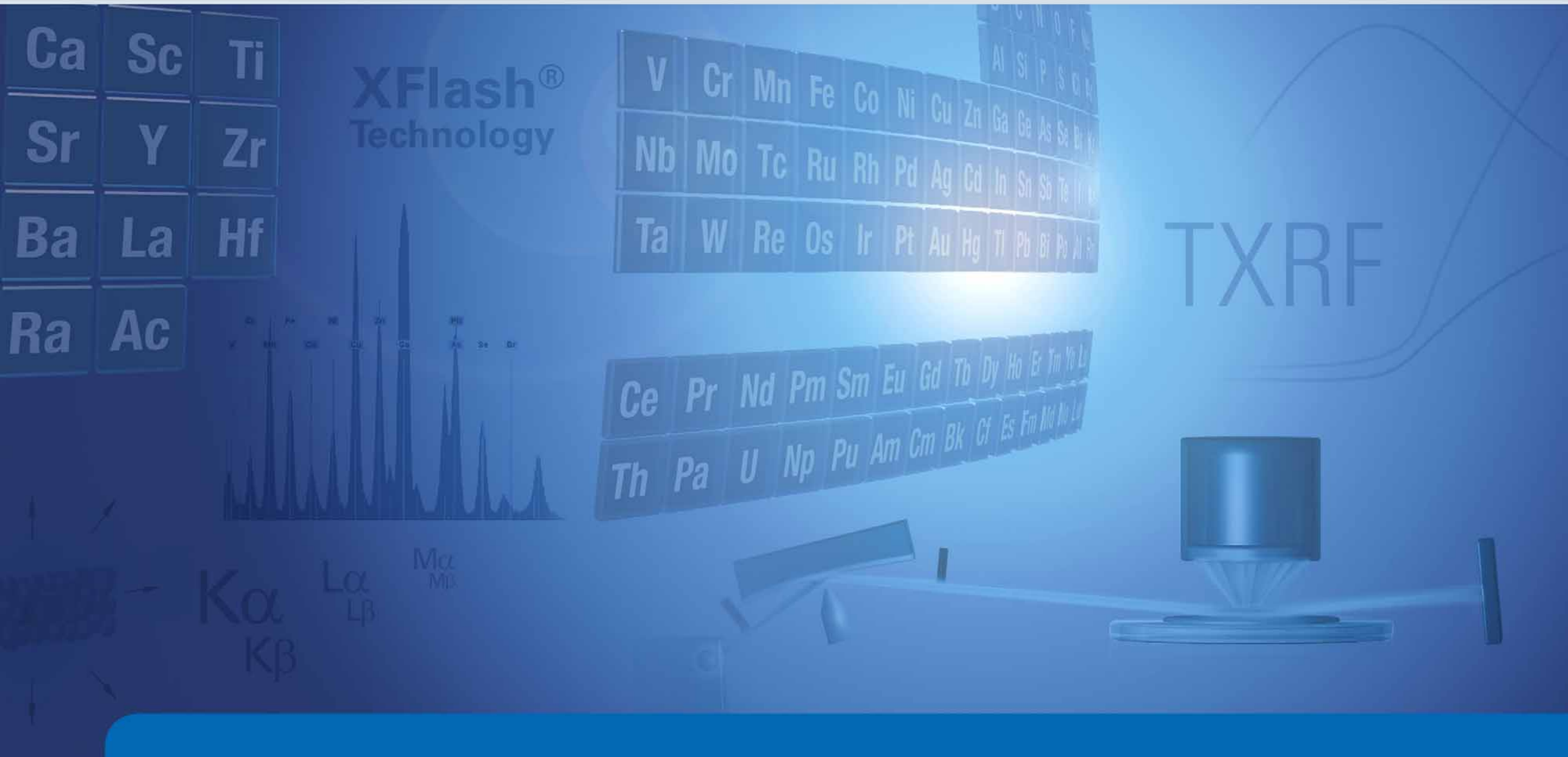
Trace Element Analysis of Industrial Wastewater and Sewage with TXRF

Bruker Nano GmbH
Berlin, Germany



Welcome

Today's Topics

- TXRF – how does it work?
- Wastewater analysis
- Water monitoring with bioindicators
- Comparison with Atomic Spectroscopy methods
- Interactive Q & A

Speakers

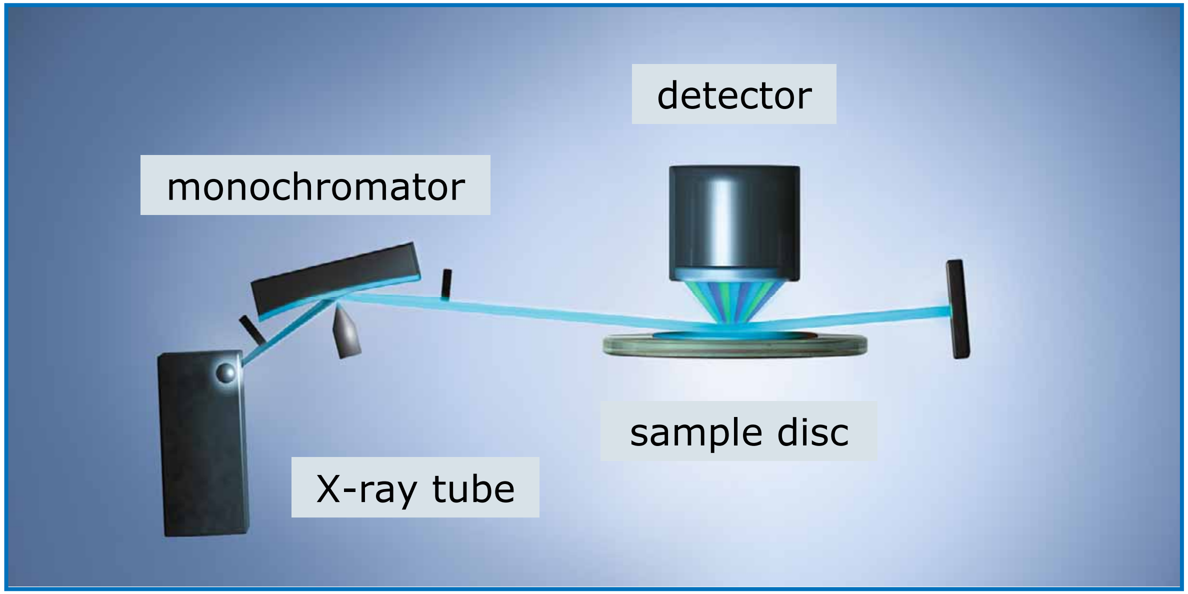
Dr. Hagen Stosnach
Applications Scientist TXRF
Berlin, Germany

Dr. Armin Gross
Global Product Manager TXRF
Berlin, Germany

TXRF – How does it work?

