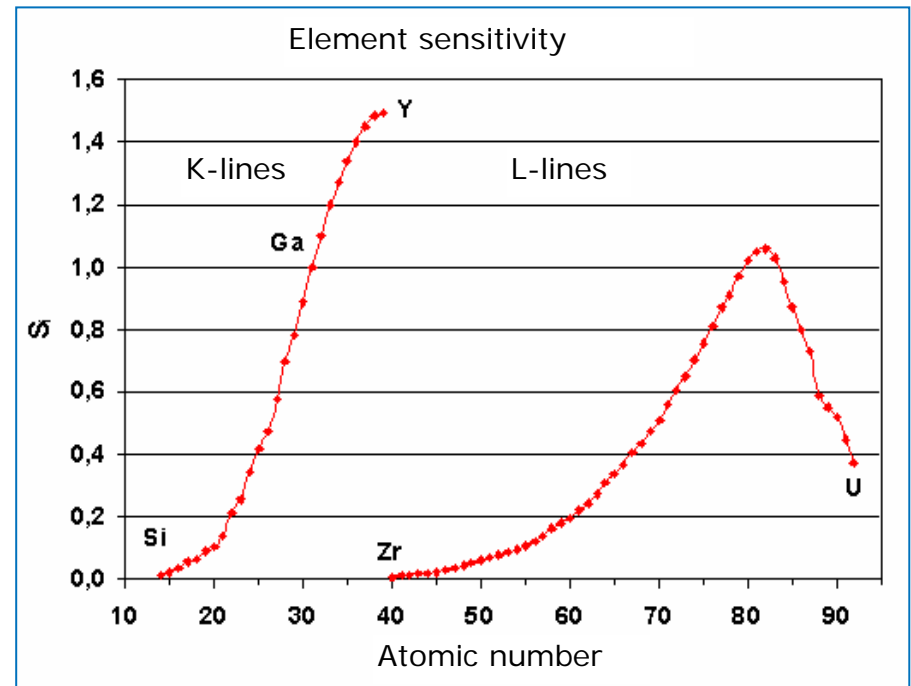
C_{IS} : Internal standard concentration

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

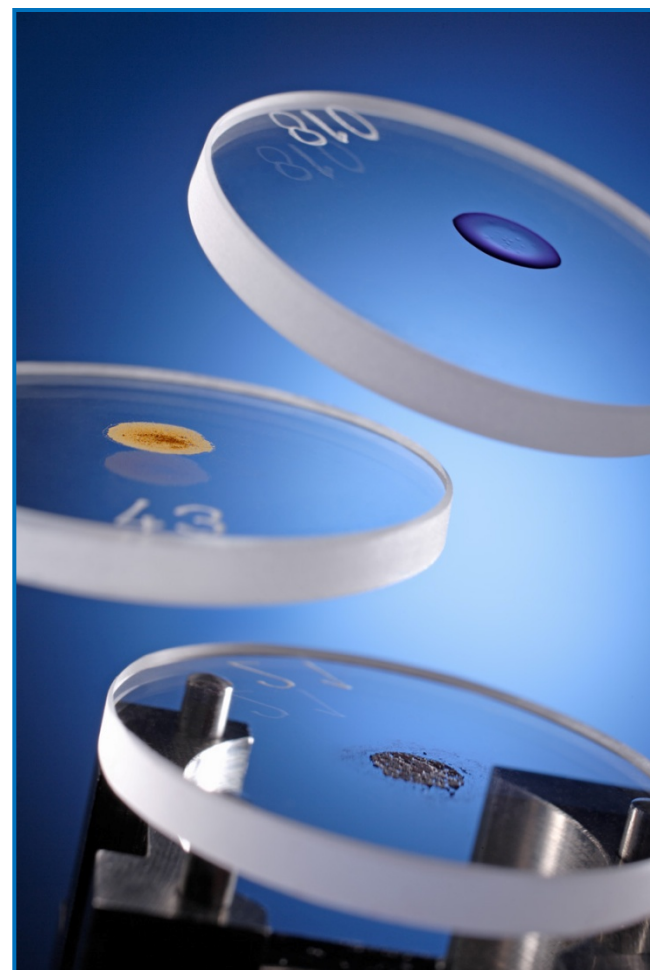


Samples for TXRF

- 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



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Ek	Cf	Es	Fm	Md	No	Lr

- Impossible to measure
- Difficult to measure
- Measured using K-lines
- Measured using L-lines

Elements measured by the W PICOFOX



H																He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Ek	Cf	Es	Fm	Md	No	Lr

- Impossible to measure
- Difficult to measure
- Measured using K-lines
- Measured using L-lines

