Sample carrier

NIST water standard

Pipetting

S2 PICOFOX

Result

Lab Report XRF 425

S2 PICOFOX
Trace Element Analysis of Fresh Water Samples by TXRF Spectrometry

Introduction

The analysis of toxic elements in fresh water samples is a very important task. Compared to common methods like Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) the application of Total Reflection X-ray Fluorescence (TXRF) spectrometry provides several benefits:

- Fast and easy sample preparation
- No external calibration necessary
- Multi-element analysis including halogenides
- Low analytical operation and maintenance costs
- Portability for on-site analysis in the field.

In this study the suitability of the TXRF spectrometer S2 PICOFOX for analyzing trace elements in fresh water samples was investigated. As test samples two certified water standards (NIST 1640 and NIST 1643d were applied.

Instrumentation

All measurements were performed using the benchtop TXRF spectrometer S2 PICOFOX. This instrument is equipped with an aircooled low power X-ray tube (Mo target), a Ni/C monochromator with 80% reflectivity and a liquid nitrogen-free Silicon Drift Detector (SDD) with an energy resolution of < 159 eV (Mn Kα).

Sample preparation and analysis

For internal calibration, 1 ml of the certified standard was mixed with 20 µl of a standard solution (Ga; 10 mg/l). 10 µl of the mixture was placed onto a quartz glass carrier and dried on a heating plate. This procedure was repeated two times resulting in a total sample amount of 30 µl on the carrier.