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

Total reflection X-ray fluorescence spectroscopy



Beam angle: 0° / 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 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

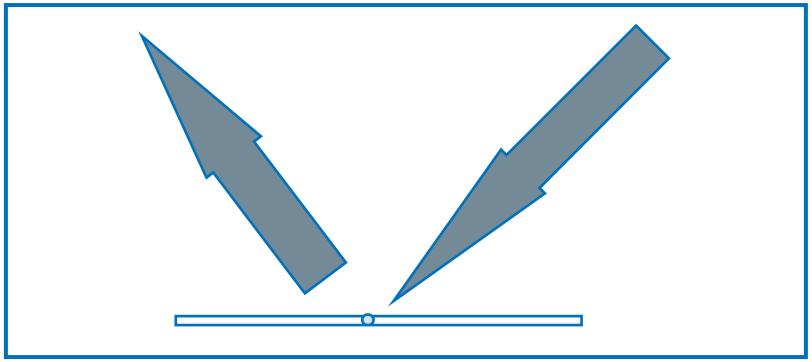
➔ Matrix effects are negligible due to thin layer

➔ Quantification is possible by internal standardization

Principles of total reflection X-ray fluorescence spectroscopy

In TXRF the samples are prepared as thin films or layers

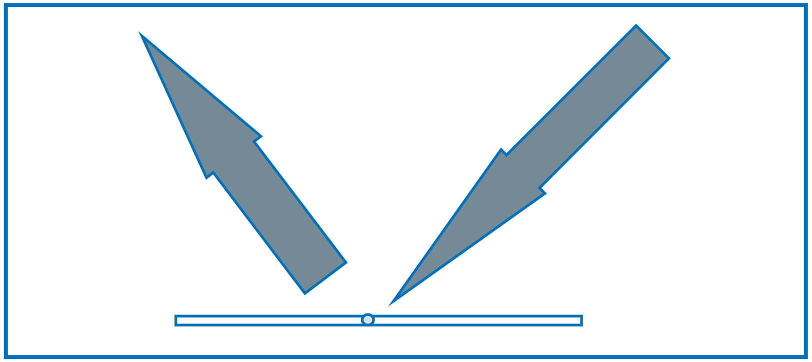
- ➔ Matrix effects are negligible
- ➔ Quantification is possible



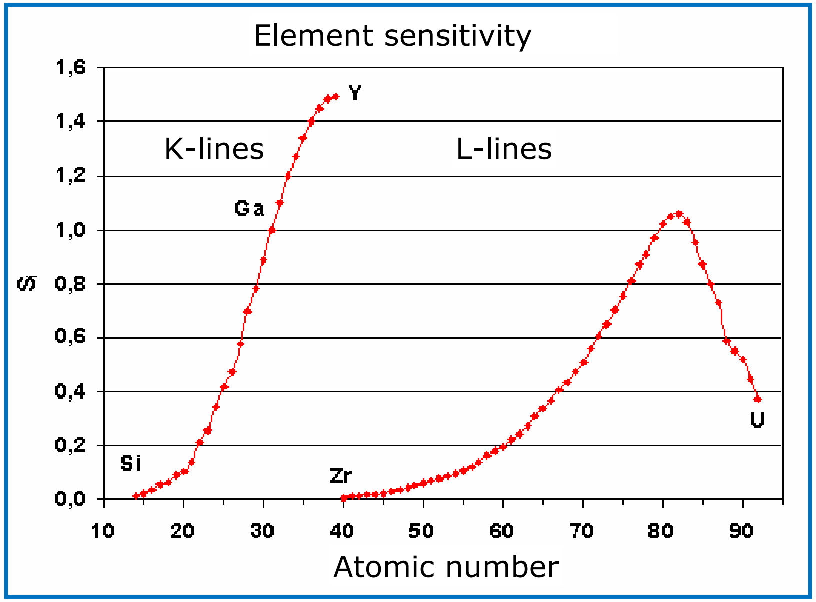
Principles of total reflection X-ray fluorescence spectroscopy

In TXRF the samples are prepared as thin films or layers

➔ Matrix effects are negligible
➔ Quantification is possible

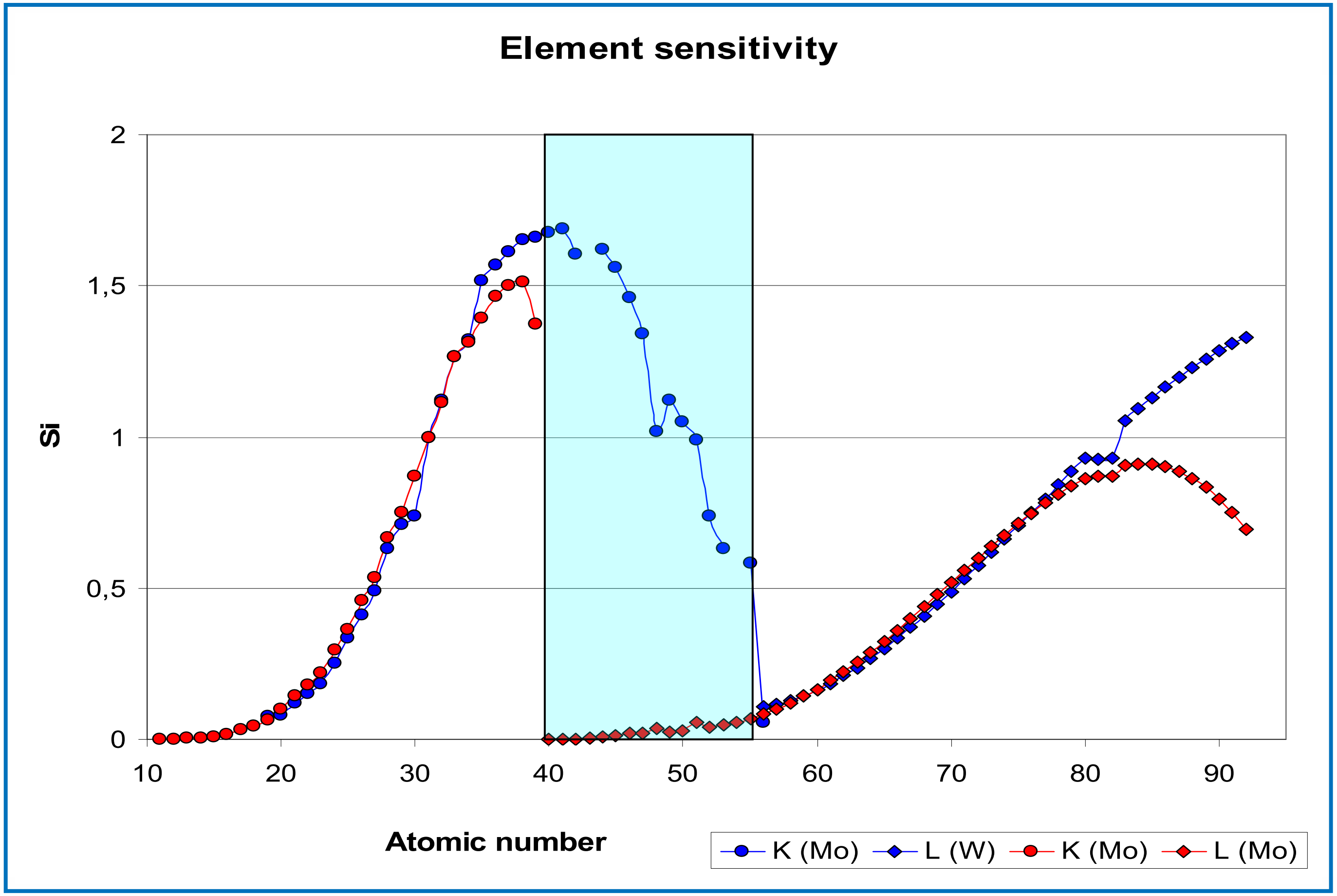


- TXRF detects elements from Na(11) to U(92)
- The element sensitivities depend on the atomic number
- The sensitivity factors are calibrated ex works
- Quantification requires the addition of one standard element