The instrument S2 PICOFOX

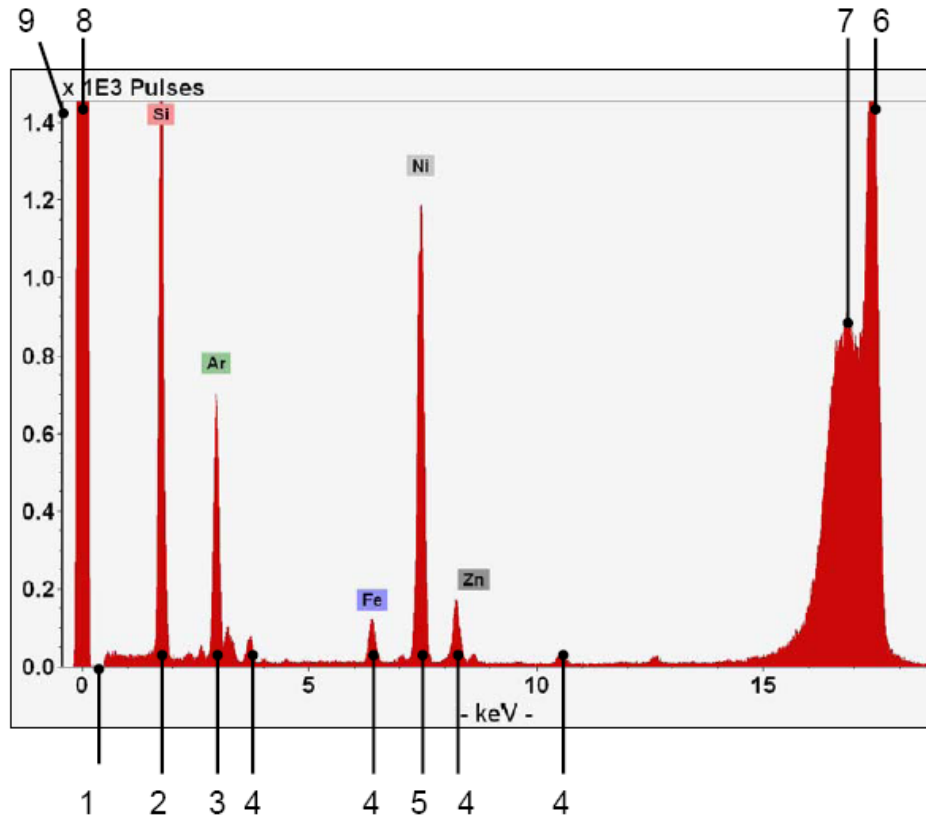


Benchtop TXRF spectrometer S2 PICOFOX

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



Our first spectrum!



1. Start of spectra
2. Si fluorescence peak of quartz glass
3. Ar fluorescence peak from air
4. Fluorescence peaks of the elements Ca, Fe, Zn, and Pb
5. $K^{\alpha 1,2}$ –fluorescence peak of the 1-ng-Ni sample
6. Characteristic Mo line from X-ray tube
7. Compton- and Rayleigh scattering peaks
8. Artificial 0 keV peak
9. Pulse scale (counts)

Evaluation of measurement data

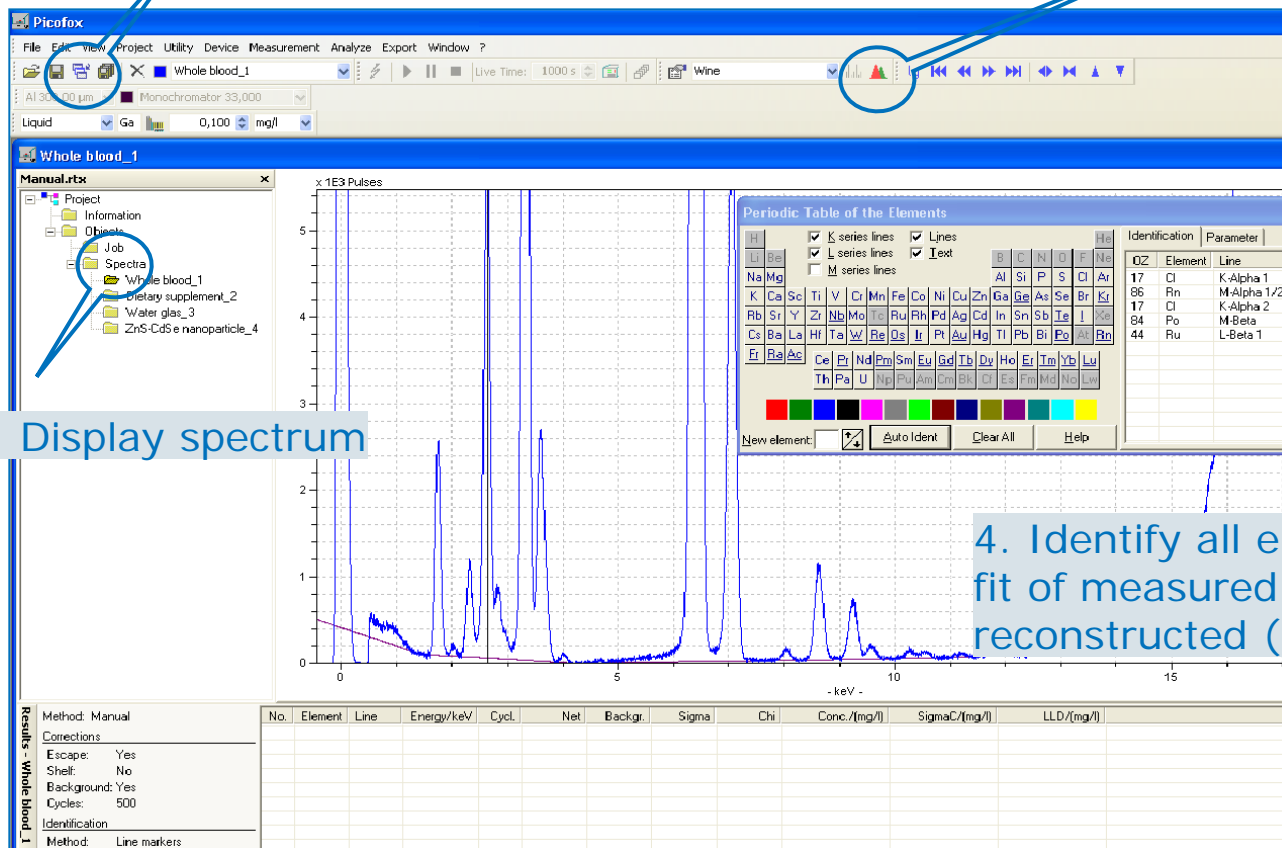


1. Open project

3. Open PSE window

2. Display spectrum

4. Identify all elements for optimum fit of measured (blue) and reconstructed (black) spectrum



Demo software available free of charge!



