A first evaluation of the analytical capabilities of the new X-ray fluorescence facility at International Atomic Energy Agency-Elettra Sincrotrone Trieste for multipurpose total reflection X-ray fluorescence analysis

Eva Marguí [a,*], Manuela Hidalgo [a], Alessandro Migliori [b], Juan José Leani [b,c], Ignasi Queralt [d], Nikolaos Kallithrakas-Kontos [e], Christina Streli [f], Josef Prost [f], Andreas Germanos Karydas [b,g]

[a] Department of Chemistry, Faculty of Sciences, University of Girona, C/M. Aurèlia Campmany, 69, 17003 Girona, Spain
[b] Nuclear Science and Instrumentation Laboratory, IAEA Laboratories, A-2444 Seibersdorf, Austria
[c] IFEG, National Scientific and Technical Research Council (CONICET), X5000HUA, Córdoba, Argentina
[d] Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona, 18-24, 08034 Barcelona, Spain
[e] Analytical and Environmental Chemistry Laboratory, Technical University of Crete, University Campus 73100, Chania, Greece
[f] Atominstitut TU Wien, Stadionallee 2, 1020 Wien, Austria
[g] Institute of Nuclear and Particle Physics, National Centre for Scientific Research, 'Demokritos', Patr. Grigoriou E' & 27 Neapoleos St, 153 41 Agia Paraskevi, Greece

ARTICLE INFO

ABSTRACT

The aim of the work is to present a systematic evaluation of the analytical capabilities of the new X-ray fluorescence facility jointly operated between the International Atomic Energy Agency and the Elettra Sincrotrone Trieste for multipurpose total reflection X-ray fluorescence analysis.

The analytical performance of the XRF beamline end-station (IAEAXspe) was systematically evaluated under TXRF excitation geometry by analyzing different types of aqueous (lake, waste and fresh water) and solid (soil, vegetal, biological) certified reference materials using an excitation energy of 13.0 keV (for the purpose of multielemental analysis). The results obtained for both types of samples in terms of limits of detection and accuracy were also compared with those obtained using laboratory X-ray tube based TXRF systems with different features (including Mo and W X-ray tube systems). Taking advantage of the possibility to work under high vacuum, the IAEAXspe set-up instrumental sensitivity was also determined using an excitation energy of 6.2 keV to explore the possibilities for light elements determination.

A clear improvement of the element detection limits is achieved when comparing this facility to conventional X-ray tube based TXRF systems highlighting the benefits of using the monoenergetic synchrotron exciting radiation and the ultra-high vacuum chamber in comparison with conventional laboratory systems.

The results of the present work are discussed in view of further exploitation of the facility for different environmental and biological related applications.

1. Introduction

There is a growing need for element trace analysis at levels lower than one part per million by weight in nearly every scientific field. A significant contribution in these areas can be given by the application of synchrotron radiation (SR) based X-ray spectrometry techniques which can provide, with high sensitivity, spatially resolved element information down to the nanometer depth scale [1]. In combination with X-ray absorption/emission spectroscopy techniques, SR can also provide chemical speciation information which is valuable in many environmental, biological as well as material science studies [2]. In fact, during the last few years a considerable number of scientific manuscripts devoted to the use of SR-based techniques in many fields have been published as it is reported in some comprehensive reviews on this subject [3,4].

In spite of the usefulness of SR based X-ray spectrometry techniques, it should be stressed that a limited number of synchrotron facilities are available globally and beam time can be obtained only on the basis of the scientific merit of proposals, thus providing limited opportunities for hands on training. This situation creates a major gap for scientists who have limited experience and resources to access and utilize the SR technology and associated techniques. In response to these needs, the International Atomic Energy Agency (IAEA) developed a multi-

technique X-ray Spectrometry instrument (IAEAXspe) that was set up and commissioned at the X-ray fluorescence beamline of Elettra Sincrotrone Trieste [5,6]. The facility allows performing measurements in different X-ray spectrometry techniques, including microscopic X-ray fluorescence analysis (μ-XRF), total reflection X-ray fluorescence analysis (TXRF), grazing incidence/exit X-ray fluorescence analysis (GI-XRF/GE-XRF) and X-ray reflectometry (XRR) in conjunction with X-ray Absorption Near Edge Structure spectroscopy (XANES).

The aim of the present manuscript is to present a systematic evaluation of the analytical capabilities of the IAEAXspe beamline end station for multielemental determination under TXRF conditions. Usually, the simultaneous multielement capability, the low detection limits for many elements and the easy quantification through internal standardization has promoted the use of TXRF for the analysis of both liquid and solid samples in many fields [7–10]. In the case of solid samples, usually a digestion procedure is applied before the TXRF analysis in order to transform the solid sample into a liquid. Recent publications have also shown the possibilities to analyze directly solid samples by means of suspension preparation as a simple and cost-effective approach [7]. However, the limits of detection and the precision of the obtained results when using suspension preparation are usually worse than those associated using conventional sample treatments for solid samples such as digestion [10].

To perform analysis under total-reflection conditions, samples must be provided as thin films. This is typically done by depositing 5–50 μL of solution on a reflective carrier (usually a Si crystal or quartz) and subsequently drying of the drop. Under glancing angles of incidence, below the critical angle that fulfils the condition for external total reflection of the exciting beam on the carrier surface (~0.1°), the incident photons penetrate at shallow depths (~few nm) within the sample carrier. Thus, the amount of the scattered radiation recorded by the X-ray detector, usually placed perpendicularly with respect to the carrier surface, is negligible, whereas the majority of the scattered intensity is symmetrically reflected away from the detector field of view leading to improved detection limits compared to conventional XRF systems [11].

SR is highly beneficial for TXRF and for angle-dependent XRF analysis in general, since its unique properties (e.g., high intensity, linear polarization, low divergence and natural collimation) [12,13]. The analytical performance of the IAEAXspe beamline end-station was systematically evaluated under TXRF excitation geometry by analyzing different types of aqueous (lake, waste and fresh water) and solid (soil, vegetal, biological) certified reference materials using an excitation energy of 13.0 keV (for the purpose of multielemental analysis). The results obtained for both types of samples in terms of limits of detection and accuracy were also compared with those obtained using laboratory X-ray tube based TXRF systems with different features. Taking advantage of the possibility to work under high vacuum, the set-up instrumental sensitivity was also determined using an excitation energy of 6.2 keV to explore the possibilities for light elements determination.

2. Materials and methods

2.1. Reagents, materials and apparatus

Stock solutions of 1000 ± 0.5 mg L^{-1} (Spectroscan, TEKNOLAB A/S, Norway) of appropriate elements were used to prepare standard solutions. High purity water used for dilution of stock solutions was obtained from a Milli-Q purifier system operated at 18 MΩ (Millipore Corp., Bedford, MA). Carbon tetrachloride and ammonium pyrrolidine dithiocarbamate (APDC) used for liquid phase microextraction were of analytical grade quality (Sigma-Aldrich, Spain). pH values of solutions were adjusted by addition of ammonia and nitric acid solutions (Merck, Spain). Triton™ X-100 (laboratory grade, Sigma-Aldrich) was used for the preparation of solid sample suspensions. Solid samples were also digested using an Ethos Plus Milestone microwave with HPR-1000/10S high pressure rotor (Sorisole, Bergamo, Italy) and all

reagents used for sample microwave digestion were analytical grade Suprapur quality: nitric acid (Merck, Darmstadt, Germany), hydrofluoric acid, boric acid and hydrogen peroxide (Sigma-Aldrich, Spain).

Quartz glass discs with a diameter of 30 mm and a thickness of 3 mm ± 0.1 mm were used as sample carriers for TXRF measurements. In the case of solid samples digested using hydrofluoric acid, acrylic glass reflectors of the same dimensions were used instead.

The multielemental atomic spectroscopy standard solution V (Fluka 70008) from Sigma-Aldrich was used to estimate elemental sensitivity factors. In addition, several aqueous and solid certified reference materials (CRMs) and an aqueous sample (IAEA S1) from the Interlaboratory Quality Evaluation organized by the IAEA in 2014 were measured to provide figures of merit regarding the analytical capabilities of the TXRF setup configuration of the IAEAXspe beamline endstation. The CRMs employed for such purpose were: TMDA 64.2 (Lake water) from the National Water Research Institute, Environment Canada (Burlington); SPS-WW2 Waste water Level 2 by Spectrapure Standards AS (Oslo, Norway); SRM 1643e (Trace elements in fresh water) from the National Institute of Standards and Technology (NIST); SO-1 (Soil CRM) from Natural Resources Canada (NRCan); NCS ZC 73031(carrot) from China National Analysis Center for Iron and Steel and GBW08571 (Mussel muscle tissue) from the National Research Centre for Certified Reference Materials (Beijing, China).

2.2. Sample preparation for TXRF analysis

In the following section, a detailed description of the sample preparation procedure for the TXRF analysis of liquid and solid samples is presented. It is interesting to remark that after the deposition and drying of each sample on the sample carrier, this carrier was analyzed using the IAEAXspe beamline end-station as well as different laboratory TXRF instruments (see Section 2.3 for details).

2.2.1. Liquid samples

Aqueous samples for TXRF analysis were prepared as follows: an appropriate amount of a 1000 ± 0.5 mg L^{-1} Ga solution (to reach a final Ga concentration of 1 mg L^{-1}) was added to 1 mL of the target sample for internal standardization. The resulting solution was then thoroughly homogenized (using vortex mixer) and an aliquot of 10 μL was transferred onto a quartz glass sample carrier and dried using an infrared lamp.

