Mercury Analysis in Food, Environmental and Medical Samples with TXRF

Bruker Nano GmbH, Berlin, Germany

Webinar 09.12.2020

Welcome

Today's Topics

- TXRF – how does it work?
- Mercury – Where does it come from and where does it go?
- TXRF analysis of mercury
- Comparison with Atomic Spectroscopy methods
- Interactive Q & A

Speakers

Dr. Hagen Stosnach
Applications Scientist TXRF
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Global Product Manager TXRF
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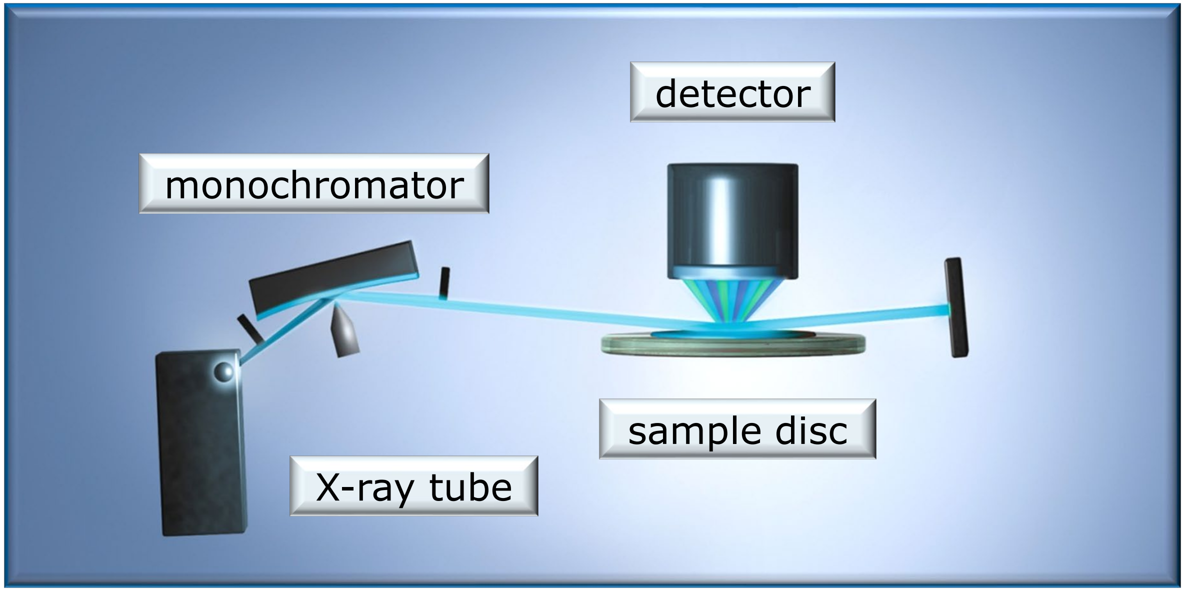
TXRF – How does it work?

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

Total reflection X-ray fluorescence spectroscopy



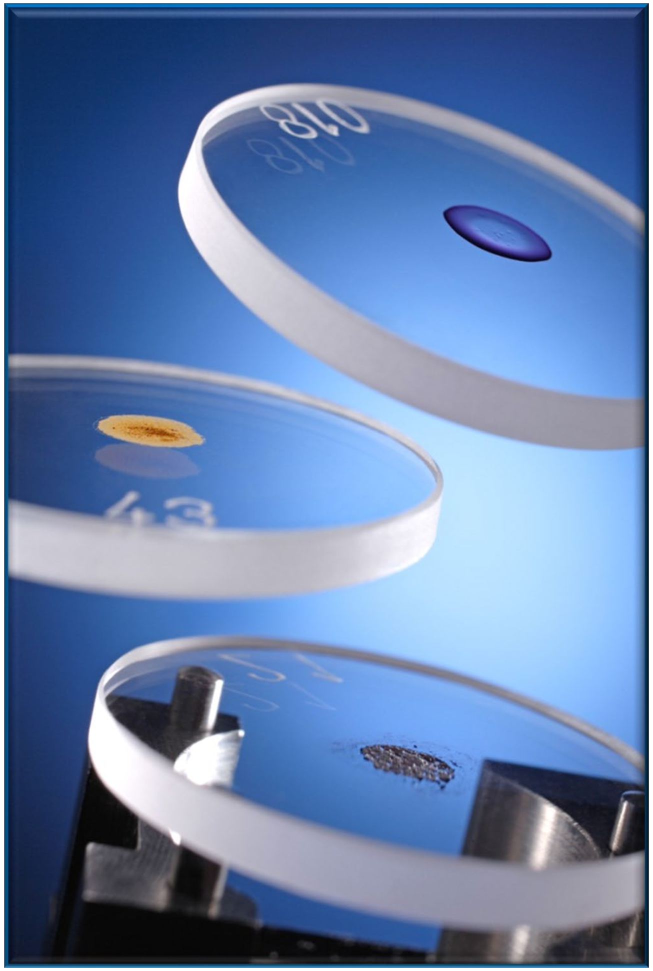
Beam angle: 0° / 90°

- 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

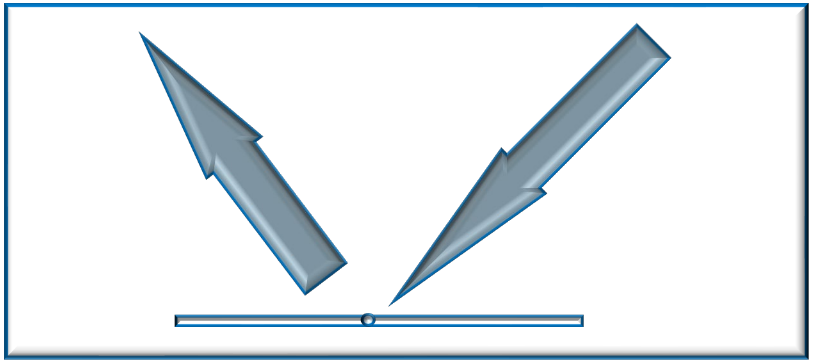
→ Matrix effects are negligible due to thin layer

