Rapid on-site trace element analysis of wastewater, sewage and industrial effluents

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Bruker Nano GmbH, Berlin
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Innovation with Integrity

Welcome

Speakers

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Berlin, Germany

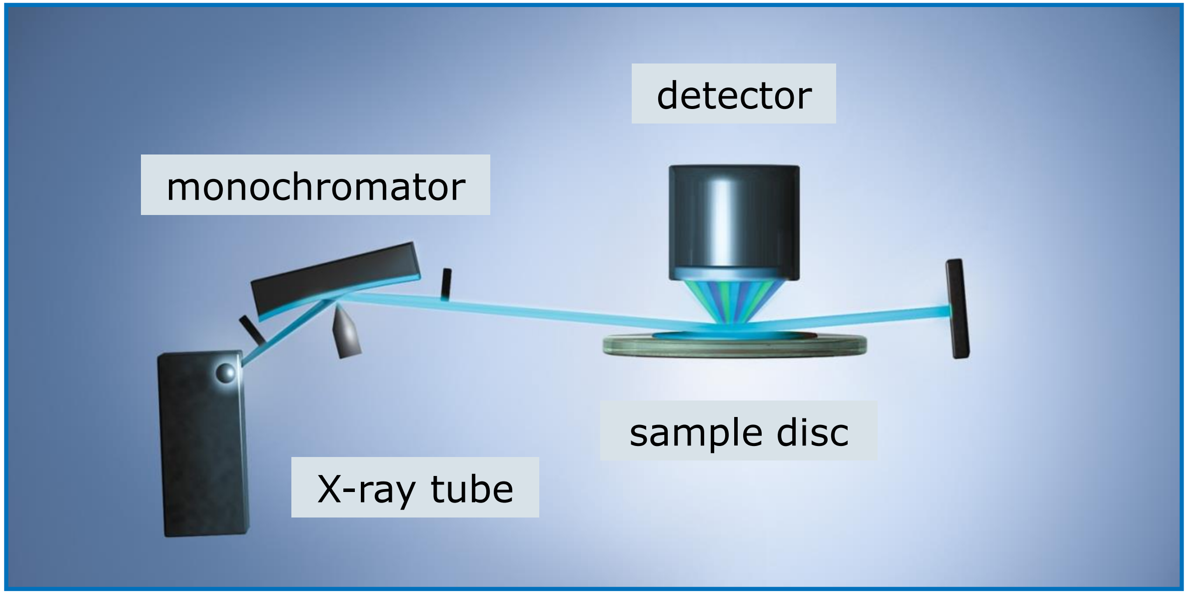
Itinerary

- Introduction
- Principles of TXRF
- Water and wastewater application examples
- Standardization of TXRF
- Comparison with Atomic Spectroscopy methods
- Q & A

Principles of TXRF

Principles of TXRF
Technical background

Total reflection X-ray fluorescence spectroscopy

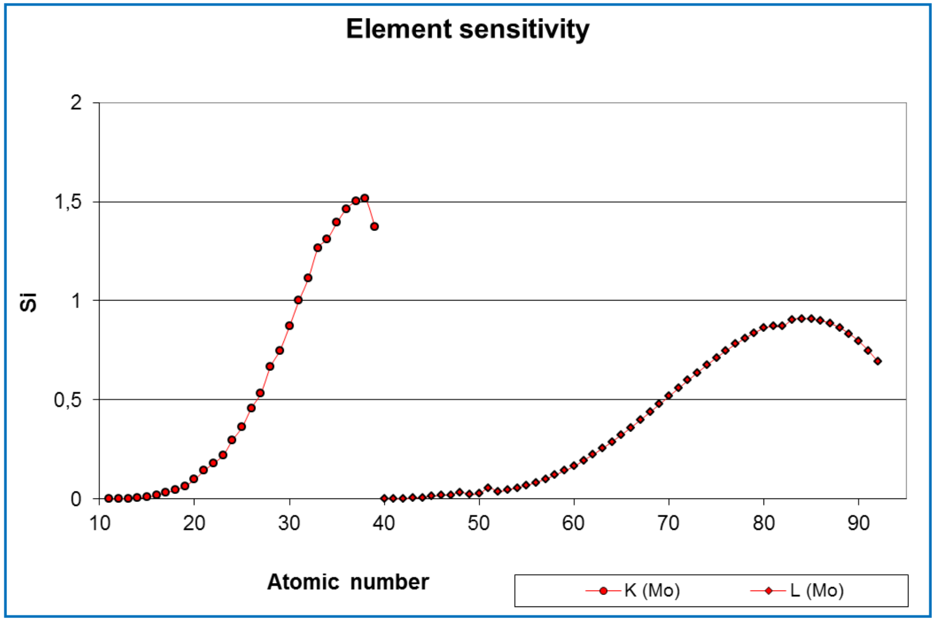


Beam angle: 0˚ / 90˚

- 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
- Matrix effects are negligible

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 countrate
N_{IS}: Internal standard net countrate
S_i: Element sensitivity factor
S_{IS}: Internal standard sensitivity factor

Principles of TXRF
Bruker Product Portfolio

S2 PICOFOX - Unique benefits

• Most compact design	transportable, for on-site analysis
• Fixed excitation mode	easy to use, most suitable for teaching
• >270 installations worldwide	well established technology
• Attractive pricing	most valuable TXRF solution

Principles of TXRF
Bruker Product Portfolio

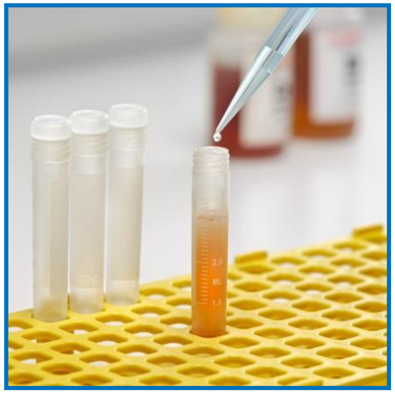
S4 T-STAR - Unique benefits

• Multiple excitation modes	to detect most elements of the PSE
• Large area detectors	improved sensitivity for lowest limits of detection
• Motorized beam path	automatic beam adjustment and QC procedures
• Large sample capacity	up to 90 sample discs, multi-user operation
• Most modern software	instrument status display statistical functions

