Actinide L-line ED-XRF and Hybrid K-edge Densitometer spectra processing

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Abstract. Numerous R&D studies are carried out in the glove-boxes or hot cells of the CEA Atalante analysis laboratory at Marcoule (France). Most of the samples need to be measured in aqueous or organic liquid phase.

The concentrations of the main actinides of interest (U, Np, Pu, Am and Cm) are determined by XRF in a hot cell equipped with a device dedicated specifically to actinide analyses via their L-line X-ray between 13 and 15 keV. In order to limit the counting rate of many radioactive emitters (X-ray and gamma emitters) in the analysis solution and the continuous spectrum, a graphite monochromator is placed between the sample and detector. Commercial or free software packages currently available for processing X-ray spectra are designed for a specific instrument and/or do not take into account the special feature of our system, i.e. the presence of a monochromator. Therefore, new X-ray analysis software was developed for this particular system, taking matrix effect corrections into account.

For samples with U and/or Pu in high concentrations, the hybrid K-edge densitometer is used. A new software program was also developed. For K-edge densitometry spectra processing, no calibration process is used. Spectra processing is based on a theoretical equation and uses the XCOM database for mass attenuation coefficients. Spectra obtained using a K-edge densitometer from the Rokkasho Safeguards Analytical Laboratory were processed with this software, and a very good agreement was found with IDTIMS results. The new graphical user interface enables manual correction of the defined edge. For the XRF spectra processing, new algorithms are used to define the base line and to find/integrate peaks.

With the XRF and K-edge densitometer in the laboratory, U and Pu concentrations can be measured from 0.5 mg.L⁻¹ to several hundreds of g.L⁻¹.

1. Introduction

The Laboratory of Analysis and Materials Metrology (LAMM) in the CEA Atalante complex at Marcoule (France) carries out numerous R&D studies run in glove-boxes or hot cells. Most of the samples are measured in aqueous or organic liquid phase. For radioactive samples coming from high-level test materials, it is best for analyses to be carried out in shielded cells. Two NDA devices are used: L-line ED-XRF and Hybrid K-edge densitometer. These analytical systems have special characteristics, and while commercial spectroscopy workstations are used for acquisition and IT data recording, no free or commercial programs are available for the data processing. Thus, specific software has had to be developed for processing our spectra.

The Python(x,y) package [1] was used to develop the spectrum processing software. The PyMCA [2] module was used to estimate the mass attenuation coefficients. This module uses the data of the XCOM database [3]. The Python language is easy to learn and a wide scientific library is available, making it very convenient for scientists.

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2. L-Line ED-XRF

2.1 Experimental

The X-ray generator and X-ray tube (Rh anode, 3 kW, 75 µm) are marketed by PANalytical. Two X-ray tube configurations are used in the laboratory: 50 kV/30 mA and 30 kV/10 mA. The primary X-ray photon beam is filtered by an Rh target (200 µm) producing an almost monochromatic beam. The detector is a hyper-pure Ge crystal (Eurisys EGX 30-05, active area 30 mm²) cooled with liquid nitrogen. The acquisition electronics were recently replaced by a Canberra DSA-1000 coupled with Genie 2000 software. The sample is transferred pneumatically from a shielded cell to the analytical equipment. The device, set up behind the shielded line, is itself also fully shielded (Pb protection). Figure 1 illustrates the device used for this study, in a system designed in the 1990s.

![Simplified diagram of the nuclearized high activity X-Ray Fluorescence device. The collimator between the vial and the monochromator is not shown.](image)

The samples are packaged in small polypropylene vials 1.5 cm in diameter and 1.5 mm thick. The primary X-ray beam reaches the sample vial laterally after passing through the 1 mm thick stainless steel pneumatic transfer tube. Given these dimensions, the sample is regarded as thick. Furthermore, the presence of many attenuators along the X-ray beam limit the actinide quantification threshold to about 0.5 mg·L⁻¹.

