TXRF

Towards PPT Concentrations Using a High Efficiency Module

Application Note # XRF 78

The benefits of TXRF over conventional XRF include a significant enhancement in fluorescence yield, greatly reduced background noise, and consequently much higher sensitivities to elements present even in trace amounts.

The S2 PICOFOX is a portable benchtop TXRF spectrometer featuring an air-cooled low power X-ray tube and a liquid nitrogen-free Silicon Drift Detector (SDD). Further improvement in sensitivity is gained through the selection of more brilliant X-ray tubes and the development of detectors with increased active areas.

The S2 PICOFOX is available in a standard configuration for applications with average requirements on detection limits and/or measurement times. However, a High Efficiency Module (HEM), which includes a micro-focus X-ray tube and large-area detector, provides enhanced sensitivity. The technical parameters of both instrument versions are summarized in Table 1.

For this study a set of mono-element standards and a fresh water reference standard (NIST 1640) were analysed for a comparison of detection limits.

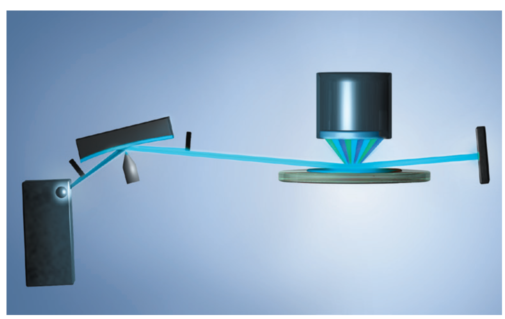

Figure 1
Schematic representation of Total Reflection X-ray Fluorescence Analysis

Table 1
Technical specifications of the S2 PICOFOX – standard configuration versus High Efficiency Module configuration

	Standard Configuration	High Efficiency Module
X-ray tube	Fine focus	Micro-focus
Spot size	1.0 x 0.1 mm	50 x 50 µm
Power	50 W (max. 50 kV, 1 mA)	30 W (max. 50 kV, 0.6 mA)
Mono-chromator	Multilayer, flat 17.5 keV	Multilayer, curved 17.5 keV
Detector	XFlash® Si Drift, 10 mm² act. area	XFlash® Si Drift, 30 mm² act. area

Sample preparation and measurements

The mono element standards were available as 1 g/l standard solutions. These were diluted with ultrapure water to obtain concentrations in the range of the expected detection limits.

10 µl of these solutions were transferred to quartz glass discs and dried in a desiccator.

The NIST 1640 reference standard was prepared by triple pipetting and drying of 10 µl of sample solution on a quartz glass sample carrier, which results in a total of 30 µl sample solution. Measurement time for all samples was 1000 s. The X-ray tube parameters were set to 50 kV, 1 mA (standard configuration) or 50 kV, 0.6 mA (HEM), respectively.

Results

A spectrum of a typical measurement is shown in Figure 4. Diagrams of the data are presented in Figure 2 and 3. The quantitative results are outlined in Tables 2 and 3 on the back side.

All LOD values were calculated with the following formula (Klockenkämper, 1997):

$$LOD(\mu g/l) = 3 \cdot \frac{c(\mu g/l)}{I_{net}\,(cts)} \cdot \sqrt{2 \cdot I_{bg}\,(cts)}$$

c: Concentration (µg/l)
I_{net}: Net intensity (cts)
I_{bg}: Background intensity (cts)

As shown in Figures 2 and 3, the detection limits of the S2 PICOFOX equipped with the High Efficiency Module are improved by a factor of 10 or more. This improvement decreases for elements with low energy fluorescence lines due to other physical effects like fluorescence absorption or quantum efficiency.