Principles of total reflection X-ray fluorescence spectroscopy

- Mo tube offers lowest LLD
- W tube suitable for elements with Z = 41 to 53 (Nb to I)



The instrument S2 PICOFOX

Benchtop TXRF spectrometer
S2 PICOFOX

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

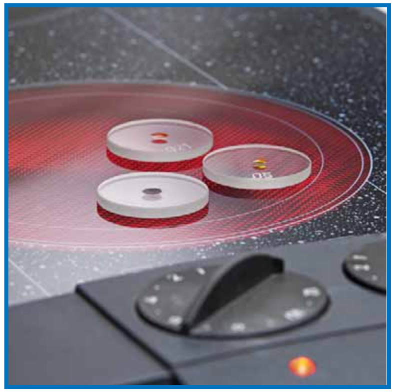
Wastewater analysis by TXRF spectrometry

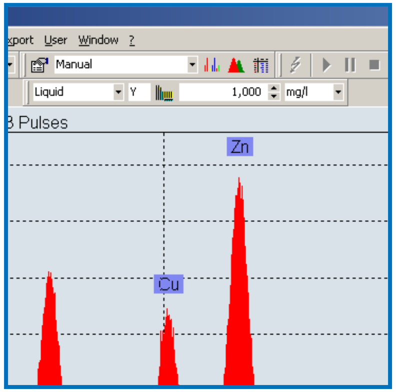
Sample preparation
Suspensions and particulate matter

Suspensions can be analyzed right after dilution

Dilute sample with distilled water → Add internal standard → Homogenize → Pipette on carrier

Sample preparation
Suspensions and particulate matter





Dry through heat/vacuum → Load the instrument → Start data aquisition

Industrial wastewater
Cement

Situation

- Discharge of wastewater from a cement plant
- Threshold value of 500 µg/L Pb to be fulfilled by law

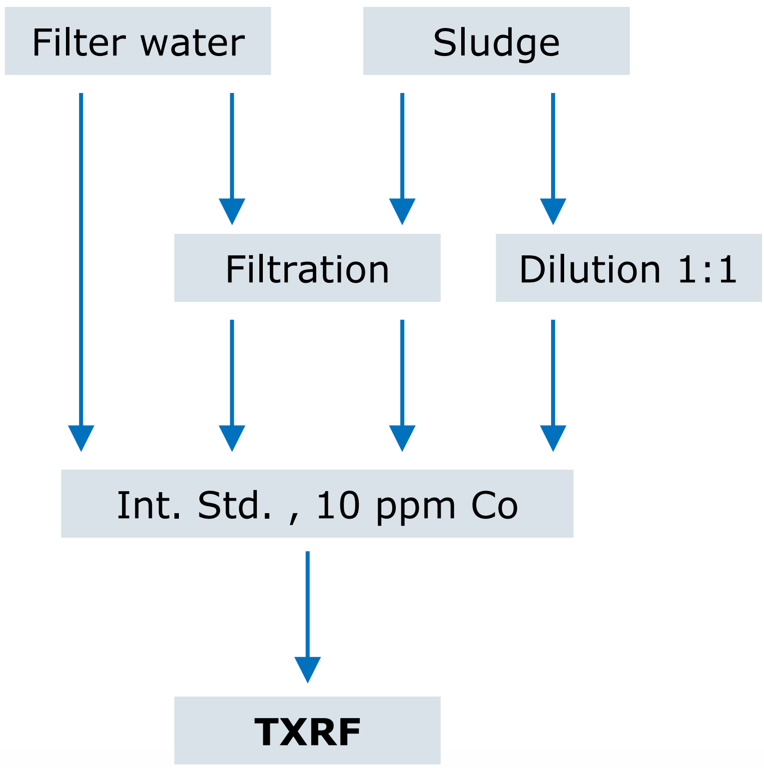
Analytical task

- Filter water with fine particles
- Thickened sludge as a suspension

(cc) pd

Industrial wastewater
Cement

Measurements and sample preparation



Industrial wastewater
Cement

Results

- Filtered samples (with particles or clear) fulfill threshold values
- Raw sludge is close or above the limits filtration removes lead-containing solids
- The analysis of further elements is possible (not shown)

Pb (µg/L)	Filtered sewage	Filtered with particles	Sludge filtered	Sludge suspension
Conc. (sample 1)	n.d.	4.0	9.4	411
LLD (sample 1)	n.d.	2.5	2.0	9.5
Conc. (sample 2)	n.d.	n.d.	13	938
LLD (sample 2)	n.d.	n.d.	2.2	16

Industrial wastewater
Petro

Situation

- Control of wastewater in the petrochemical industry

Analytical task

- Analysis of wastewater
  special interest in V, Mn, Ni, Hg

(cc) Leonard

Industrial wastewater
Petro

Measurements and sample preparation

Wastewater

↓

Int. Std., 10 ppm Ga

↓

TXRF

Industrial wastewater
Petro

Results

- The elements V, Mn, Ni and Hg could be detected down low ppb
- The analysis of further elements is possible (not shown)

Conc. (µg/L)	Sample 1	Sample 2	Sample 3	Sample 4
V	< NWG	1.9	79	15
Mn	104	1.3	904	9.9
Ni	1.3	0.68	< NWG	5.4
Hg	< NWG	0.46	< NWG	4.0

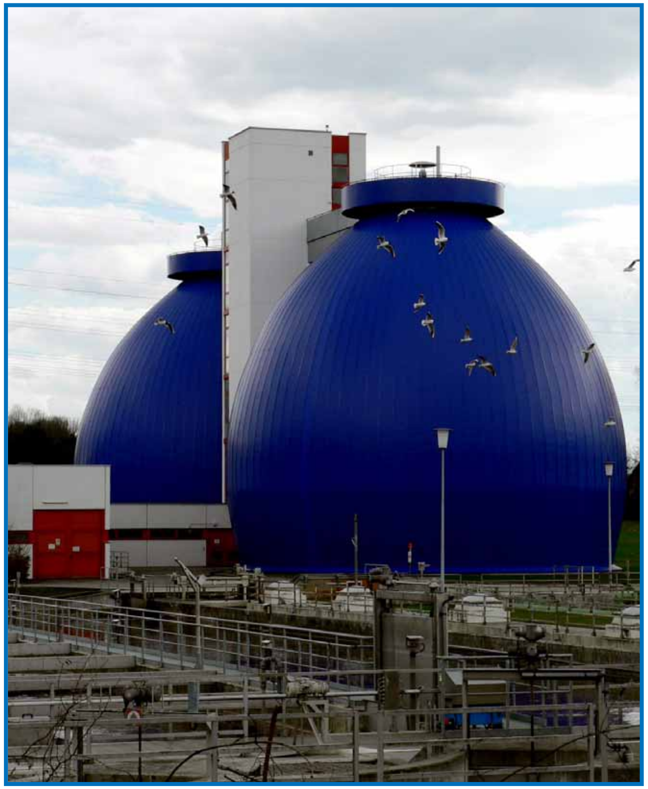
Industrial wastewater
Oil/solvent mixtures

