Application of X-ray fluorescence techniques for the determination of hazardous and essential trace elements in environmental and biological materials

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Abstract The utilization of X-ray fluorescence technique for the determination of trace element concentrations in environmental and biological samples is presented. The analytical methods used include energy dispersive X-ray fluorescence with polarizing secondary targets, total reflection X-ray fluorescence, direct in-situ X-ray fluorescence, and micro-beam X-ray fluorescence spectrometry. These methods were applied to analysis of different samples including soil, water, plant material and airborne particulate matter collected on polycarbonate filters. The performance and achieved detection limits of elements for different techniques, established by measuring appropriate reference standards, are presented. Also described is the utilization of microbeam X-ray fluorescence technique for studying element distribution in heterogeneous samples and investigating the 2D- and 3D-morphology of minute samples by means of computerized X-ray absorption and X-ray fluorescence tomography. The different X-ray techniques have their unique advantages. The micro-beam X-ray fluorescence set-up has an advantage of producing very well collimated primary X-ray beam (about 15 µm in diameter), in front of which the analyzed sample can be precisely positioned, providing local information about the sample composition. The energy dispersive X-ray fluorescence with secondary targets offers rapid analysis of broad range of elements (Na-U) combined with a simple sample preparation method. Total reflection X-ray fluorescence technique, characterized by the lowest detection limits of elements, has its leading edge in analysis of liquid samples, and dealing with particle size effects in air particulates collected on filter papers. In-situ X-ray fluorescence spectrometers are truly portable and enable on the spot, in field analysis. It is shown that the combination of several XRF methods allows for a better characterization of a variety of materials, e.g. solids, liquids, and minute heterogeneous samples.

Key words biological material • environmental materials • X-ray fluorescence analysis

Introduction

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Environmental pollution effects emanating from natural or anthropogenic sources manifest eventually in the atmospheric, aquatic, and terrestrial media. Hence, for a holistic approach to environmental pollution studies, a wide range of representative samples need to be analyzed in sufficient quantities over a broad scope of parameters. This will involve the measurement of large quantities of different kinds of samples. Adequate information has to be generated at the pollution monitoring level, in order to comprehensively characterize the pollutants being monitored. Such information will enable pollution pathways to be established and also serve as input for effective pollution management and control. It may also be necessary, at times, to be able to keep custody of the analyzed samples due to legal or other reasons. The above situation and conditions impose the requirements for a fast, non-destructive, and simultaneous multi-elemental method of analysis. Energy dispersive X-ray fluorescence spectrometry and related techniques meet these requirements, and have some unique advantages. In the last 20 years the energy dispersive X-ray fluorescence (EDXRF) spectrometry has been developed intensively. Recently, the advances made in semiconductor detectors, in digital signal processing and in computercontrolled data acquisition systems have widened the applicability of the technique allowing construction of lowcost, desktop size spectrometers capable of reliable and fast determination of element concentrations in different kinds of matrices [4, 8]. The main advantages of the EDXRF technique over other methods of elemental analysis are its multi-elemental capacity, simple or wellestablished sample preparation methods and good detection limits of elements. Also important are low maintenance costs allowing the EDXRF technique to be employed in many low-budget laboratories through the world. It is relatively easy, by utilizing standard components available on the market, to assemble a stand-alone, laboratory X-ray spectrometer. The IAEA, through various technical cooperation projects, supports local XRF laboratories, providing analytical software and assistance in the maintenance of the spectrometric equipment. The Agency is also involved in professional training of laboratory staff. For supporting these activities the IAEA has established an XRF laboratory, which is a part of the IAEA Laboratories, Seibersdorf, Austria.