The monochromator is cylindrical. Internally, it is made with thin strips of graphite. In order to avoid direct X-rays, two tungsten discs with a smaller diameter are placed axially at each end of the cylinder. This device was custom-made. Thus, the energy range studied is restricted by the monochromator, and the elements of interest (U, Pu, Np) in this range have one L-line with an apparent emission rate exceeding 95%. For example, only the L3O45 lines between 13.6 and 14.3 keV are visible for U and Pu respectively, while their theoretical emission rates are 44% and 45%, again respectively. For an X-ray beam at 50 kV and 30 mA, their respective L3O1 lines at 17.2 and 18.3 keV with theoretical emission rates of 23% and 21% are visible only at concentrations greater than 5 g·L⁻¹ and represent less than 5% of the apparent total emission. For an X-ray beam at 30 kV/10 mA and up to 10 g·L⁻¹ of U or Pu, no secondary line is visible; for a 20 g·L⁻¹ Pu concentration, the secondary lines represent less than 0.2‰ of the maximum intensity of the main line.

Analysis of high atomic number elements in a limited energy range through a monochromator means our system is extremely specific: the “apparent” element spectrum contains only a single main line. Our experience has shown that the secondary fluorescence phenomena are negligible, and hence they are disregarded hereafter.
The name “L-line ED-XRF” indicates the device’s specificity: the use of a monochromator in order to focus on an energetic range corresponding to actinide L-line X-rays.

### 2.2 Data Processing

Most free or commercial software available for XRF data processing are specifically for one particular device and/or are based on the use of the relative X-ray emission rates of elements. In our case, the presence of a monochromator changes the appearance of these ratios, and in-house data processing software has been developed [4].

The basic principle is to deconvolute the spectrum as a linear combination of elementary spectra (see Figure 2). The resulting fit is very close to the experimental curve and the residual curve is less than 5% on the spectral range studied.

![Spectrum for a nuclear fuel dissolution solution sample taken from a liquid-liquid extraction test.](image)

To make this possible, a library of standard samples was needed, but not just a simple record of standard spectra fingerprints. For each standard element, calibration was carried out for every channel (multichannel analyzer), linking intensity and concentration by a nonlinear function because of an auto-attenuation effect for the highest concentration, see Figure 3. Thus the calibration file is a huge array containing all the parameters of calibration function for every channel and every standard.

A new approach has been proposed for matrix correction effects, similar to that of Lachance-Traill established for solid samples, but dedicated to liquid samples. This correction requires an accurate description of the sample matrix analyzed and the use of data from the XCOM mass attenuation coefficients database. Another advantage is the possibility to use a calibration file with another sample matrix that that of the standard sample. For example, an organic sample analysis can give a reasonably accurate result providing that the matrix has been accurately described. This is particularly useful for R&D studies, as a rapid estimation of results can be obtained without a long calibration process.
Figure 3. Example of U calibration curve. The curve is drawn at the maximum intensity of the L-line X-ray for U (E=13.6 keV).

An example is given in Table 1 below: a test of spent fuel residue dissolution in presence of a high amount of AgO (~100 g/L) in HNO₃ 6 M media. Calibration was done in HNO₃ 3 M media. The matrix effects correction takes into account the presence of AgO and the difference in acid media concentration.

Table 1. Validation of the proposed method.

<table>
<thead>
<tr>
<th>Description of media used for correction</th>
<th>Element selected</th>
<th>EDXRF (mg.L⁻¹)</th>
<th>ID-TIMS (mg.L⁻¹)</th>
<th>Relative deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without correction</td>
<td>With correction</td>
<td>Without correction</td>
<td>With correction</td>
</tr>
<tr>
<td>HNO₃ 6 M</td>
<td>U</td>
<td>33.3</td>
<td>102.8</td>
<td>109.2 ± 2.2</td>
</tr>
<tr>
<td>AgO 100 g.L⁻¹</td>
<td>Pu</td>
<td>18.7</td>
<td>57.8</td>
<td>59.8 ± 1.2</td>
</tr>
</tbody>
</table>

2.3 Estimated uncertainty

Uncertainty estimation is a complex step. To date, studies have concerned dispersion due to vial positioning in the counting station, and the electronics and detector. This dispersion is less than 2%. However, many parameters are involved in the uncertainty such as the calibration parameters, the number of elements selected in the deconvolution process, etc. The studies are continuing in our laboratory. For the moment, an uncertainty of 10% has been retained, given the feedback obtained so far.

