



# Analytical performance of a versatile laboratory microscopic X-ray fluorescence system for metal uptake studies on argillaceous rocks



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## ABSTRACT

Laboratory-scale microscopic X-ray fluorescence (micro-XRF) plays an increasingly important role in various fields where multielemental investigations of samples are indispensable. In case of geological samples, the reasonable detection limits (LOD) and spatial resolutions are necessary to identify the trace element content in microcrystalline level. The present study focuses on the analytical performance of a versatile laboratory-scale micro-XRF system with various options of X-ray sources and detectors to find the optimal experimental configuration in terms of sensitivities and LOD for selected elements in loaded petrographic thin sections. The method was tested for sorption studies involving thin sections prepared from cores of Boda Claystone Formation, which is a potential site for a high-level radioactive waste repository. Loaded ions in the sorption measurements were Cs(I) and Ni(II) chemically representing fission and corrosion products. Based on the collected elemental maps, the correlation between the elements representative of main rock components and the selected loaded ion was studied. For the elements of interest, Cs(I) and Ni(II) low-power iMOXS source with polycapillary and silicon drift detector was found to be the best configuration to reach the optimal LOD values. Laboratory micro-XRF was excellent to identify the responsible key minerals for the uptake of Cs(I). In case of nickel, careful corrections were needed because of the relatively high Ca content of the rock samples. The results were compared to synchrotron radiation micro-XRF.

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## 1. Introduction

Due to the rapid development of X-ray optics, microscopic X-ray fluorescence (micro-XRF) that was feasible only at synchrotron radiation (SR) sources became available as laboratory size or even portable equipments. The earliest laboratory micro-XRF equipments were based on high-power, water-cooled X-ray tubes and straight or conical monochromators. Standard long-fine-focus (LFF) X-ray diffraction (XRD) glass tubes [1,2] or rotating anode X-ray tubes [3] were used as X-ray sources and a spatial resolution of a few tens of micrometers could be reached. Another important step toward compact laboratory or portable micro-XRF equipment was initiated by the development of focusing polycapillary lenses [4,5,6], low-power air-cooled microfocussing X-ray tubes [7] and compact energy-dispersive X-ray detectors without requiring liquid-nitrogen cooling.

Micro-XRF equipments are operational at several laboratories [8,9,10], and commercial equipments are also available. Laboratory and portable micro-XRF has been applied in several research fields, such as forensic science [11] and archeometry [6,12], and applications to environmental sciences were recently reviewed [13].

Geologists and geochemists have recently realized the advantageous properties of laboratory micro-XRF due to the capability of 2D elemental mapping with reasonable spatial resolution and suitable minimum detection limits to perform even trace element analysis at the microcrystalline

level. Synchrotron micro-XRF was the preferred analytical tool of geochemists for similar experiments, whereas in the last decade, laboratory micro-XRF elemental mapping provided outstanding results for the study of laminated sediment records [14,15], and recently a reaction zone of metamorphic rock was investigated by compositional imaging [16].

Sorption of metal ions from groundwater/pore water in heterogeneous rock systems is of high importance for many environmental problems related to waste deposition. The distribution coefficient ( $K_d$ ) between solid and liquid phases is a crucial parameter describing sorption on macroscopic scale; however, to understand the essential uptake mechanism, the microheterogeneity of the rock has to be taken into consideration. The uses of petrographic thin sections instead of crushed rock samples widen the possibility of analytical measurements while retaining the original microstructure of the rock. It allows the re-location of the same areas on the samples for different microscopy techniques. Thin sections in sorption experiments are treated with different solutions containing key metal ions to study the sorption capability of the different mineral phases present in the rock. The concentrations of the metal ions in the solutions involved should be, on the one hand, sufficiently low in order to avoid precipitation on the surface of the thin section and, on the other hand, sufficiently high to produce adequate load for application of microspectroscopic methods. The element of interest will be present in minor or trace concentration level

heterogeneously distributed in the sample after the sorption experiment [17,18]. Due to its high dynamic range, micro-XRF spectroscopy is a suitable tool to detect simultaneously the distribution of the sorbed elements and the main elements corresponding to rock-forming minerals [19].

Generally, a micro-XRF system is suitable for investigating various samples, but for each application the lateral resolution has to be in compromise with the sensitivity being limited by the X-ray intensity. In case of geological samples that require multielemental analysis, the grain size of mineral phases is in a wide range between 100 nm and 100  $\mu\text{m}$  [18]. To satisfy the challenges arising from the variety of the samples, the laboratory-scale micro-XRF system has to be versatile, and the changes between the sources and the detectors have to be simple and fast just like in case of the samples.

The present paper discusses the analytical performance of a versatile laboratory micro-XRF system with exchangeable X-ray sources and detectors, combining the advantages of sources based on high-power X-ray tubes and a state-of-the-art low-power microfocus X-ray source. The applicability of the system to 2D elemental mapping of geological samples of petrographic thin sections is presented with the aim of sorption studies, with comparison to micro-XRF using synchrotron radiation. The performance of the laboratory micro-XRF method is demonstrated for studies of clay-rich rock systems that are of interest for management of municipal, industrial, and radioactive waste. Thin sections were prepared from the Boda Claystone Formation (BCF), which is a suitable host rock for high-level radioactive waste (HLW) repository in Hungary. The samples were subjected to sorption experiments using inactive Cs(I), Ni(II), and natural U(VI), chemically representing fission and corrosion products as well as transuranium elements of interest for HLW repository.