All the experimental work has been carried out and the results were obtained at the IAEA XRF Laboratory. The Laboratory is equipped with a commercial XRF system taking most of the routine analytical work, and several inhouse designed EDXRF spectrometers. The configuration of the in-house designed spectrometers can easily be adapted making them very suitable for training the Agency's fellows, validating new analytical approaches, and for analysis of "difficult" samples, which due to different reasons cannot be analyzed with the commercial system [1, 2, 9, 10]. The analytical techniques available include conventional EDXRF with secondary targets, total reflection X-ray fluorescence (TXRF), micro-beam XRF (µXRF), and radioisotope based direct *in-situ* portable XRF (PXRF) spectrometry. The μ XRF spectrometer is also utilized to perform X-ray computerized tomographic (μCT) imaging. Using these techniques, determination of hazardous and essential trace elements in environmental and biological samples and characterization of heterogeneous samples has been carried out. In Table 1, an overview of the samples analyzed and techniques used is shown. In addition, the results of analysis of several reference materials will be also presented.

Table 1. Samples and spectrometric techniques used.

Sample	EDXRF	TXRF	PXRF	μXRF	μCΤ
	sec. target				
Biological matrix					
rice	•				
lichen	•				
human bone					•
Environmental matrice	es				
soil	•				
sediments	•				
air aerosols	•				
uranium contaminat	ed			•	
soil					
tap water		•			

Experimental

The XRF analyses have been performed utilizing several XRF methods and spectrometers. Depending on the spectrometer used, the analyzed samples were prepared as pressed pellets, particulate deposits on polycarbonate filters (EDXRF), liquids – after chemical decomposition in a microwave acid digestion system (TXRF) or filtered deposits following a chemical preconcentration procedure (EDXRF and TXRF), loose powders (PXRF), individual grains deposited on a Mylar foil (μ XRF), and minute samples mounted individually (μ CT). The spectrometers' configuration and measuring conditions were as described below.

Spectrometers and measuring conditions

EDXRF spectrometers with secondary targets

Two such spectrometers were used. The first system, a commercial apparatus, consisted of a Pd-anode X-ray tube (300 W), five secondary targets (Al₂O₃, Co, Mo, Pd, Highly Oriented Pyrolytic Graphite (HOPG)), a Si(Li) detector (FWHM of 150 eV at 5.9 keV, 20 mm² active area, 8 µm Be window). The measurements were carried in vacuum, the analysis time per sample was 1800 s (overall real time of measurements with all five sec. targets) and the tube HV settings, depending on the secondary target, were the following: 52.5 kV/Al_2O_3 , 30 kV/Co, 30 kV/Mo, 44 kV/Pd, and 15 kV/HOPG. The analysis was controlled by a PC data acquisition system. The analyzed samples were prepared in the form of pressed pellets with the diameter equal to 32 mm. The quantitative analysis procedure used in the commercial spectrometer was based on backscatter fundamental parameter approach [8]. For the purpose of a direct analysis of air aerosols deposited on polycarbonate filters an in-house built EDXRF sec. target spectrometer has been used. The spectrometer consisted of a Mo-anode X-ray tube (3000 W), a Mo secondary target, a Si(Li) detector (FWHM of 170 eV at 5.9 keV, 30 mm² active area, 8 μ m Be window) with accompanying NIM electronics connected to a PC-based multichannel analyzer (MCA) system. The measurements were carried out in vacuum for 10,000 s per sample. The tube operating conditions were 45 kV/40 mA.

TXRF spectrometer

A system designed and assembled at the IAEA Laboratories (see Fig. 1). The spectrometer consists of a TXRF vacuum chamber attached to a Mo-anode X-ray tube (3000 W). The chamber was equipped with a motorized cut-off reflector and motorized sample stage allowing for remote adjustments of the grazing angle. A detailed description of the TXRF chamber can be found elsewhere [3]. The X-ray spectra were collected by the Si(Li) detector with FWHM = 170 eV at 5.9 keV, 30 mm² active area, 8 μ m Be window. The critical angle adjustment and data acquisition was carried out under control of a PC running SPECTOR software [5]. The X-ray tube was operated at 45 kV/40 mA and the measuring time varied between 100–500 s per sample.

For the purpose of cadmium determination in tap water samples, the cut-off reflector was removed. It was replaced



Fig. 1. TXRF spectrometer.

by a sample carrier. Bringing the sample carrier closer to the X-ray tube allowed efficient excitation of Cd- $K\alpha$ line.