A dispersive liquid–liquid microextraction procedure (DLLME) using APDC as the complexing agent was employed to separate and preconcentrate Cd from water samples prior to TXRF analysis. Specific details about the preconcentration procedure can be found in Ref. [14]. Briefly, 5 mL of the aqueous solution was placed in a conical glass tube to which 50 mL of 0.01 M nitric acid were added to adjust the pH (pH = 3). Next, a mixture containing 500 mL of APDC 0.01% in methanol (chelating agent + disperser solvent) and 50 mL of carbon tetrachloride (extraction solvent) was injected rapidly into the sample solution by means of a micropipette. The mixture was then centrifuged at 4000 rpm for 5 min to achieve phase separation. This resulted in a small volume (≈35 μL) of organic phase, containing the CdPDC complex, settling at the bottom of the tube. An aliquot of 20 μL of the preconcentrated sample was transferred onto a pre-heated quartz sample carrier and dried under a laminar flow hood for subsequent TXRF analysis.

A dispersive microsolid phase extraction (DMSPE) using mercapto-modified graphene oxide nanosheets (GO-SH) as adsorbent was used for multielemental ultratrace determination of metal and metalloids. Specific details about the synthesis and characterization of this novel adsorbent can be found elsewhere [15]. The preconcentration procedure consists of injecting 200 μL of GO-SH suspension (5 mg mL^{-1} GO-SH) into 75 mL of analyzed solution (pH adjusted to 5 using 0.1 mol L^{-1} HNO$_3$ and 0.1 mol L^{-1} NH$_3$). The rapid injection of

Table 1
Instrumental parameters and measurement conditions.

IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste (TXRF-1)	
Energy range	3.6–14.5 keV
Resolving power ($\Delta E/E$)	1.4×10^{-4}
Beam size	260 μm (H) × 130 μm (V)
Optics	Double crystal Si(111) monochromator
Excitation angle	0.01–0.15° (adjusted for each sample)
Detector	SDD, 30 mm², 131 eV resolution at Mn-K$_\alpha$
Working environment	Ultra-high vacuum
Measurement time	Depends on the scans performed for each sample and element signals in the analyzed sample:
	- Lake water (CRM TMDA 64.2): 2000s (8 scans)
	- Fresh water (NIST1643e): 1440s (6 scans)
	- Waste water (SPS WW2): 1300s (13 scans)
	- Aqueous sample (IAEA S1): 1440s (12 scans)
	- CRM SO-1 (soil), digestion: 570s (19 scans)
	- CRM SO-1 (soil), suspension: 480s (24 scans)
	- CRM NCS ZC73031 (carrot), digestion: 600s (5 scans)
	- CRM NCS ZC73031 (carrot), suspension: 1500s (25 scans)
	- CRM GBW08571 (mussel muscle tissue), digestion: 1200s (20 scans)
	- CRM GBW08571 (mussel muscle tissue), suspension: 1170s (26 scans)

S2 PICOFOX TXRF benchtop spectrometer (TXRF-2)	
X-ray tube anode	W
Power	50 W
Optics	Multilayer monochromator (35.0 keV)
Excitation angle	≈0.1° (fixed)
Detector	SDD, 10 mm², <160 eV resolution at Mn-K$_\alpha$
Working environment	Air
Measurement time	2000 s

TXRF module designed and produced at the Atominstitut, Vienna (TXRF-3)	
X-ray tube anode	Ag
Power	1.5 kW
Optics	Quartz cut-off reflector
Excitation angle	0.1° (fixed)
Detector	Si-PIN, 25 mm², 190 eV resolution at Mn-K$_\alpha$
Working environment	Air
Measurement time	2000 s

Atomika 8030C TXRF spectrometer (TXRF-4)	
X-ray tube anode	Mo
Power	3 kW
Optics	Double W/C multilayer monochromator (17.4 keV)
Excitation angle	≈0.1° (adjusted for each sample)
Detector	Si(Li), 80 mm², 150 eV resolution at Mn-K$_\alpha$
Working environment	Air
Measurement time	1000 s

Fig. 1. TXRF element sensitivities expressed as cps/mg kg^{-1} determined for Kα and Lα-lines excitation (IAEAXspe end-station of the XRF beamline at Elettra Sincrotrone Trieste). Measurement time: 600 s (10 scans). Legend: squares (Excitation energy: 6.2 keV), diamonds (Excitation energy: 13.0 keV).
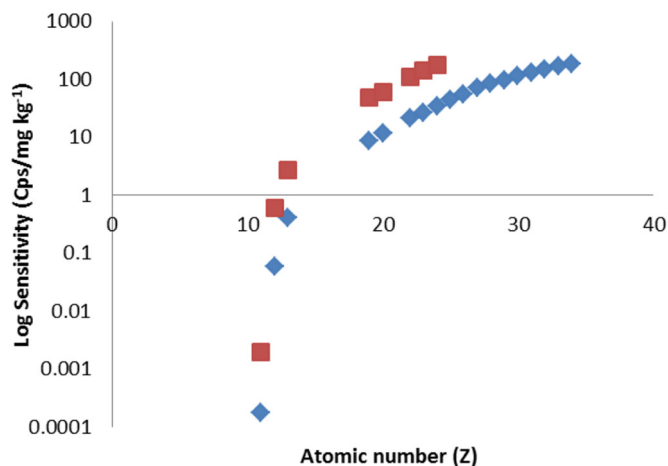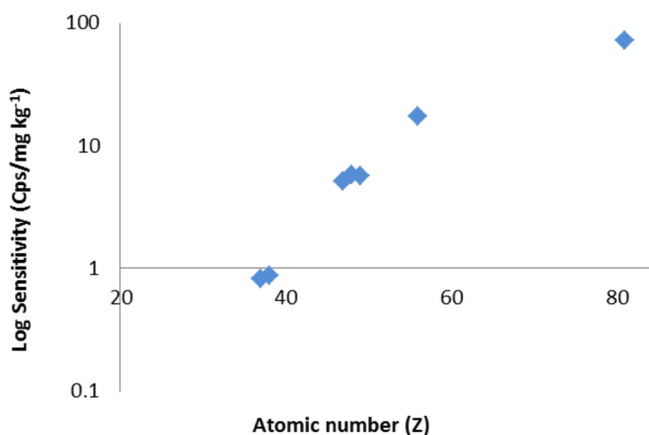
GO-SH suspension promotes instant interaction between metal ions and GO-SH nanosheets dispersed throughout the sample. After 10 min the sample was filtered and the membrane filter with collected GO-SH was placed in a 3 mL Eppendorf containing 0.5 mL of 2 μg mL^{-1} Y (internal standard) in 2 mol L^{-1} HNO$_3$. The closed Eppendorf was placed in an ultrasonic bath for 2 min. After homogenization, a suspension of 10 μL was transferred onto a siliconized quartz reflector and dried under an IR lamp for subsequent TXRF analysis.

2.2.2. Solid samples

Solid samples, including vegetables and soils, were prepared as suspensions and digested samples for the later TXRF analysis.

A study of the shape and element distribution of the deposited residue on the quartz reflector was performed by micro X-ray fluorescence spectrometry using a commercial spectrometer (M4 Tornado, Bruker). In this system, the X-ray tube is a lower-power micro-focus side window Rh tube cooled by air. The generator is able to operate in the ranges 10–50 kV and 100–600 μA. A poly-capillary opticsis used to obtain a spot size down to 25 μm for Mo K$_\alpha$. Detection of fluorescence radiation is performed by an energy-dispersive SDD with 30 mm² sensitive area and energy resolution of 142 eV for Mn K$_\alpha$. The system also allows to work under vacuum conditions. Samples imaging was performed with scan resolution of 700 × 700 pixel, step size of 15 μm and a dwell time of 0.76 ms/pixel.

2.2.2.1. Solid suspensions.
Sample suspensions were prepared by weighing 50 mg of sample and adding 1 mL of mL Triton™ X-100 1% (in water). Then, Ga was added to the slurry sample for internal standardization (final Ga amount 10 μg). The resulting solution was thoroughly homogenized by 5 min of sonication in an ultrasonic bath. After that, 5 μL of the internal standardized sample was deposited on a quartz reflector and dried using an IR lamp for further TXRF analysis.

