Improving the detection limit of the Radiochemistry end-station

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EXAFS spectroscopy is the method of choice for chemical speciation in environmental samples, which are typically characterized by multi-elemental matrices and the presence of aqueous, sorbed and mineral species at the same time. Especially for elements like the actinides, which are toxic at even extremely low concentrations, one demand can never be fulfilled by EXAFS with full satisfaction: lower detection limits. Up to know, we could investigate uranium speciation in simple laboratory samples like kaolinite at concentrations below 100 mg/kg. However, first tests showed that uranium in a soil matrix needed to be present at concentrations above 1000 mg/kg to provide spectral quality sufficient for uranium speciation. The major problem was that the U-L3 fluorescence line in such samples was hidden behind the - often stronger - neighboring K-lines of Rb and Sr. Since many samples of interest contain uranium at maximum concentrations of 50 to 500 mg/kg, EXAFS spectroscopy could not be performed with the existing experimental setup. At this point, it was necessary to acquire a new multi-element detector with higher energy resolution without cutting down on count rate. The installation of this new detector involved not only electronic instrumentation and software development, but - due to the complex radiochemical safety installations at the Radiochemistry end-station - also mechanical engineering. This work which is described in the following has been performed by the Department of Research Technology at the FZR in collaboration with the Institute of Radiochemistry.

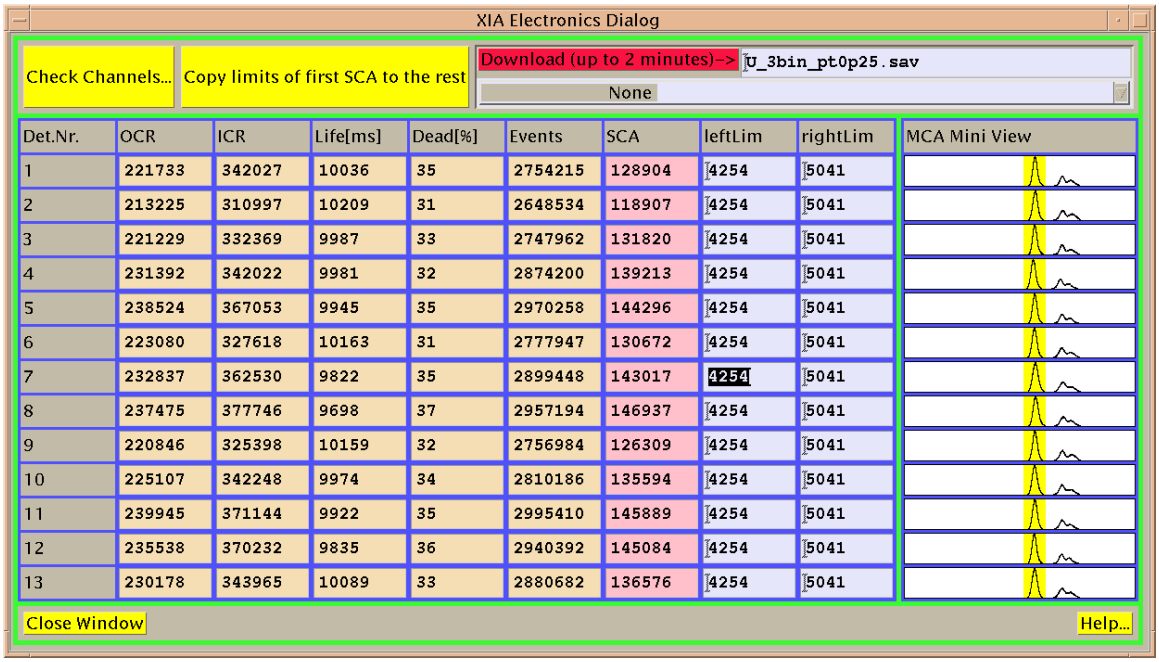
The new detector and its electronics

We acquired an advanced hard X-ray, 13-element LEGe detector (Canberra) [3]. Each of the elements has an active thickness of 10 mm and an area of 100 mm2. We have measured average energy resolutions of 156 and 311 eV at shaping times of 3 and 0.25 μs, respectively. The reset periods of the pre-amplifiers are in the range of 250 to 850 ms. The detector is equipped with a custom-designed, small multi-attitude cryostat to allow for multiple detector orientations in the narrow Radiochemistry hutch. The detector is equipped with an automatic LN2 filling station.

The detector is instrumented with a high-rate digital multi-channel analysis spectrometer from X-ray Instrumentation Associates (XIA) [6] which is particularly well suited for EXAFS with multi-element detectors. Each channel operates with a digitally-based X-ray processor (DXP). The DXP offers complete computer control over all amplifier and spectrometer controls including gains, shaping times, and pile-up inspection criteria. The DXP digital filter typically increases throughput by a factor of two over the available analog system at comparable energy resolution but at lower cost per channel.

Software development

The new 13-element Ge detector has been integrated in the measurement program XATROS [5] using the device server XIADS [7] developed at the ESRF. XATROS imports the functionality of this device server. XATROS provides functionality to perform scans and to check these detectors. Checks and settings of the SCAs (single channel analyzer) are supported by visualizations of the statistics parameters and the SCA limits and their contents/counts as text widgets (Fig. 1). Additionally there are mini views of the spectra of each of the thirteen channels. There is also the possibility to get a detailed graphical presentation of each of the thirteen channels. The SCA limits can be set both in the text widgets and in the graphical representation. XATROS is also able to switch easily between the new detector and its electronics and the older one which can be used alternatively.