→ 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

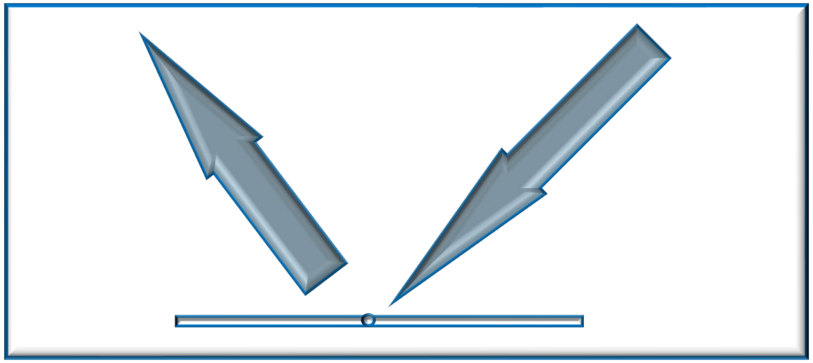
- ➔ Matrix effects are negligible
- ➔ Quantification is possible



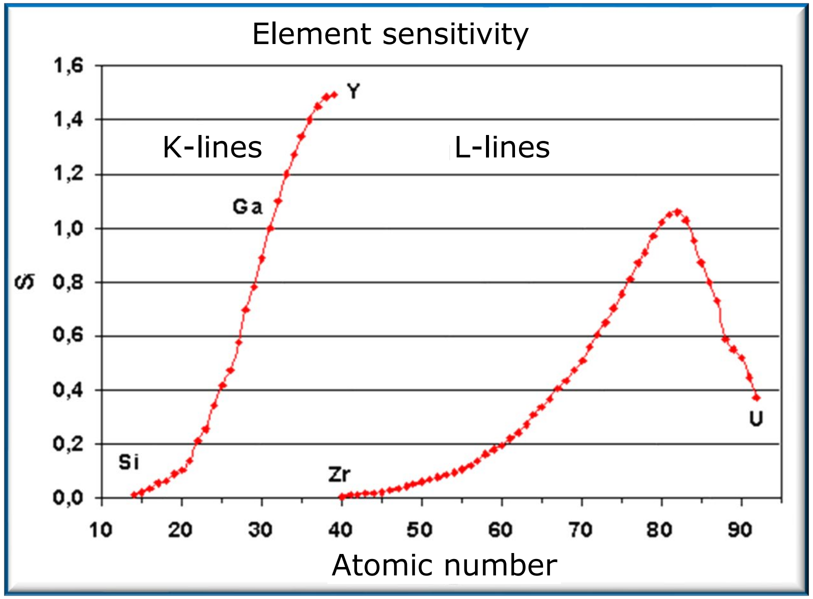
Principles of total reflection X-ray fluorescence spectroscopy

In TXRF the samples are prepared as thin films or layers

- ➔ Matrix effects are negligible
- ➔ Quantification is possible

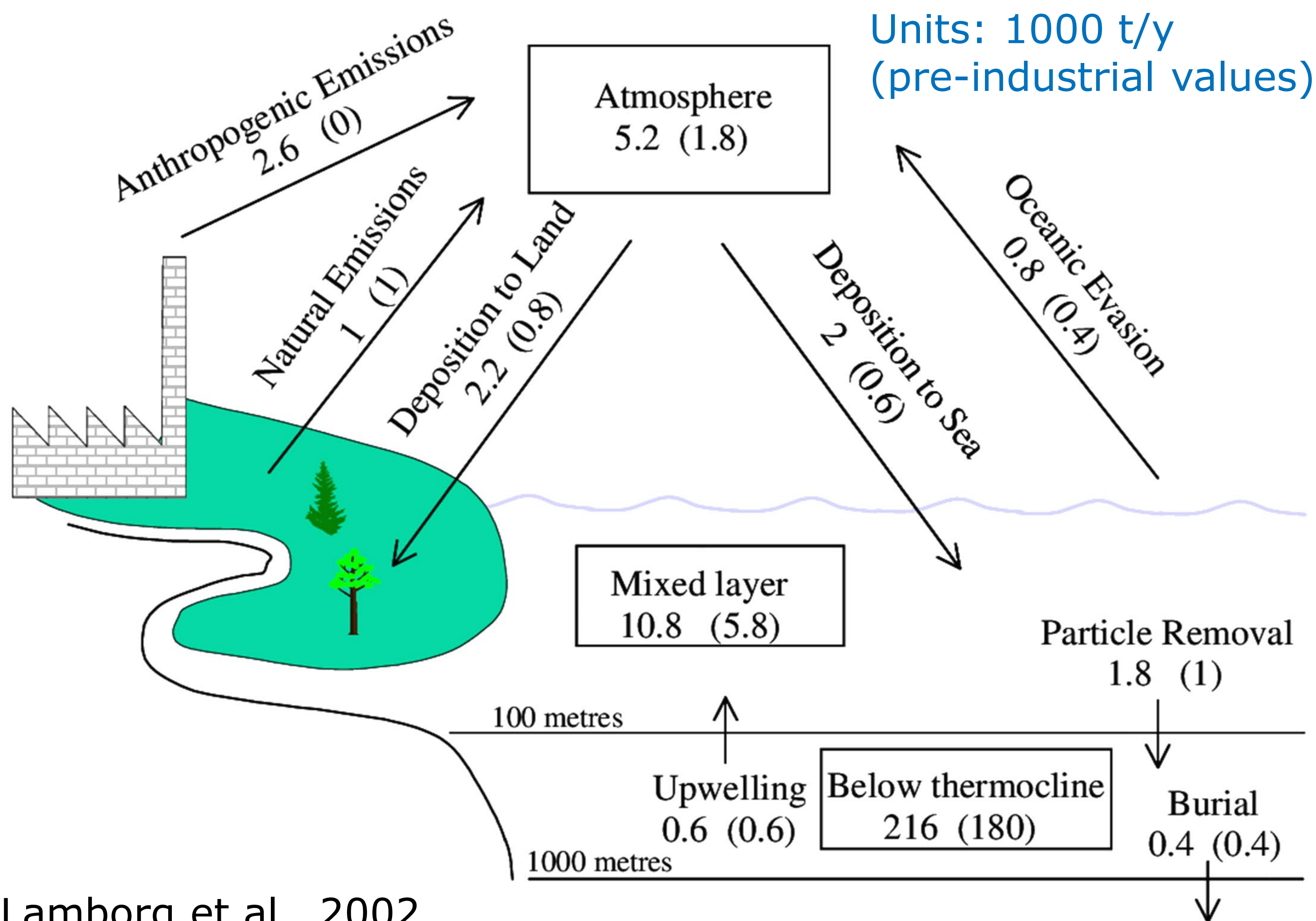


- TXRF detects elements from Na(11) to U(92)
- The element sensitivities depend on the atomic number
- The sensitivity factors are calibrated ex works
- Quantification requires the addition of one standard element



Mercury – Where does it come from and where does it go?