2.2.2.2. Digested solid samples.
A microwave acid digestion, based on the EPA method 3052, was employed for the preparation of plant material. About of 250 mg of sample was added in a PTFE vessel with 9 mL of HNO$_3$ and 2 mL of H$_2$O$_2$. The vessels were closed and heated following a two-stage digestion program consisting of a first step of 5 min to reach 180 °C and a second step of 10 min at 180 °C. After cooling,
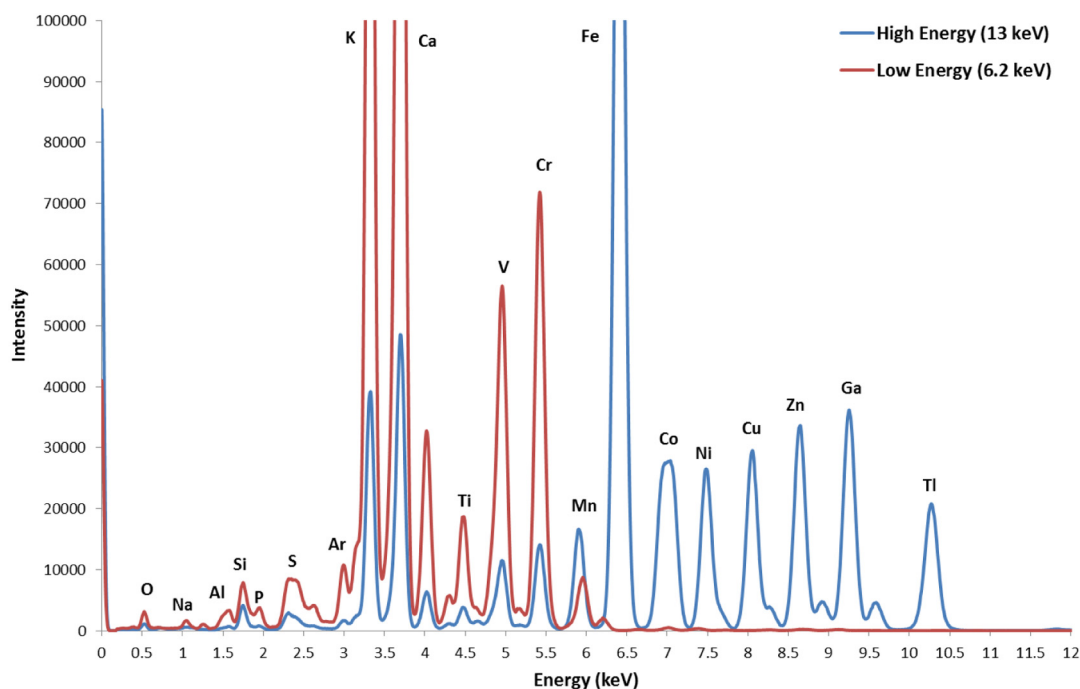
Fig. 2. TXRF spectra (IAEAXspe end-station of the XRF beamline at Elettra Sincrotrone Trieste) for a multielemental Standard (Fluka 70008) analysis using 13.0 keV and 6.2 keV excitation energies. Measurement time: 600 s (10 scans).

digested sample solutions were transferred to a 30 mL flask and diluted with ultrapure deionized water.

Taking into account the complexity of soil samples, a more aggressive microwave digestion using hydrofluoric acid was necessary to decompose this type of samples. Digestions were prepared by weighing in a Teflon vessel 250 mg of sample and adding 9 mL of concentrated HNO_3, 3 mL concentrated HF and 1 mL of H_2O_2. The vessels were capped and heated following a two-stage digestion program consisting of a first step of 15 min to reach 130 °C and a second step of 15 min to reach 200 °C. Following the matrix decomposition with HF, extracts were additionally treated with 0.5 mL 5% (v/v) H_3BO_3 and heated during 15 min at 180 °C to allow the complexation of fluoride. Finally, digests were transferred into a 50 mL flask and brought to volume with ultrapure deionized water.

From each sample digest (vegetation/soil samples) an aliquot of 1 mL was fortified with a suitable volume of a Ga solution (internal standard) to have a final concentration of 10 mg L^{-1}. The sample deposition volume and drying mode to perform TXRF analysis were the same as for the suspended samples.

2.3. Instrumentation, spectra evaluation and data treatment

In the following sections a summarized description of the IAEA end-station (IAEAXspe) of the XRF beamline at Elettra Sincrotrone Trieste as well as the laboratory TXRF instruments used for comparison purposes is reported. Specific instrumental parameters and measurement conditions are summarized in Table 1.

2.3.1. IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste (TXRF-1)

The IAEAXspe end-station consists of an ultra-high vacuum chamber that includes as main instrument a seven-axis motorized manipulator for the precise positioning of sample and monitoring photodiodes with respect to the exciting beam direction. This beamline offers, at its present configuration, tunable SR excitation in the energy range from 3.7 to 14 keV by means of a double crystal Si(111) monochromator with a resolving power of 1.4×10^{-4}. The beam size at the sample position is equal to about 200 μm (H) × 100 μm (V) and XRF spectra are acquired by an ultra-thin Silicon Drift Detector (SDD, Bruker Nano GmbH, X-Flash 5030) with a nominal area of 30 mm², 450 μm crystal thickness, an energy resolution of 131 eV (FWHM) at the Mn Kα (5.9 keV) line and equipped with a thin polymer window (Super Light Energy Window). Specific details on the end-station hardware components and X-ray detectors, the control and data acquisition software can be found elsewhere [5,6]. It should be pointed out that during the present experimental work the SDD was placed at 10 mm away from the sample surface, whereas the use of an aperture with 2.25 mm in diameter (attached to the magnetic trap placed in front of the SDD window) restricted significantly the solid angle of detection.

Taking into account the size of the exciting beam, several measurements across the vertical direction over the propagation plane were carried out in order to ensure the analysis of the whole sample area on the reflector. Therefore, spectral evaluation was made using the respective accumulated spectrum. The evaluation of the TXRF spectra and the determination of the analyte net peak areas were performed using the software WinQXAS version 1.30 by the IAEA.

2.3.2. S2 PICOFOX benchtop TXRF spectrometer (TXRF-2)

S2 PICOFOX (Bruker Nano GmbH) is a commercial benchtop TXRF system. One of the advantages of this spectrometer compared to other existing systems is that it is equipped with an air-cooled low-power X-ray tube and a Peltier-cooled silicon drift detector and thus, no cooling media and gas consumption are required. As it is shown in Table 1, the anode material of the X-ray tube in the TXRF instrument is tungsten (W). This fact allows performing TXRF analysis using K-lines of high atomic number elements such as Sn and Cd (in conventional Mo-based X-ray tubes the less intense L-lines have to be used for this purpose) and thus the limits of detection for heavy elements are improved. However, limits of detection for the 4th period elements (Z = 19–35) are higher than those associated with Mo anode X-ray tubes [16].

The evaluation of TXRF spectra and the determination of the analytes net peak areas were performed using the provided software (SpectraPlus 5.3, Bruker AXS Microanalysis GmbH, Berlin, Germany) linked to the system. In more specific, for the evaluation of net peak
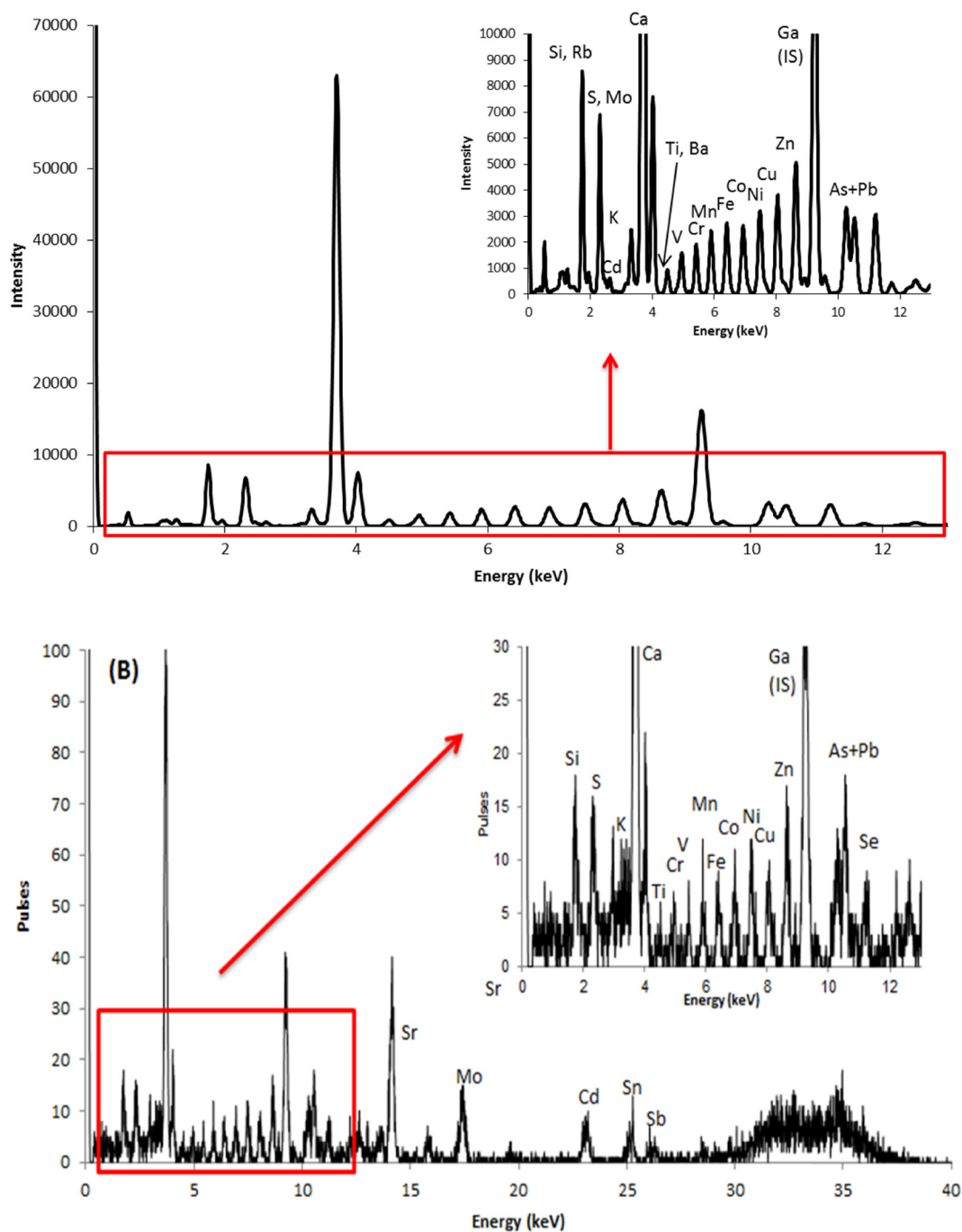
Fig. 3. TXRF spectra obtained for the analysis of the certified reference material TMDA 64.2 (Lake Ontario Water) using: (A) IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste under total reflection conditions at 13.0 keV (TXRF-1), (B) S2 PICOFOX TXRF benchtop spectrometer (TXRF-2). For specific system details and measurement time see Table 1.

areas the software applies a deconvolution routine which employs measured mono-element profiles.