2.4 Conclusion

This device is suitable for actinide analysis (U, Np, Pu, Am, Cm) in the 0.5 mg/L to 20 g/L range. Other elements are analyzed in the energetic windows of the monochromator via their K-lines, such as Br, Rb, Sr, Y, and Zr. The data processing requires a good knowledge of the sample matrix in order to apply the suitable matrix effect correction.
3. Hybrid K-edge Densitometer

In this study, the X-ray tube has a W anode. The X-ray tube configuration used in the laboratory is 150 kV/17 mA, and there is no filter on the primary X-ray photon beam. The detectors are hyper-pure Ge crystal (Eurisys EGX 30-05, active area 30 mm$^2$) cooled with liquid nitrogen. The acquisition electronics were recently replaced by a Canberra DSA-1000 coupled with Genie 2000 software. The sample is transferred pneumatically from a shielded cell to the analytical device, which is located behind the shielded line and is also fully shielded (Pb protection). Figure 4 illustrates the device as used for this study. This system was designed in the 1990s.

![Image of LAMM HKED device](image)

Figure 4. The LAMM HKED device.

The samples are packaged in small polypropylene vials 1.5cm in diameter and 1.5mm thick. The primary X-ray beam reaches the sample vial laterally after passing through the stainless steel pneumatic transfer tube (1mm thick). A stainless steel filter on the K-edge pathway, also called absorption pathway, avoids “blinding” the detector.

This device was custom-made in house by the CEA. The polypropylene vials were specially made to specifications with a low diameter tolerance, as the pathway length through the vial is a very important parameter for K-edge data processing. From a theoretical equation and supposing there is no other error source, it is easy to show that $s_C/C = s_x/x$, where $C$ is the concentration of the element measured, $x$ the pathway length in the vial, and $s$ their respective standard deviations. A tolerance of 1% on vial diameter then means a 1% variation in the estimated value.

3.1 Data Processing

K-edge data processing is based on Ottmar and Collins’ work [5-6]. A theoretical model was chosen for use. Mass attenuation coefficients from the XCOM database were used except for the coefficient change at element edges, where Ottmar’s values were adopted [5]. Thus, no calibration is needed for K-edge measurement. A very good agreement was found with reference solutions (CETAMA U and Pu standards). One of the improvements provided by our software is the possibility to interactively adjust the height edge determination by moving the points delimiting the portion of the curve used to make a linear fit on either side of the discontinuity. The advantage of this manual adjustment is an easier spectra processing with any U-Pu mass ratio.

A very good accuracy was obtained with less than 2% deviation, without any optimization for parameters such as temperature nor a blank spectrum acquisition, as this spectrum is acquired with the same intensity as the sample.

![Image of experimental U and Pu edge determination](image)

Figure 5. Experimental U and Pu edge determination from K-edge spectra processing.
In order to test the robustness of our software, a blind test was carried out with spectra provided by the IAEA OSL (Japan). Only the path length in the vial, the sample intensity measurement and the blank spectra were given. The results obtained are given in Table 2 and show very good agreement.

Table 2. Comparison of results obtained with our software on spectra provided (K-edge densitometer in Rokkasho Safeguards Analytical Laboratory) and ID-TIMS.

<table>
<thead>
<tr>
<th>K-edge data processing (CEA)</th>
<th>ID-TIMS (IAEA - Japan)</th>
<th>Relative deviation K-edge/ID-TIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (g/L) Pu (g/L)</td>
<td>U (g/L) Pu (g/L)</td>
<td>U Pu</td>
</tr>
<tr>
<td>284.5 163.0</td>
<td>283.62 163.56</td>
<td>0.31% -0.36%</td>
</tr>
<tr>
<td>61.0 35.2</td>
<td>60.89 35.11</td>
<td>0.15% 0.37%</td>
</tr>
<tr>
<td>143.7 82.5</td>
<td>142.18 81.99</td>
<td>1.06% 0.62%</td>
</tr>
<tr>
<td>179.7 103.5</td>
<td>180.01 103.58</td>
<td>-0.20% -0.09%</td>
</tr>
<tr>
<td>212.5 104.4</td>
<td>212.38 104.30</td>
<td>0.03% 0.05%</td>
</tr>
<tr>
<td>167.5 81.6</td>
<td>167.57 82.22</td>
<td>-0.04% -0.71%</td>
</tr>
</tbody>
</table>

For XRF measurements in hybrid mode, the principle is to create a relative calibration between U and Pu. Thus, knowing the law linking the areas of U and Pu peaks ($S_U$ and $S_{Pu}$) with their concentrations, $f(U,Pu)$ vs $g(S_U, S_{Pu})$, it is possible to estimate U (or Pu) concentration by XRF measurement if the Pu (or U) concentration is measured by absorption. The choice of reference element is left to the user.