Mercury
Background information

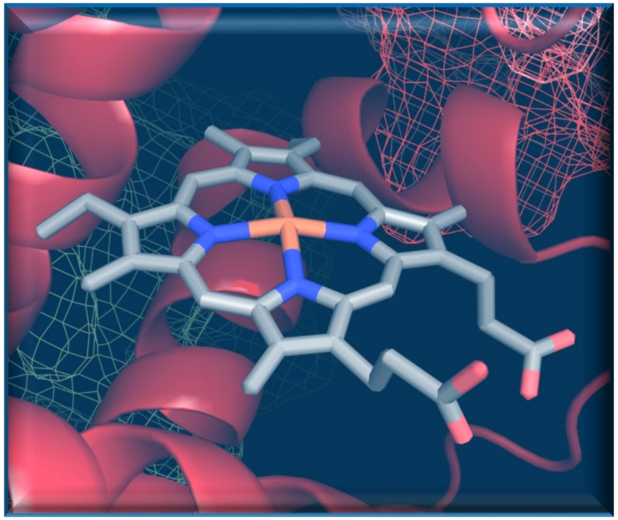


Lamborg et al., 2002

Mercury
Background information

Sources for mercury uptake

- Fish & other seafood, non-alcoholic beverages and composite food are the most important contributors to inorganic mercury dietary exposure



Toxicity of mercury

- The critical target for toxicity is the kidney
- Other targets include the liver, nervous system, immune system, reproductive and developmental systems
- Methylmercury is able to enter the hair follicle, and to cross the placenta as well as the blood-brain and blood-cerebrospinal fluid barriers, allowing accumulation in hair, the foetus and the brain

Mercury

Background information

Regulations

Maximum levels for mercury in certain foods
(Commission Regulation (EC) No 1881/2006)

3.3	**Mercury**	**Maximum level (mg/kg wet weight)**
3.3.1	Fishery products ([26]) and muscle meat of fish ([24]) ([25]), excluding species listed in 3.3.2. The maximum level applies to crustaceans, excluding the brown meat of crab and excluding head and thorax meat of lobster and similar large crustaceans (*Nephropidae* and *Palinuridae*)	0,50
3.3.2	Muscle meat of the following fish ([24]) ([25]): anglerfish (*Lophius species*) atlantic catfish (*Anarhichas lupus*) bonito (*Sarda sarda*) eel (*Anguilla species*) emperor, orange roughy, rosy soldierfish (*Hoplostethus species*) grenadier (*Coryphaenoides rupestris*) halibut (*Hippoglossus hippoglossus*) marlin (*Makaira species*) megrim (*Lepidorhombus species*) mullet (*Mullus species*) pike (*Esox lucius*) plain bonito (*Orcynopsis unicolor*) poor cod (*Tricopterus minutes*) portuguese dogfish (*Centroscymnus coelolepis*) rays (*Raja species*) redfish (*Sebastes marinus, S. mentella, S. viviparus*) sail fish (*Istiophorus platypterus*) scabbard fish (*Lepidopus caudatus, Aphanopus carbo*) seabream, pandora (*Pagellus species*) shark (all species) snake mackerel or butterfish (*Lepidocybium flavobrunneum, Ruvettus pretiosus, Gempylus serpens*) sturgeon (*Acipenser species*) swordfish (*Xiphias gladius*) tuna (*Thunnus species, Euthynnus species, Katsuwonus pelamis*)	1,0

Mercury
Background information

Regulations

- US EPA Safe Drinking Water Act: Maximum level 2 µg/l
- German drinking water regulation: Maximum level 1 µg/l
- International norms for beverages: Maximum levels 5 – 50 µg/l

Mercury analysis by TXRF - Instrumentation

Mercury analysis
Instrumentation

S2 PICOFOX

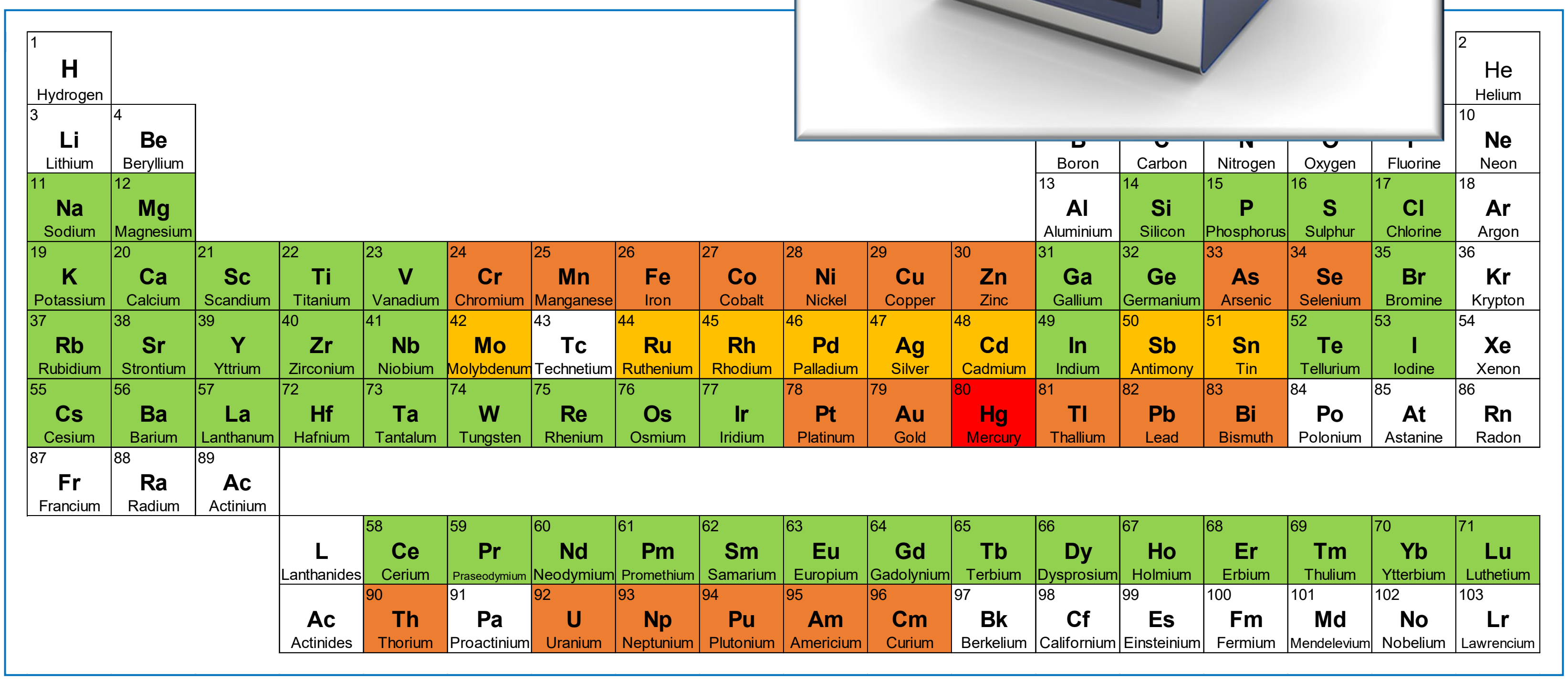
- Mo tube, 50 kV/1000 µA
- 60 mm² XFlash SDD
- 25 position sample changer