Situation

- Before discharging liquid mixtures of oils and solvents the content of heavy metals has to be verified

Analytical task

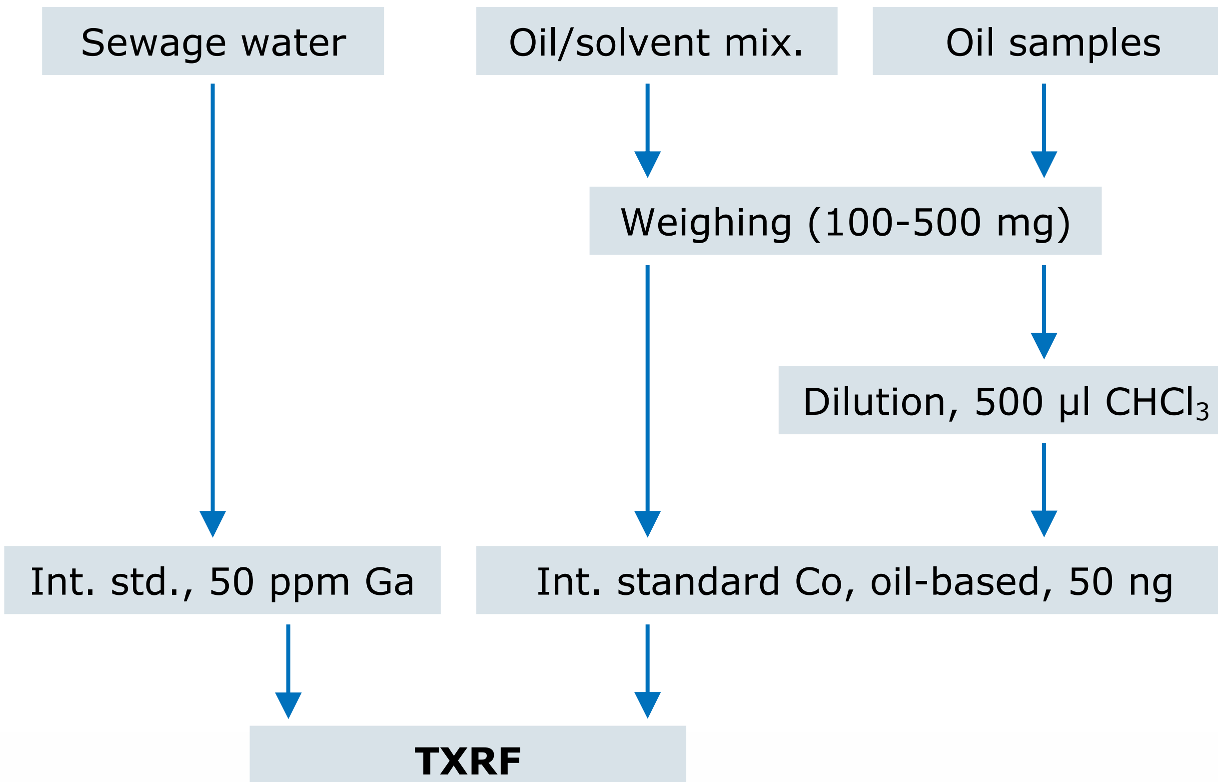
- All sewages have to be tested for the entire element range
- Therefore, all samples were analyzed by two instruments subsequently:
  W unit for elements from Mo to Sb,
  Mo unit for all other elements



(cc) Michael Meding

Industrial wastewater
Oil/solvent mixtures

Measurements and sample preparation



Industrial wastewater
Oil/solvent mixtures

Results – sewage

- All elements from P to Hg were quantitatively analyzed
- Detection limits were < 10 ppb for most elements (Z > 19)
- Detection limits measured by the W unit were higher but fulfilled the required limits (e.g. Cd < 80 ppb, Sb < 160 ppb)

Industrial wastewater
Oil/solvent mixtures

Results – oil samples and mixtures

- Best detection limits were in the range from 15 to 60 ppb (e.g. Br, Se, As, Zn, Ni, Cu)
- LLD measured by the W unit depend on sample type:
- Cd: 0.3 ppm in solvent, 1–2 ppm in oils and mixtures
- Sb: 0.6 ppm in solvent, 4 ppm in oils
- Mo: 0.2 ppm in solvent, 1 ppm in oils and mixtures

Improved sample preparation for achieving lower LLD is possible

Industrial wastewater
TiO_2 production

Situation

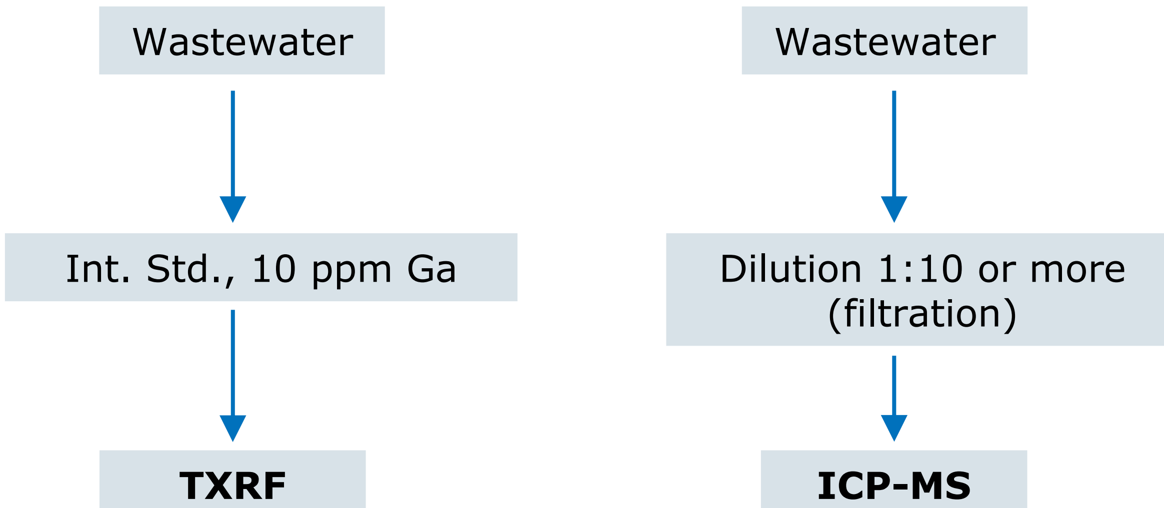
- Before discharging the concentrations of several heavy metals they must be analyzed in order to fulfill legislative norms

Analytical task

- Wastewater has to be analyzed with regard to limit values for
  - Cr < 0,5 mg/l
  - Cd < 5,0 µg/l
  - Hg < 1,0 µg/l
- Concentrations in the mg/l range of additional elements (Fe, Ti and V) have to be supervised