Preparation of wastewater and sludges

Sample preparation workflow
Suspensions and particulate matter

Suspensions can be analyzed right after dilution

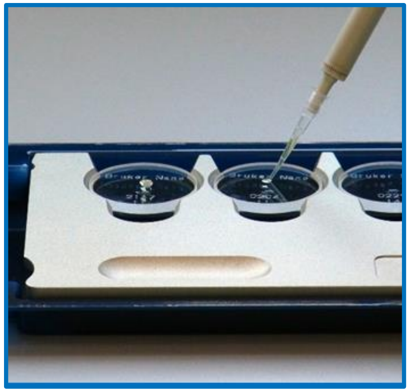


Dilute sample with distilled water

Add internal standard and drying agent

Homogenize

Sample preparation workflow
Suspensions and particulate matter



Pipette on carrier

Dry by vacuum

Load system and start measurement

Accessories for optimized workflow

- T-Box: carriers are stored safely
  - Reduces risk of contamination
- T-DRY drying station
  - Direct drying of up to 9 trays (81 samples)
  - No direct disc handling for contamination prevention

Typical measurements of wastewater by TXRF

Wastewater
Objective

Samples

- 4 artificially spiked sewage samples with high matrix content (Na, Mg, S, Cl, K, Ca)
- 1 certified wastewater standard SPS WW2

Analytical task

- Analysis of toxic elements
  Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Te, Ba, Hg, Tl, Pb and Bi

Wastewater
Sample preparation

Sample preparation

- Aliquotation of 1 ml sewage sample
- Addition of 10 µl internal standard
  - Sc (1 g/l) → W-L excitation
  - Ga (0,1 g/l) → Mo excitation
  - Pd (1 g/l) → W-Brems excitation
- Addition of 100 µl polyvinyl alcohol solution (0,1 g/l) for homogeneous sample drying
- Homogenization in automatic sample shaker
- Preparation of 10 µl sample onto siliconized quartz glass carriers
- Drying in vacuum
- Two samples prepared nine-fold for MLD, all others measured in triplicate

Wastewater
Spectrometer configuration

S2 PICOFOX

- Mo tube, 50 kV/600 µA
  - Mo-K excitation, 17,5 keV
- 30 mm^2 XFlash SDD
- 25 position sample changer

Wastewater
Spectrometer configuration

S2 PICOFOX

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S4 T·STAR

- Mo tube, 50 kV/1000 µA
  - Mo-K excitation, 17,5 keV
- W-tube, 50 kV/1000 µA
  - W-Brems excitation, 35 keV
  - W-L excitation, 8,4 kev
- 60 mm² XFlash SDD
- 90 position sample changer

Wastewater Measurements

Element range

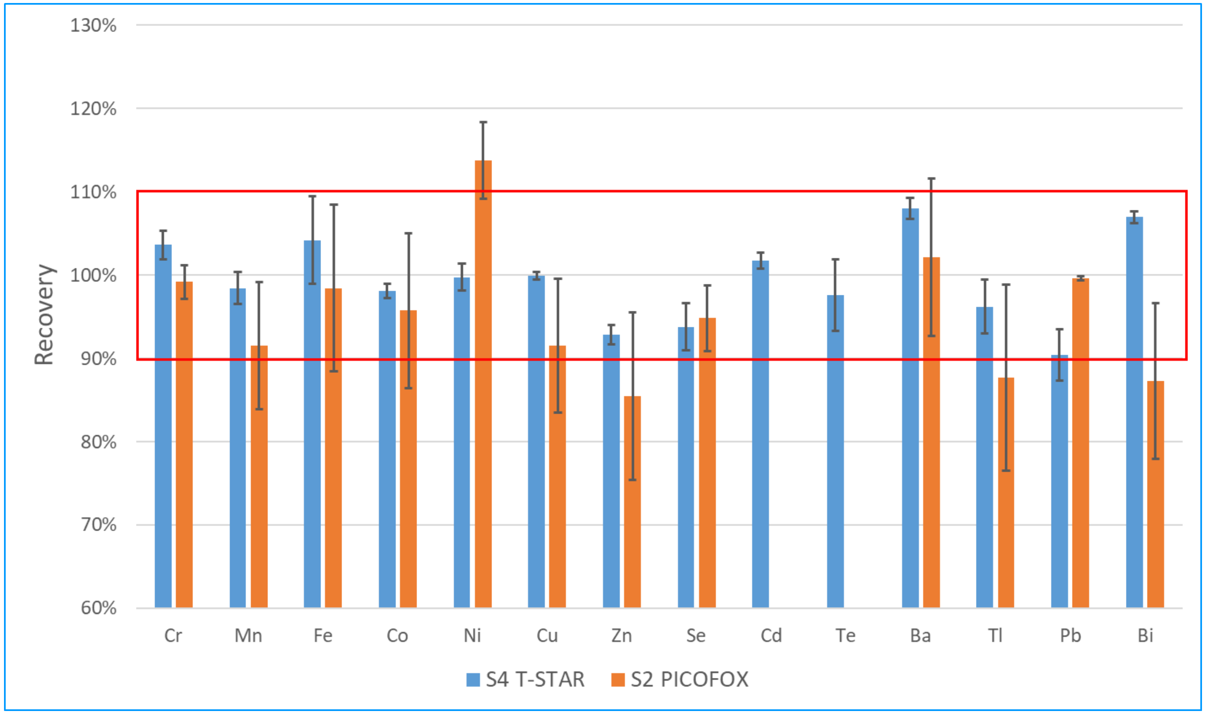
1 **H** Hydrogen																	2 He Helium
3 **Li** Lithium	4 **Be** Beryllium											5 **B** Boron	6 **C** Carbon	7 **N** Nitrogen	8 **O** Oxygen	9 **F** Fluorine	10 **Ne** Neon
11 **Na** Sodium	12 **Mg** Magnesium											13 **Al** Aluminium	14 **Si** Silicon	15 **P** Phosphorus	16 **S** Sulphur	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