Sample Preparation

Sample Carrier

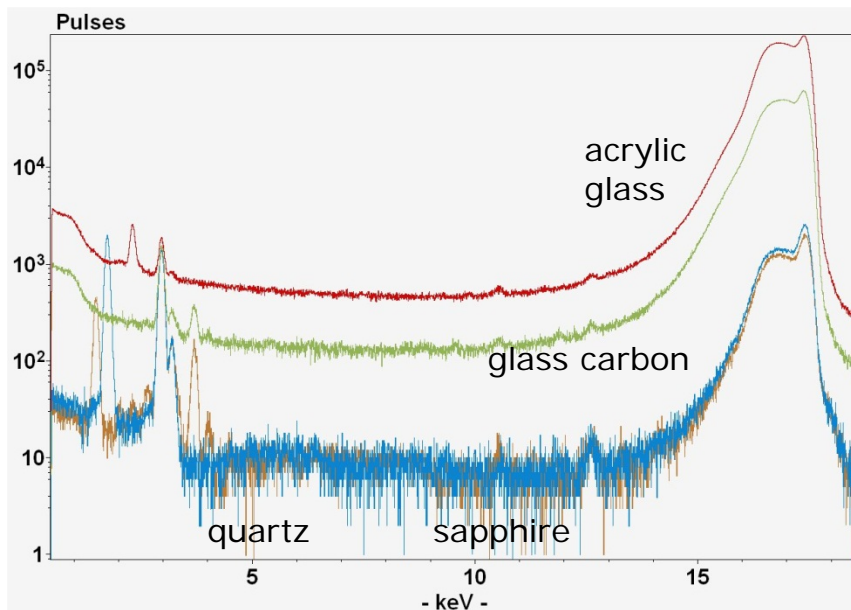


quartz glass

glass carbon

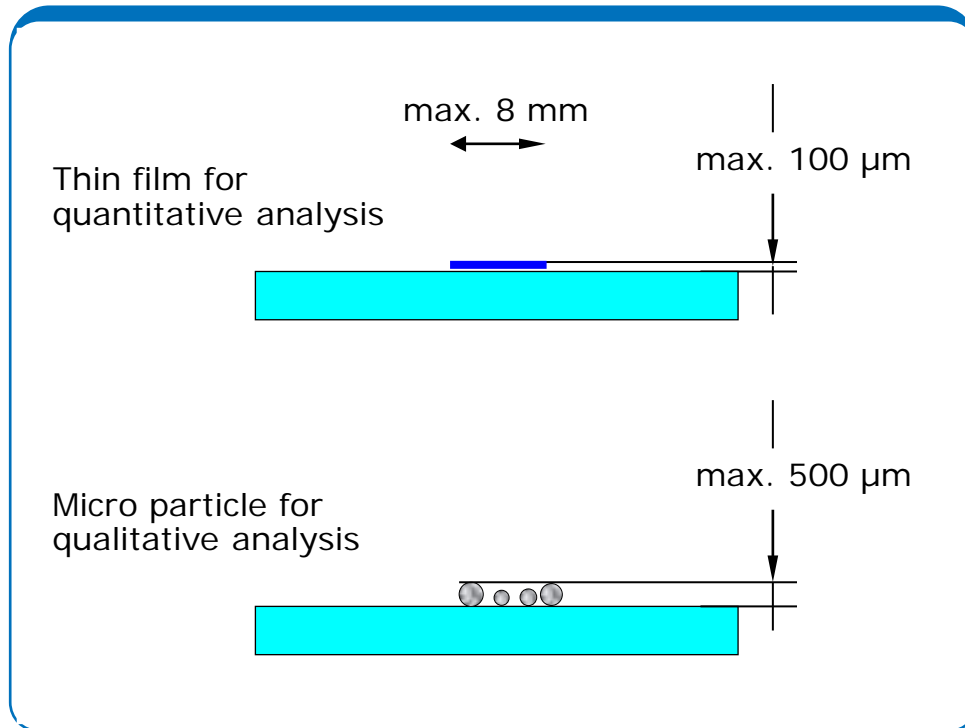
acrylic glass

sapphire



Chemical TXRF

Sample preparation



Basics

Samples for TXRF analysis must be prepared as thin films or micro particles

Sample preparation

Liquid and digested samples



You'll need just a few steps for the preparation of liquid samples



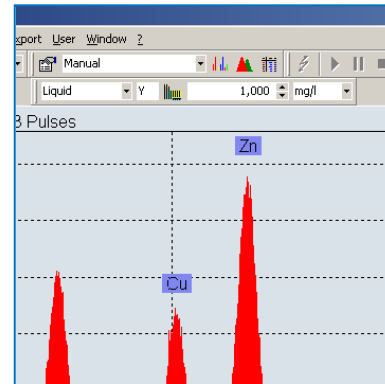
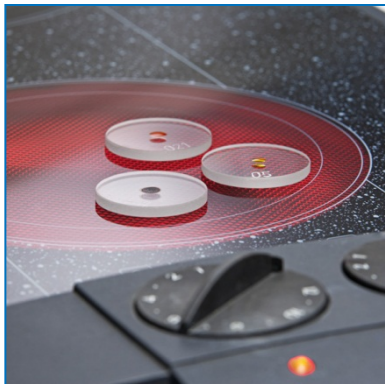
- fill sample in micro tube
 - add internal standard
 - homogenize

Note: high matrix samples may require a dilution step

- pipette on carrier

Sample preparation

Final steps



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

Sample preparation

Suspensions



Suspensions can be analyzed right after dilution



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

Sample preparation

Solid and powder samples I



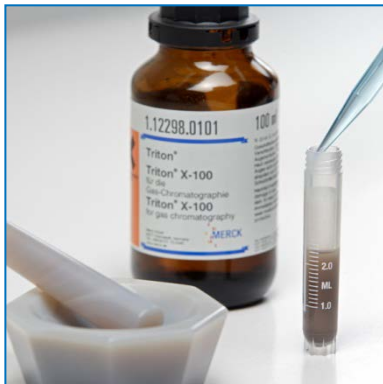
Solids are ground to fine particle size and resuspended for direct analysis without digestion



- fill powder in mortar
 - grind carefully ($<50\ \mu\text{m}$)
 - weigh about 20-50 mg
 - transfer to tube

Sample preparation

Solid and powder samples II



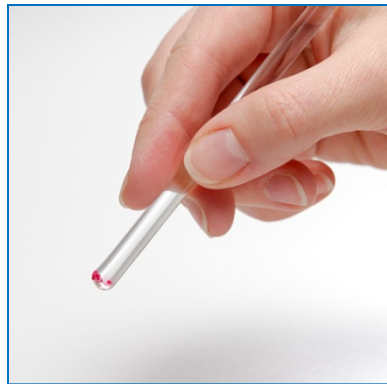
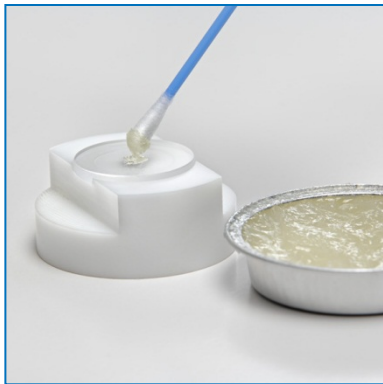
- suspend in detergent solution
 - add standard
- homogenize
- pipette on carrier

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

Audience Poll



Please use your mouse to answer the question on your screen:

What type of instrumentation do you currently use for elemental analysis of environmental samples (check all that apply):

- ICP-MS
- ICP-OES
- AAS
- ED-XRF
- WD-XRF
- TXRF
- Other



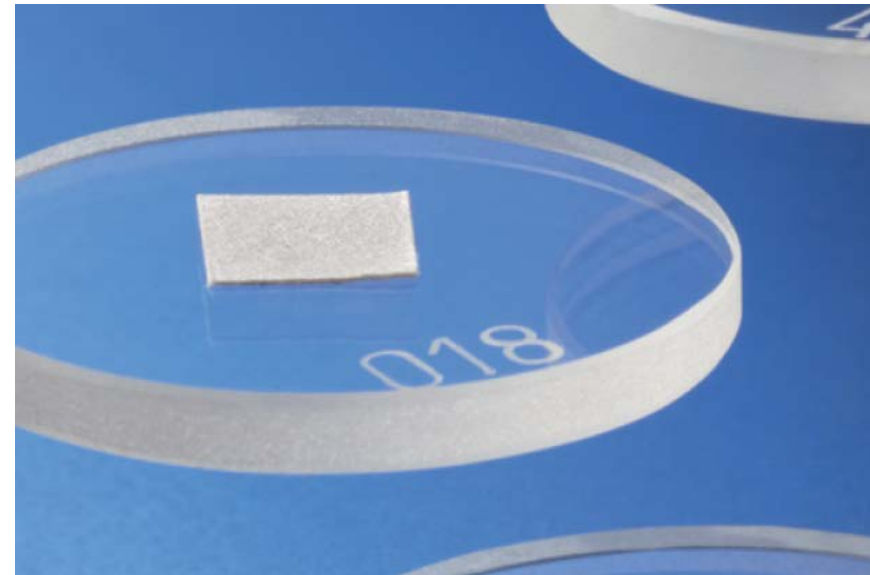
Air – Heavy Metals in Aerosols

Analysis of Filter Samples

Introduction



- Analysis of filters is crucial for environmental and health
 - Grain Size
 - Organics
 - **Heavy Metals**
- No requirements for time consuming digestions
- Fast non-destructive analysis of Al-U from emissions
- Filter samples collected from various European sources from a Cascade Impactor



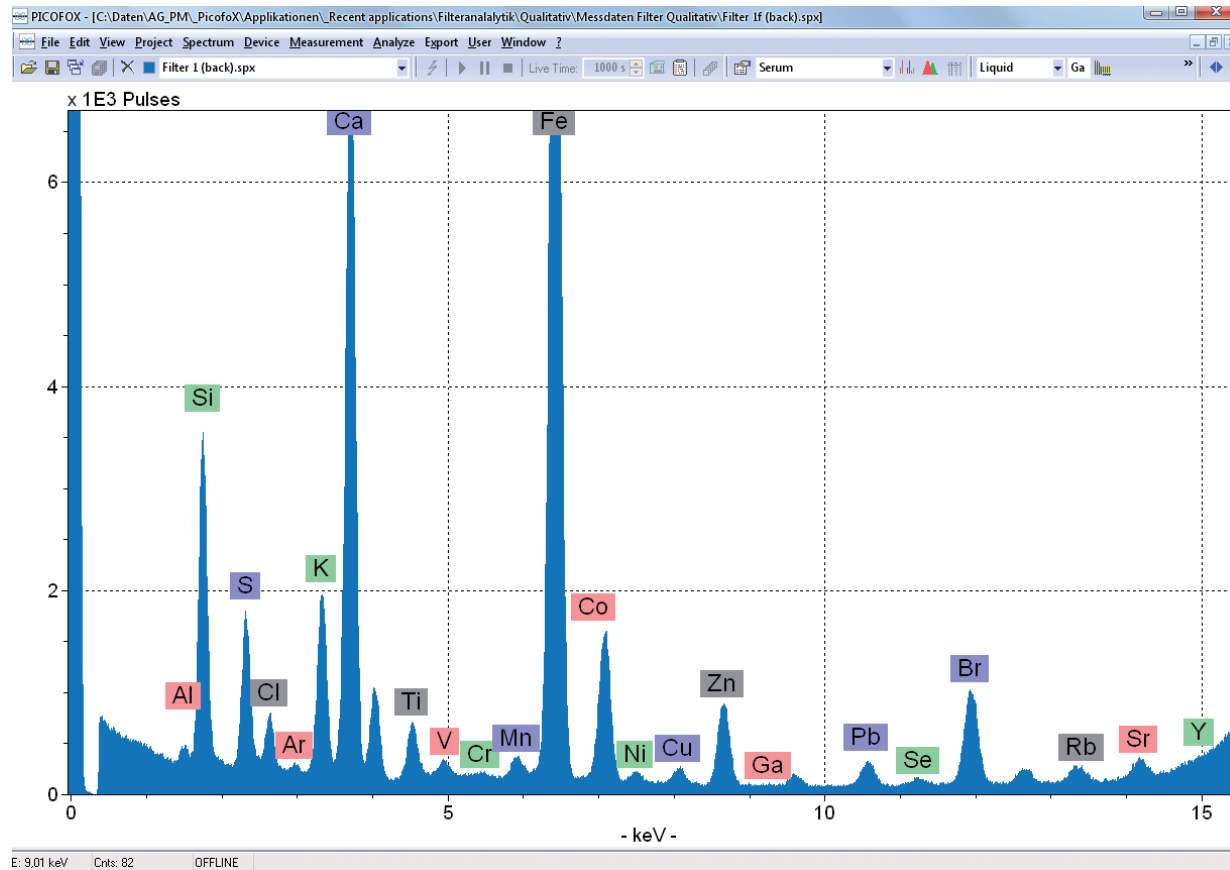
Analysis of Filter Samples

Sample Preparation



Qualitative Analysis

1. 3 x 3 mm section of filter was cut from filter
2. Fixed onto sample carrier by desiccator grease
3. Blank filter was first analyzed
4. Analyzed for 1000 seconds



