Continuum Background Contributions in K-edge Densitometry

Jozsef Zsigrai, Magdalena Toma, Arnaud Le Terrier, Artur Muehleisen
European Commission, Joint Research Centre (JRC)
Karlsruhe, Germany

K-edge densitometry is a key technique for safeguarding uranium (U) and plutonium (Pu) in nuclear reprocessing and fuel production. It uses X-ray spectrometry to measure the transmission of X-rays around the K-edge of uranium or plutonium. To improve the uncertainty and robustness of the technique, the influence of two contributions to the spectral continuum background in X-ray transmission spectra of U and Pu was studied: random coincidence summing and the scattering step background. These effects occur when the transmitted X-ray photons and the photons from the Cd-109 source, used for gain stabilization, interact with the detector. This work studied the impact of these effects on the U and Pu concentration measured by K-edge densitometry. It was concluded that the scattering background due to the presence of Cd-109 has the highest impact on the measured concentrations.

1. Introduction

Hybrid K-edge densitometry (HKED) is the leading major technique for measuring uranium (U) and plutonium (Pu) concentration in samples from nuclear reprocessing and nuclear fuel production. The analysts of the JRC analyse hundreds of uranium and plutonium samples for safeguards purposes each year in the EURATOM on-site laboratory in La Hague, France, and in the analytical laboratory in Karlsruhe, Germany, using the HKED method. However, the HKED instruments must be recalibrated every 3-4 months. The described work aims to reduce the frequency of recalibrations and to make the method more robust.

HKED is a combination of two techniques: X-ray transmission measurement around the K-edge energy of actinide elements ("KED branch") and the measurement of the K-shell X-ray fluorescence of these elements ("XRF branch"). Routine HKED analyses are currently done using software developed in the 1990s, running on the obsolete OpenVMS operating system [1].

The calibration factor of the KED branch ("$\Delta\mu$") in the OpenVMS-based software must be occasionally adjusted because the results become biased. The bias is always in the same direction. This calibration drift is due to the decay of the ^{109}Cd source used for gain stabilization. As the source decays, its contribution to the overall spectrum continuum changes, affecting the spectra analysis.

Another variable part of the spectral continuum comes from random coincidence summing. As long as all KED measurements, including the calibration measurement, are recorded with the same total count rate, the variation of the continuum due to random coincidence summing can be neglected. However, the total count rate during the sample measurement differs sometimes from the total count rate of the calibration measurement. This can be due, for example, to the uranium concentration in the sample being very different from the concentration in the calibration sample. The presence of other heavy elements in the matrix and the decay of the ^{109}Cd source also impact the total count rate. Thus, the influence of random coincidence summing may be different for different measurements.

The JRC has developed new prototype software to analyse KED spectra from HKED instruments. The developed software has been tested on Windows and Linux and can achieve the same or better results as the traditional OpenVMS-based software. It has new features to better account for removing the spectral continuum in the analysis process. This paper presents those new features.

2. Method

To remove the effect of the ^{109}Cd decay and random coincidence summing (RCS), we subtract suitably normalized background spectra from the sample spectrum and the blank reference spectrum, channel by channel.

An initial ^{109}Cd spectrum is obtained by recording a spectrum without sample and without X-rays. Then this spectrum can be used with any subsequent sample analysis as long as the setup has no major changes. Major changes here mean, for example, replacing the absorbers between the ^{109}Cd source and the detector, changing the position of the ^{109}Cd source relative to the detector, or replacing the detector. In principle, replacing the ^{109}Cd source would not mean a major change, but that replacement might affect the position of the source, or with a new source, we might need fewer absorbers. Therefore, recording a fresh ^{109}Cd spectrum after replacing the ^{109}Cd source is good practice.