Light elements   Toxic elements   Toxic elements S4 T-STAR only

Wastewater
Results

Recovery rates

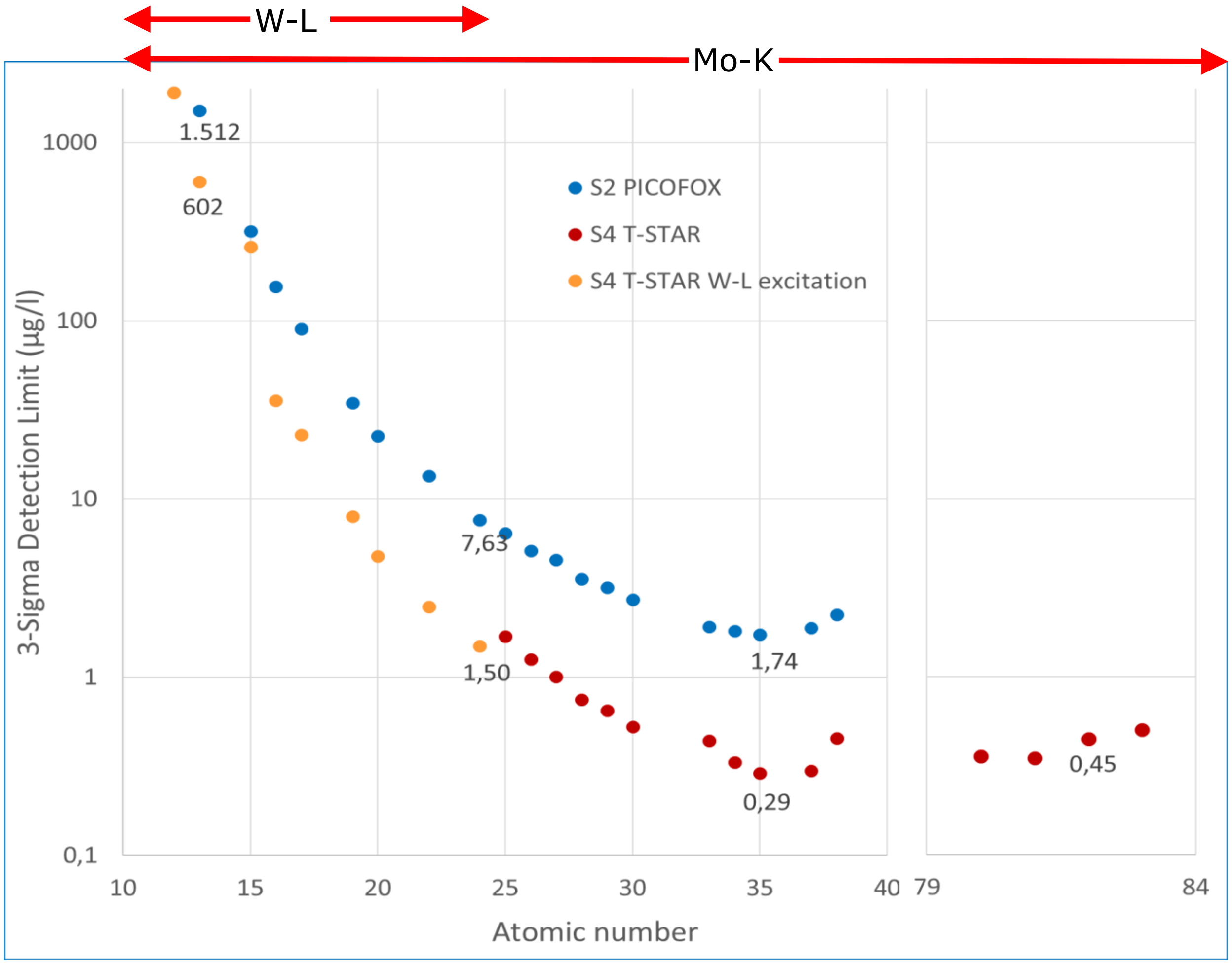
- S2 PICOFOX gives recovery rates of 100 ± 15%
- S4 T·STAR: most results within a confidence limit of ± 5% (all ± 10%)
- Standard deviation also improved with S4 T·STAR



Wastewater
Results

Detection limits

- 3-sigma detection limits of both systems applying the Mo-K excitation
- W-L excitation improves light element detection by a factor of 4 to 10

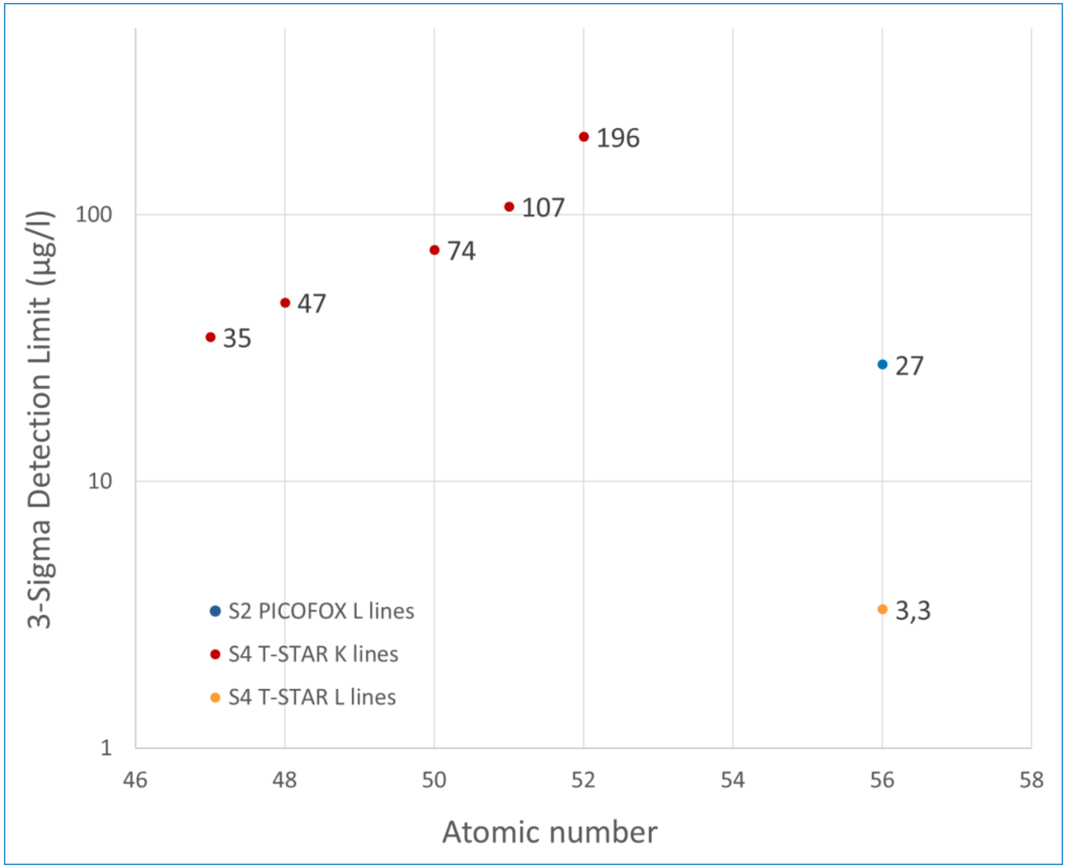


Representative values for Al, Cr, Br and Pb

Wastewater
Results

Detection limits

- Only the S4 T·STAR offers a W-Brems excitation for detection of element K-lines from Zr to I
- LOD are higher compared to Mo excitation, but without line inter-ferences and sufficient to fulfill regulatory demands for wastewaters