Det.Nr.	OCR	ICR	Life[ms]	Dead[%]	Events	SCA	leftLim	rightLim	MCA Mini View
1	221733	342027	10036	35	2754215	128904	4254	5041	
2	213225	310997	10209	31	2648534	118907	4254	5041	
3	221229	332369	9987	33	2747962	131820	4254	5041	
4	231392	342022	9981	32	2874200	139213	4254	5041	
5	238524	367053	9945	35	2970258	144296	4254	5041	
6	223080	327618	10163	31	2777947	130672	4254	5041	
7	232837	362530	9822	35	2899448	143017	4254	5041	
8	237475	377746	9698	37	2957194	146937	4254	5041	
9	220846	325398	10159	32	2756984	126309	4254	5041	
10	225107	342248	9974	34	2810186	135594	4254	5041	
11	239945	371144	9922	35	2995410	145889	4254	5041	
12	235538	370232	9835	36	2940392	145084	4254	5041	
13	230178	343965	10089	33	2880682	136576	4254	5041	

Fig. 1. Online visualization of the output of each of the 13 detector channels by the application software XATROS.

Upgrade of glovebox and positioning systems

The beamline's central glovebox with its negative air pressure gradient towards the Radiochemistry hutch has to present a safe sample confinement during the EXAFS measurements. This is realized by a bay-window extension of the box, which protrudes into the beam path (pink in Fig. 2). Beam transmission from the first ionization chamber (I0) to the sample inside the glove box, and then from the sample to the second and third ionization chambers again outside of the glove box is realized with Kapton windows. A third Kapton window behind the sample position and normal to the beam enables fluorescence detection by the fluorescence detector.

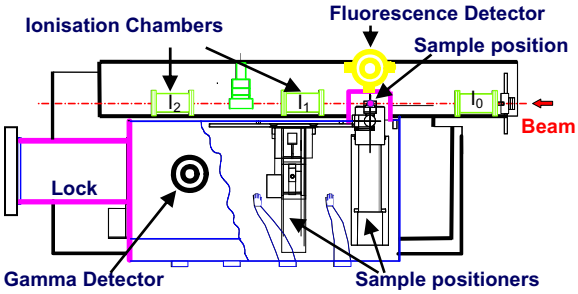


Fig. 2. New glove box design.

The new design had to fulfill several demands. First, simplification of the box interior to ease decontamination in case of a radioactive spill. Second, a larger fluorescence window to allow for an unrestricted, even illumination of all 13 detector elements. Third, a unification of the sample positioning system to ease exchange of the various sample holders, electrochemical cell and the cryostat, and to ease a potential decontamination of the box.

Point 1 was realized by creating a new box extension with a simpler cubic shape and without any further protruding parts. For point 2, we enlarged the diameter of all windows, not only to improve illumination of the fluorescence detector, but also to be able to have the beam and the sample as close as possible to the fluorescence detector for ultra-dilute samples. For point 3, we have extended and unified the control units for the positioning

systems (sample holders and detectors) inside and outside of the glove box. Generally, PEGASUS control units of the MICOS company [1] are now applied. By developing a new software (Device Server PEGASUS [2]) we ensured that these new systems could also be used inside of the existing software systems without the need to change them. A new sample positioning holder is still under development, which will avoid the use of two independent systems, and will be installed in 2005.

Gas flow controllers for the transmission detectors

To improve the sensitivity of the ionization chambers, a new panel with gas flow controllers for the automated and precise adjustment of gas compositions was installed [4]. Using He, N_2 and Ar gas, gas mixtures can be adjusted to have 15-20 % beam absorption in I_0 and 30-40 % beam absorption in I_1 and I_2.

First results

Figure 3 shows typical energy-dispersive XRF spectra of a uranium mine sample collected with the new detector. The uranium L3-line overlaps strongly with the K-line of Rb, and may be even influenced by a strong Sr K-line. Such a situation is quite typical for geological samples where feldspar and other K and Ca-rich minerals contribute to Rb and Sr concentrations in the low g/kg range. The XRF collected at an extended time of 60 s shows that that the U-L_3 line can be separated from the Rb and Sr K-lines using a relatively narrow SCA window. The shoulder can also be separated at a common EXAFS data collection time of 5 s. This is quite remarkable insofar as the shaping time of 0.25 μs represents the condition for optimum count rate, but the worst case in terms of energy resolution.

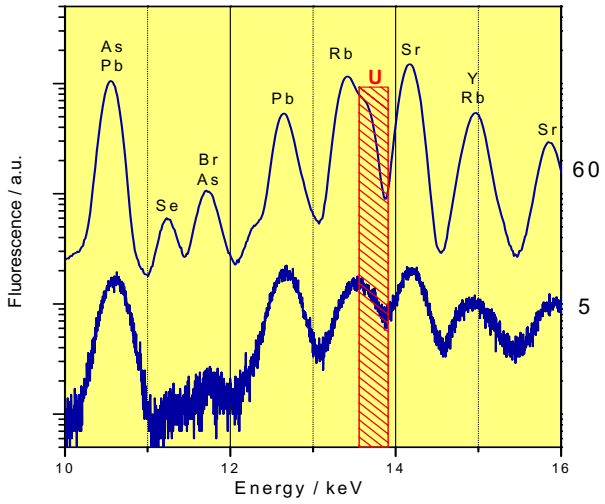


Fig. 3. Typical XRF of Freital mine tailing samples collected with the new detector using a shaping time of 0.25 μs.

The Experimental Report 20-01-626 in this volume demonstrates that EXAFS spectra of several samples from mine tailings and contaminated soils could be successfully collected within a reasonable data collection time (5-8 hours). In such difficult sample matrices we now routinely achieve a lower detection limit of 200 mg/kg uranium.

References

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