## 2. Materials and methods

### 2.1. Laboratory micro-XRF

The implemented laboratory micro-XRF equipment includes five main parts: (i) an X-ray source with appropriate X-ray optics (capillaries) necessary for producing a microfocused X-ray beam and a water/air cooling system to prevent the overheating of the X-ray source; (ii) a camera to observe the actual sample; (iii) a detector system to detect the characteristic and scattered X-rays; (iv) a sample stage with translation and rotation axes and stepping motors which are responsible for sample movement; and (v) a controlling system which contains a computer with a control software for recording and evaluating the results. Since the X-ray source cannot be moved, recording of 2D elemental maps is performed through movement of the sample across a stationary X-ray microbeam.

In order to generate a microfocused beam, various sources can be used in the laboratory. The change of the setup is simple, and only a calibration process is necessary before measurements. For these experiments, a new low-power and a conventional high-power X-ray source were used. The low-power source is an air-cooled modular X-ray source (iMOXS, IfG, Berlin, Germany) [7] with a rhodium (Rh) anode microfocus X-ray tube (MCBM 50 0.6 B, RTW, Germany), which is a brilliant low-power microfocus equipment. A polycapillary minilens (IfG, Berlin, Germany) specially designed for the microfocus X-ray tube was used as X-ray optics in this case. The diameter of the focal spot of the microbeam varied between 20 and 30  $\mu\text{m}$ , depending on the X-ray energy [5]. Between the X-ray tube and the polycapillary, an optional beam filter can be adjusted by means of a filter wheel. The high-power X-ray source (HPS) is a water-cooled system comprising a tube housing (Type S, Siemens, Karlsruhe, Germany), which can accommodate standard X-ray diffraction tubes with various anodes. Long-fine-focus glass tubes of chromium (Cr, Siemens), molybdenum (Mo, Seifert), and tungsten (W, Panalytical) anodes were used for the present work. Tapered glass monocabillaries (XCO, Gothenburg, Sweden) were

used as X-ray optics resulting in X-ray microbeams of 90  $\mu\text{m}$ , 60  $\mu\text{m}$ , and 30  $\mu\text{m}$ .

A WAT-902A (Watec, Yamagata-Ken, Japan) black-and-white CCD camera is used for visualization of the sample, with composite video signal compliant with NTSC/RS-170 standard. The sample table is mounted to an assembly of three linear positioning slides (Parker Daedal, Irwin, PA, USA) in Cartesian geometry, driven by Nanotec (Munich, Germany) stepping motors. The slides have a 100 mm travel range (50 mm in the focusing direction) and a repeatability of 2  $\mu\text{m}$ /25 mm travel. In addition, a rotation stage (DMT 40, Owis, Staufen, Germany) with a 40 arcsec resolution is mounted to the sample table allowing fine adjustment of the sample and tomography measurements. The sample stage is set up in such a way that the incoming beam is perpendicular to the sample plane; therefore, the angle between the detector and the incoming beam is 45°. Although the geometry is not ideal regarding scattering background in the X-ray spectra, the setup allows investigating large objects increasing the versatility of the system [8]. The geometry has a further restriction, the visualization of the sample can only be performed at a position different from the measuring position. For this reason, the vector for the movement from camera to capillary position and back has to be recalibrated after changing the X-ray microbeam source.

Two types of X-ray detectors were used to detect the emitted characteristic X-rays, a Peltier-cooled Si drift detector (SDD) with an active area of 30 mm<sup>2</sup> (KETEK, Munich, Germany) and a liquid nitrogen cooled intrinsic germanium (IGX) detector (PGT, Princeton, USA) with an active area of 50 mm<sup>2</sup>.

The measurement process is computer controlled by an in-house developed software specifically designed for the system. It controls the sample stage and the spectrum acquisition process and displays the optical image of the sample. The control software was developed under LabVIEW environment (National Instruments, Austin, TX, USA), supported by most hardware developing companies, yielding a cost-effective, user-friendly solution. [10,20]. For this reason, main parts of the hardware inside the control computer were selected based on this requirement. The stepping motors of the three translation and one rotation axes are controlled by an NI 7330 motion controller card (National Instruments, Austin, TX, USA), which is programmable using LabVIEW. A suitable frame-grabber card (DFG/SV1/PCIe, The Imaging Source) with LabVIEW driver is used to digitize the image. The spectrum acquisition process requires communication with the multichannel analyzer (MCA) in the control software, which has two options. The KETEK SDD is equipped with a digital pulse processor (DPP) built in the detector housing. For the KETEK SDD, communication with the DPP server was solved in LabVIEW through a DLL interface and LabVIEW driver provided by the manufacturer. The second case is the S8000 system (PGT, Princeton, USA), which contains an analog amplifier, an analog-digital converter (ADC), and an MCA. In that case, the LabVIEW driver had to be written in house for communication with the MCA. The S8000 system has a further advantage that it can be used not only with the PGT IGX detector, but also other detectors providing analog signals.

The system can conduct three types of scans, namely, area scans, line scans, and tomography. The most commonly used scan type is area scan, where the area defined by the two cursors on the optical image is scanned with a pre-defined stepsize. Line scan option allows a movement trajectory of the sample with an arbitrary direction within the sample plane. The points of the trajectory are defined based on the two cursors set by the user on the optical image and a given stepsize. Tomography is a special two-dimensional scan comprising a rotation and a translation dimension where the same horizontal line-scan is executed for all angle positions. For this reason, a separate module had to be developed for tomography. Several scans of the same type can be defined on one optical image and the system runs the scans sequentially. The stepsize and spectral collection time for one pixel is restricted to be the same for all scans in one run. Spectra are saved for each pixel

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