Wastewater
Mercury analysis

Results of Hg analysis

- Hg analysis requires fixation
  - Addition of thiourea solution (1 mM)
- Low detection limits can be achieved with both systems
  - S2 PICOFOX: < 5 µg/l
  - S4 T-STAR: < 0,5 µg/l
- Only spikes of 100 ppb could be quantified accurately

Wastewater
Summary

Summary

- At typical concentration ranges of wastewaters Cr, Mn, Fe, Co, Ni, Cu, Zn, Ba, Tl, Pb and Bi can be analyzed with both systems
- Due to the improved sensitivity the S4 T-STAR has advantages for
  - The analysis of Al with W-L excitation
  - As and Se in the lower µg/l range (< 1 ppb)
  - Cd and Te using W-Brems excitation

Rapid analysis of dissolved water samples

Rapid water analysis
The challenge

Samples

- Target elements:
  Ti, Cr, V, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb, Pb
- Measurements with new S4 T-STAR,
  Mo and W excitation

Issues of ICP analysis

- Time for sample preparation,
  need results within 30 min
- No lab infrastructure at measurement sites

Samples

- Standard samples containing 0,5 mg/kg
  target elements
- Samples with unknown element concentrations

Rapid water analysis
Sample preparation / measurement

- Transfer of 1 ml sample to vial
- + 100 µl PVA-solution / 10 mg/l Y
- Homogenization
- Transfer of 10 µl to sample carrier
- Drying by vacuum
- Measurement with Mo excitation
- Automatic excitation change
- Measurement with W excitation

Rapid water analysis
Results

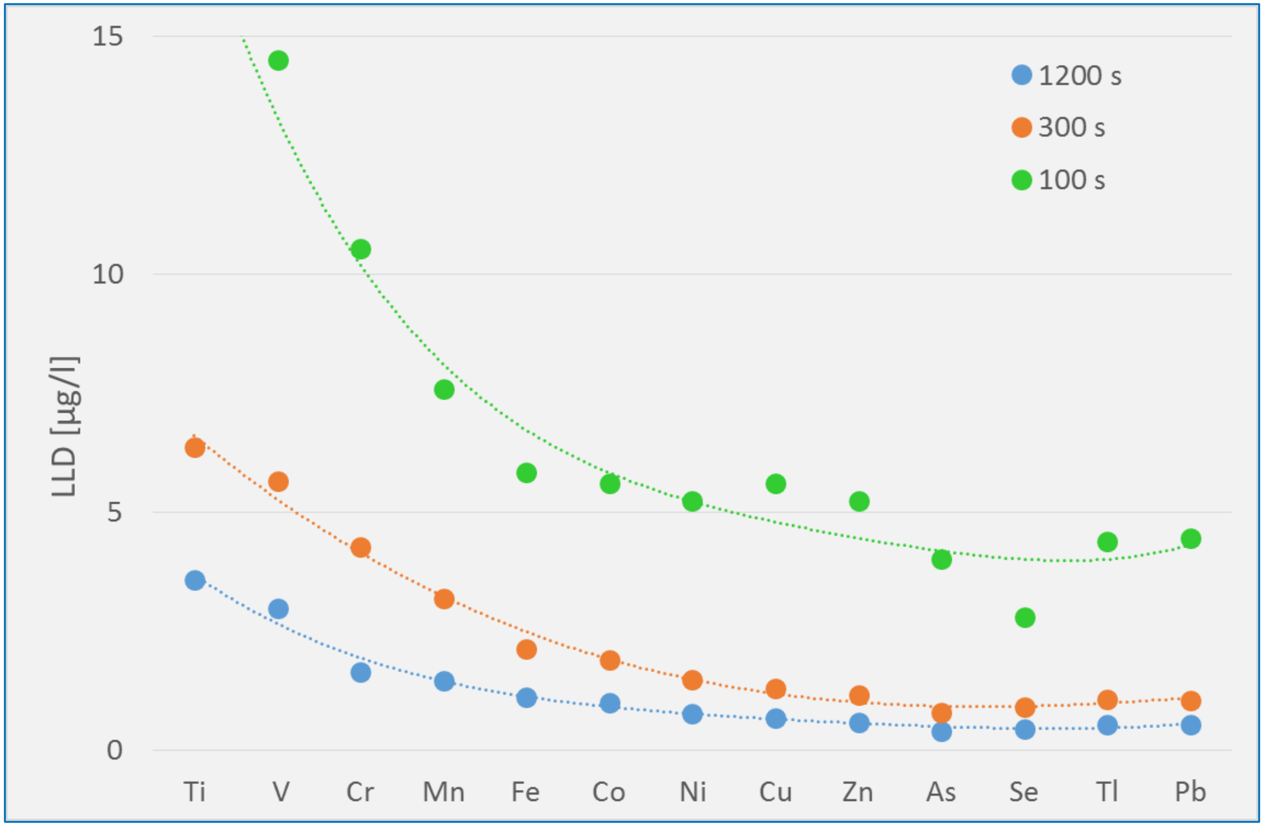
Name	Excitation	0.5 ppm - 100s (µg/l)			0.5 ppm - 200s (µg/l)			0.5 ppm - 300s (µg/l)		
		Average	SD	LLD	Average	SD	LLD	Average	SD	LLD
Mg	Mo-K	34388	9544	62554	13303	1207	45152	15236	6233	35873
Cl	Mo-K	3476	1091	222	3631	1347	156	3491	1236	126
K	Mo-K	7087	145	112	7013	262	79	7084	206	64
Ca	Mo-K	827	67	66	863	118	47	893	101	38
Ti	Mo-K	675	16	17	682	19	12	658	20	9,8
V	Mo-K	534	11	15	544	7,3	10	540	3,7	8,3
Cr	Mo-K	479	14	11	503	11	7,3	496	15	6,0
Mn	Mo-K	498	12	7,6	496	14	5,3	484	8,2	4,2
Fe	Mo-K	607	14	5,9	609	15	4,1	604	11	3,3
Co	Mo-K	472	4,4	5,6	471	14	3,9	469	7,1	3,1
Ni	Mo-K	475	9,6	5,3	475	6,2	3,6	475	12	2,9
Cu	Mo-K	477	7,4	5,6	487	8,6	3,9	486	8,6	3,1
Zn	Mo-K	713	11	5,2	723	22	3,7	718	21	2,9
As	Mo-K	468	7,6	4,0	464	7,5	2,8	465	14	2,3
Se	Mo-K	458	6,8	2,8	456	10	2,0	454	6,2	1,6
Br	Mo-K	13	8,6	4,1	16	8,3	2,9	15	8,4	2,3
Rb	Mo-K	9,8	0,63	1,9	9,6	0,33	1,3	9,7	0,22	1,1
Y (i.s.)	Mo-K	1000		5,1	1000		3,6	1000		2,9
Tl	Mo-K	400	12	4,4	405	12	3,1	403	9,9	2,5
Pb	Mo-K	541	14	4,5	552	18	3,1	549	15	2,5