1 H Hydrogen																	He Helium
3 Li Lithium	4 Be Beryllium											B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine	0 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sb Antimony	51 Sn Tin	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astanine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium															
			L Lanthanides	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolynium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Luthetium
			Ac Actinides	90 Th Thorium	91 Pa Proactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Mercury analysis
Instrumentation

S4 T-STAR

- Mo- and W-tube, 50 kV/1000 µA
- Mo-K, W-L and W-Brems excitation
- 90 position sample changer



Mercury analysis by TXRF – Water and environment

Mercury analysis
Water and food samples

Background

Drinking water:

- Strict public limit values for various metals

Element	Limit value (µg/l)
Cu	2000
Mn	50
Fe	200
Ni	200
As	10
Cd	3
Hg	**1**
Pb	10
U	10

Example:
German drinking water regulation

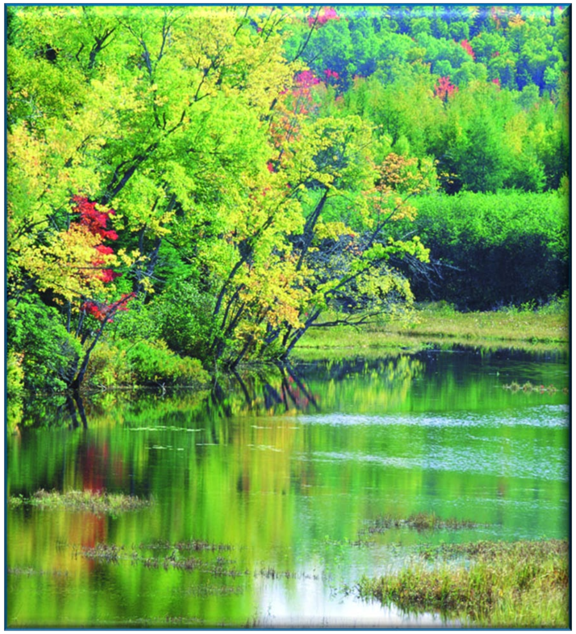
Mercury analysis
Water and food samples

Background

High-end laboratories for drinking water

- Very high sample throughput
- Only analysis of drinking water

→ In most cases application of ICP-MS



Water analysis in environmental research

- Normal sample throughput
- Water with different matrices and various content of solid matter
- Demand for the analysis of biomonitors
- Sometimes demand for mobile on-/near-site analysis

→ TXRF more suitable than other methods like ICP-MS

Mercury analysis
Water

Sample preparation

- Aliquotation of 1 ml sample
- Addition of EDTA- or thioureane solution for Hg-fixation
- Addition of gallium solution for internal standardization
- Homogenization, transfer of 10 µl onto sample carrier
- Drying
- Measurement

Mercury analysis
Water

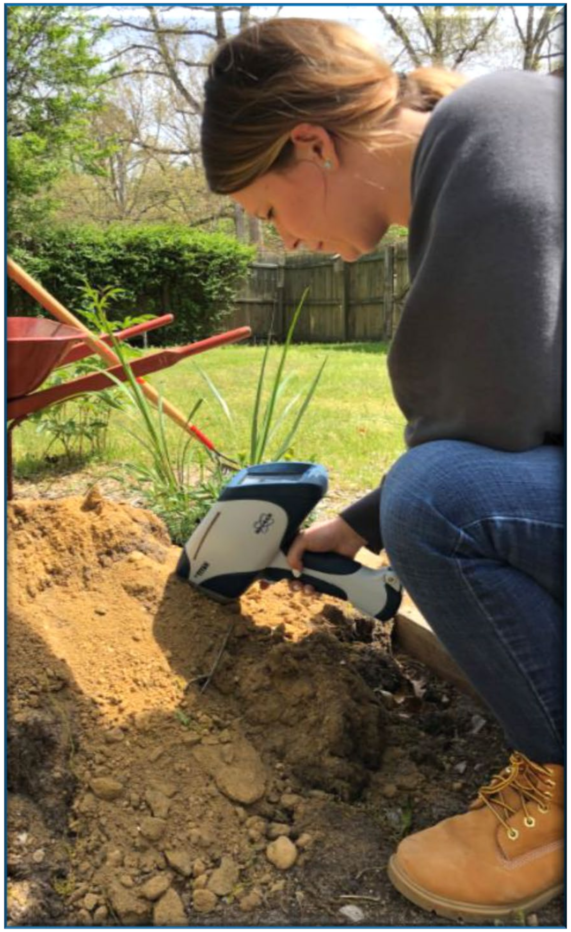
Results

	LLD Water (µg/l)		LLD Sewage (µg/l)	
	S2 PICOFOX	S4 T-STAR	S2 PICOFOX	S4 T-STAR
Manganese	0,62	0,35	1,4	0,88
Iron	0,49	0,27	1,1	0,72
Nickel	0,33	0,18	0,73	0,49
Copper	0,29	0,17	0,63	0,44
Arsenic	0,15	0,10	0,27	0,21
Cadmium	n. d.	51	n. d.	64
Mercury	**0,22**	**0,11**	**0,42**	**0,26**
Lead	0,20	0,11	0,37	0,23
Uranium	0,34	0,28	0,34	0,30

Mercury analysis
Soil

Background

- Heavy metal distribution in soils is often very inhomogeneous
- Typical TXRF analysis of soils only analysed minute sample amounts
→ only screening analysis is possible
- For soil samples the application of handheld XRF is more suitable.
These also fulfill several international norms (e.g. US EPA Method 6200-05, EN 15309—07, ISO 13196:2013)