2.3.3. TXRF module designed and produced at the Atominstitut (TXRF-3)

A TXRF module designed and produced at the Atominstitut (TU Wien, Austria) was also used for comparison purposes [17]. In this system, X-rays are produced by a fine-focus silver anode X-ray tube (Seifert FK 60-04 AG) connected with aSeifert IsaDebyeflx 3000 high-voltage generator. The produced X-rays are detected by an AMPTEK XR-100CR Si-PIN X-ray detector with a 25 mm^2 surface area, 1mil thickness Be window and a resolution of 190 eV at 5.9 keV. Other instrumental parameters and measurement conditions are displayed in Table 1.

The evaluation of the TXRF spectra was performed using the AXIL software distributed by the IAEA [18].

2.3.4. Atomika 8030C TXRF spectrometer (TXRF-4)

The high power TXRF commercial instrument TXRF 8030C spectrometer (Atomika Instruments GmbH) is equipped with a 3 kW X-ray tube with a Mo/W alloy anode and a double-W/C multilayer monochromator, adjusted to obtain an excitation energy of 17.4 keV (Mo K$_\alpha$). In this equipment, the characteristic radiation emitted by the elements present in the sample is detected by a Si(Li) detector with an active area of 80mm^2 and a resolution of 150 eV at 5.9 keV. The measurements were performed working at 50 kV and the current was adjusted

Table 2
Limits of detection (in µg L^{-1}) estimated from the analysis of the certified reference materials TMDA 64.2 (Lake water) and NIST 1643e (Fresh water) using the systems TXRF-1, TXRF-2 and TXRF-4 (for specific details and measurement time see Table 1).

Element	Lake water (CRM TMDA 64.2)[a]			Fresh water (NIST1643e)[a]		
	TXRF-1	TXRF-2	TXRF-4	TXRF-1	TXRF-2	TXRF-4
Na	n.c.	n.c.	n.c.	600		
Mg	n.c.	n.c.	n.c.	120		
Al	31	n.d.	n.d.	n.c.	n.c.	n.c.
K	n.c.	n.c.	n.c.	2.9	460	41
Ca	n.c.	n.c.	n.c.	2.2	367	45
Ti	1.6	n.d.	19	n.c.	n.c.	n.c.
V	1.4	102	22	1.0	n.d.	n.d.
Cr	1.0	55	19	0.7	n.d.	10
Mn	0.7	29	17	0.4	n.d.	9
Fe	0.5	36	7	0.2	13	3
Co	0.5	26	11	0.2	9	8
Ni	0.4	27	9	0.2	14	6
Cu	0.4	29	8	0.1	9	3
Zn	0.3	21	6	0.09	9	4
As	0.1	21	3	0.9	10	4
Se	0.09	25	5	n.c.	n.c.	n.c.
Rb		n.d.	13	n.c.	n.c.	n.c.
Sr		16	4	n.c.	n.c.	n.c.
Cd	4.2	10		n.c.	n.c.	n.c.
Sn	3.8	15		n.c.	n.c.	n.c.
Sb	1.5	17		n.c.	n.c.	n.c.
Ba	2.3	n.d.	6.6	1.5	n.d.	125
Tl	0.1	n.d.	11	0.1	n.d.	11

[a] Certified values are displayed in Table 3, n.d.: not detected, n.c.: not certified.

automatically as a trade-off between the detector dead time and total analysis time. Additional details are summarized in Table 1.

The evaluation of TXRF spectra was performed using the provided software linked to the system.

2.4. Quantification

For all the TXRF systems considered (TXRF-1, TXRF-2, TXRF-3 and TXRF-4) element quantification was carried out by internal standardization (Expression (1)):

$$C_i = (N_i C_{is} S_{is})/(N_{is} S_i) \qquad (1)$$

where C_i: analyte concentration, N_i: analyte net peak area, C_{is}: internal standard concentration, S_{is}: instrumental sensitivity for the internal standard, N_{is}: Internal standard net peak area, S_i: instrumental sensitivity for the analyte.

In the case of instruments TXRF-2 and TXRF-4, sensitivity factors linked to the commercial instrumental software were employed for quantification purposes and the concentration uncertainty was calculated directly by the software routine linked to the system. When using the other non-commercial systems, the sensitivity factors for each element were experimentally calculated by analyzing the multielemental standard Fluka 70,008 (TXRF-1) or a set of mono-elemental standard solutions (TXRF-3). In this case, the estimation of concentration uncertainties was calculated by random error propagation.

3. Results and discussion

3.1. Sensitivity evaluation of the IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste (TXRF-1)

In order to exploit the benefits of incident beam energy tunability delivered by the XRF beamline, the TXRF elemental sensitivities were evaluated by measuring the multielemental atomic spectroscopy standard solution V (Fluka 70008) at two different exciting energies: 13.0 keV (for multielemental analysis purposes) and 6.2 keV (for light

element determination). The TXRF elemental sensitivities for K-Lines (Kα) and L-lines (Lα), expressed in (in cps/mg kg^{-1}), are reported in Fig. 1, whereas the respective accumulated TXRF spectra are also shown in Fig. 2.

As it can be seen, a clear improvement is observed for the determination of low Z elements sensitivities (Z = 11–24) when the sample is excited at 6.2 keV. In this sense, it is also interesting to remark the benefits of using a detector with very thin polymer window under vacuum for the determination of light elements. Using the higher exciting energy of 13.0 keV it was possible to determine elemental sensitivities for elements up to Z = 34 using K-lines and from Rb (Z = 37) up to Tl (Z = 81) using L-Lines.

As aforementioned, the sensitivity curves displayed in Fig. 1 were obtained using exciting energies of 13.0 keV and 6.2 keV. However, element sensitivities can be improved using better excitation/detection conditions for specific applications. For instance, by decreasing the SDD distance from the sample surface, for example from 10 mm to 5 mm, removing the magnetic trap, adding a thicker window to stop electrons reaching the Si crystal [5] and using an excitation energy of 10.5 keV the sensitivity for Zn-K determination can be improved more than an order of magnitude.

3.2. Analysis of liquid samples

3.2.1. Direct analysis of water samples

In Fig. 3, TXRF spectra obtained for the analysis of the CRM TMDA 64.2 (Lake water) using the IAEAXspe endstation at Elettra Sincrotrone Trieste under total reflection conditions using an excitation energy of 13.0 keV (TXRF-1) and the S2 PICOFOX TXRF benchtop spectrometer equipped with a low power W X-ray tube (TXRF-2) are displayed. As it can be noticed, using the TXRF-2 system, high Z elements such as Cd, Sn, Sb can be identified using their K-lines, which is an optimum condition for a more effective determination of these elements. However, for the determination of light, medium-Z elements a clear improvement of the sensitivity is obtained when using synchrotron radiation. For a better comparison of the analytical capabilities of both systems, limits of detection calculated from the analysis of the CRMs TMDA 64.2 (Lake water) as well as the CRM NIST 1643e (Fresh water) are reported in Table 2. For comparison purposes, limits of detection associated to the TXRF-4 system (Mo X-ray tube, 3 kW) are also displayed in this table. In all cases, LODs were estimated from the resulting spectrum according to the 3σ criteria. As it can be seen, light elements such as Na, Mg and Al can be only detected using the system TXRF-1 which is equipped with an ultra-high vacuum (UHV) chamber. In this sense it is also important to remark that these limits of detection (LODs) can be further improved (in addition to the solid angle improvement mentioned above) by selecting a lower energy for the synchrotron beam, closer to the absorption edges of the interested elements. Limits of detection for other light elements such as K and Ca could be estimated from the analysis of the fresh water CRM. As it is shown from the obtained values, LODs using TXRF-1 were around 150 and 20 times lower than using the systems TXRF-2 (W-Xay tube, 50 W) and TXRF-4 (Mo X-ray tube, 3 kW), respectively.

The LODs obtained for medium-Z elements (Z = 24–34) using the TXRF-1 set-up were in all cases lower than 1 µg L^{-1} and for some elements such as Cu around 0.1 µg L^{-1}. These limits are suitable for most environmental applications dealing with the determination of heavy metals and metalloids and are much better than those obtained using the X-ray tube systems TXRF-2 and TXRF-4. For these systems, LODs were between 50 and 70 times and 15–30 times higher, respectively, depending on the element and type of water. Finally, the LODs for high Z-elements are also clearly improved using synchrotron radiation (TXRF-1). For high-Z element such as Cd, Sb and Sn the improvement factor (2−11) is not so high because, as aforementioned, using the laboratory system equipped with a W X-ray tube (TXRF-2) these elements can be determined through their K-lines which are excited better than

Table 3
Results obtained for the analysis of water samples by using the target TXRF systems. For specific details and measurement time see Table 1.