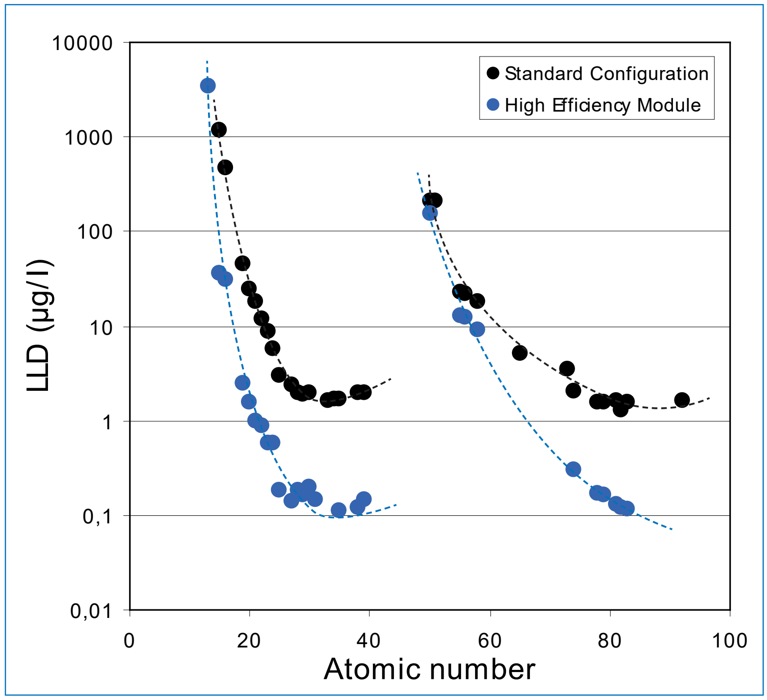

Figure 2
LOD values for mono-element standards analysed by the S2 PICOFOX TXRF spectrometer

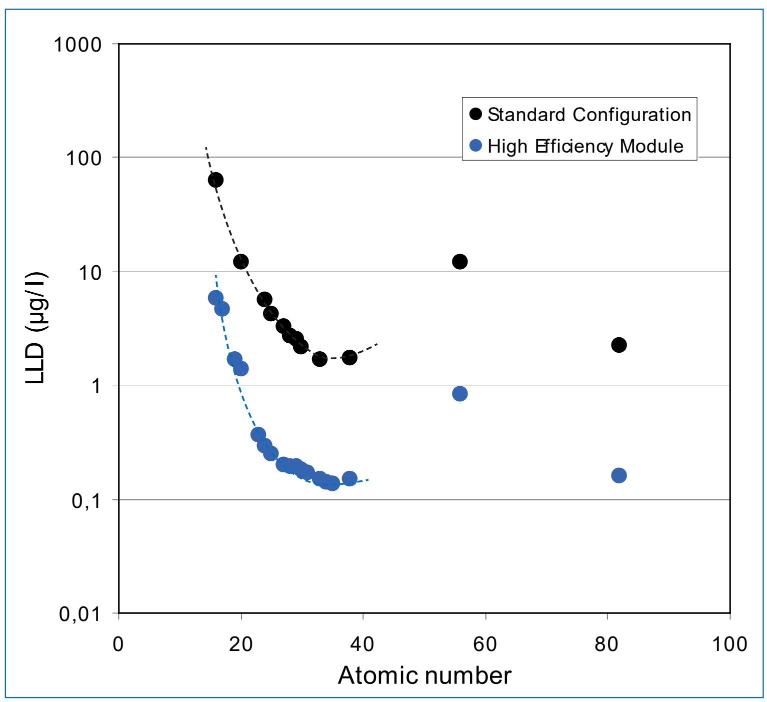

Figure 3
LOD values for the reference standard NIST 1640 analysed by the S2 PICOFOX