Mercury analysis by TXRF – Food and beverages

Mercury analysis
Non-alcoholic beverages

Iced tea - Motivation

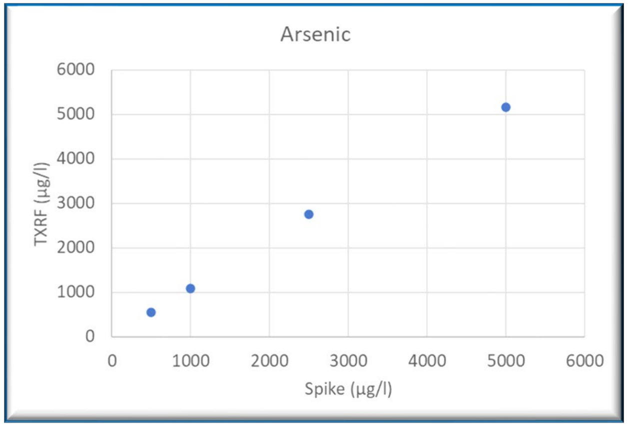
Iced tea is a widely consumed non-alcoholic beverage and challenging for trace element analysis because of the high sugar matrix

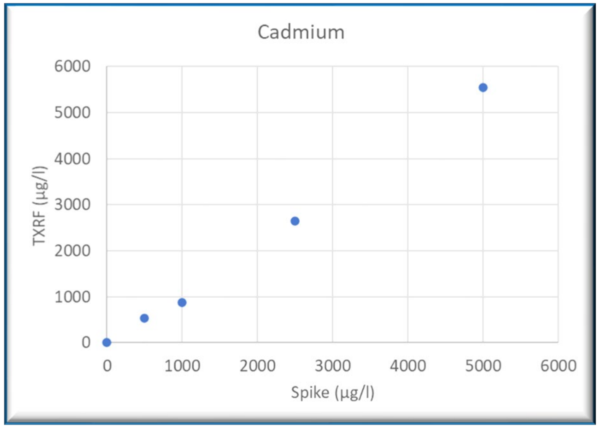
Sample preparation

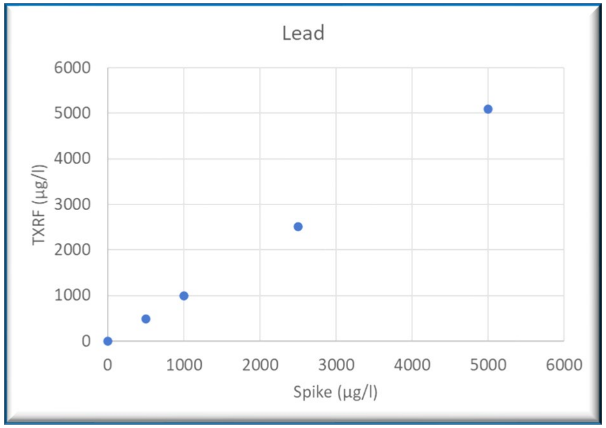
- Spiking of an iced tea samples with As, Cd, Hg and Pb
- Internal standardization with Ga and Pd
- Addition of polyvinyl alcohol solution
- Homogenization
- Preparation of 10 µl on quartz glass sample carriers

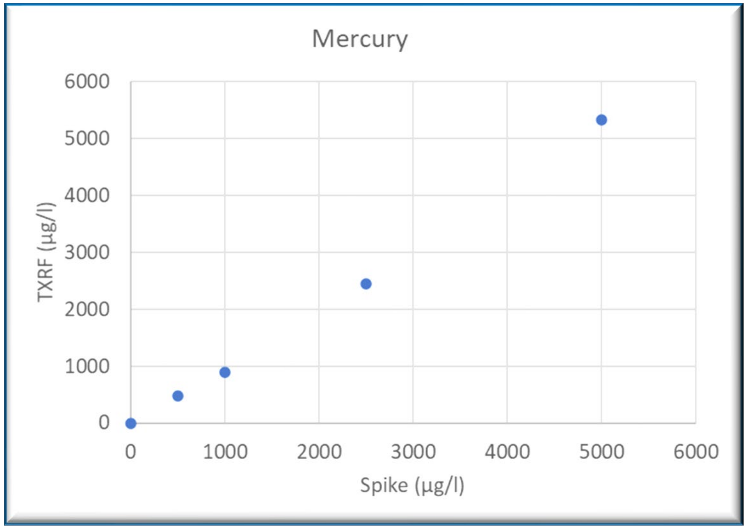
Mercury analysis
Non-alcoholic beverages