Name	Excitation	0.5 ppm - 300s (µg/l)			0.5 ppm - 600s (µg/l)			0.5 ppm - 1000s (µg/l)		
		Average	SD	LLD	Average	SD	LLD	Average	SD	LLD
Mo	W-Brems	165	30	29	162	31	24	160	21	17
Ag	W-Brems	168	36	58	179	95	50	188	47	33
Cd	W-Brems	< LLD		81	114	62	70	104	40	46

Rapid water analysis
Detection limits Mo excitation

Sample 0.5 ppm standard mixture

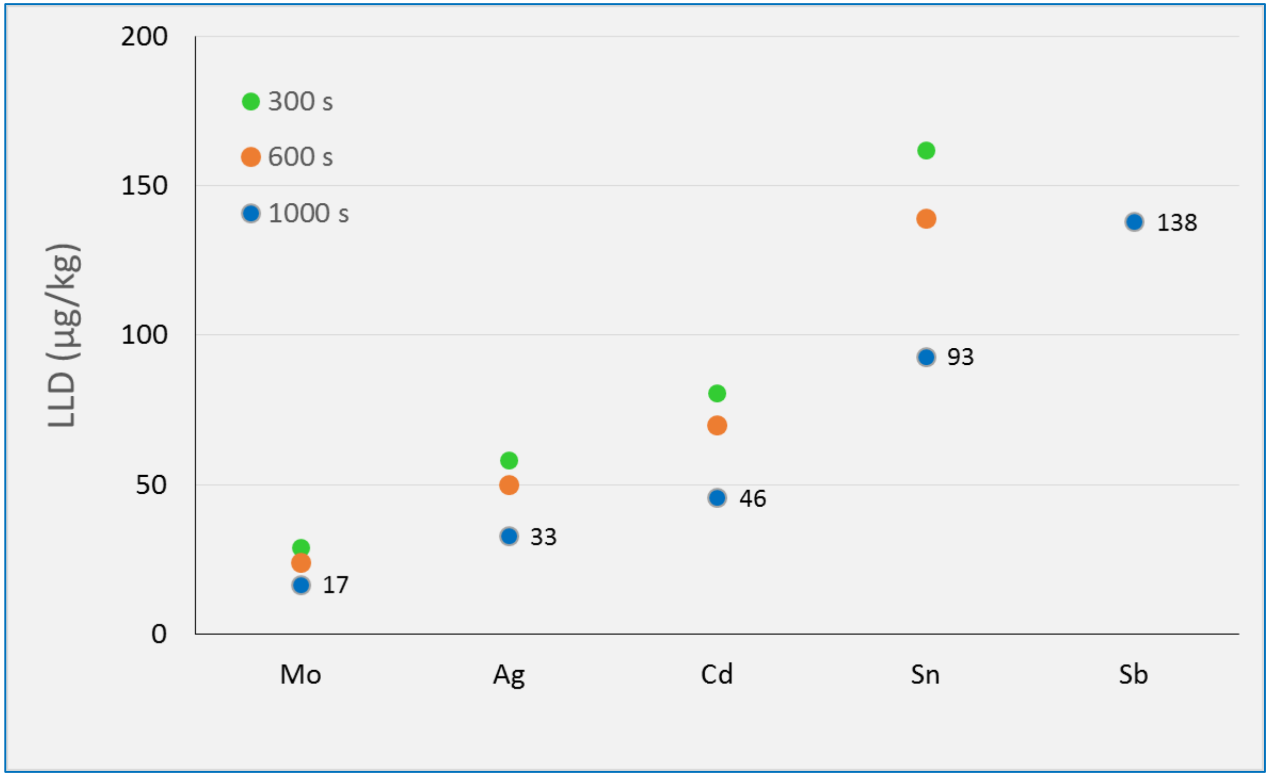
- Mo excitation: 100 s measurement time sufficient
- Detection limits close or below 10 ppb
- Longer measurement times will improve standard deviation



Rapid water analysis
Detection limits W-Brems excitation

Sample 0.5 ppm standard mixture

- W-Brems excitation: less than 5 min measurement time for sub-ppm levels
- Longer times needed only for low levels below 100 ppb



Rapid water analysis
Lead time for 10 samples

Step	Time
Transfer of 1 ml sample to vial	01:00 min
+ 100 µl PVA-solution / 10 mg/l Y	02:00 min
Homogenization	02:30 min
Transfer of 10 µl to sample carrier	03:30 min
Drying by vacuum	09:00 min
Measurement with Mo excitation	11:00 min
Automatic excitation change	12:00 min
Measurement with W excitation	17:00 min

Rapid water analysis
Conclusion

- The entire element range from Al to U can be accurately quantified in wastewaters, sludges and effluents
- From sampling to final results in less than 30 minutes
- The analysis close to the sampling site is possible – just a power supply is required