	Lake water (TMDA 64.2)					Waste water (SPS WW2)					Fresh water (NIST 1643)					Aqueous sample (IAEA S1)				
	Certified values (mg L⁻¹)	TXRF-1 (mg L⁻¹)	TXRF-2 (mg L⁻¹)	TXRF-3 (mg L⁻¹)	TXRF-4 (mg L⁻¹)	Certified values (mg L⁻¹)	TXRF-1 (mg L⁻¹)	TXRF-2 (mg L⁻¹)	TXRF-3 (mg L⁻¹)	TXRF-4 (mg L⁻¹)	Certified values (µg L⁻¹)	TXRF-1 (µg L⁻¹)	TXRF-2 (µg L⁻¹)	TXRF-3 (µg L⁻¹)	TXRF-4 (µg L⁻¹)	Certified values (mg L⁻¹)	TXRF-1 (mg L⁻¹)	TXRF-2 (mg L⁻¹)	TXRF-3 (mg L⁻¹)	TXRF-4 (mg L⁻¹)
K											1.984 ± 0.029[a]	2.2 ± 0.1[a]	1.6 ± 0.3[a]	1.5 ± 0.4[a]	2.14 ± 0.06[a]	10	15.4 ± 0.9	26.0 ± 1.0	10 ± 1	11.4 ± 0.2
Ca											31.5 ± 1.1[a]	34 ± 2[a]	24.6 ± 1.0[a]	24.4 ± 4[a]	33.1 ± 0.5[a]	10	15.5 ± 0.9	10.4 ± 0.6	11 ± 1	20.1 ± 0.3
Ti	0.128 ± 0.0091	0.139 ± 0.007		0.20 ± 0.04	0.20 ± 0.02															
V	0.289 ± 0.021	0.29 ± 0.02	0.30 ± 0.08		0.27 ± 0.03	0.50 ± 0.03	0.52 ± 0.04	0.7 ± 0.1	0.20 ± 0.04	0.56 ± 0.03	36.93 ± 0.57	27 ± 2	22 ± 6	45 ± 1						
Cr	0.29 ± 0.0196	0.29 ± 0.02	0.28 ± 0.05	0.31 ± 0.06	0.32 ± 0.02	1.00 ± 0.01	1.1 ± 0.08	1.2 ± 0.1	1.0 ± 0.2	1.07 ± 0.04	19.9 ± 0.2	16 ± 1			30 ± 6	10	10.8 ± 0.8	10.5 ± 0.3	10 ± 1	10.29 ± 0.05
Mn	0.295 ± 0.0215	0.31 ± 0.02	0.37 ± 0.05		0.26 ± 0.01	2.00 ± 0.01	2.1 ± 0.1	2.2 ± 0.1	1.5 ± 0.3	2.06 ± 0.04	38.02 ± 0.04	32 ± 2			43 ± 8	10	10.1 ± 0.7	10.4 ± 0.3	10 ± 1	9.70 ± 0.08
Fe	0.306 ± 0.0274	0.31 ± 0.02	0.30 ± 0.04	0.10 ± 0.02	0.47 ± 0.02	5.00 ± 0.025	5.2 ± 0.2	5.5 ± 0.2	5.0 ± 0.5	5.32 ± 0.02	95.7 ± 0.14	107 ± 5	170 ± 30		280 ± 30	10	10.2 ± 0.5	10.1 ± 0.2	10 ± 1	10.81 ± 0.07
Co	0.254 ± 0.0176	0.25 ± 0.02	0.32 ± 0.04		0.22 ± 0.01	0.300 ± 0.002	0.31 ± 0.02	0.32 ± 0.05		0.313 ± 0.005	26.4 ± 0.32	25 ± 2	60 ± 20		24 ± 8	10	9.0 ± 0.6	10.9 ± 0.2	10 ± 1	10.60 ± 0.06
Ni	0.263 ± 0.0193	0.27 ± 0.02	0.29 ± 0.04	0.4 ± 0.1	0.26 ± 0.01	5.00 ± 0.025	5.1 ± 0.3	5.3 ± 0.2	4.9 ± 0.5	5.49 ± 0.02	60.89 ± 0.67	64 ± 4	80 ± 20		64 ± 3	10	9.3 ± 0.6	10.2 ± 0.2	10 ± 1	11.13 ± 0.05
Cu	0.275 ± 0.0233	0.29 ± 0.02	0.25 ± 0.03	0.33 ± 0.06	0.28 ± 0.01	2.00 ± 0.01	2.0 ± 0.1	2.0 ± 0.1	2.2 ± 0.4	2.19 ± 0.02	22.2 ± 0.3	027 ± 2	40 ± 10		33 ± 5	10	9.5 ± 0.6	10.2 ± 0.2	10 ± 1	10.24 ± 0.06
Zn	0.31 ± 0.0277	0.33 ± 0.02	0.34 ± 0.03	0.16 ± 0.04	0.33 ± 0.02	3.00 ± 0.015	2.9 ± 0.2	3.1 ± 0.1	2.4 ± 0.4	3.18 ± 0.01	76.5 ± 2.1	116 ± 7	110 ± 20		90 ± 8	10	9.0 ± 0.5	10.2 ± 0.2	10 ± 1	10.84 ± 0.08
As	0.162 ± 0.0154	0.13 ± 0.02	0.13 ± 0.02		0.18 ± 0.01	0.500 ± 0.003	0.5 ± 0.2	0.49 ± 0.03		0.53 ± 0.01	58.98 ± 0.700	27 ± 7	80 ± 10		60 ± 04					
Se	0.155 ± 0.0183	0.15 ± 0.02	0.12 ± 0.02		0.14 ± 0.01															
Rb	0.0306 ± 0.0029				0.03 ± 0.02															
Sr	0.641 ± 0.0465		0.64 ± 0.04		0.50 ± 0.01											10		10.7 ± 0.1		8.08 ± 0.09
Mo	0.29 ± 0.0254	0.15 ± 0.03																		
Ag											1.036 ± 0.073					10	15 ± 4	11.4 ± 0.2		
Cd	0.266 ± 0.0213	0.5 ± 0.1	0.32 ± 0.03			0.100 ± 0.005	0.11 ± 0.05	0.17 ± 0.02			6.408 ± 0.071					10	12 ± 3	10.3 ± 0.2		
In																10		10.8 ± 0.2		
Sn	0.289 ± 0.037		0.28 ± 0.03																	
Sb	0.128 ± 0.0122		0.13 ± 0.02																	
Ba	0.29 ± 0.0235	0.26 ± 0.04									531 ± 6	420 ± 70			600 ± 20					
Tl	0.146 ± 0.0138	0.16 ± 0.01	0.16 ± 0.02		0.12 ± 0.01						7.263 ± 0.094	7 ± 1				10	8.0 ± 0.6	10.4 ± 0.2	11 ± 1	8.08 ± 0.09

Results were obtained by analyzing the same reflector. Concentration uncertainties (±) correspond to error propagation taking into account the formula used for internal standard quantification (Expression (1)).

Legend: TXRF-1: IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste, TXRF-2: S2 PICOFOX TXRF benchtop spectrometer, TXRF-3: TXRF module designed and produced by the Atominstitut, Vienna, TXRF-4: Atomika 8030C TXRF spectrometer.
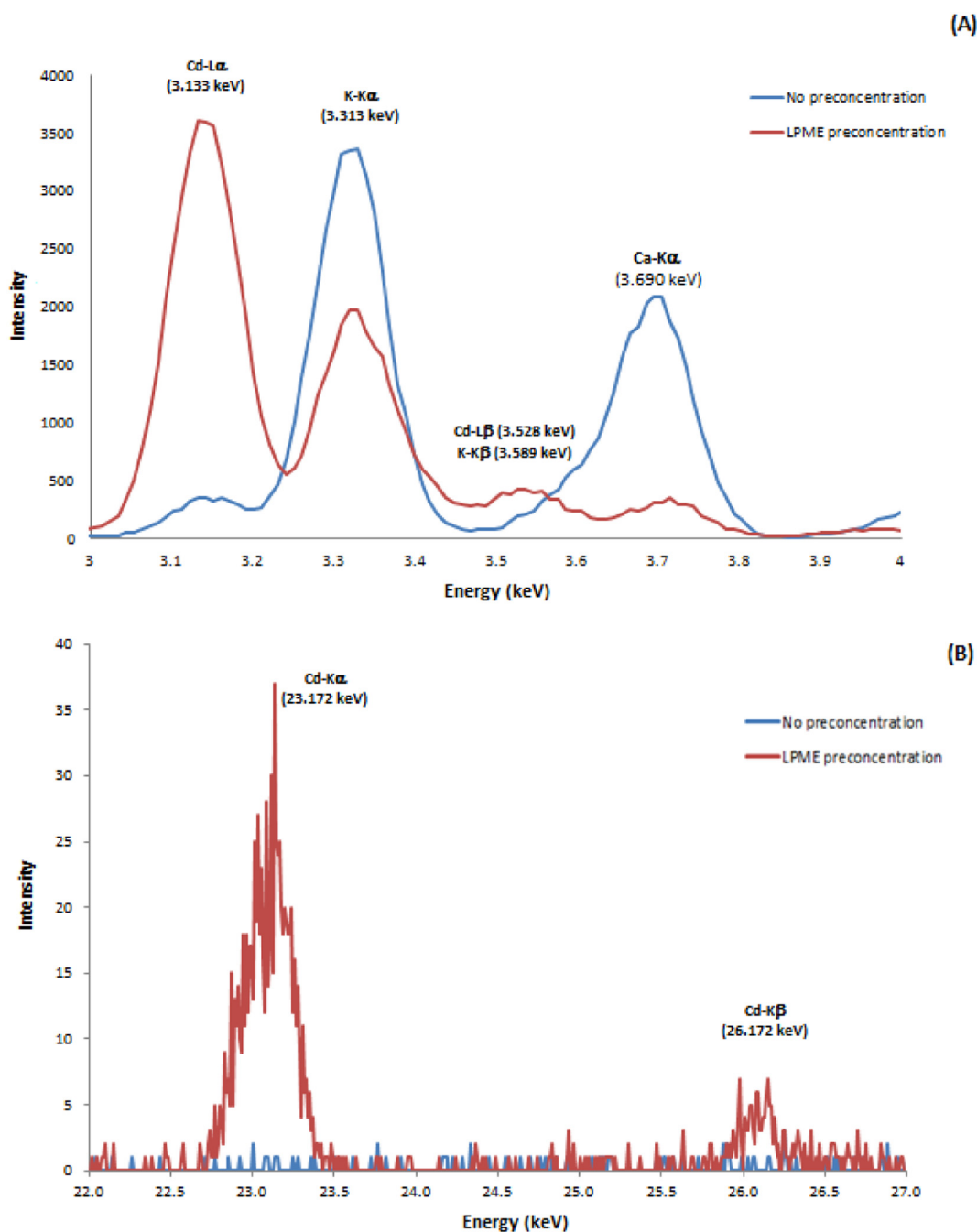
[a] Results reported in mg L⁻¹.