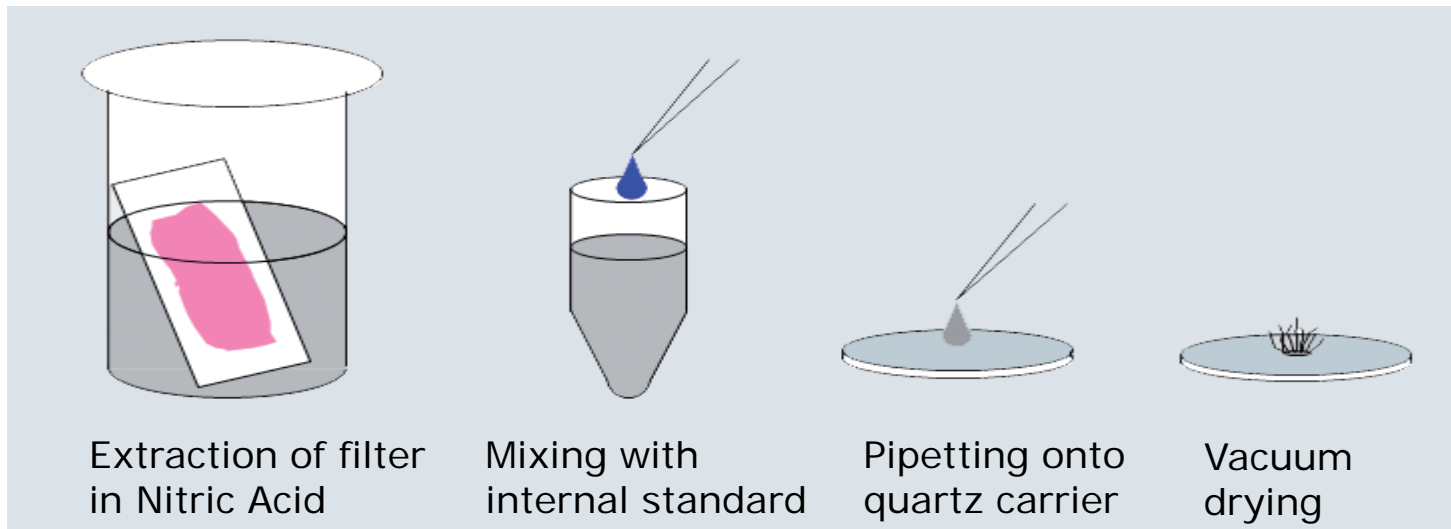
Analysis of Filter Samples

Sample Preparation



Quantitative Analysis

1. Sample was transferred to clean beaker filled with 5 mL nitric acid and treated in an ultrasonic bath for 5 minutes
2. Aliquot of 1 mL of extraction was transferred to a vial
3. 10 μ l internal standard Gallium was added
4. Homogenized and 10 μ l was pipetted onto carrier
5. Sample carrier was dried in a desiccator



Analysis of Filter Samples Results



- Large number of elements ranging from Mg to Pb were detected and quantified
- Results compared to blank filter samples
- Software allows output in absolute values (μg) or mass per filter area ($\mu\text{g}/\text{cm}^2$)
- No need for an external calibration
- Samples were prepared in under 10 minutes

Element	Filter 2 (mg/l)	Filter f1 (mg/l)	Blank filter (mg/l)
Mg	not detected	22.5	not detected
P	not detected	1.20	not detected
S	31.1	1.80	not detected
Cl	6.82	0.471	0.680
K	24.1	5.79	not detected
Ca	80.6	3.82	0.185
Ti	not detected	0.108	not detected
V	not detected	0.034	not detected
Cr	0.876	< LLD	not detected
Mn	0.241	0.022	not detected
Fe	29.4	0.957	0.048
Ni	0.439	0.005	not detected
Cu	1.18	2.21	not detected
Zn	4.93	0.242	0.021
As	not detected	0.003	not detected
Br	0.296	0.015	0.016
Rb	< LLD	0.003	not detected
Sr	0.160	0.012	not detected
Ba	1.86	not detected	not detected
Pb	0.697	0.017	not detected

Land - Monitoring with BioIndicators

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 sublethal metal concentrations?
- Methods for fast screening?

Water monitoring with bioindicators

What are biofilms?