For statistical evaluation 10 samples were prepared for each of the two reference standards. Measurement times were 1000 seconds.
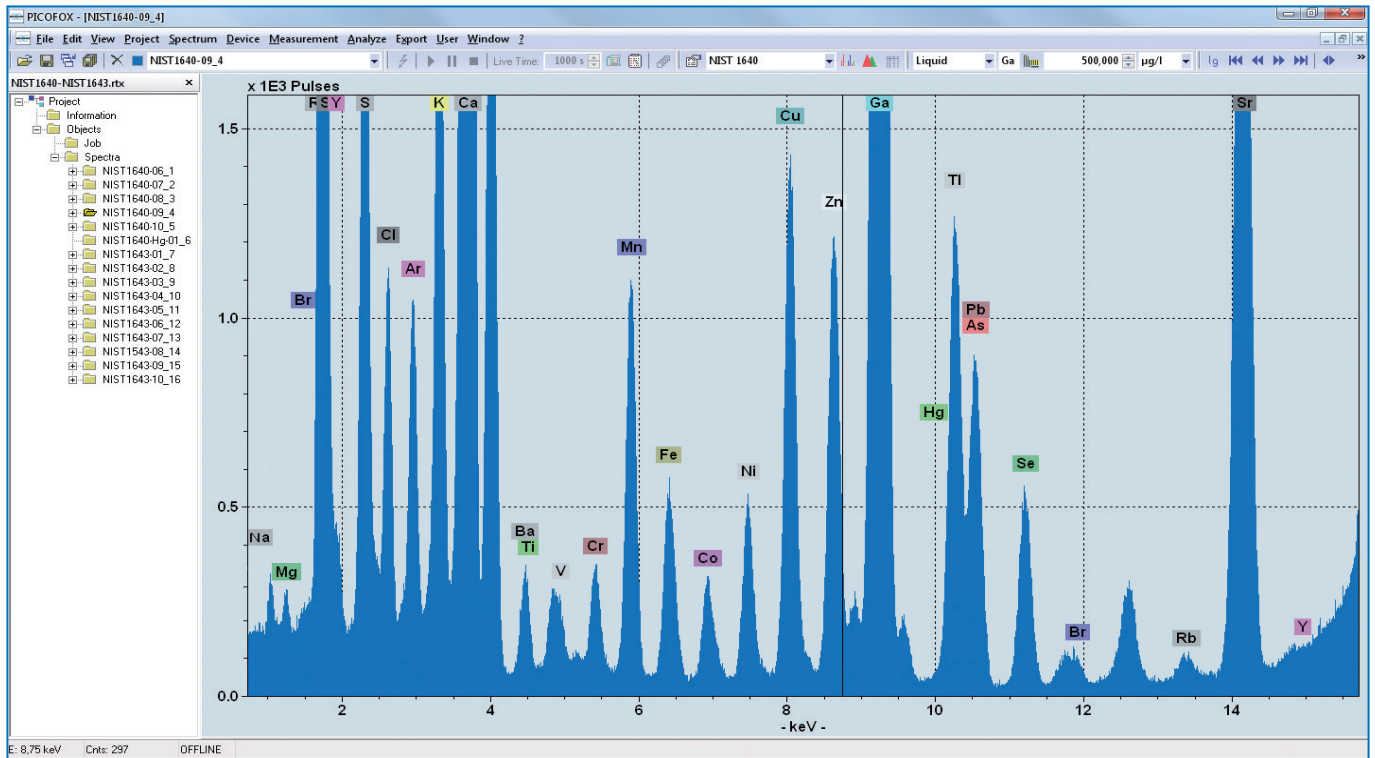
Figure 1: Typical TXRF spectrum of the NIST 1640 freshwater reference standard, measurement time 1000 s
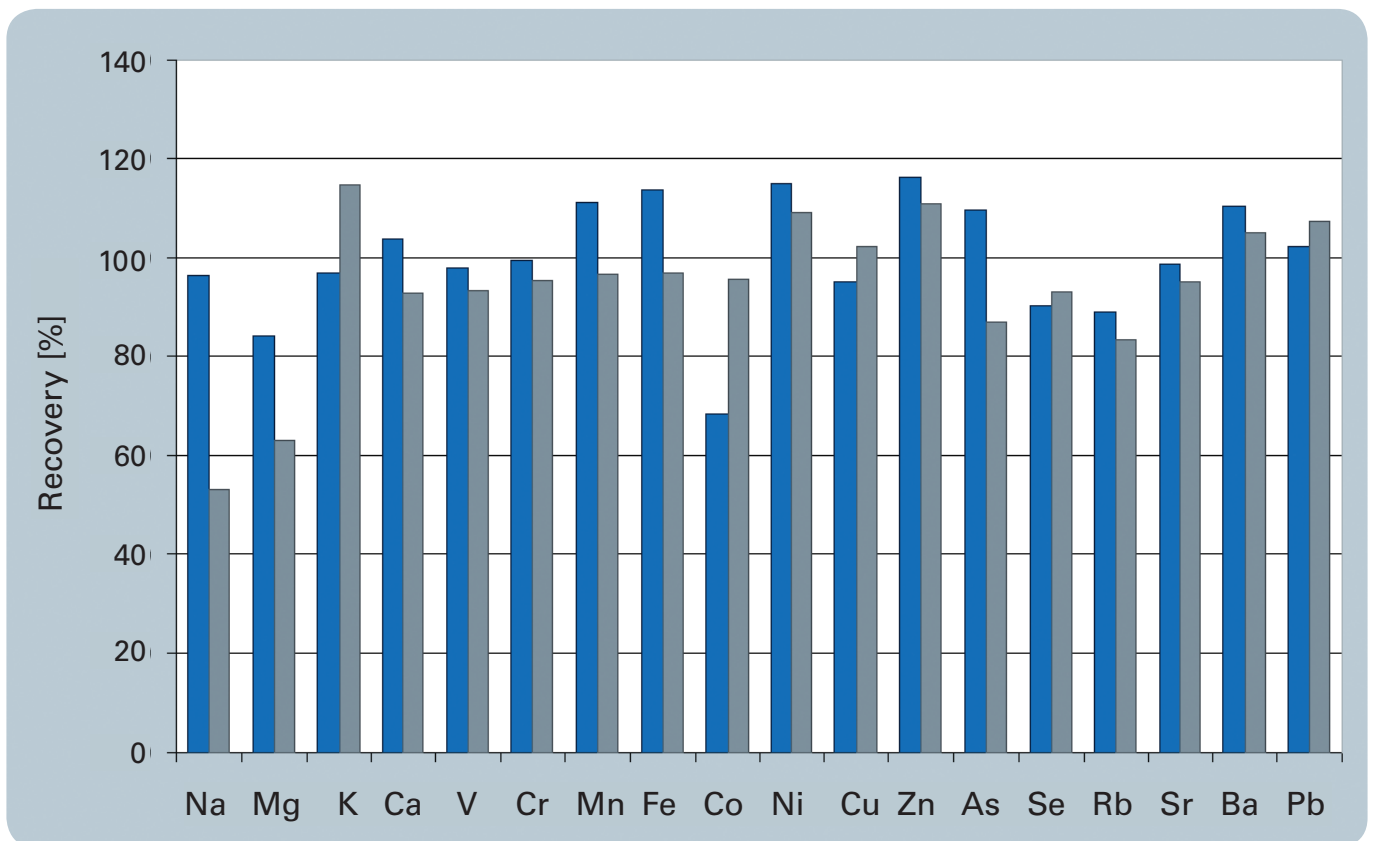