Fig. 4. Comparison between TXRF spectra obtained for the direct analysis of an aqueous standard containing 10 μg L^{-1} of Cd and after the LPME preconcentration procedure (A) IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste under total reflection conditions at 6.2 keV (TXRF-1), (B) S2 PICOFOX TXRF benchtop spectrometer (TXRF-2). Measurement time: TXRF-1 system (standard without LPME: 1440s (8 scans), standard after LPME: 600 s (10 scans), TXRF-2 system (standard without and after LPME: 2000s).

their respective L-lines used for determination of these elements using the TXRF-1 and TXRF-4 systems. However, for the determination of high-Z elements such as Ba and Tl, the LODs for the TXRF-1 system are <3 μg L^{-1} and significantly lower than those associated to the TXRF-4 system (7–125 μg L^{-1}). These elements cannot be detected using the TXRF-2 system in any of the analyzed water CRMs and thus the respective LODs could not be estimated.

In order to investigate the actual capability of the synchrotron set-up (TXRF-1) for multielemental analysis of water samples, several multielemental CRMs with different matrices (lake, waste, fresh water) and an aqueous standard were analyzed and the obtained results are reported in Table 3. For comparison purposes, the actual samples deposited on the same reflector following the procedure described in

Section 2.2.1, were also analyzed using other laboratory TXRF systems (TXRF-2, TXRF-3 and TXRF-4) and results have been also included in Table 3. As it can be noticed, matrix effects for the elements reported in Table 3 in the different types of water are negligible for all the studied systems and the same trends were found regardless of the aqueous sample considered. The worst results for the determination of light elements such as K and Ca were obtained when using the benchtop system. For medium Z-elements good agreement (within 10%) was assessed in most cases for all the considered TXRF systems. For samples containing element with very low concentration levels (i.e., Fresh water CRM) better results were obtained when using the synchrotron set-up (TXRF-1). More accurate results for the determination of high Z elements (i.e. Cd, Sn, Sb) were obtained when employing the system TXRF-2, due to the
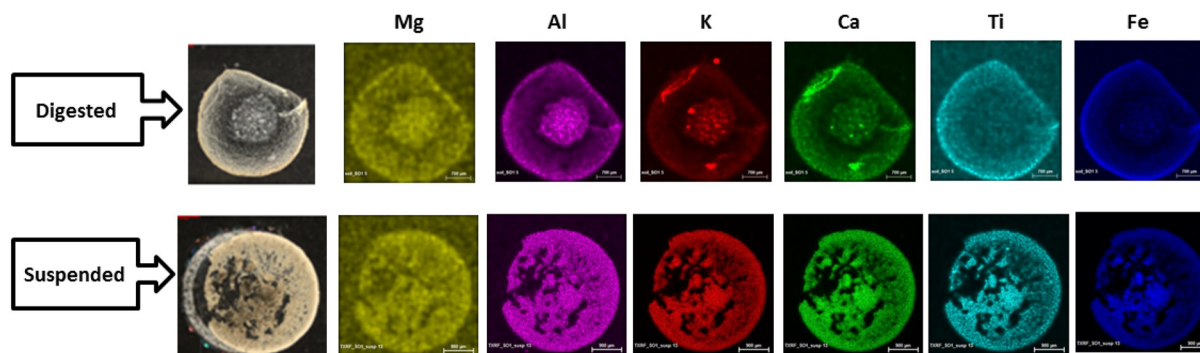
Fig. 5. Two-dimensional mappings for Mg, Al, K, Ca, Ti and Fe distribution in the residue deposited on a quartz reflector both after digestion or suspension of the certified reference material SO1 (soil) obtained by micro X-ray fluorescence spectrometry (M4 Tornado, Bruker). See Section 2.2.2 for instrumental details. Scale information: Digested samples (scale: 700 μm), Suspended samples (scale: 900 μm).

possibility to quantify these elements through their K-lines avoiding common overlaps associated with the detection of L-lines. For other high Z elements such as Ba and Tl the best agreement was obtained when using the TXRF-1 system even at very low concentration levels (see Table 3 for details).

3.2.2. Analysis of preconcentrated liquid samples

A large number of sample treatment procedures have been developed to preconcentrate analytes prior to the TXRF measurements [19]. In this respect it is important to remark the recent development of faster, simpler, inexpensive and more environmentally-friendly analytical procedures for metal preconcentration within the framework of the so-called "green analytical chemistry" such as liquid-phase microextraction (LPME), as well as dispersive micro-solid phase extraction (DMSPE) using nanomaterials as adsorbents. These procedures have been proved to be particularly especially suitable when are combined with benchtop TXRF systems, which offer extreme operational simplicity withlow-cost compact design (no cooling media or gas consumption are required for operation), but limited sensitivity compared with high-scale instrumentation. In fact, in two recent publications, we have demonstrated the usefulness of a LPME procedure for the determination of ultratrace levels of Cd in aqueous samples [14] and a DMSPE using mercapto-modified graphene oxide nanosheets for multi-element (Co, Ni, Cu, As, Cd and Pb) analysis of water samples [15].

In order to study the benefits of the LPME procedure in combination with the SR set-up (TXRF-1), an aqueous standard containing 10 μg L^{-1} of Cd was measured directly and after using the aforementioned preconcentration procedure (see Section 2.2.1 for details). For comparison purposes, the same samples were also analyzed using the benchtop TXRF system (TXRF-2). As it can be seen form the TXRF spectra displayed in Fig. 4, the cadmium analytical response is clearly improved after the preconcentration procedure in both cases with limits of detection for Cd of 0.015 μg L^{-1} (TXRF-1) and 0.1 μg L^{-1} (TXRF-2). An additional advantage of the LPME procedure is the elimination of the potassium content from the water sample (only the Cd is isolated to the organic phase) and this fact clearly reduces the overlapping issues between Cd-L$_\beta$ and K-K$_\alpha$ lines when using the TXRF-1 system (see Fig. 4A). However, it is interesting to remark that when using the SR set-up the energy of the excitation beam can be also adjusted (i.e., at 3.55 keV) in order to detect Cd avoiding the overlapping with the K-K$_\alpha$ line.

The possibility to use a DMSPE procedure using modified graphene oxide nanosheets in combination with the SR set-up (TXRF-1) was also evaluated by analyzing a preconcentrated aqueous standard containing 2 μg L^{-1} of Co, Ni, Cu, As and Cd. The LODs for all elements were below 0.003 μg L^{-1} except for Cd (0.03 μg L^{-1}). As it can be seen in Table 2, these values are almost two orders of magnitude lower in comparison with those obtained for the direct analysis of water samples (without preconcentration). This fact highlights the benefits of using this preconcentration approach for simultaneous determination of

several elements in water samples using synchrotron radiation with fixed excitation energy (in this case 13.0 keV). The obtained limits of detection using the combination DMSPE+TXRF-1 were also compared with those obtained using the system (TXRF-2). In general LODs for the studied analytes were 70–80 times lower using the system TXRF-1, except for Cd. As mentioned abovein the TXRF-2 system, cadmium is determined through its K-lines which are excited much better than the respective L-lines measured using the TXRF-1. Therefore, the corresponding limits of detection for Cd were improved only by a factor of 2 using the SR set-up (TXRF-1).

3.3. Analysis of solid samples

To study the analytical capabilities of the IAEAXspe end-station of the XRF beamline at Elettra Sincrotrone Trieste (TXRF-1) for multielemental analysis of environmental solid samples, several certified reference materials with different matrices (soil, vegetation and biological) were analyzed. In all cases, solid samples were prepared as suspensions or as solutions after digestion according to the procedures described in Section 2.2.2.