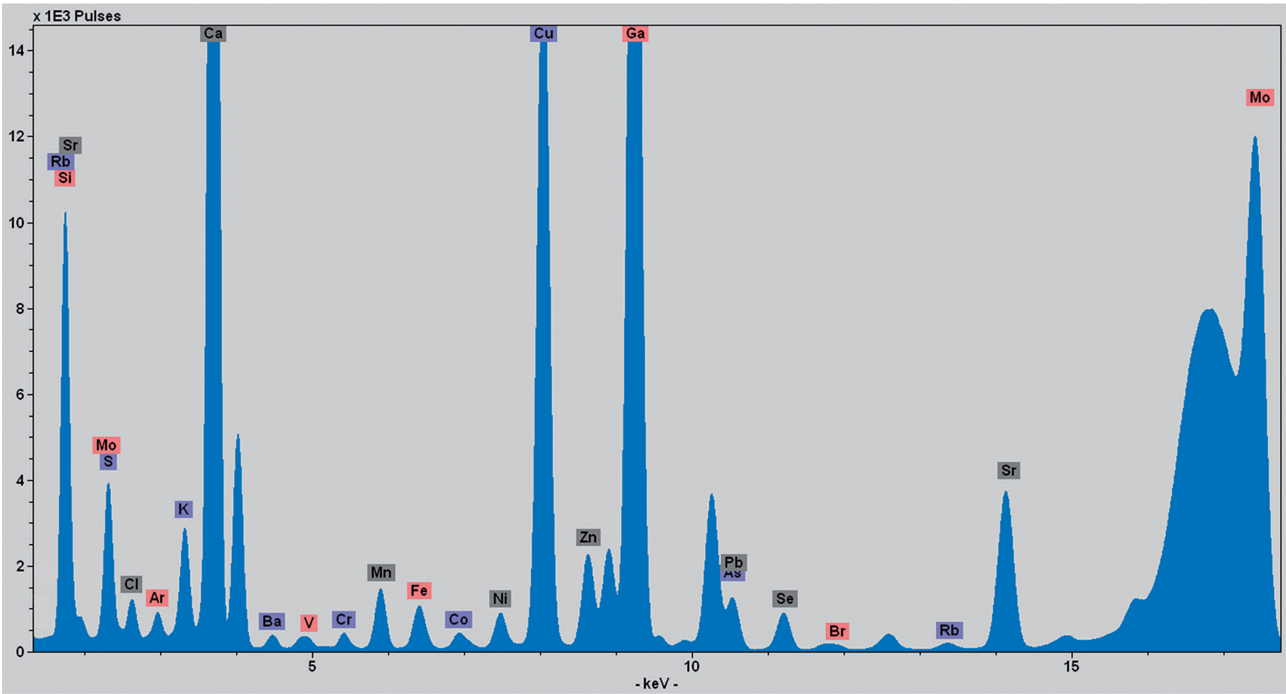

Figure 4

TXRF spectrum of the reference standard NIST 1640, measured with High Efficiency Module

Conclusion

This study demonstrates the outstanding performance of the portable TXRF spectrometer S2 PICOFOX.

Even with the S2 PICOFOX standard configuration, detection limits down to 2 ppb can be obtained for real water samples (NIST 1640). When the spectrometer is equipped with a more brilliant X-ray tube and a large-area detector – the High Efficiency Module – the detection limits approach 100 ppt. This represents a 20 times increase in sensitivity!

The S2 PICOFOX with High Efficiency Module provides low detection limits with the smallest sample amounts. For certain elements, the lowest detectable absolute mass is just 1 pg! The detection limits of other elements may be restricted by the instrument's compact, non-vacuum chamber design.

LOD NIST 1640 (µg/l)			
Element	**(Z)**	**Standard Configuration**	**High Efficiency Module**
S	(16)	63	5.9
Cl	(17)	n/a	4.6
K	(19)	n/a	1.7
Ca	(20)	12	1.4
V	(23)	n/a	0.37
Cr	(24)	5.6	0.29
Mn	(25)	4.2	0.25
Co	(27)	3.2	0.20
Ni	(28)	2.7	0.19
Cu	(29)	2.5	0.19
Zn	(30)	2.2	0.18
Ga	(31)	n/a	0.17
As	(33)	1.7	0.15
Se	(34)	n/a	0.14
Br	(35)	n/a	0.14
Sr	(38)	1.7	0.15
Ba	(56)	12	0.83
Pb	(82)	2.2	0.16

LOD mono-element standards (µg/l)			
Element	**(Z)**	**Standard Configuration**	**High Efficiency Module**
P	(15)	1179	36
S	(16)	470	31
K	(19)	46	2.5
Ca	(20)	25	1.6
Sc	(21)	18	1.0
Ti	(22)	12	0.87
V	(23)	8.6	0.58
Cr	(24)	5.7	0.58
Mn	(25)	3.0	0.19
Co	(27)	2.4	0.14
Ni	(28)	1.9	0.18
Cu	(29)	1.9	0.17
Zn	(30)	1.9	0.20
Ga	(31)	n/a	0.15
Br	(35)	1.7	0.11
Sr	(38)	1.9	0.12
Y	(39)	2.0	0.15
Cd	(48)	226	293
In	(49)	212	239
Sn	(50)	206	154
Cs	(55)	23	13
Ba	(56)	22	12
Ce	(58)	18	9.2
W	(74)	2.0	0.30
Pt	(78)	1.6	0.17
Au	(79)	1.6	0.17
Tl	(81)	1.6	0.13
Pb	(82)	1.3	0.12
Bi	(83)	1.6	0.12

Table 2 (left)
Results of LOD measurements for the reference standard NIST 1640

Table 3 (right)
Results of LOD measurements for mono-element standards

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