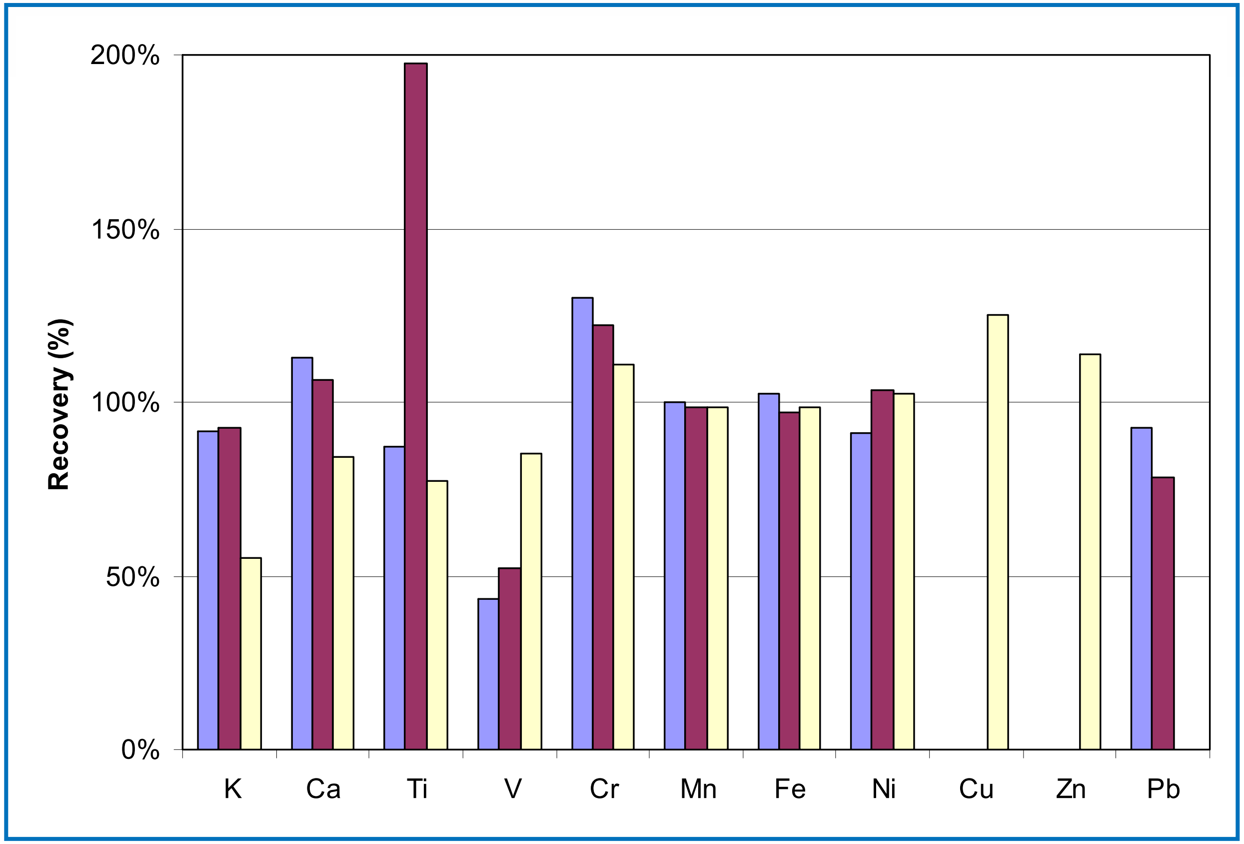
Industrial wastewater
TiO_2 production

Measurements and sample preparation



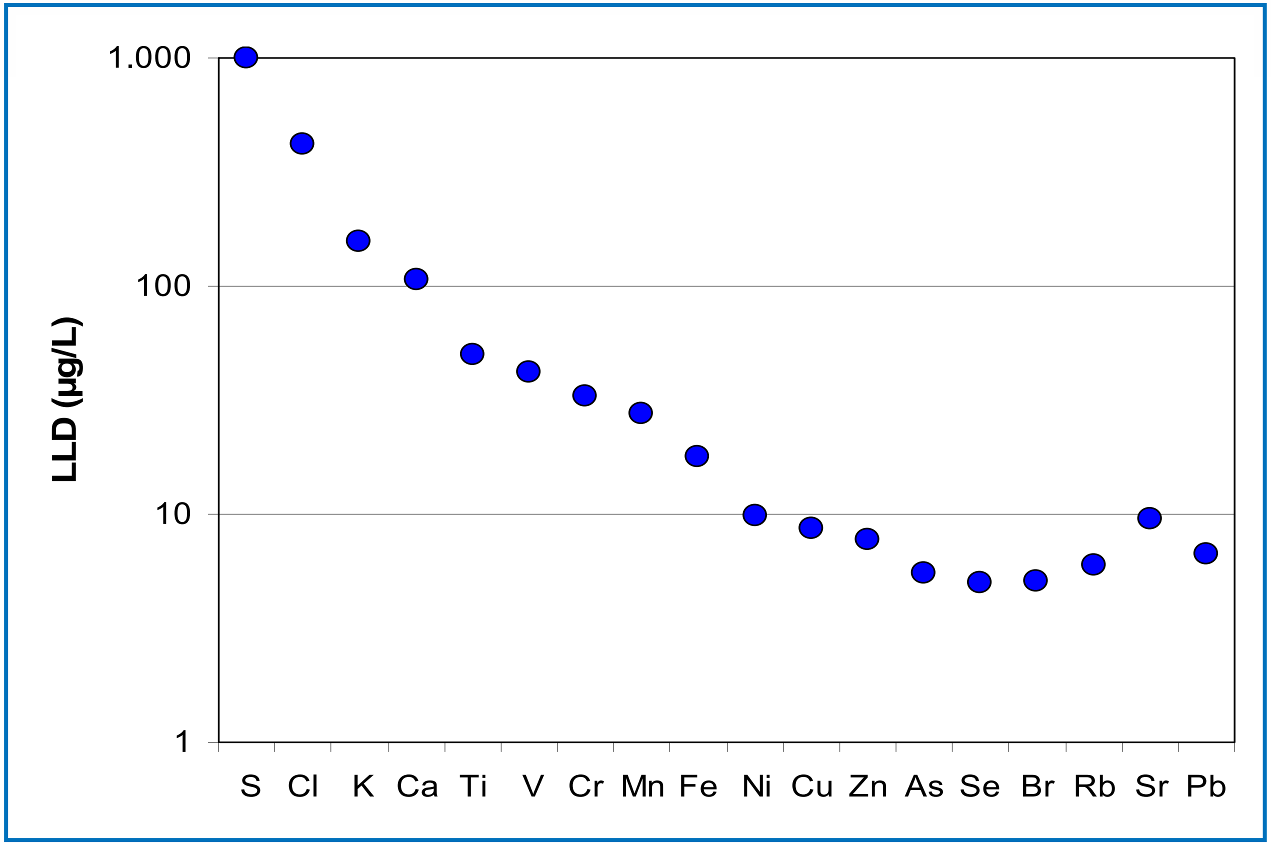
Industrial wastewater
TiO_2 production

- Fast screening of wastewater delivers comparable results of TXRF and ICP-MS
- TXRF: Cd and Hg (conc. range 30 to 70 ppb) were not detectable due to line overlaps
- ICP-MS: S, Cl, Br, Rb, Sr were not detectable