PXRF spectrometer

Radioisotope-based portable spectrometer designed and assembled at the IAEA Laboratories (see Fig. 2). The spectrometer can be applied directly to the soil surface and can also be used to analyze loose powder samples loaded in plastic sample cups. Up to three sources (⁵⁵Fe, ¹⁰⁹Cd, and ²⁴¹Am) can be installed in a revolving wheel for consecutive sample excitation. The results presented in this paper were obtained by using a ¹⁰⁹Cd radioisotope source of activity equal to 925 MBq (February 2002) for exciting the X-ray fluorescence radiation. The X-ray spectra were collected by a Si-PIN photodiode detector supplied from a battery operated integrated power supply/amplifier attached to a battery operated MCA. Data acquisition was controlled by a palmtop computer. The spectrometer performance has been validated by analyzing a broad spectrum of reference materials in the form of loose powders and by carrying out in-situ element determination in surface soil.

$\mu XRF/\mu CT$ spectrometer

A micro-beam scanning spectrometer system [6]. The spectrometer consists of a high-power X-ray tube fitted with capillary optics (single tapered glass capillary or poly-

capillary lens) producing a very fine collimated beam of X-rays. The minimum diagonal dimension of the beam spot, FWHM - as measured on the sample surface, is equal to about 12 μ m. Different anode tubes can be easily installed allowing optimization of excitation conditions. The sample is mounted in front of the beam on a motorized sample stage. The stage has four degrees of freedom - three translation and one rotation axis. The precision of positioning the sample is about $1-2 \mu m$. The system is equipped with two X-ray detectors, the Si(Li) detector (FWHM = 160 eV at 5.9 keV, 80 mm², 8 μ m Be window) and a thermoelectrically cooled, silicon drift (SD) detector (FWHM = 170 eV at 5.9 keV, 2 mm^2 , $8 \mu \text{m}$ Be window). The scanning and the data acquisition is controlled by PC running SPECTOR software. The advantageous feature of this system, as compared to other X-ray tube based micro-beam spectrometers, are its two detectors, which can be operated simultaneously. The Si(Li) detector collects the X-ray fluorescence spectra of the sample and the SD detector, operated at 0.25 µs peak shaping time, measures the direct beam transmitted through the analyzed sample. Coupled to a gated integrator amplifier and fast ADC (Wilkinson type - 500 MHz), the SD detector can be operated at 10^5 cps output counting rate. The system has been used for examining the presence of U-rich particles in a contaminated soil dust sample and for obtaining 3D µCT images of an osteoporotic bone fragment. A top-view picture of the micro-beam spectrometer is shown in Fig. 3.

Sample preparation

The samples were prepared in various ways depending on the sample type, available amount, and the selected spectrometer to carry out the analysis [3, 7]. Table 2 summarizes the procedures used for sample preparation.

Biological samples

The biological matrices analyzed included rice, lichen, and a bone fragment. The rice seeds were ground to a fine powder, and then taking 7 g portions, pellets of 32 mm were pressed. Separate sub-samples were taken for estimating "constant dry-mass" of the analyzed material. The rice samples were analyzed by on EDXRF sec. target method and a commercial spectrometer. The lichen samples, a proficiency test material, were obtained in





Fig. 2. Portable, battery operated XRF spectrometer during direct *in-situ* element determination in surface soil.



Fig. 3. Micro-beam XRF/CT spectrometer.

the powdered form. They were pelletized following the procedure described for rice samples (excluding grinding step) and analyzed by the EDXRF secondary target method. Simultaneously, 500 mg portions were put into PTFE vessels and underwent closed acid digestion, with a mixture of nitric acid and hydrogen peroxide, in a microwave system. After digestion, the samples were spiked with internal standard solution, several microlitres were pipetted onto quartz sample carriers, dried on a hot plate and measured in a TXRF spectrometer.