Figure 2: Recovery data for the freshwater reference samples NIST 1640 (blue columns) and NIST 1643d (grey columns)

Element	NIST 1640 cert.		NIST 1640 TXRF				NIST 1643d cert.		NIST 1643d TXRF			
	Conc.	+/-	Conc.	+/-	Recovery	LLD	Conc.	+/-	Conc.	+/-	Recovery	LLD
	[µg/l]	[µg/l]	(µg/l)	(µg/l)	(%)	(µg/l)	[µg/l]	[µg/l]	(µg/l)	(µg/l)	(%)	(µg/l)
Na	29350	310	28285	766	96.4	1142	22070	640	11751	2052	53.2	4243
Mg	5819	56	4890	157	84.0	250	7989	35	5032	457	63.0	923
S	n/a	n/a	5012	21	--	9.5	n/a	n/a	151	16.8	--	34.4
Cl	n/a	n/a	2121	10.0	--	5.2	n/a	n/a	1142	14.1		21.6
K	994	27	963	3.0	96.9	1.3	2356	35	2700	11.6	114.6	9.2
Ca	7045	89	7300	10.8	103.6	2.1	31040	500	28773	39.8	92.7	6.6
Ti	n/a	n/a	4.2	0.48	--	0.94	n/a	n/a	3.5	1.0	--	2.1
V	13.0	0.37	12.7	0.48	97.9	0.84	35.1	1.4	32.8	0.98	93.4	1.7
Cr	38.6	1.6	38	0.53	99.4	0.65	18.5	0.2	17.6	0.76	95.2	1.4
Mn	122	1.1	135	0.80	111.4	0.46	37.7	0.83	36.3	0.66	96.4	0.97
Fe	34.3	1.6	39.0	0.37	113.7	0.32	91.2	3.9	88.4	0.76	96.9	0.75
Co	20.3	0.31	13.8	0.18	68.3	0.19	25.0	0.59	23.9	0.43	95.8	0.62
Ni	27.4	0.8	31.5	0.28	115.0	0.22	58.1	2.7	63.4	0.55	109.1	0.54
Cu	85.2	1.2	80.9	0.55	94.9	0.25	20.5	3.8	21.0	0.33	102.3	0.46
Zn	53.2	1.1	61.9	0.32	116.3	0.16	72.5	0.65	80.3	0.51	110.8	0.40
As	26.7	0.41	29.2	0.21	109.7	0.13	56.0	0.73	48.6	0.33	86.8	0.26
Se	22.0	0.51	19.8	0.28	90.3	0.18	11.4	0.17	10.6	10.6	93.0	0.25
Br	n/a	n/a	1.91	0.06	--	0.10	n/a	n/a	0.38	0.11	--	0.23
Rb	2.00	0.02	1.78	0.06	89.1	0.10	13	n/a	10.8	0.17	83.3	0.23
Sr	124.2	0.7	123	0.37	98.9	0.14	295	3.4	280	0.80	94.9	0.28
Y	n/a	n/a	0.76	0.12	--	0.25	n/a	n/a	0.77	0.21	--	0.43
Ba	148	2.2	163	1.59	110.3	1.46	507	8.9	531	3.8	104.9	3.6
Tl	n/a	n/a	n/a	n/a	--	--	7.28	0.25	3.65	0.21	50.2	0.41
Pb	27.89	0.14	28.5	0.21	102.2	0.12	18.2	0.64	19.5	0.26	107.3	0.32
Bi	n/a	n/a	n/a	n/a	--	--	13	n/a	12.6	0.24	96.7	0.35

Results

A typical TXRF spectrum of the NIST standard 1640 is shown in Figure 1. Recovery data of all measured elements for both standards are displayed in Figure 2. The complete results including recovery data with regard to the certified values and detection limits are summarized in the table.