Firstly, a study of the shape and element distribution of the deposited residue (after suspension or digestion of the solid sample) on the quartz reflector was performed by μ-XRF analysis. As an example, in Fig. 5, two-dimensional mappings for Mg, Al, K, Ca, Ti and Fe in the residues deposited on the quartz reflector both after digestion or suspension of the certified reference material SO-1 (soil) are displayed. As it is shown, significant differences were found in terms of residue distribution and shape on the reflector depending on the sample treatment procedure. In the digested sample, elements were more accumulated in the center part of the residue and to the external border of the drop. Otherwise, in the case of suspended sample, there was not a clear trend regarding element distribution but the residue on the reflector was not as homogeneous as the one obtained after a digestion process of the solid sample. These findings highlight the necessity to analyze the whole sample area on the reflector to obtain representative element concentrations. For this reason, quantification using the TXRF-1 system was carried out based on the accumulated spectrum resulted from several scan measurements perpendicular to horizontal plane and covering the entire area of the sample residue.

The results obtained for the analysis of several solid certified reference materials after digestion or suspension preparation using the TXRF-1 system are shown in Fig. 6. For comparison purposes, the same samples were also analyzed using the TXRF-2 system. As it can be seen, light elements (such as Mg) as expected can be detected only under vacuum conditions and using an ultra-thin window SDD at the synchrotron set-up (TXRF-1). For other light elements such as K and Ca, better results were also achieved using the TXRF-1 system. It is apparent that TXRF determination of these elements under air conditions (TXRF-2 system) led to a clear underestimation of their concentrations,
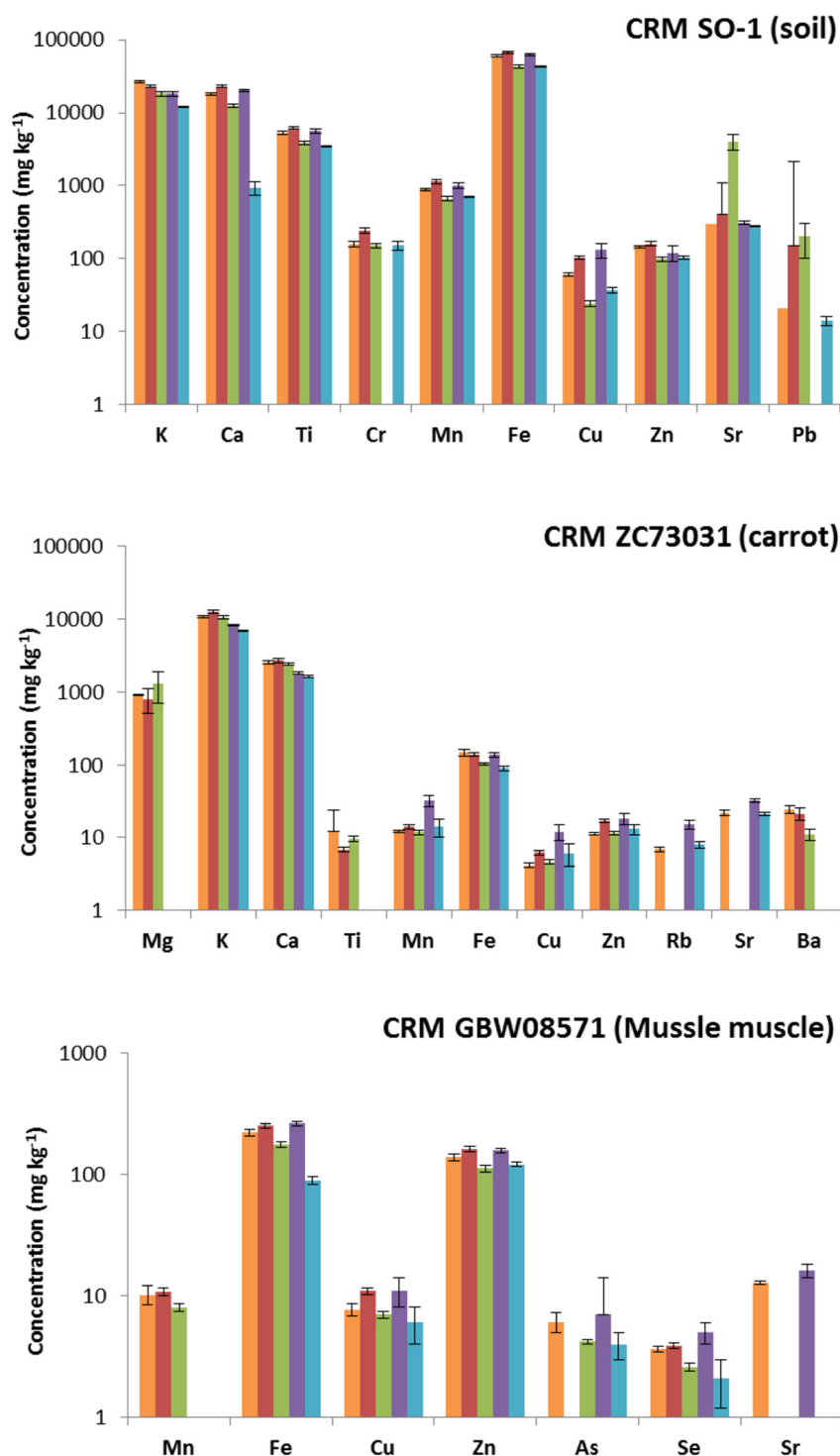
Fig. 6. Results obtained for the analysis of several solid certified reference materials using the IAEAXspe end-station of the XRF beamline at Elettra Sincrotrone Trieste under total reflection conditions at 13.0 keV (TXRF-1) and S2 PICOFOX TXRF benchtop spectrometer (TXRF-2). For specific system details and measurement time see Table 1. Error bars correspond to error propagation taking into account the formula used for internal standard quantification (Expression (1)). Legend: Orange (certified values), Brown-red (TXRF-1 digestion), Green (TXRF-1 suspension), Purple (TXRF-2 digestion) and Blue (TXRF-2 suspension). For the interpretation of the references to color in this figure legend, the reader is referred to the web version of this article. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

above all when solid samples are prepared as suspensions. For the quantification of medium-Z elements (Ti-Se) comparable results were obtained for both TXRF-1 and TXRF-2 systems and both sample treatment strategies. However, more accurate results were found for low concentration levels (ultratraces) when using TXRF-1 set-up (see for example the determination of Se in the CRM-GBW08571, Mussel muscle tissue).

Heavier elements such as Ba (Z = 56) could be only determined using the TXRF-1 system and quantitative results were obtained by applying the digestion procedure as solid sample treatment. On the contrary, quantitative determination of Pb (Z = 82) was only possible using TXRF-2 system.

From the TXRF spectra obtained in the analysis of the solid certified reference materials, limits of detection were also estimated (see

Table 4

Limits of detection (in mg kg^{-1}) estimated for the analysis of the solid certified reference materials SO-1 (soil), NCS ZC73031 (carrot) and GBW08571 (mussel muscle tissue) using the systems TXRF-1 (Excitation energy: 13.0 keV) and TXRF-2 (for specific system details and measurement time see Table 1).

Element.	CRM SO-1 (soil)				CRM NCS ZC73031 (carrot)				CRM GBW08571 (mussel muscle tissue)			
	TXRF-1 Dig.	TXRF-1 Susp.	TXRF-2 Dig.	TXRF-2 Susp.	TXRF-1 Dig.	TXRF-1 Susp.	TXRF-2 Dig.	TXRF-2 Susp.	TXRF-1 Dig.	TXRF-1 Susp.	TXRF-2 Dig.	TXRF-2 Susp.
Mg					170	84						
K	31	10	2035	197	0.9	1.0	124	129				
Ca	15	7	970	136	0.7	0.7	100	99				
Ti	9	4	493	60	0.5	0.4						
Cr	4	2		25								
Mn	4	2	146	22	0.1	0.1	3	7	0.2	0.2		
Fe	3	1	113	19	0.1	0.1	6	10	0.1	0.1	5	8
Co												
Ni												
Cu	0.9	0.9	23	8	0.04	0.04	2	2	0.1	0.1	3	4
Zn	1.2	0.4	50	5	0.03	0.04	3	2	0.1	0.1	3	3
As									0.03	0.03	2	3
Se									0.03	0.02	0.9	3
Rb							0.5	1				
Sr			20	2			0.7				4	
Ba					0.4	0.5						
Pb				4.6								

Dig: digestion (Dilution factors: soil → 0.25 g/50 mL, carrot and mussel → 0.25 g/25 mL), Susp.: suspension (Dilution factor: 50 mg/1 mL).

Table 4). In this sense it is interesting to remark the different dilution factor associated to the digestion or suspension procedures used to prepare the solid samples (Digestion: soil → 0.25 g/50 mL, carrot and mussel → 0.25 g/25 mL, Suspension: 50 mg/1 mL). In the case of digested samples, a clear reduction of the TXRF spectrum background is observed. Nevertheless, due to the higher dilution factor of the digestion procedure, the limits of detection were estimated to be similar or even slightly worse than those obtained for the solid suspended samples. As expected, limits of detection reported in Table 4 associated to biological sample (carrot and mussel muscle) analysis are lower than those calculated from soil analysis. For instance, limits of detection for medium-Z elements such as Cu and Zn are twenty times lower in the considered biological matrices in comparison with the soil CRM when using the TXRF-1 system. The lower limits of detection are related to the fact that the matrix of a biological sample is much lighter (i.e. it has a lower average atomic number) than a soil sample. For this reason, the mass attenuation coefficient for the exciting X-ray beam is much smaller in a biological matrix compared to a solid one, leading also to smaller self-attenuation correction factor for the exciting beam. Moreover, the high intensity of the relatively dominant Fe-K peaks in the soil sample spectrum further contribute to an increased background below the X-ray peaks of elements with Z < 26 [20].