The empirical law $f(U,Pu)$ vs $g(S_U, S_{Pu})$ was modified compared to that proposed by Ottmar, in order to obtain the best results whatever the mass ratio between U and Pu ($5<U/Pu<600$). It should be emphasized that the use of several published algorithms was implemented for processing XRF spectra: among these, an algorithm for background removal and another for peak search and integration (see Figure 6). For every peak, the baseline definition can be improved, as well as the integration parameters.
Figure 6. Example of XRF Spectrum with automatic baseline definition, as well as peak searching and integration. Standard sample in HNO$_3$ 3 M: U=5 g/L and Pu=0.5 g/L.

Several standards were measured and their XRF spectra processed with our software by using U as reference value (i.e. K-edge result). Results are presented in Table 3. A very good agreement was found.

Table 3. Hybrid XRF mode – Pu results obtained with our software, considering U as the reference element.

<table>
<thead>
<tr>
<th>Standards [*]</th>
<th>Experimental</th>
<th>Relative deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (g/L)</td>
<td>Pu (g/L)</td>
<td>U/Pu (g/g)</td>
</tr>
<tr>
<td>22.8</td>
<td>4.58</td>
<td>5</td>
</tr>
<tr>
<td>75.1</td>
<td>5.01</td>
<td>15</td>
</tr>
<tr>
<td>150.0</td>
<td>1.50</td>
<td>100</td>
</tr>
<tr>
<td>20.0</td>
<td>0.11</td>
<td>181.6</td>
</tr>
<tr>
<td>50.4</td>
<td>0.23</td>
<td>219.1</td>
</tr>
<tr>
<td>302.6</td>
<td>0.50</td>
<td>605.2</td>
</tr>
<tr>
<td><strong>249.1</strong></td>
<td><strong>2.45</strong></td>
<td><strong>101.7</strong></td>
</tr>
</tbody>
</table>

(*): Solution prepared by dilution of certified standards by weighing (EQRAIN standards – supplier: CEA/CETAMA). Uncertainties for these solution concentrations are less than 2%.

(**): IRMM (Institute for Reference Materials and Measurements) standard – Uncertainties given as 2% - Blank reference spectrum is unsuitable (HNO$_3$ 3M used instead of HCl medium).

3.2 Estimated uncertainty

**K-edge results.** Several comparisons were made between U and Pu results obtained by K-edge and ID-TIMS. For concentrations above 50 g/L, the expanded uncertainty (k=2) is less than 2%. Between 10 g/L and 50 g/L, an expanded uncertainty of 10% is assumed. For monitoring R&D tests, these uncertainties are sufficient and to date, no optimization has been undertaken.

**XRF results in hybrid mode.** Even if the deviations obtained in Table 3 are less than 4%, uncertainties also have to take into account those concerning the calibration process, and for the nature of the matrix. It must be remembered that matrix effects can be significant, especially with the high actinide concentrations studied, and the matrices of samples analyzed in our laboratory vary widely. An expanded uncertainty of 10% is assumed for a reference element concentration above 50 g/L. Further uncertainty studies will be undertaken.
3.3 Conclusion

This apparatus is suitable for actinide analysis (U, Pu) in the range 100 mg/L to several hundred g/L. The K-edge device enables quick analyses without prior sample treatment. It is reliable and gives a good level of accuracy.

The hybrid XRF mode is convenient for determining U (or Pu) low concentrations when high concentrations of Pu (or U) are present. Its calibration process with an empirical law can however be time-consuming and tedious, and a peak integration process needs to be further improved.

4. Conclusion and Prospects

With these two analytical devices available in a laboratory, U and Pu concentrations can be measured from 0.5 mg.L\(^{-1}\) to several hundred g.L\(^{-1}\) in various matrices. As K-edge measurements are not affected by matrix effects, it is very convenient to use this device for high concentrations of U and Pu in various media.

While the K-edge analytical device does not need standard samples, many standard samples have to be prepared for L-line XRF (elementary standards) and Hybrid XRF (mixed U, Pu standards). The calibration procedures are very long and demanding. Nevertheless, regular checks have been performed on the calibration of the two devices used over two years in the study described here, and no deviations have been found during this time.

At present, studies on the implementation of FP (fundamental parameters) algorithms and/or Monte-Carlo modeling for the two devices are continuing to run. These approaches should minimize the number of standard samples to be prepared in the future.

5. References