The decay of the ^{109}Cd source is accounted for in the following way. The net count rate in the 88 keV peak of ^{109}Cd is calculated for the pure ^{109}Cd spectrum, the KED spectrum of the sample, and the reference blank. Then the counts in each channel i of the normalized ^{109}Cd spectrum, $S_{Cd,norm}$, are calculated using the following formula

$$S_{Cd,norm}(i) = \frac{N_{KED}(88keV)}{N_{Cd}(88keV)} S_{Cd}(i),$$

where $S_{Cd}(i)$ is the number of counts in channel i in the raw ^{109}Cd spectrum, while $N_{KED}(88keV)$ and $N_{Cd}(88keV)$ are the net count rate in the 88 keV peak in the KED spectrum (of the sample or the blank) and in the raw ^{109}Cd spectrum, respectively. The expression "KED spectrum" refers to the X-ray transmission spectrum through the sample or the reference blank. The normalized ^{109}Cd spectrum corresponds to the ^{109}Cd spectrum at the date of the sample or reference blank measurement. This way, the ^{109}Cd spectrum has to be recorded only once; there is no need to record a new ^{109}Cd spectrum for each sample.

The next step is calculating the influence of random coincidence summing. The contribution of RCS is calculated for each spectrum: the normalized ^{109}Cd spectrum, the sample's KED spectrum, and the reference blank's KED spectrum.

To account for cross-coincidences between photons from the ^{109}Cd source and the X-ray tube, the following sequence should be followed:

1. Calculate the normalized (or "decayed") ^{109}Cd spectrum
2. Calculate the contribution of RCS for the normalized ^{109}Cd spectrum, the KED spectrum of the sample, and the KED spectrum of the reference blank
3. Subtract the RCS contribution from all three spectra
4. Subtract the normalized, RCS-corrected ^{109}Cd spectrum from the RCS-corrected KED spectra
5. Continue with the traditional KED analysis (subtract step background, calculate transmission etc.)

The RCS contribution to the KED spectra also includes the coincidences of ^{109}Cd photons with themselves and with the X-rays. Therefore, before subtracting the normalized ^{109}Cd spectrum, it has to be corrected for RCS effects to avoid subtracting twice the coincidences from ^{109}Cd photons with themselves. An example of a KED spectrum with the RCS contribution is shown in Figure 1.
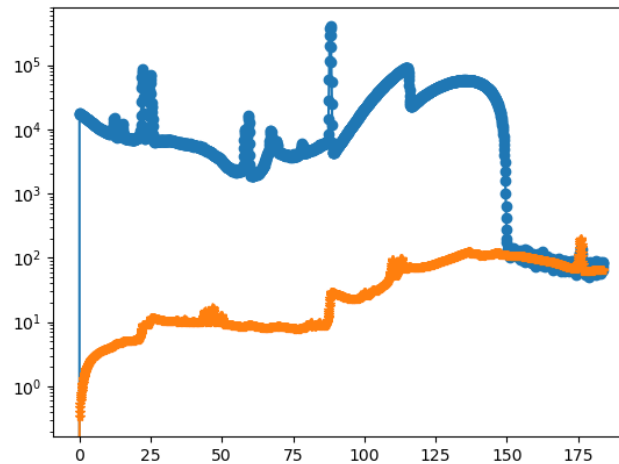

Figure 1. X-ray transmission spectrum of a uranium sample and the contribution of RCS to the spectrum (counts as a function of energy in keV)

The RCS contribution is calculated similarly as in references [2] and [3]. The calculated RCS counts also include a tailing component, as described in [3]. The parameters of the tailing function were estimated empirically by visual comparison of the calculated sum peak from the 88 keV line of ^{109}Cd to the corresponding sum peak in the real spectra. A better method is needed for determining the tailing parameters.

We treated the Compton continuum from the scattering of the X-rays by using the step background model given in [1]. Possible improvements to the step background model, based on adding tailing components to the right background window, have already been described in [2] in 1987. These improvements are not yet implemented in our algorithm.