Results – S4 T-STAR



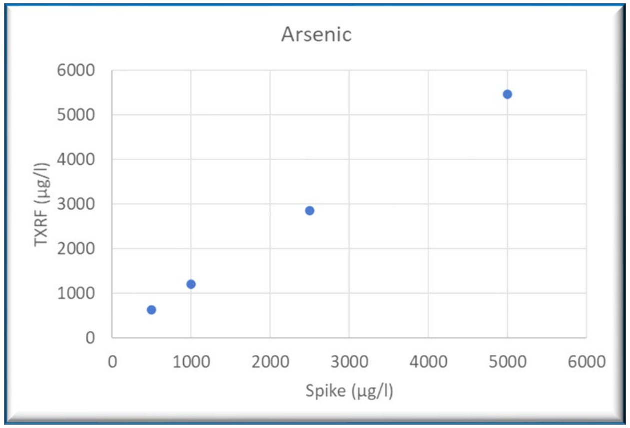


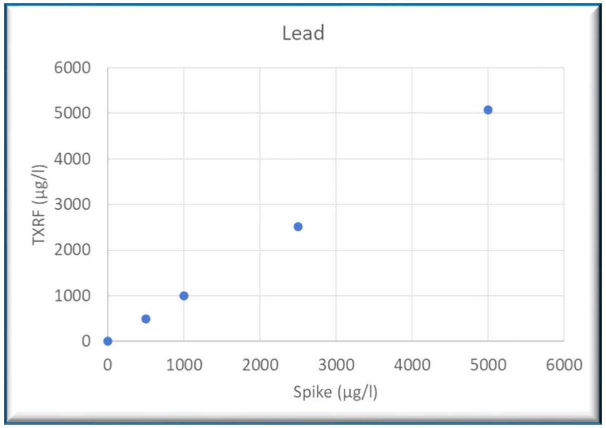


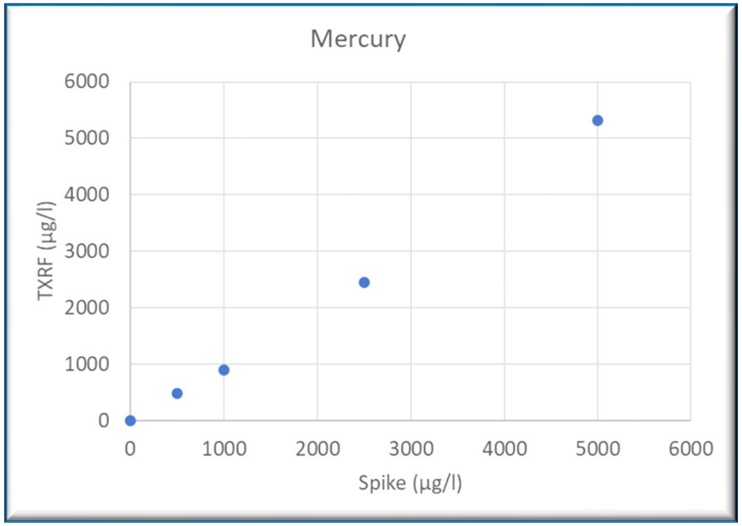


Mercury analysis
Non-alcoholic beverages

Results – S2 PICOFOX







Mercury analysis
Non-alcoholic beverages

Results

(µg/L)	LLD S2 PICOFOX	LLD S4 T-STAR
Arsenic	3,4	2,9
Cadmium	n.d.	132
Mercury	4,3	3,1
Lead	4,1	2,8

Mercury analysis
Solid food

Background

Dried food

- On a world-wide scale fish and rice are two dominant food sources
- For test purposes the certified reference materials „DORM-3“ (fish protein) and “NIST 1568a” (rice flour) were tested. Both are available as freeze-dried powders.

Mercury analysis
Solid food

Sample preparation solid food

- Grinding (< 25 µm)
- Weighing of about 100 mg into plastic tubes
- Suspension in 5 ml aqueous Triton X100 solution
- Addition of internal standard
- Homogenization, treatment in ultrasonic bath
- Preparation of 10 µl suspension on sample carrier
- Drying

Mercury analysis
Solid food

Results

	LLD S2 PICOFOX (mg/kg)		LLD S4 T-STAR (mg/kg)	
	NIST 1568a	DORM-3	NIST1568a	DORM-3
Arsenic	0,075	0,074	0,074	0,067
Cadmium	n. d.	n. d.	0,269	0,3
Mercury	**0,084**	**0,098**	**0,080**	**0,072**
Lead	0,086	0,099	0,072	0,065

Mercury analysis by TXRF – Medical analysis

Mercury analysis
Medical samples

Urine - Motivation

- Toxic metals like As and Hg are normally present in blood and serum at ppt-levels. This is too low for TXRF and is normally done by ICP-MS (TXRF is widely used in medical research for these samples for other elements like Mn, Cu, Zn and Se)
- As the kidney is the main secretion part, analysis of toxic metals in urine is of high interest
- Especially when dealing with sampling in rural regions, when intoxications must be monitored over longer time periods or samples must be stored and transported the analysis of urine samples becomes important

Mercury analysis
Medical samples

Urine - Samples

- Seronorm Urine CRM

Urine – Sample preparation

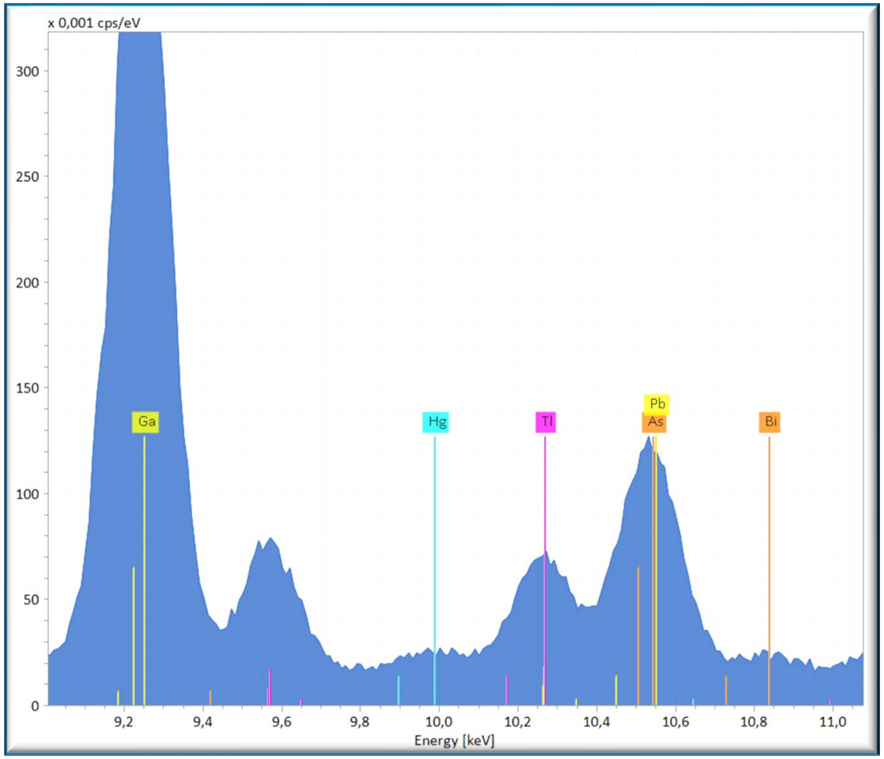
Same as for all high-matrix liquid samples

- Aliquotation
- Internal standardization
- Addition of polyvinyl alcohol solution
- Transfer of 10 µl to quartz glass sample carrier
- Drying (here on air at room temperature

Mercury analysis
Medical samples

Urine - Results

	LLD Seronorm Urine Level 2 (µg/l)	
	S2 PICOFOX	S4 T-STAR
Arsenic	2,9	2,8
Cadmium	n. d.	420
Mercury	**3,6**	**3,1**
Thallium	3,5	2,9
Lead	3,4	2,7
Bismuth	3,4	2,6



Mercury analysis
Medical samples

Hair - Motivation

- Hair is easier to collect, transport and store than other medical samples like blood or serum
- As elements are fixed in the hair, element control over longer time period is possible

Hair – Samples

- Certified reference sample NIES 13 (National Institute for Environmental Studies)
- 5 human hair samples (cleaned with acetone and ultrapure water)

Mercury analysis
Medical samples

Hair – Sample preparation by suspension

- Grinding
- Weighing of about 100 mg
- Suspension in aqueous Triton X100 solution
- Internal standardization
- Homogenization
- Transfer if 10 µl suspension to quartz glass carrier
- Drying