Industrial wastewater
TiO_2 production

- Detection limits



Water 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

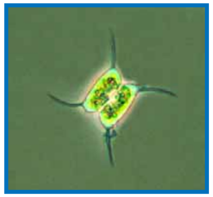
General questions

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

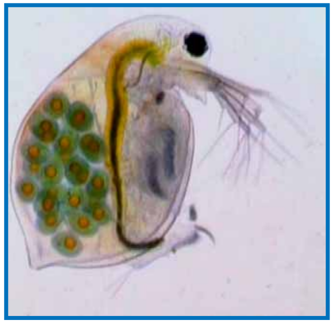
Bioaccumulation of metals in the trophic chain

Element mass fraction increases at log scale

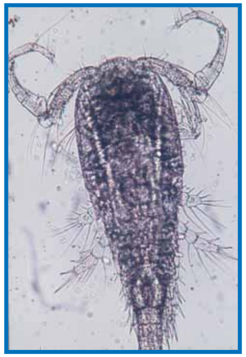
Primary producer



Primary consumer



Secondary consumer



Tertiary consumer

Metal screening of single Daphnia

Zooplankton Daphnia as bioindicator

- Describes biological availibility of heavy metals, indicator for water quality
- Measurements of single organisms (< 100 µg) after selection by type, sex, growth status
- Trace element analysis of single organisms by ICP-OES and AAS impossible

Metal screening of single Daphnia

Sample preparation

- Rinsing of Daphnia
- Freeze drying
- Selection of individual organisms, weighing and size measurement
- Fix Daphnia on quartz carrier, add HNO_3 and internal standard
- Cold Plasma Ashing (2 h, 180ºC) no loss of volatile trace element compounds

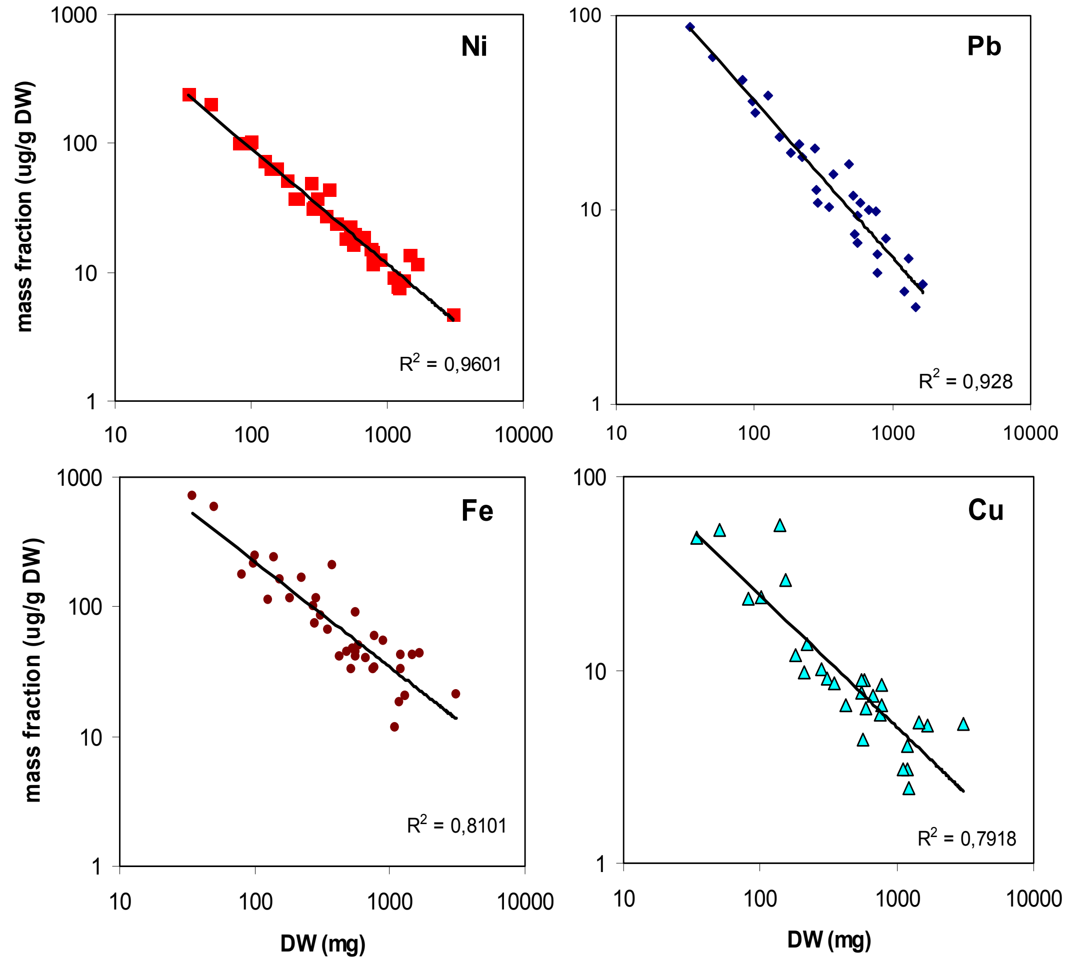
➔ CPA reduces organic matrices and lowers background counts

TXRF measurement

- Typically 1000 s

Metal screening of single Daphnia

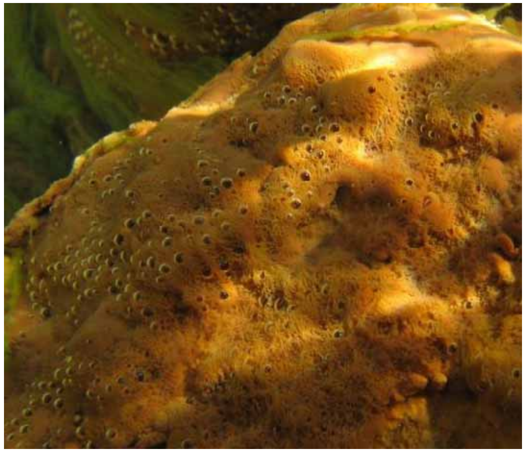
- Direct correlation of metal concentration and dry weight of bioindicator organism