Dry sample
microscopy photo

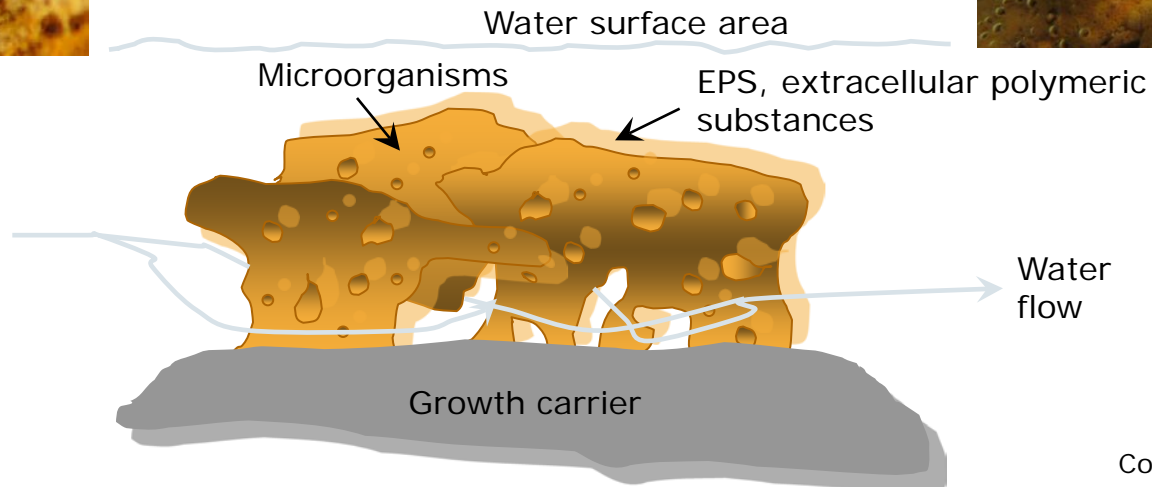


1 mm

Wet sample
underwater photo



10 mm



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

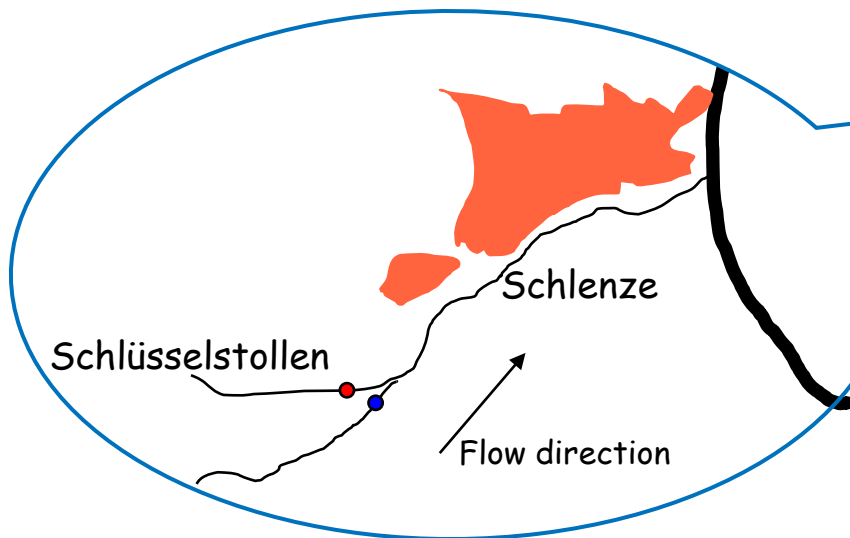
Biofilms

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



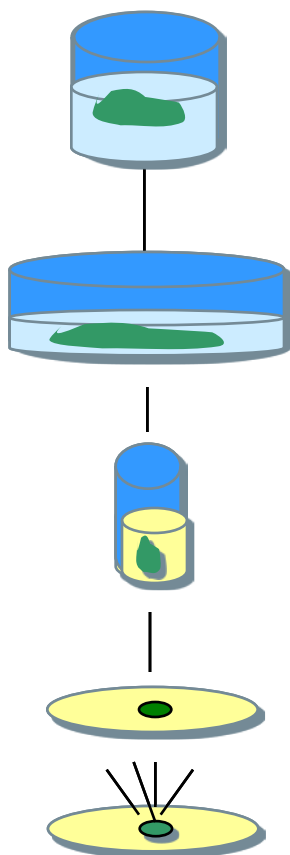
Grown on round polycarbonate slide



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 $\text{HNO}_3/\text{H}_2\text{O}_2$
- Internal standard Sc
- 10 µl sample aliquot
- Drying on a hot plate 80°C

Analysis with TXRF

Accumulation factors in water and biofilms

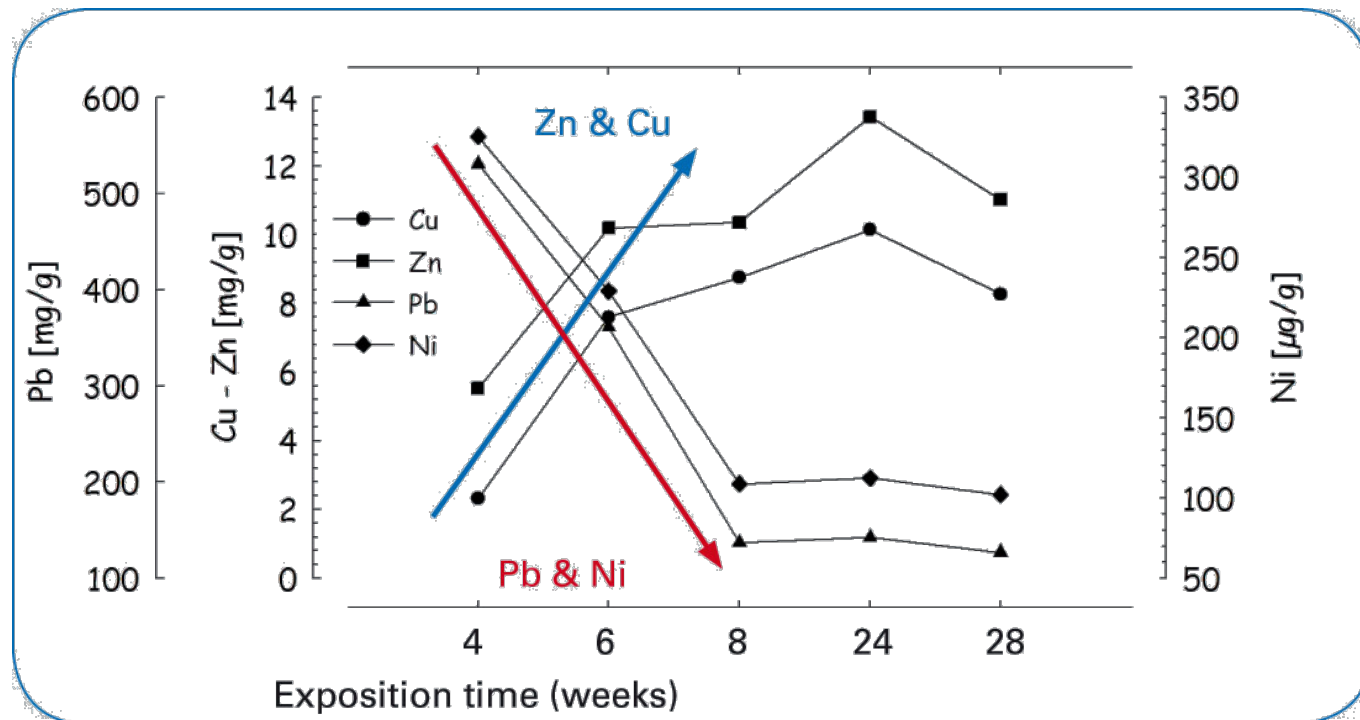


Element	Accumulation factor water*	Accumulation factor biofilm*
Pb	1400	2200
Zn	630	18
Cu	11	140
Ni	8	7

* 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

Biofilms

- Further investigations are planned on a river platform (mesocosmos) with “flow lines” simulating natural flow behaviors

Acknowledgement

- Margarete Mages, Helmholtz Centre for Environmental Research (UFZ) Magdeburg, Germany

Analysis of Plant Leaves

Introduction



- Analysis of plant materials allows us to understand:
 - Accumulation of toxic elements
 - Understand how these toxic elements are transferred from soil, water, and air through the food chain
 - Transfer of macro and trace elements used in fertilization (e.g. Br and Cl)
- Analysis of four certified reference materials were analyzed