Mercury analysis
Medical samples

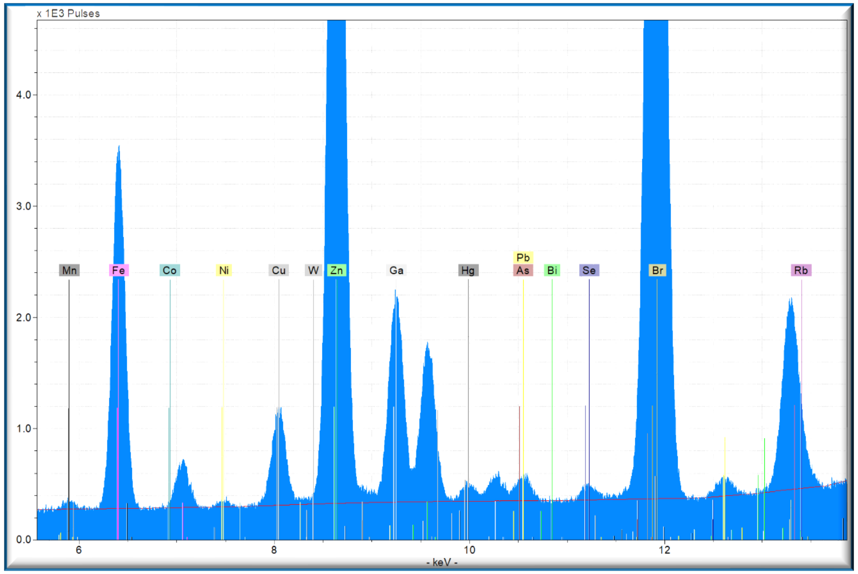
Hair – Sample preparation by acid digestion on hot plate

- Grinding
- Weighing of about 100 mg
- Digestion at 120 ° C for 2h in 1 ml HNO_3/H_2O_2 mixture (3:1), filled up to 5 ml with pure water
- Internal standardization
- Homogenization
- Transfer if 10 µl suspension to quartz glass carrier
- Drying

Mercury analysis
Medical samples

Hair - Results

LLD	S2 PICOFOX (mg/kg)		S4 T-STAR (mg/kg)	
	Digest.	Susp.	Digest.	Susp.
Manganese	0,40	0,61	0,15	0,31
Nickel	0,20	0,27	0,059	0,12
Arsenic	0,11	0,19	0,036	0,076
Cadmium	n. d.	n. d.	4,7	12,3
Mercury	**0,13**	**0,23**	**0,040**	**0,084**
Lead	0,13	0,22	0,040	0,085



Mercury analysis by TXRF – Analysis of cosmetics

Mercury analysis
Cosmetics

Mercury in cosmetics - Motivation

- Mercury is a common ingredient found in skin lightening soaps and creams
- It is also found in other cosmetics, such as eye makeup cleansing products and mascara
- Mercury can be found in cosmetics exists in two forms:
- inorganic (e.g. ammoniated mercury), which is used in skin lightening soaps and creams
- organic mercury compounds (thiomersal ethyl mercury and phenyl mercuric salts), which are used as preservatives

Mercury analysis
Cosmetics

Mercury in cosmetics - Motivation

The allowed mercury content in cosmetics is strictly regulated in many countries

Regulatory body	Hg limits for cosmetics other than eye area products
European Union	Banned
Many African nations	Banned
United States FDA	< 1 mg/kg
Health Canada	< 3 mg/kg
Phillipines FDA	< 1 mg/kg
Regulatory body	**Hg limits for eye area products**
European Union	< 70 mg/kg
United States FDA	< 65 mg/kg

Mercury analysis
Cosmetics

Sample preparation

- The complex and variable matrix of cosmetics (oil, fats, minerals and numerous organic and inorganic detergents) make the complete digestions for techniques like ICP-MS extremely difficult
- For TXRF a rather simple suspension preparation can be applied for all types of cosmetics

Measurements

- Measurements were performed with a S2 PICOFOX, applying Mo-K excitation and measurement times of 1000 s

Mercury analysis
Cosmetics

Results

Table 3 Comparison of determination results(mg/kg) of cosmetics samples by different methods

样品 Samples	Pb 本方法 TXRF	Pb 其它方法 Other method	As 本方法 TXRF	As 其它方法 Other method	Hg 本方法 TXRF	Hg 其它方法 Other method
GBW09305	39.4	37.2(Reference value)	9.1	9.9(Reference value)	–	–
GBW09306	–	–	–	–	0.64	0.67(Reference value)
GBW09307	–	–	–	–	1.33	1.35(Reference value)
洁面膏 Face wash gel	1.25	1.20 (ICP-MS)	–	–	1.20	1.16 (ICP-MS)
护臀膏 Bottom Butte	–	–	1.30	1.24 (ICP-MS)	–	–
日霜 Day cream *	0.62	0.60 (Added value)	0.58	0.60 (Added value)	0.57	0.60 (Added value)
美白霜 Whitening cream	6.71	6.84 (ICP-MS)	–	–	–	–

*：空白样品加标(Spiked blank sample)。

Wang, Q. et al. (2018): „Determination of Lead, Arsenic and Mercury in Cream Cosmetics by Total Reflection X-Ray Fluorescence Spectrometry Using Suspension Sampling", Chinese Journal of Analytical Chemistry, 4, 517-523

Mercury analysis
Cosmetics

Summary

- TXRF is suitable for the analysis and control of Hg (and other toxic metals) in all types of cosmetics
- The applied sample preparation is fast, easy and does not need any toxic or dangerous chemicals

Outlook

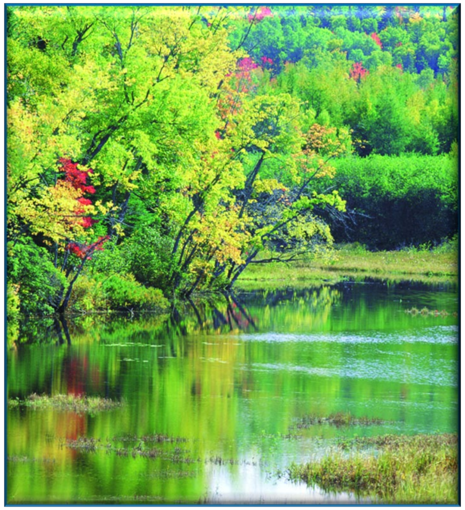
- Detailed work on the analysis of toxic metals in cosmetics (optimisation of sample preparation procedures, development of SOPs, publications) in cooperation with external partners are planned for Q1 2021