Measurement of light elements in water

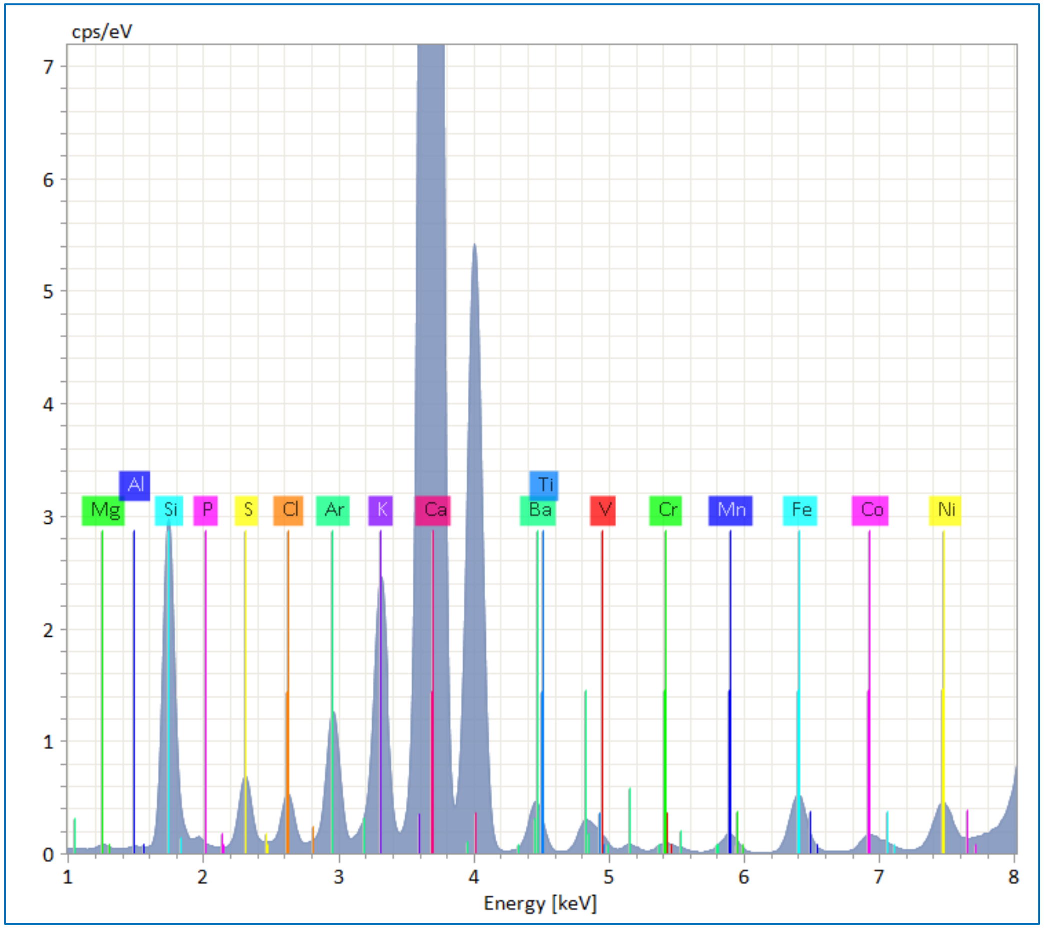
Light elements in water
Objective

Determination of detection limits

- Sample: NIST 1643d water standard
  Typical element concentration 10 to 100 µg/l
- Measurements:
  - Original standard
  - 1:10 diluted standard
- Spectrometer S4 T·STAR
  - W-L excitation (8,4 keV)
  - 60 mm² XFlash SDD
- Measurement time: 1000 s
  measurements were done in triplicate