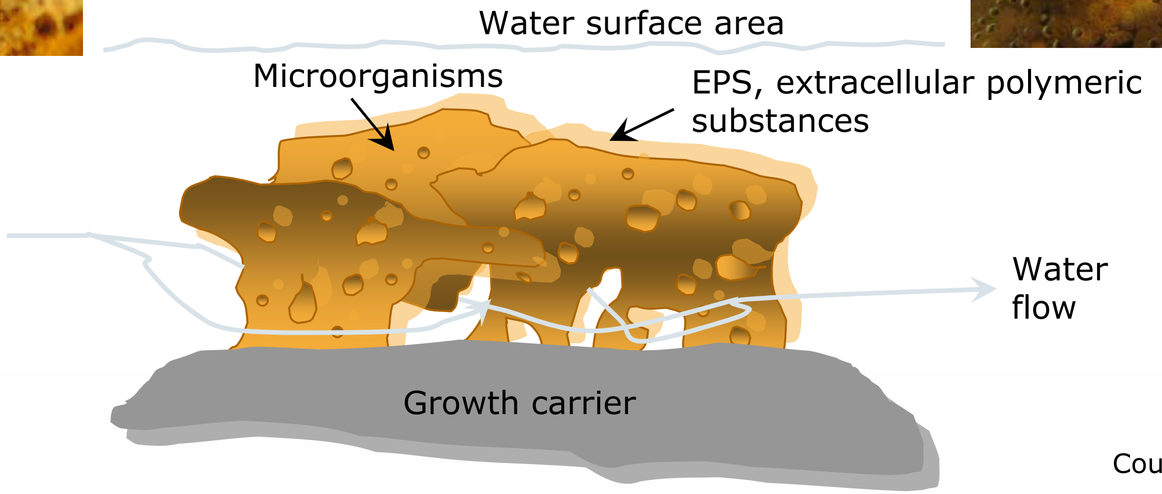


Water monitoring with bioindicators
What are biofilms?

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 pathogenes in hospitals

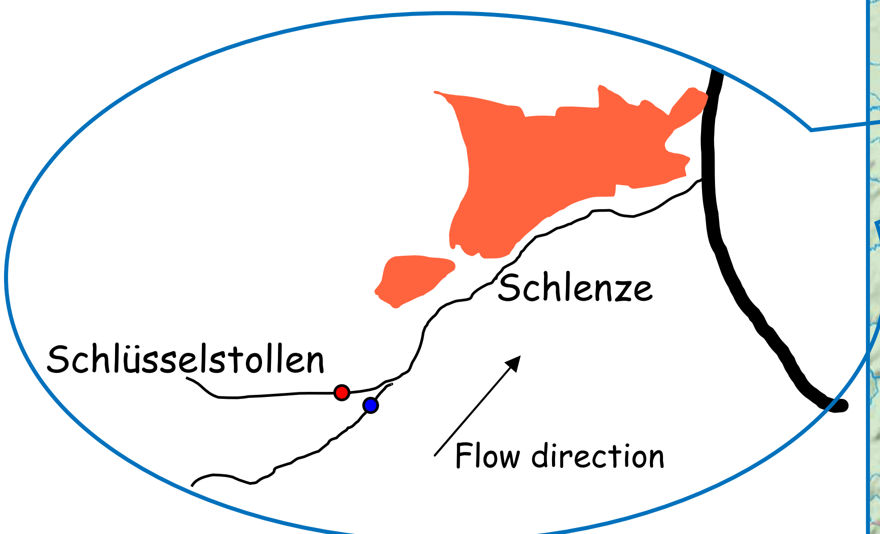
Application of biofilms

- 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 bronce age



Courtesy of UFZ Magdeburg

Biofilms
Sampling location

Sampling location "Schlüsselstollen"

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

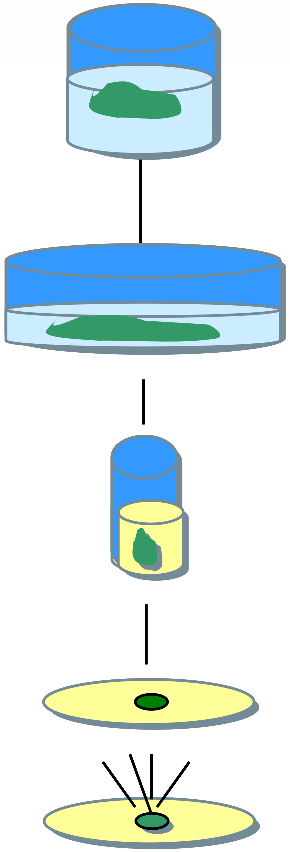
Courtesy of UFZ Magdeburg

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

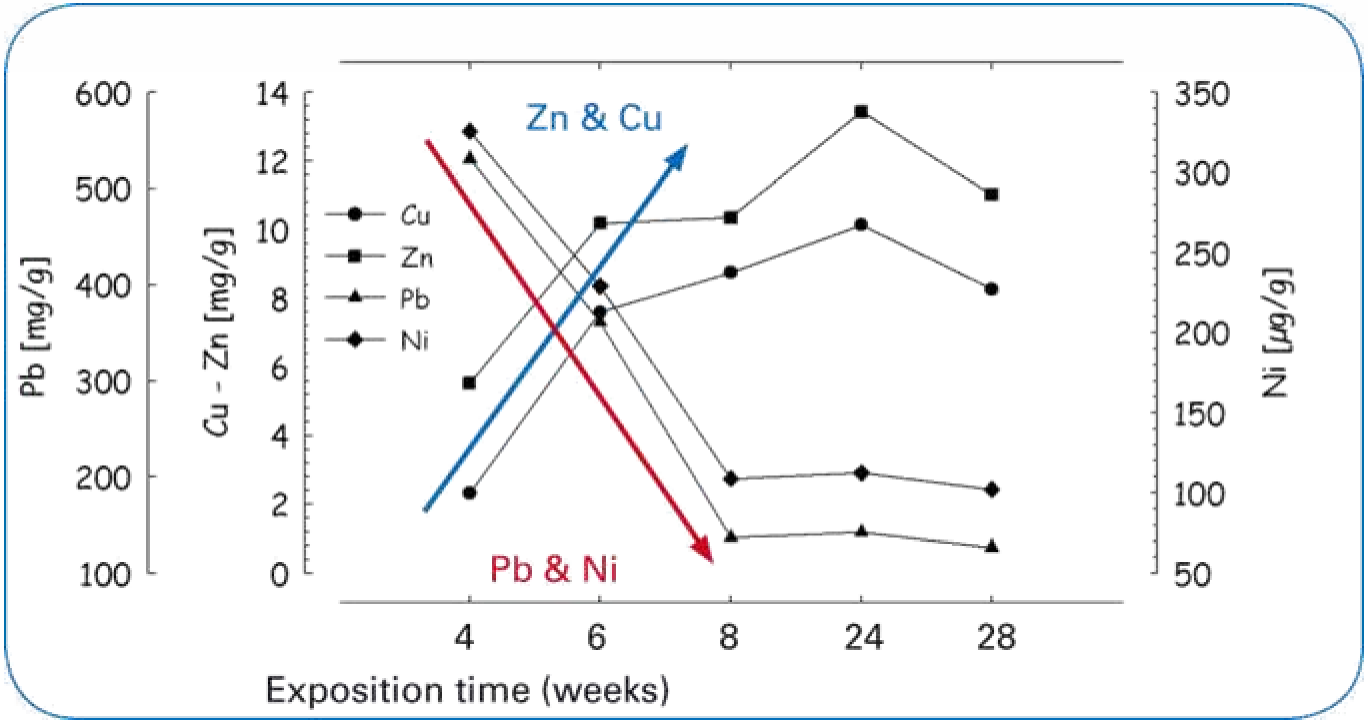
Accumulation factors in water and biofilms

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

Outlook

Biofilms

- Further investigations are planned on a river platform (meso cosmos) with “flow lines” simulating natural flow behaviours