Light elements like Li, Be and B were not detectable in both samples or were present in concentrations below the detection limit (Al). Ag, Cd and Sb were not detected because of the Mo-excitation.

These elements can be analyzed by the weak L-lines, which are overlapped by strong Ca and K signals. The use of a Mo tube also prevents the analysis of Mo.

Na and Mg could be detected in many cases with a good recovery. But taking the standard deviations into account, the values show a very wide variation.

Good recovery data can be observed for K, Ca, V, Mn, Ni, Cu, As, Se, Rb, Sr, Ba, Pb and with restrictions for Cr. In sample NIST 1643d complex line overlaps, especially with Tl lead to distinct deviations from the reference values.

The elements P, S, Cl, Ti, Br and Y were detected in both samples. Because no certified reference values are available for these, no recovery data could be determined.

Regarding the detection limits (Figure 3) it is obvious that these are in the medium to low µg/l range for most of the detectable elements.

The deviation of the detection limits originates in part from the different measurement times. The general differences between both samples are caused by the distinctly higher matrix concentration (mainly Ca and Fe) of sample NIST 1643d.

Conclusions

The results of this study show that the S2 PICOFOX is capable of the analysis of trace elements in fresh water samples, even when present in the low µg/l range.

Future developments will be focussed on the improvement of the spectral deconvolution as well as the implementation of a helium purge system to increase the sensitivity for light elements. Alternative radiation sources like W will improve the K-line detection of elements with high atomic numbers (Ag, Cd, Sn).

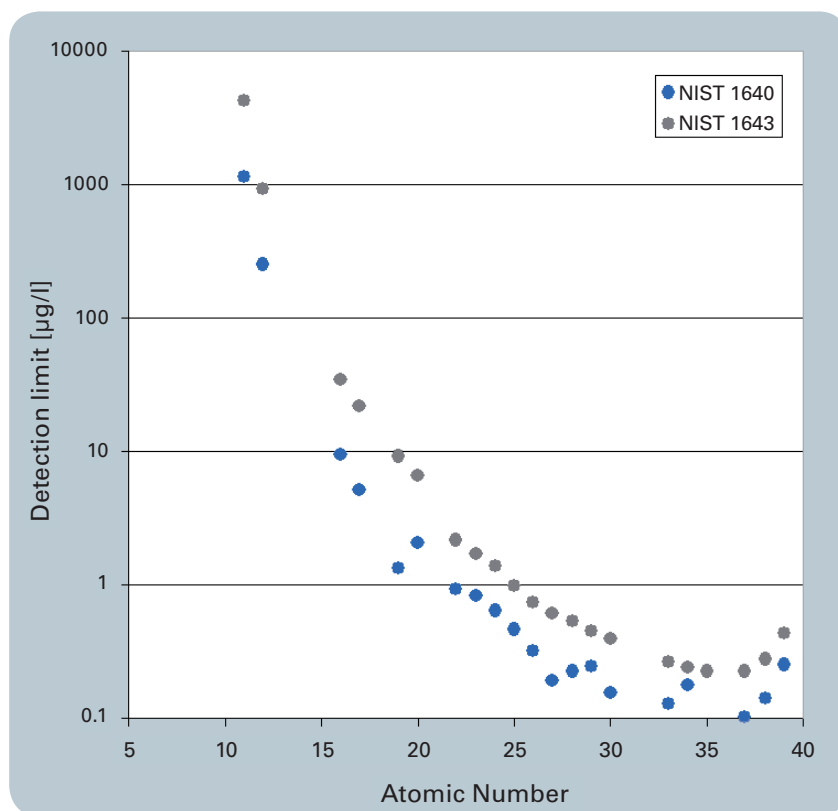## Author

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Figure 3: TXRF Detection limits for NIST fresh water reference samples