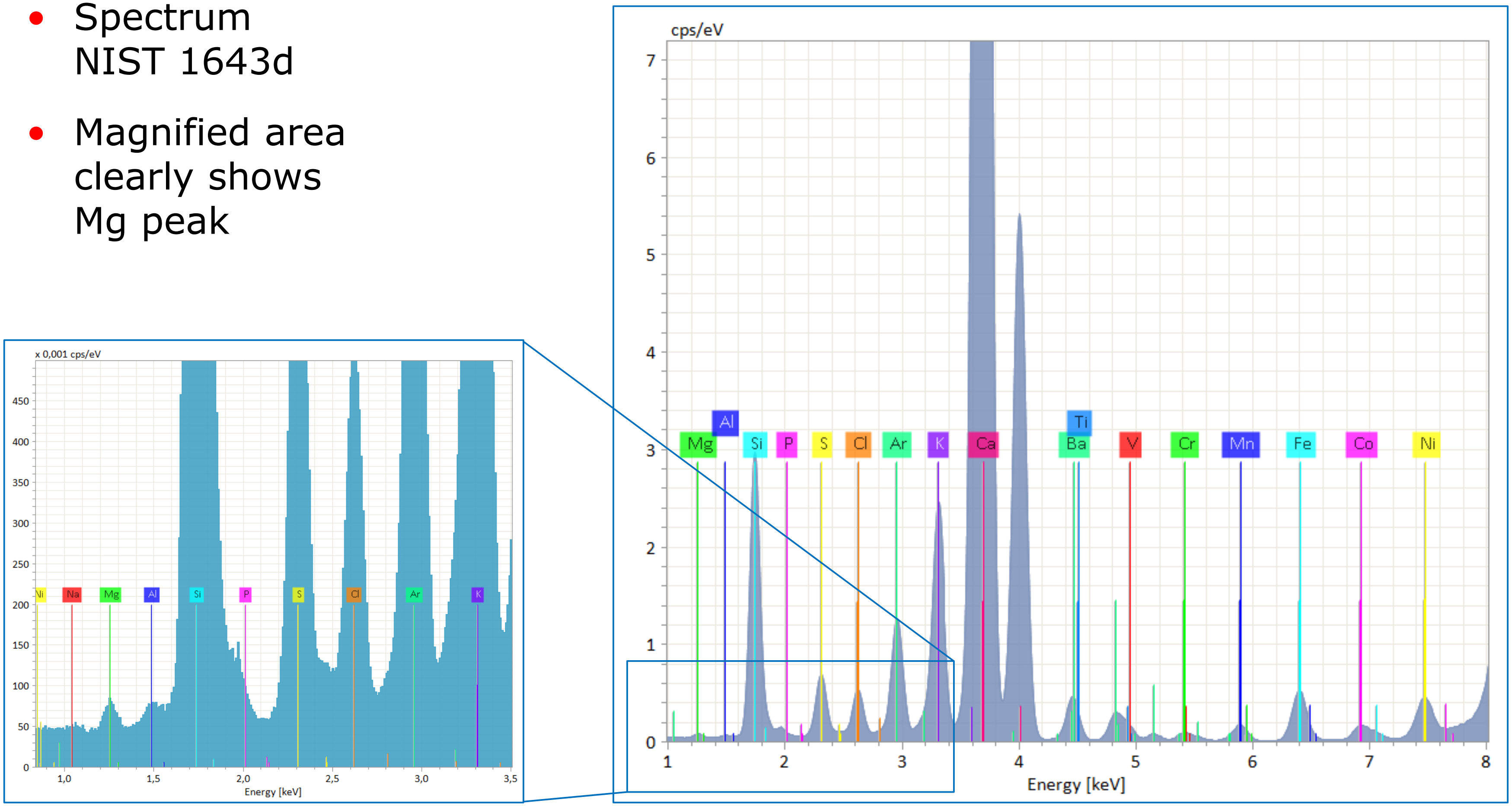
Light elements in water
Results

- Spectrum
  NIST 1643d



Light elements in water
Results

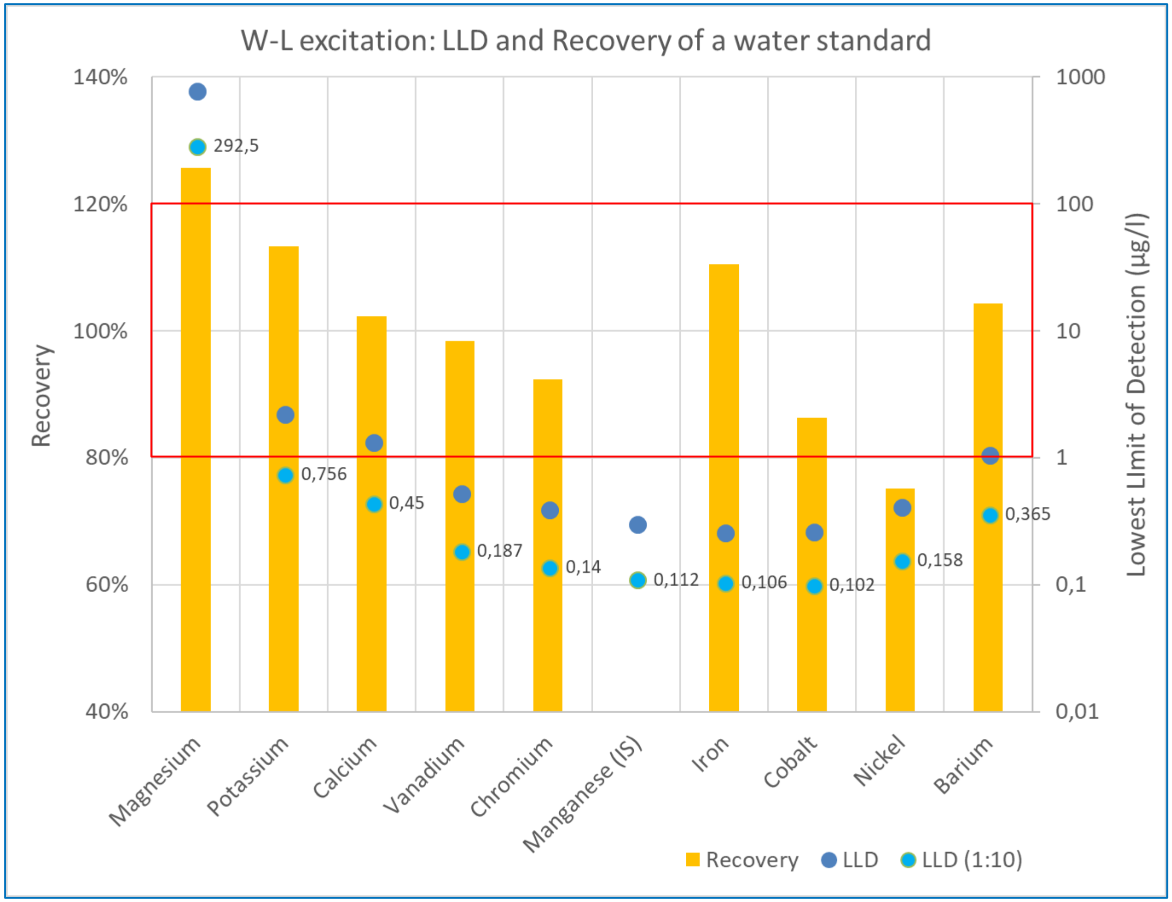
- Spectrum
  NIST 1643d
- Magnified area clearly shows Mg peak