Acknowledgement

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

Comparison with Atomic Spectroscopy

TXRF vs. AAS/ICP-OES

TXRF

- Small footprint/portable
- Microgram sample size
- %-ppb levels
- Single std. calibration
- Low maintenance
- Non-destructive
- Fast learning curve
- Fast sample prep

AAS/ICP-OES

- Large, fixed installation
- Milligram sample size
- ppm – sub ppb levels
- Multi-standard calibration
- High maintenance
- Destructive
- Long learning curve
- Laborious sample prep

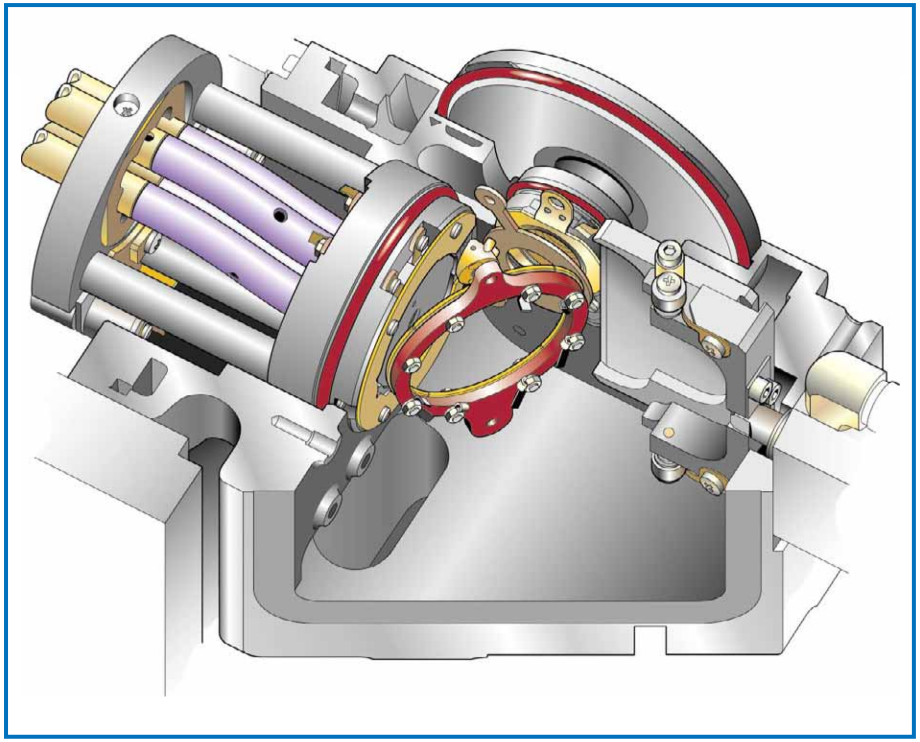
Want ICP-MS?
Bruker 820-MS

- Low DLs <1ppt for some elements in solution
- Wide range of elements (>75)
- Isotopic analysis capability

Innovative Ion optics
90° design

Ionen mirror

- Parabolic electrostatic field
- Reflects and focusses ions *(patented)*



Hollow structure of the ion mirror

- Photons and uncharged particles pass without contact

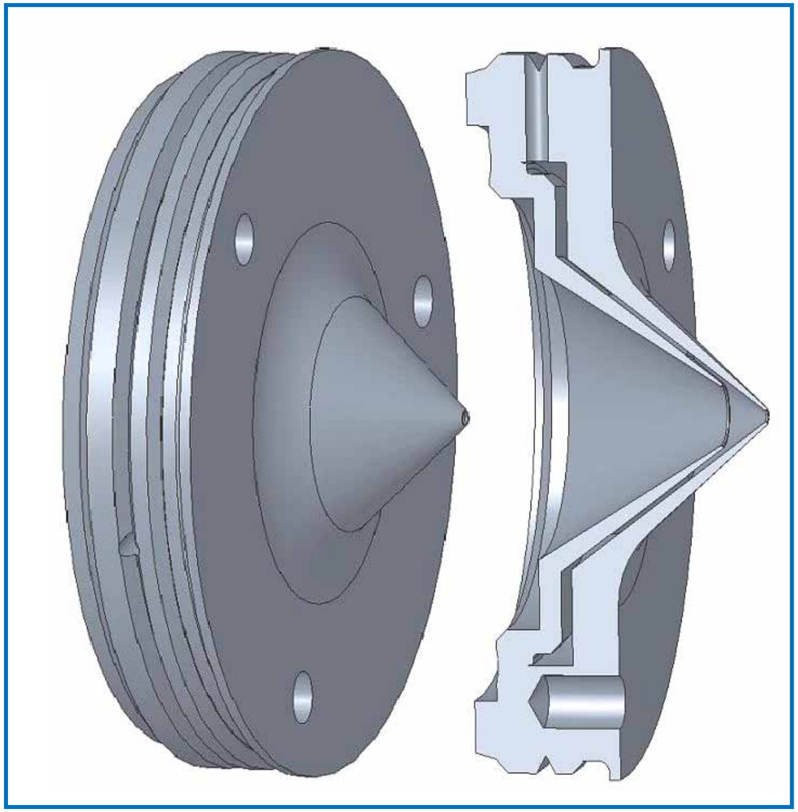
Arrangement of turbo pump

- optimal conditions for vacuum
- removes unwanted particles

Convenient technology
Collision Reaction Interface – CRI

Bruker's answer to common interferences?

- The Collision/Reaction Interface (CRI)
- H_2 gas injected to react with Ar^+ and ArX^+ molecular ions
- He gas used to separate other interferences
- Improved detection limits for several key elements (^{40}Ca, ^{56}Fe, ^{75}As, ^{80}Se)
- Increased productivity, most suitable for routine applications
- Fast and reproducible switching of CRI modes



Application labs in your neighborhood

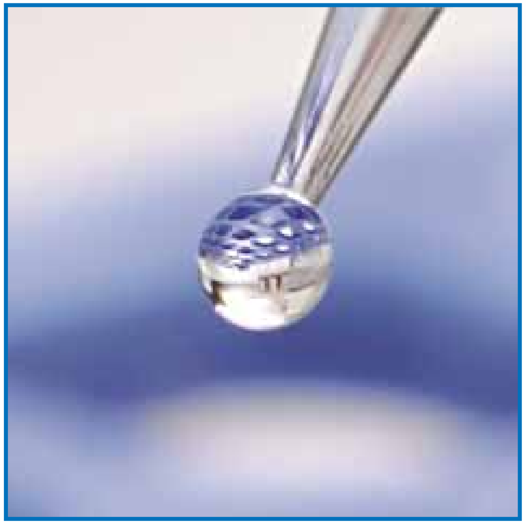
Application labs with TXRF and ICP-MS at work
or coming soon …

- Berlin, Germany
- Coventry, UK
- Paris, France
- Milton, Canada
- Houston, Texas, USA
- Melbourne, Australia
- Seoul, Korea

Q & A

Any Questions?

Please **type in** the questions you may have for our speakers in the **Questions form** and click **Submit**



Thank you for your attention!

Upcoming:

14th International Conference on
Total Reflection X-ray Fluorescence
and Related Methods
06–10 June 2011, Dortmund, Germany

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