The fragment of an osteoporotic human bone has been prepared to perform 3D μ CT imaging of the bone structure. The bone fragment has been lyophilized. A sub-section of the bone was cut out using a diamond rotary saw. The bone was mounted on a 0.5 mm graphite holder and then underwent a CT scanning procedure in the micro-beam spectrometer.

Environmental samples

The environmental samples included soil, sediment, tap water, air aerosols, and uranium contaminated soil dust.

The soil and sediments samples were prepared in the form of pellets by pressing the powdered homogeneous S. A. Bamford *et al*.

material into a thick pellet directly or after addition of a binder in the form of boric acid or cellulose. Then, the samples were measured in the commercial EDXRF secondary target spectrometer.

The samples analyzed with PXRF spectrometer were in the form of loose powders and a local, Seibersdorf surface soil was analyzed directly *in-situ*.

A chemical preconcentration procedure was combined with TXRF for the determination of Cd, Cr(III), Cr(VI), As(III), and As(V) in tap water. For cadmium determination a chelating agent (1% aqueous solution of APDC) was added to the tap water following co-precipitation of the organometallic complexes with Ag as a carrier at pH equal to 4 (adjusted with nitric acid). The precipitate was collected on a Millipore filter of 0.22 µm pore size and dried in a vacuum chamber. In the next step, 1 mL of nitric acid, spiked with Ga internal standard, was poured through the filter. From the filtrate 0.5–1 µL aliquots were pipetted onto a quartz sample carriers and dried on a hot plate. The dried residue was measured in the TXRF spectrometer. Preconcentration of Cr(III) and Cr(VI) was carried out by co-precipitation with cobalt-APDC at two different pH values: 9 and 4, respectively. Aqueous ammonia and nitric acid used for adjusting appropriate pH levels. After drying, 1 mL of nitric acid was poured through the filters and microlitre aliquots of the filtrate were pipetted onto quartz sample carriers, dried and analyzed. For the determination of As(III), complexation with APDC and co-precipitation using silver as a carrier element, at pH = 2, was applied. Hydrochloric acid solution (HCl) or aqueous ammonia (NH₄OH) were used to adjust the pH value. For determination of As(V), the precipitation was preceded by the reduction of As(V) to As(III) by using potassium iodide and ascorbic acid solutions. The precipitate was filtered, poured with nitric acid. From the filtrate samples were prepared and measured in the TXRF spectrometer in a similar way as described for the other species.

Air aerosol samples were analyzed firstly without any preparation in an in-house designed EDXRF sec. target spectrometer. After EDXRF analysis, the filters were digested in a closed microwave system and spiked with cobalt internal standard solution. From the spiked solution, 2 μ L aliquots were pipetted onto quartz sample carriers and measured in the TXRF spectrometer.

Uranium contaminated soil dust particles were fixed on the surface of a 2.5 μ m thick Mylar foil mounted in

Table 2. Samples and methods of sample preparation [3, 7].

Sample	Not any (PXRF, EDXRF)	Little (PXRF, µXRF, µCT)	Pelletizing (EDXRF)	Digestion (TXRF)	Preconcentration (TXRF)
Biological matrices rice lichen human bone		Lyophilization	Pellet, no binder Pellet, no binder	Closed acid digestion Closed acid digestion	
Environmental matrices soil sediments	Direct in-situ	Loose powder	Pellet, no binder Pellet, with and without binder		
air aerosols uranium contaminated soi tap water	Direct on filter	Deposition on foil	"Hilout billubi	Closed acid digestion	Co-precipitation



Fig. 4. Variability of element concentrations in the rice samples.

a plastic frame. The diameter of the particulate matter deposit was equal to about 1 cm. The sample was mounted in the μ XRF spectrometer and a pre-scan was made covering 5 mm × 5 mm deposit area (51 pixels × 51 pixels). The measuring time per pixel was set to 1 s and 0.3 s for the Si(Li) and SD detectors, respectively. By examining the transmission and fluorescence signals, a sub-area (1.5 mm × 2.5 mm) containing heavy, U-rich particles was selected and scanned using higher resolution (251 pixels × 251 pixels) and longer measuring times (5 s per pixel for fluorescence and 2 s per pixel for transmission signal).