3. Results

Figure 2 shows the difference between the uranium concentrations measured by KED and the reference concentration measured by isotope dilution mass spectrometry (IDMS) for several samples. It demonstrates that ^{109}Cd spectrum subtraction makes it possible to obtain good results with a single KED calibration factor ("Δμ"), which does not change over time. The outlier in the non-extrapolated mode is a sample that contained gadolinium in its matrix. In extrapolated mode, there are no outliers because the extrapolated mode is less sensitive to matrix effects, as expected.
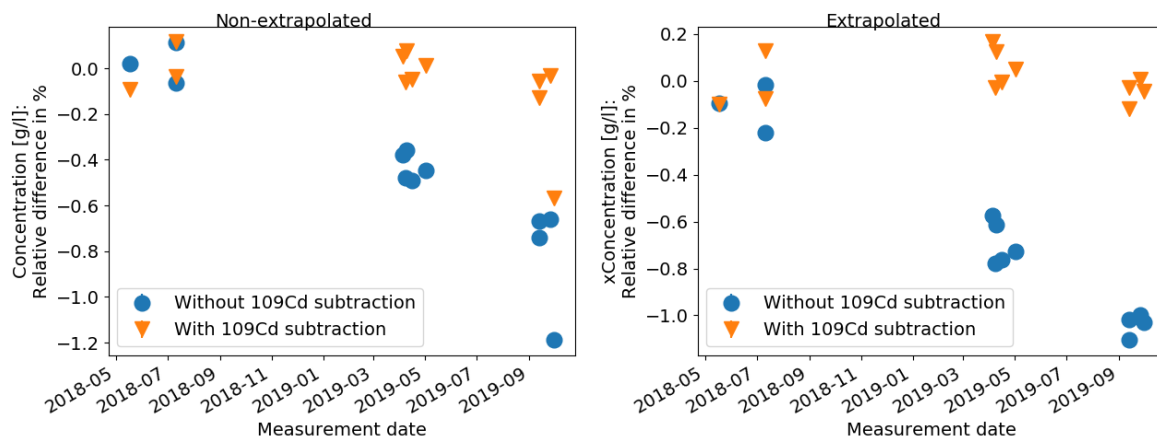
Figure 2 Relative difference between the U concentration calculated by our program and the reference value from mass spectrometry, for a set of pure U solutions, as a function of the measurement date, with and without ^{109}Cd subtraction. Each point is the average of three replicates. The same calibration factor was used for all measurements. Left: non-extrapolated mode. Right: extrapolated mode.

To illustrate further the influence of the ^{109}Cd source, we look at the results obtained with an internal quality control sample, shown in Figure 3. We do not know the exact reference concentration of this sample, so we only focus on the stability of the measured concentration. We obtained all results in Figure 3 using the same calibration factor.

Without ^{109}Cd subtraction, the measured uranium concentration decreases with time. This is due to the decay of the ^{109}Cd source. As the ^{109}Cd source decays, its contribution to the background continuum decreases, affecting the evaluation of the spectrum. This dataset's outliers around June - July 2018 are due to our experiments with an old, weaker ^{109}Cd source.

With ^{109}Cd subtraction, the measured concentration slightly increases with time. This is probably due to the evaporation of the solvent from the sample. There are no outliers in this dataset for June - July 2018. The concentrations obtained with a weaker ^{109}Cd source in June – July 2018 are the same as those obtained with a stronger source.
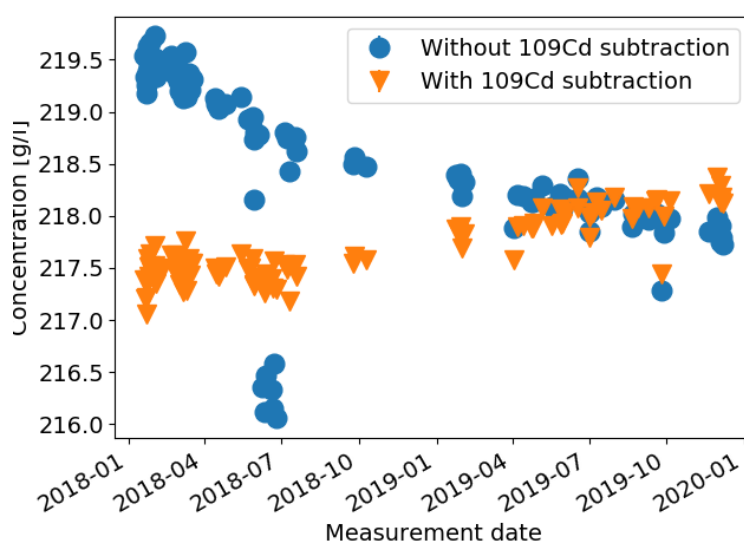

Figure 3 Variation of the measured uranium concentration of the internal standard.

The above results show that the performance of the KED algorithm can be easily improved by [109]Cd subtraction, which was impossible with the OpenVMS software.