NIST 1573 – Tomato
Leaves



NIST 1515 – Apple
Leaves



NIST 1547 - Peach
Leaves



NIST 1572 – Citrus
Leaves

Analysis of Plant Leaves

Sample Preparation



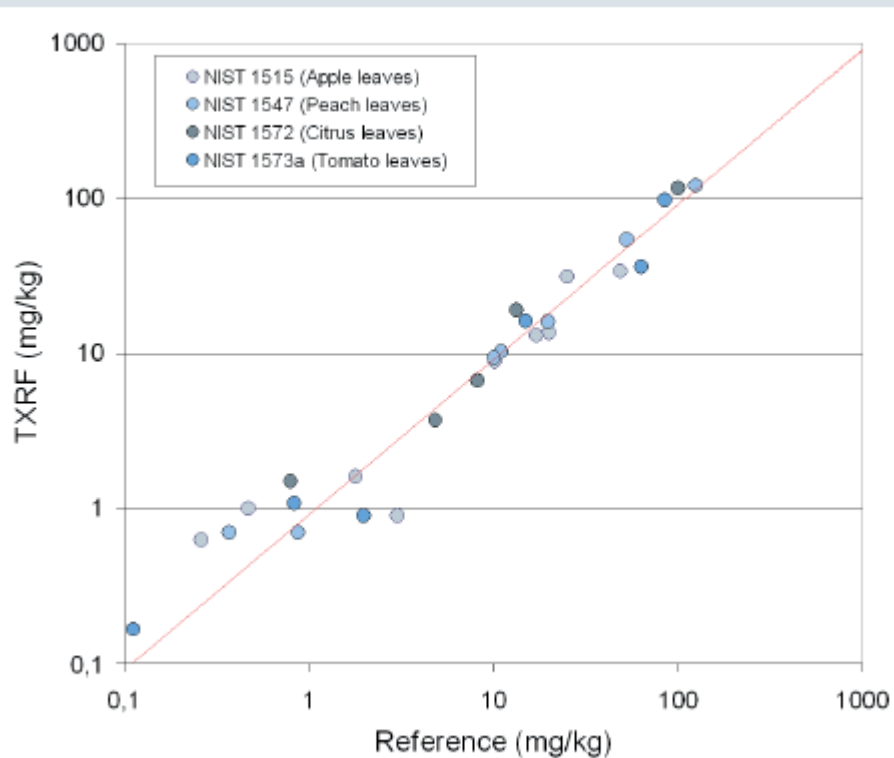
Procedure

1. Samples ground in mixer mill (Retsch MM400, Zr grinding jar) for 3 min. at 30 Hz.
2. Amount of 60 – 70 mg of ground powder was weighed
3. Weighed amount transferred to a polypropylene cryo-tube and suspended in 2.5 ml of a 1 vol% aqueous Triton X-100 solution
4. 10 μ l of a gallium solution was added
5. To separate grains, samples were placed in an ultrasonic bath for 15 minutes
6. 10 μ l of sample suspension was transferred to siliconized quartz disk and dried in a vacuum
7. Tenfold preparation at 1000 s each to test reproducibility

Analysis of Plant Leaves Results

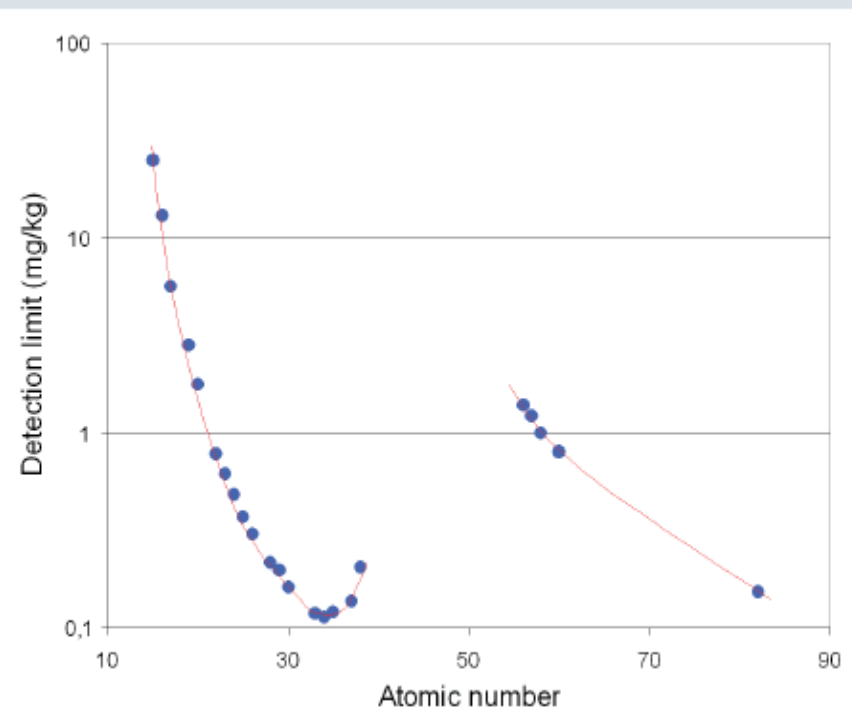


Comparison of TXRF and reference concentrations



Comparison of TXRF and reference values for trace elements (i.e. V, Br, Rb, La, Ce, Pb, Nd, As, Ba)

Detection limits for trace elements in plant material



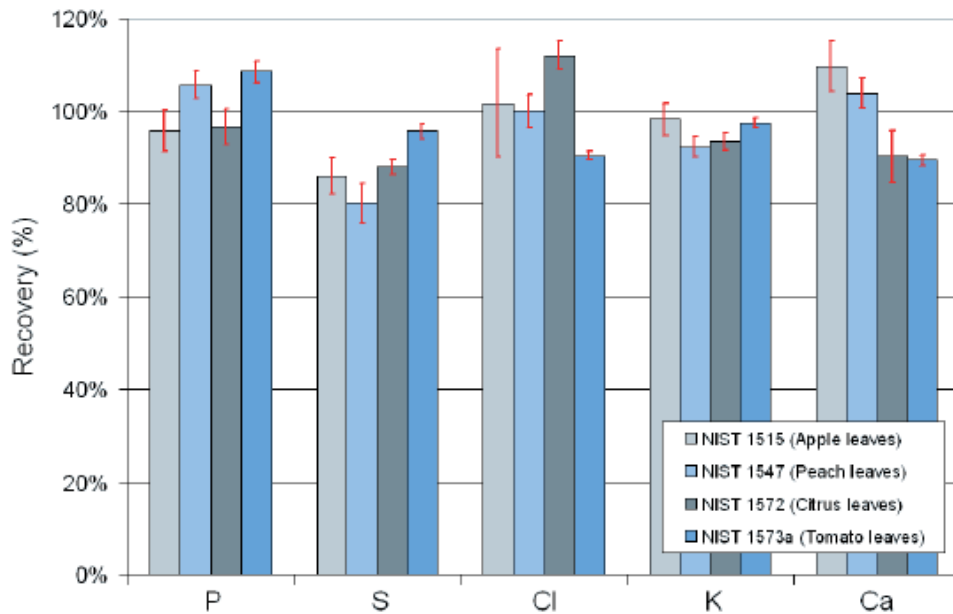
3 sigma detection limits for trace elements in plant standards by TXRF