Mercury analysis by TXRF - Summary

Mercury analysis
Summary

Environmental analysis

- TXRF is suitable for the analysis of Hg and other metals in water samples from fresh water to highly contaminated sewages
- All different kinds of biomonitors (plants, algae, biofilms etc.) can be analysed for environmental research and control



Food and beverages

- Beverages can easily be analysed into the sub mg/l range for Hg and other toxic elements like As and Pb
- Fast screening for toxic elements in solid foodstuff is possible after an easy sample preparation, avoiding complex digestion procedures

Mercury analysis
Summary

Medical research

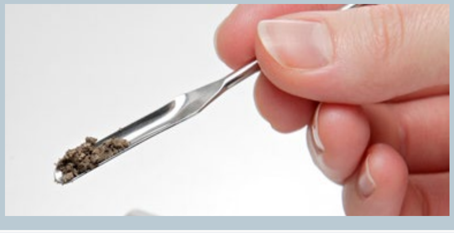
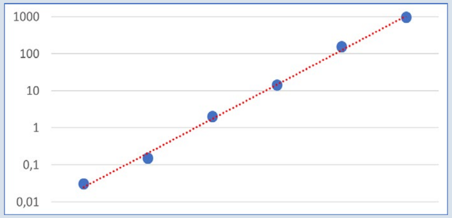
- Hg and other metals can easily be analysed in urine and hair samples applying fast and easy preparation techniques

Cosmetics

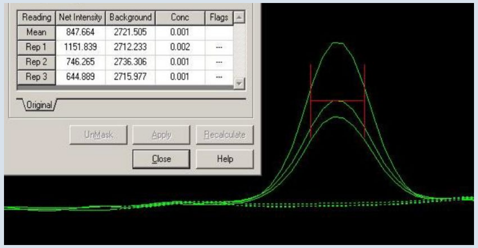
- Hg and other metals like As and Pb can be analysed in various types of cosmetics for control of regulatory limits avoiding time consuming and expensive preparation techniques

Comparison with Atomic Spectroscopy

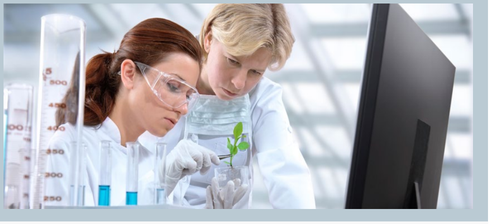
Feature comparison
TXRF versus ICP

Topic	Feature	Benefit	
Suspensions, solid samples	direct analysis without sample digestion possible	saves time and avoids use of hazardous chemicals	
Solid, valuable samples	non-destructive analysis possible (semi-quantitative)	samples are not destroyed and can be used for other purposes	
Linear range	high linear quantify-cation range from sub-ppb to low %	avoids multiple calibrations or measurements; full results after one run	

Feature comparison
TXRF versus ICP

Topic	Feature	Benefit	
Media, disposables	no consumption of media (e.g. carrier gases, chemicals, standards), no need for periodic replacement of parts (lamps, nebulizer)	cost saving; no special infrastructure (gas lines) required	
Quantification	by internal standardization, instrument calibrated ex works	simple; time saving, no daily calibration required	
Memory effects	No memory effects	ICP: intense purging of the system, risk of carryover from previous samples	

Feature comparison
TXRF versus ICP

Topic	Feature	Benefit	
System maintenance and cleaning	QC system check automated, no cleaning of specific parts required	ICP requires daily/weekly system checks	
Ease of operation	simple, suitable for academic training	technicians are able to use TXRF; ICP typically used by (scientific) experts	
Footprint	compact benchtop instrument, foot print 693 x 528 mm	saves lab space	

Cost comparison
TXRF versus ICP-MS

Total (5 years)	S4 T·STAR	ICP-MS	Remarks
Installation	136.900 €	188.100 €	incl. peripheral devices
Operation costs	64.600 €	179.000 €	disposables, gas, media, standards etc.
Man hours	82.000 €	134.000 €	100 k€/a, 220 working days, 20 samples/d
Total	**283.500 €**	**501.100 €**	
Costs / sample	12,89 €	22,78 €	

Sources: Automotive study 2015
EPA study
ICP-OES cost calculator Spectro
Discussion forums
Bruker data

More detailed PPT and Excel sheet available

Technology comparison
Day-to-day checks

Technology comparison
Daily checks

ICP	TXRF
Setup before analysis	
Inspect torch for injector blockage	Check system status
Check nebulizer for blockage	Select excitation
Inspect peristaltic pump tubing	
Check exhaust system operating	
Rinse between samples (ICP-MS)	
After analysis / end of day	
Aspirate rinse solution	
Release pressure and detach pump	
Empty waste vessel	
Wipe down exterior surfaces	Wipe off exterior surfaces
Leave system in stand-by mode	Automatic system stand-by

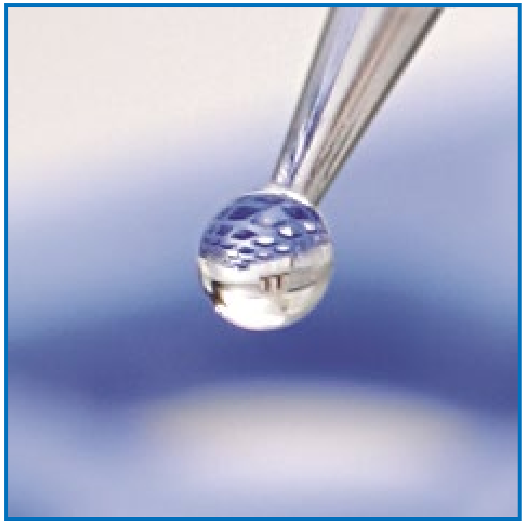
Technology comparison
Weekly/monthly checks

ICP	TXRF
Clean torch and test plasma ignites after reconnection	Sensitivity test (automatic!)
Clean nebulizer frequently (ICP-MS)	Start auto beam adjustment, when sensitivity is decreasing
Check sample introduction tubing, O-rings	
Inspect cone or snout and clean, if needed; check vacuum after reconnection	
Check/replace graphite gasket (ICP-MS)	
Inspect torch bonnet (radial ICP, -MS)	
Clean spray chamber	Check auto beam adjustment
Check/clean nebulizer (ICP-OES)	
Inspect induction coil	
Check/clean air filter for cooling air	
Check/clean water level and air filter on water chiller	

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!

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