Subtracting the RCS contribution does not significantly impact the calculated uranium concentration. To investigate the effect of RCS, the same internal quality control sample was measured several times using different X-ray tube currents. Figure 4 shows the relative difference of the calculated U concentration with and without RCS correction as a function of the total count rate. As expected, the magnitude of the RCS correction depends on the count rate. However, it is very small, as seen in Figure 4.
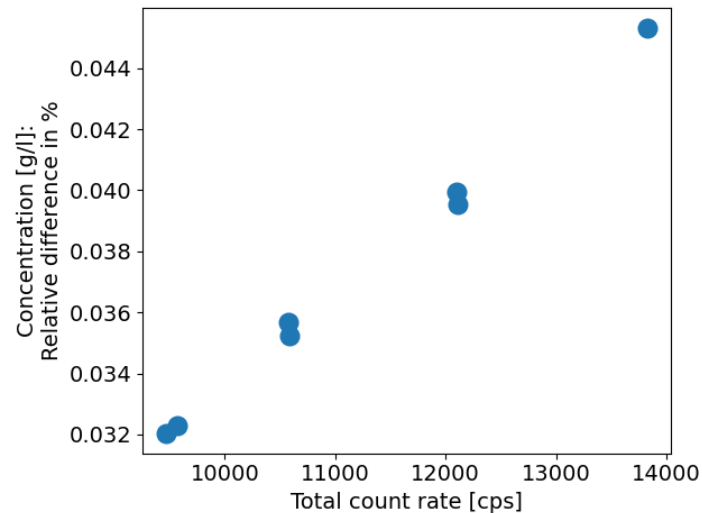

Figure 4 Difference of calculated U concentration with and without RCS correction, as a function of total count rate

In Figure 5, the RCS correction slightly reduces the dependence of the calculated concentration on the total count rate. However, this RCS correction is insufficient to completely remove the dependence on the total count rate. This result is consistent with the data in Figure 12 of reference [2].
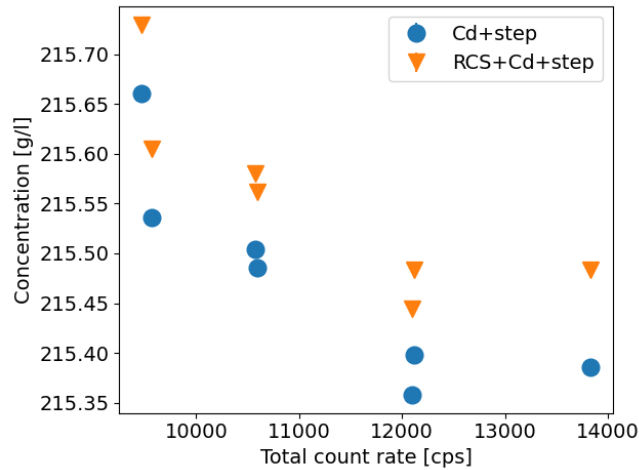
Figure 5 Uranium concentration calculated with and without RCS correction as a function of total count rate. The Compton continuum from X-ray scattering (step) and ^{109}Cd spectrum are always subtracted.

To further reduce the dependence of the reported concentration on the total count rate, we plan to implement the modified step background model for the Compton continuum, mentioned in [2]. This means adding a fast and slow tailing contribution to the right-hand side window of the step background region.

4. Conclusion

The drift of the KED calibration factor due to the decay of the ^{109}Cd source can be completely removed by subtracting a suitably normalized ^{109}Cd spectrum from the KED spectra. However, the dependence of the calibration factor on the total count rate can only be slightly reduced by correcting for RCS effects. That is, the RCS correction is insufficient to remove the dependence on the count rate. Further studies related to continuum subtraction in KED spectra are ongoing to decrease the dependence of the KED calibration factor on the total count rate.

References

[1] Ottmar H, Eberle H, The Hybrid K-Edge / K-XRF Densitometer: Principles - Design – Performance, Report KfK 4590, Kernforschungszentrum Karlsruhe (1991)

[2] Eberle H, Matussek P, Michel-Piper I, Ottmar H, Evaluation of High-Rate Pulse Processing in K-Edge Densitometry, Report KfK 4291, Kernforschungszentrum Karlsruhe (1987)

[3] McElroy RD Jr, Performance Evaluation of the ORNL Multi-Elemental KED (MEKED) Analysis Algorithms, Report ORNL/TM-2018/878 (2018)