Light elements in water
Results

Recovery and detection limits

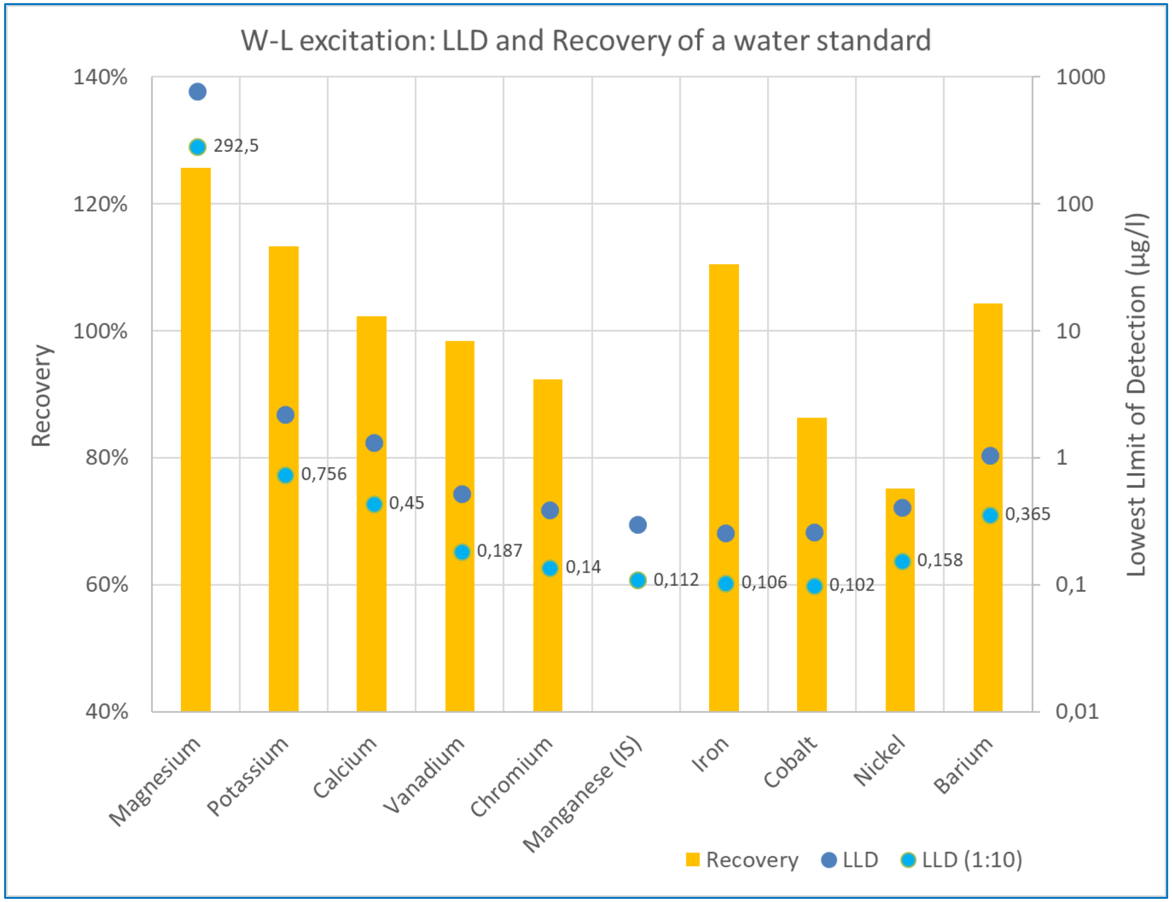
- Almost all elements show recovery within 100% +/- 20%
  - Low Ni due to overlap with Compton peak



Light elements in water
Results

Recovery and detection limits

- Almost all elements show recovery within 100% +/- 20%
  - Low Ni due to overlap with Compton peak
- Detection limits typically below 1 ppb (K to Ni)
- Mg lightest element to be quantified with LOD < 300 ppb
- Al: LOD = 109 ppb, too close to certified amount of 128 ppb



Outlook

Outlook
Future TXRF projects

Brumadinho dam disaster

- The dam disaster in the region Minas Gerais, Brazil, occurred on 25 January 2019
- A tailings dam at an iron ore mine suffered a catastrophic failure. The dam released a mudflow of 12M m³. 270 people died as a result of the collapse.

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Outlook
Future TXRF projects

Brumadinho dam disaster

- In June 2020 a S4 T-STAR will be installed at the Universidade Federal de Minas Gerais (UMFG), Departamento de Química
- A large number of sewage samples, soils and biological materials must be analyzed
- Objective is the method development for fast screening with minimal sample preparation by TXRF

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Standardization of TXRF

Standardization of TXRF
Current activities

Normative work

- ISO TS 18507-2015: „Technical Specification for the use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis"
- ISO 20289:2018:„Total Reflection X-Ray fluorescence analysis of water"

Standardization of TXRF
Current activities

Normative work

- ISO TS 18507-2015: „Technical Specification for the use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis"
- ISO 20289:2018:„Total Reflection X-Ray fluorescence analysis of water"

CA18130 - The "European Network for Chemical Elemental Analysis by TXRF" Action aims to

- coordinate research and building capacity
- to develop and assess new instrumentation, protocols, methods for determination of potentially toxic elements

The Action will

- create an infrastructure for scientific communication, exchange, collaboration
- enhance technical standards and analytical science, fostering research activities, combining partners' expertise

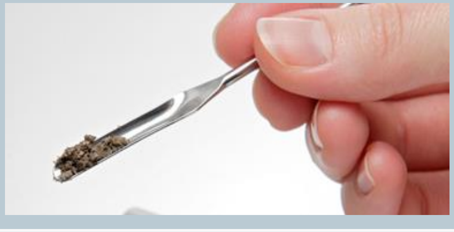
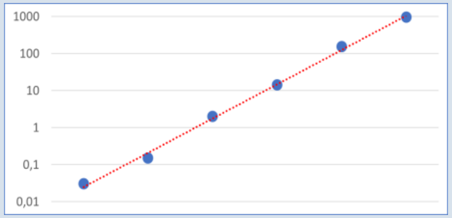
COST =
European Cooperation in Science and Technology

CA18130
03/2019 – 03/2022

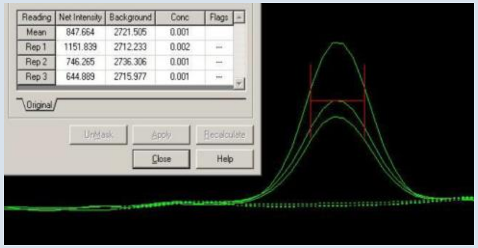
https://enforcetxrf.eu/

Comparison with Atomic Spectroscopy

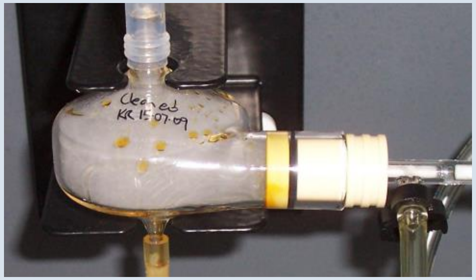
Feature comparison
TXRF versus ICP

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

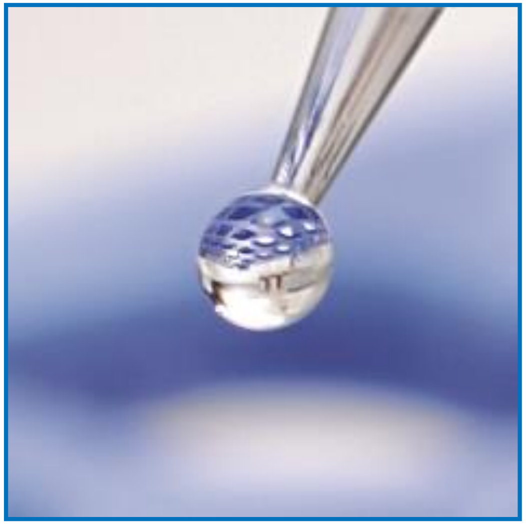
Technology comparison
Weekly/monthly checks

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 Box** and click **Submit**



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