Results

Twenty rice samples, including two commercially available rice products, were analyzed by the EDXRF secondary target technique. The following elements were determined: P, K, Ca, Mn, Fe, Zn, Br, and Rb. The variability of the element concentrations in the analyzed rice samples is shown in Fig. 4.

The lichen samples were analyzed by the EDXRF sec. target and by TXRF techniques. For each technique, a different sample preparation method was applied. Concentra-



Fig. 5. Correlation between the element concentrations in lichen samples determined by EDXRF sec. target and TXRF techniques.



Fig. 6. Correlation between the determined and given concentrations of elements. The results of analysis performed by EDXRF sec. target and TXRF techniques.

tions of the following elements were determined: V, Mn, Fe, Cu, Zn, Sr, Ba, and Pb. Vanadium and barium were determined only by the EDXRF method. A comparison of the results obtained by both techniques is presented in Fig. 5.

In order to validate the analytical procedures applied for rice and lichen analysis, two control materials were analyzed and the results compared with certified values. The control samples were prepared from the IAEA-H-10 *Hay Powder* and IAEA-336 *Lichen reference materials*. The obtained results are presented in Fig. 6.

The commercial EDXRF sec. target spectrometer has also been employed to determine major, minor and trace elements in soil, marine and glacier sediments. Concentrations of the following elements were determined: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, I, Ba, La, Ce, Pb, Th, U. The performance of the EDXRF secondary target spectrometer was examined by analyzing several environmental and geological reference materials. The correlation between the determined and given concentrations is



Fig. 7. Correlation between given and determined concentrations of elements based on the measurement of three control samples, IAEA-*Soil*-7 RM, CERAMIC-1 SARM 69 RM, and Penrhyn Slate proficiency test sample.



Fig. 8. Correlation between the given and determined concentration of elements obtained from the analysis of loose powder samples prepared from reference materials and measured by PXRF spectrometer.

presented in Fig. 7. The results in this figure were obtained from measurements of IAEA-Soil-7, CERAMIC-1 SARM 69



Fig. 9. Comparison of the results obtained during direct *in-situ* determination and after processing the sample in the laboratory. The analyses performed with the use of PXRF spectrometer.



Fig. 10. The X-ray spectra of air aerosol samples obtained with EDXRF secondary target (direct analysis) and TXRF (after digesting the samples) spectrometers.



Fig. 11. Element concentrations in air obtained by TXRF and EDXRF sec. target techniques. The air aerosols were collected in dichotomous air sampler.



Fig. 12. Correlation between given and determined element loadings on NIST SRM 2783 *Air Particulate on Filter Media*. The analysis was performed with EDXRF sec. target spectrometer.



Fig. 13. Results of speciation analysis of tap water samples containing know additions of Cr(III), Cr(VI), As(III), As(V), and Cd species. The analyses were performed with TXRF technique.



Fig. 14. Distribution of particles, shown by the Mo- $K\alpha$ transmission signal, and identified U-rich/As-rich, K-rich, Fe-rich, and Ca-rich particles identified by their X-ray fluorescence spectra.

reference materials, and a Penrhyn Slate proficiency test sample.

The PXRF spectrometer was also used for element determination in environmental samples. The results of validation of the spectrometer performance are shown in Fig. 8. The PXRF spectrometer has also been applied for direct *in-situ* element determination in surface soil. Following the *in-situ* measurements, the soil samples were taken to the laboratory and the analysis has been repeated after processing the soil material. The results of this exercise are shown in Fig. 9.