Analysis of Plant Leaves

Conclusion



Recovery of macronutrients by TXRF



Recovery of macronutrients in plant standards ranging from 300 mg/kg to 5%

- Simple grinding and suspension are only requirements for multi element analysis
- Only requires small amount of sample for rare plants or medicinal herbs
- One analysis for:
 - Macros (P, S, Cl, K, Ca)
 - Transition metals (Mn, Fe, Cu, and Zn)
 - Trace elements (Cr, As, Se, Br, Rb, Ba, La, Tl, Pb, Ce, Nd, etc.)
- Analysis of Halogens is possible



Water - Effluent Analysis and Monitoring with BioIndicators

Liquid Samples

Industrial effluents



Situation

- Control of wastewater and runoff from Industrial and petrochemical industries per Catalonia Water Agency

Analytical task

- Threshold values for multiple elements in water, sewage, soils, etc.
- Need accurate, easy-to-use, cost effective technique to ensure they are below threshold levels

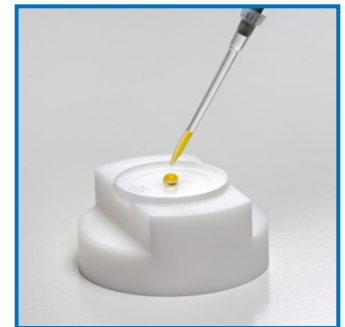
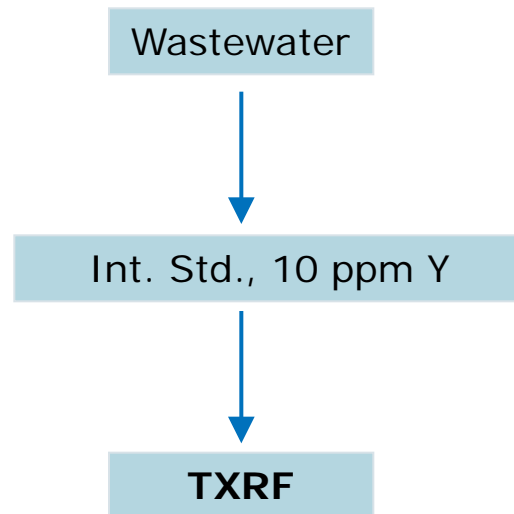


(cc) Leonard

Liquid Samples Industrial effluents



Measurements and sample preparation



Liquid Samples

Industrial effluents



- Level of Detection was well below limit value
- Level of Detection only showed slight improvement with Microwave Digestion of sewage sample
- Analyzed using W tube at 1000s
- Analyzed sewage, water, and filtrates
- Complimentary tool to digestion techniques such as ICP-MS for Industrial treatment plants

Element	Limit value	Limits of detection (TXRF analysis)	
		Without treatment	Microwave digestion
Cr	3	0.24	0.24
Mn	2	0.17	0.12
Fe	5	0.09	0.07
Ni	5	0.11	0.07
Cu	3	0.10	0.06
Zn	10	0.08	0.05
As	1	0.03	0.02
Se ^a	0.5	0.02	0.09
Cd	0.5	0.009	0.003
Sn ^a	5	0.04	0.03
Ba ^a	10	0.49	0.48
Pb	1	0.01	0.01

- Concentrations expressed as mg/L⁻¹
- Concentration limits for heavy metals in industrial waste water effluents according to the regulation from the Catalonia Water Agency (Spain) and calculated detection limits from the analysis of the waste water reference material SPS-WW2 by TXRF

* Acknowledgements to E. Margui – Institute of Earth Sciences Barcelona, Spain

Liquid Samples

Industrial effluents



When applied to trace element analysis of fresh water and sewage samples, TXRF offers the following benefits:

- Flexibility with regard to sample type
 - Raw sewage
 - Industrial Wastewater and effluents
 - Contaminated soils
 - Filtered sewage
 - Fresh water
 - Sewage filtrates
- Easy multi-element analysis without external calibration – Allows for prescreening of unknown samples
- Low maintenance costs
- Small size of the system (mobile use)



Let's compare...

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 ₂ H 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	

Any questions?

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S2 PICOFOX Publications



Application Notes:

- Lab Report XRF 428 – Qualitative and Quantitative of Filter Samples
- Lab Report XRF 423 – Analysis of Heavy Metals in Sewage Samples
- Lab Report XRF 425 – Trace Element Analysis of Fresh Water
- Lab Report XRF 445 – Trace Element Analysis of Plant Material
- Lab Report XRF 450 – Rapid Screening of Nutrient Relevant Elements in Fish
- Lab Report XRF 430 – Mercury in Nutrition

Recent Publications

- E. Bontempi et. al. "Total Reflection X-ray fluorescence (TXRF) for direct analysis of aerosol particle samples", *Environment Technology*, 31:5, 467-477
- M. Mages "The use of portable total reflection X-ray fluorescence spectrometer for field investigation", *Spectrochimica Acta* 58 2129-2138
- L. Borgese et. Al "Total Reflection X-ray fluorescence (TXRF): a mature technique for environmental chemical nanoscale metrology", *Measurement Science and Technology*, 20 084027, 2009

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Webinar	Content	Webinar	Content
Nov 20, 2012	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	Dec 13, 2010	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
TXRF for Trace Element Analysis of Air, Land and Water		Trace Element Analysis of Industrial Wastewater and Sewage with TXRF and ICP-MS	

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