Regarding the comparison of the LODs estimated for the TXRF-1 and TXRF-2 systems for solid sample analysis, similar conclusions to the ones reported for the analysis of water samples can be drawn. As reported in the Table 4, the limits of detection for these elements are in the range of 0.7–0.9 mg kg^{-1} using the synchrotron TXRF-1 set-up and between 100 and 124 mg kg^{-1} using the TXRF-2 instrument, working under air conditions. The LODs for medium-Z elements are also improved by a factor of around 20 (soil sample) and 30–50 (biological samples) using the synchrotron TXRF-1 set-up, except for the Rb, Sr and Pb determination. Finally, the detection of high-Z elements (i.e. Ba) at levels lower than 0.5 mg kg^{-1} is only feasible using the TXRF-1 set-up. It was not possible to evaluate the limit of detection for Ba when using the benchtop spectrometer (TXRF-2) since this element was not detected in the resulting CRM-ZC73031 (carrot) TXRF spectrum.

4. Conclusions

In this contribution a first evaluation of the analytical capabilities of the IAEASpe beamline endstation at IAEA-Elettra Sincrotrone for multielemental analysis of different types of aqueous and solid samples under TXRF conditions is presented.

Using an excitation energy of 13.0 keV elements from Z = 11 up to Z = 34 using K-lines and from Rb (Z = 37) up to Tl (Z = 81) using L-Lines can be quantitatively determined under vacuum conditions and using an ultra-thin window SDD.

A clear improvement of the element detection limits is achieved when comparing this facility to conventional X-ray tube based TXRF systems (operated with Mo and W X-ray anodes) highlighting the benefits of using the monoenergetic synchrotron exciting radiation in comparison with conventional laboratory systems. The determination of light elements (Z < 23) can be assessed at levels around 3 μg L^{-1} in liquid samples and in the range of 0.7–0.9 mg kg^{-1} for geological/biological solid samples. For medium-Z elements (Z: 23–34) the associated LoD are in all cases lower than 1 μg L^{-1} and for some elements such as Cu around 0.1 μg L^{-1} for liquid samples, whereas for solid samples LODs are in the range of 0.03–4 mg kg^{-1} (depending on the sample type and sample preparation procedure). For heavier elements (i.e., Ba and Tl) LODs are <3 μg L^{-1} (aqueous samples) and lower than 0.5 mg kg^{-1} for solid samples.

For high-Z element such as Cd, Sb and Sn the improvement factor in the detection limits in comparison with laboratory W anode X-ray tube systems is less pronounced (factor ≈ 10) because, as aforementioned, for the determination of these elements K-lines can be used instead of L-lines, less intense and more affected by overlapping with other lines. However, the LoDs for these heavier elements can be significantly improved using more suitable excitation conditions or using preconcentration procedures in sample preparation.

From the analysis of the solid certified reference materials in general LODs obtained for biological samples (carrot and mussel muscle) are lower than those calculated for geological materials such as soils. For medium-Z elements (i.e., Cu and Zn) LODs are twenty times lower in the considered biological matrices in comparison with the soil CRM.

For all the studied aqueous and solid samples (biological/geological), quantitative results were obtained using internal standardization as the preferred quantification methodology. However, for quantitative determination it was necessary to use the sum spectrum of several measurements performed to cover the entire area of the residue, due to the inhomogeneity observed regarding the spatial distribution of the analyte and the extended shape of the residue on the reflector.

The results of the present work provide a solid ground for further advances in different environmental, biological and industrial applications of TXRF analysis. The optimization of the set-up geometrical

parameters, such as the diameter of the SDD aperture and its working distance from the sample, in conjunction with the utilization of a multi-layer monochromator that will offer much higher beam intensity, it is expected to decrease significantly the obtained LODs thus enabling ultra-trace elemental analysis under TXRF excitation conditions.

Acknowledgments

References

[1] C. Streli, P. Wobrauschek, F. Meirer, G. Pepponi, Synchrotron radiation induced TXRF, J. Anal. At. Spectrom. 23 (2008) 792–798.

[2] G. Sarret, G. Willems, M.-P. Isaure, M.A. Marcus, S.C. Fakra, H. Frerot, S. Pairis, N. Geoffroy, A. Manceau, P. Saumitou-Laprade, Zinc distribution and speciation in *Arabidopsis halleri* × *Arabidopsis lyrata* progenies presenting various zinc accumulation capacities, New Phytol. 184 (2009) 581–595.

[3] F. Meirer, A. Singh, G. Pepponi, C. Streli, T. Homma, P. Pianetta, Synchrotron radiation-induced total reflection X-ray fluorescence analysis, Trends Anal. Chem. 29 (2010) 479–496.

[4] U.E.A. Fittschen, G. Falkenberg, Trends in environmental science using microscopic X-ray fluorescence, Spectrochim. Acta B 66 (2011) 567–580.

[5] A.G. Karydas, M. Czyzycki, J.J. Leani, A. Migliori, J. Osan, M. Bogovac, P. Wrobel, N. Vakula, R. Padilla-Alvarez, R.H. Menk, M.G. Gol, M. Antonelli, M.K. Tiwari, Cl. Caliri, K. Vogel-Mikuˇs, I. Darby, R. Bernd Kaiser, An IAEA multi-technique X-ray spectrometry endstation at Elettra Sincrotrone Trieste: benchmarking results and interdisciplinary applications, J. Synchrotron Radiat. 25 (2018) 189–203.

[6] P.M. Wrobel, M. Bogovac, H. Sghaier, J.J. Leani, A. Migliori, R. Padilla-Alvarez, M. Czyzycki, J. Osan, R.B. Kaiser, A.G. Karydas, LabVIEW interface with tango control system for multi-technique X-ray spectrometry IAEA beamline end-station at Elettra Sincrotrone Trieste, Nucl. Inst. Methods Phys. Res. A 833((2016) 105–109.

[7] R. Dalipi, E. Marguí, L. Borgese, L.E. Depero, Multielement analysis of vegetal food-stuff by means of low power total reflection X-ray fluorescence (TXRF) spectrometry, Food Chem. 218((2017) 348–355.

[8] H. Gallardo, I. Queralt, J. Tapias, L. Candela, E. Marguí, Bromine and bromide content in soils: analytical approach from total reflection X-ray fluorescence spectrometry, Chemosphere 156((2016) 294–301.

[9] C. Streli, Recent advances in TXRF analysis, Appl. Spectrosc. Rev. 41 (2006) 473–489.

[10] E. Marguí, G.H. Floor, M. Hidalgo, P. Kregsamer, G. Román-Ross, C. Streli, I. Queralt, Analytical possibilities of total reflection X-ray spectrometry (TXRF) for trace selenium determination in soils, Anal. Chem. 82 (2010) 7744–7751.

[11] E. Marguí, R. Van Grieken, X-ray Fluorescence Spectrometry and Related Techniques: An Introduction, Momentum Press, LLC, 2013.

[12] F. Meirer, C. Streli, G. Pepponi, P. Wobrauschek, M.A. Zaitz, C. Horntrich, G. Falkenberg, Feasibility study of SR-TXRF-XANES analysis for iron contaminations on a silicon wafer surface, Surf. Interface Anal. 40 (2008) 1571–1576.

[13] C. Streli, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Zaray, A new SR-TXRF vacuum chamber for ultra-trace analysis at HASYLAB, Beamline L, X-Ray Spectrom. 34 (2005) 451–455.

[14] E. Marguí, I. Queralt, M. Hidalgo, Determination of cadmium at ultratrace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid–liquid microextraction, J. At. Anal. Spectrom. 28 (2013) 266–273.

[15] R. Sitko, P. Janik, B. Zawisza, E. Talik, E. Marguí, I. Queralt, Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection X-ray fluorescence spectrometry and mercapto-modified graphene oxide nanosheets as a novel adsorbent, Anal. Chem. 87 (2015) 3535–3542.

[16] R. Dalipi, E. Marguí, L. Borgese, F. Bilo, L.E. Depero, Analytical performance of bench-top total reflection X-ray fluorescence instrumentation of multielemental analysis of wine samples, Spectrochim. Acta B 120 (2016) 34–43.

[17] P. Wobrauschek, P. Kregsamer, Total reflection X-ray fluorescence analysis with polarized X-rays, a compact attachment unit, and high energy X-rays, Spectrochim. Acta B 44 (1989) 453–460.

[18] P. Van Espen, K. Janssens, J. Nobels, AXIL-PC, software for the analysis of complex X-ray spectra, Chemom. Intell. Lab. Syst. 1 (1986) 109–114.

[19] E. Marguí, B. Zawisza, R. Sitko, Trace and ultratrace analysis of liquid samples by X-ray fluorescence spectrometry, Trends Anal. Chem. 53((2014) 73–83.

[20] E. Marguí, G.H. Floor, M. Hidalgo, P. Kregsamer, G. Román-Ross, C. Streli, I. Queralt, Analytical possibilities of total reflection X-ray spectrometry (TXRF) for trace selenium determination in soils, Anal. Chem. 82 (2010) 7744–7751.