The air aerosols deposited on polycarbonate filters have been analyzed by using the EDXRF secondary target and TXRF techniques. In Fig. 10, the X-ray fluorescence spectra of the two aerosol particle fractions, obtained with the EDXRF secondary target and TXRF spectrometers, are shown. A comparison of the results of the element determination in the air aerosols is presented in Fig. 11. The determination of elements in air aerosols deposited on polycarbonate filters has been validated by analysis of a NIST SRM 2783 *Air Particulate on Filter Media*. The reference material was analyzed directly by the EDXRF secondary target technique. The correlation between given and the determined element loadings is presented in Fig. 12.

The chemical preconcentration method for the determination of Cd, Cr(III), Cr(VI), As(III), and As(V) was followed by TXRF analysis of the obtained filtrate samples. The recovery of the preconcentration procedure was investigated. The obtained results are shown in Fig. 13.

The µXRF technique has been applied for identification of U-rich particles in contaminated soil dust. The results of an area scan (2.5 mm \times 1.5 mm/251 steps \times 251 steps; step size: $dx = 10 \ \mu\text{m}$, $dy = 6 \ \mu\text{m}$; measuring time per pixel: t = 5 s for fluorescence signal, t = 2 s for transmission signal live time) are presented. The obtained maps of element distributions, showing U-rich and also other types of particles, are shown in Fig. 14. By examining Figs. 14 and 15, a clear coincidence between U and As was observed. The μ XRF system was also used to perform μ CT 3D-imaging of the porous structure of an osteoporotic bone fragment. The CT scan was performed (64 2D projections, every 2D projection contained 64×64 rays). A filtered backprojection algorithm was used to reconstruct the crosssection images of the bone, and then volumetric rendering was applied to obtain 3D reconstruction of the bone fragment. The reconstructed bone structure is shown in Fig. 16.

Conclusions

Using the different kinds of XRF spectrometers available at the XRF laboratory, the Agency's Seibersdorf Laboratories, it has been shown that elements ranging from Na–U can be analyzed with little or no sample preparation. The biological samples analyzed included rice, lichen, and osteoporotic human bone. The different X-ray spectrometric techniques enabled the determination of essential trace elements such as Fe and Zn in the rice samples, and to carry out a 3D visualization of the bone structure. Analysis of the environmental samples of soil, sediments, air aerosols, uranium contaminated soil, and drinking water also exhibited the capabilities of the XRF techniques for determination of major, minor and trace elements. The concentration of the following elements were determined: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn,



Fig. 15. X-Ray spectra of the identified particle types in the uranium contaminated soil dust.



Fig. 16. Tomographic reconstruction of an osteoporotic bone fragment.

Ga, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, I, Ba, La, Ce, Pb, Th, and U. The µXRF analysis additionally enabled the identification of particle types (K-, Fe-, Ca-, As-, and U-rich particles) in the uranium contaminated soil dust. In order to validate the quantitative methods used, the following biological and environmental reference materials were also analyzed: IAEA-H-10 Hay Powder, IAEA-336 Lichen, IAEA-Soil-7, Penrhyn Slate (a proficiency test sample), CERAMIC-1 SARM 69, and NIST SRM 2783 Air Particulate on Filter Media. The correlation between the determined and given concentration of elements was found to be satisfactory for the reference materials analyzed, with correlation factors within the range 0.996-1.07. Hence, access to different types of XRF spectrometers allows comprehensive analysis of both bulk and particulate samples, and the availability of a truly portable XRF spectrometer enables on-the-spot analysis and decisions to be taken in the field.

The presented results of analysis and applications of XRF and related techniques show that X-ray spectrometric methods can handle many analytical problems. The XRF methods have been successfully applied in the analysis of biological and environmental samples. The measurements have been performed by using commercial as well as inhouse designed and assembled X-ray spectrometers. The commercial system was found very efficient in analyzing large sample batches, whereas the non-commercial spectrometers were more suitable for the analysis of "difficult" samples, or where a special measuring configuration was required. The unique features of the μ XRF system make them very useful in forensic studies but also they are well suited for investigating environmental pollution. Moreover, without any additional effort, except adapting the controlling

software, such system can be used in tomographic mode giving a unique opportunity in studying morphology, porosity and other fields where 3D visualization of the structure of minute objects may be of importance.

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