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OAK RIDGE NATIONAL LABORATORY
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Robert D. McElroy, Oak Ridge National Laboratory

Introduction

The CHKED software replicates functionality of the older VMS based HKED software and incorporates additional analysis algorithms and analysis tools. When the traditional HKED analyses are selected, the CHKED software appears to faithfully reproduce the measurement results as reported by the older software. The CHKED software includes a Multi-Elemental K-Edge (MEKED) analysis based in part on algorithms devised at Los Alamos National Laboratory. In principle, the MEKED analysis represents a significant advance over the traditional HKED analysis, providing a capability to analyze the actinide concentrations from complex solutions such as low U:Pu ratios (e.g. U:Pu = 1:1) including additional minor actinide components such as Np and Am. However, this MEKED analysis is somewhat limited by reliance on a Region of Interest (ROI) analysis of the spectrum, the need for extensive calibration measurements and a simplistic interpretation of the KED transmission spectrum. Finally, MEKED algorithm set associated with the CHKED software acquired by Oak Ridge National Laboratory (ORNL) from Canberra Industries, does not seem to be “finished” (e.g. the MEKED analysis provides concentration results for only 2 actinides). These limitations are discussed in the sections below.

MEKED analysis

The MEKED analysis expands the traditional ROI approach through the inclusion of additional ROIs corresponding to the various K-edge transitions associated with the actinides. The traditional KED analysis assumes that only a single dominant actinide (typically U) is present in the solution and that any other actinides are of sufficiently low concentration as to not perturb the interrogating X-ray flux. However, the presence of the actinides in the solution effectively alters the interrogating X-ray energy distribution and introduces potentially large biases in the assay results unless this effect is properly accounted for in the analysis. The CHKED algorithms attempt to correct for the presence of additional actinides by introducing an attenuation matrix.

The generalized MEKED approach involves the following steps[1]:

1. Continuum Background Subtraction
2. Determine HV endpoint energies
3. *First Pass Transmission determination and determination of current beam ratio (α)*
    - *Measured transmission ratios are determined rather than calculated from beam currents. A correction ratio is determined for each element. This has the benefit that it will tend to*

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[1] From Canberra CHKED training materials, presented by Marcel Villani at ORNL (2013).

   correct for variations in the energy distribution of the interrogating X-ray source (that is aging of the tube).
   - *An initial density is computed*
4. *2^{nd} Pass Transmission determination and solve generalized MEKED equation*
5. Enrichment correction
6. Temperature Correction

Steps 1, 2, 5 and 6 follow the same methodology as the traditional KED transmission analysis. Biases associated with the continuum background subtraction are discussed in Appendix A. The steps 3 and 4 constitute the MEKED analysis enhancements.

Generalized MEKED Equations

The Canberra Hybrid K-Edge Densitometry User's Manual states that the elemental concentrations (ρ_i) are solved by the following densitometry equations:

$$\begin{pmatrix} \Delta\mu_{1,1} & \Delta\mu_{1,2} & \Delta\mu_{1,3} & \Delta\mu_{1,4} & \Delta\mu_{1,5} & \Delta\mu_{1,6} \\ \Delta\mu_{2,1} & \Delta\mu_{2,2} & \Delta\mu_{2,3} & \Delta\mu_{2,4} & \Delta\mu_{2,5} & \Delta\mu_{2,6} \\ \Delta\mu_{3,1} & \Delta\mu_{3,2} & \Delta\mu_{3,3} & \Delta\mu_{3,4} & \Delta\mu_{3,5} & \Delta\mu_{3,6} \\ \Delta\mu_{4,1} & \Delta\mu_{4,2} & \Delta\mu_{4,3} & \Delta\mu_{4,4} & \Delta\mu_{4,5} & \Delta\mu_{4,6} \\ \Delta\mu_{5,1} & \Delta\mu_{5,2} & \Delta\mu_{5,3} & \Delta\mu_{5,4} & \Delta\mu_{5,5} & \Delta\mu_{5,6} \\ \Delta\mu_{6,1} & \Delta\mu_{6,2} & \Delta\mu_{6,3} & \Delta\mu_{6,4} & \Delta\mu_{6,5} & \Delta\mu_{6,6} \end{pmatrix} \cdot \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \\ \rho_5 \\ \rho_6 \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix}$$

Where $C_j = \frac{1}{x}\left[\exp\left(A_{j+}\right) - \exp\left(A_{j-}\right)\right]$, x is the sample vial thickness, and $A_{j\pm} = \ln\left(ln(1/T)\right)$, at energy $E_{j\pm}$ bracketing the K-edge energy of **each major element** (or region-of interest).

Multi-Elemental Analysis Limitations

There are a number of small issues with the MEKED analysis

1. The MEKED is not truly multi-elemental

   Our studies (based on V1.0 software) indicate that the MEKED analysis is only applied to two elements. Data for "minor elements" can be entered into the declarations but it is not clear from the documentation or the performance of the software how the minor elements are accounted for in the analysis.

   Declarations and Certificates

   The CHKED MEKED software only determines concentration results for the three elements (2 major plus 1 minor or 1 major plus 2 minor) listed in the declaration and certificate files. While it is possible to assign calibration parameters for 6 elements (Th, U, Pu, Np, Am, Cm) using the CHKED software, it was only possible to assign 3 elements to a declaration or certificate. In the case of MOX items, this would typically mean assigning U and Pu and then choosing between Am and Np as the third element.

2. MEKED Major Element Analysis

   Since the software only allows definition of 2 major elements, the implication is that the Multi-elemental analysis is only applied to two actinides and that the special case where there are only 2 major actinides is the only case addressed by this software. The *Canberra Hybrid K-Edge Densitometry User's Manual* defines this equation as

$$\begin{pmatrix} \Delta\mu_{1,1} & \Delta\mu_{1,2} \\ \Delta\mu_{2,1} & \Delta\mu_{2,2} \end{pmatrix} \cdot \begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

The appeal of this representation is that it may be solved for the major actinide concentrations rather simply as set of 2 linear equations.

However, it may be that the minor elements are included as "known" relative concentrations when applying the larger general attenuation matrix. We did not fined definitive documentation to determine how the analysis actually works.

<u>Potential impact of the minor actinides on the major actinide results</u>
By examining the impact of the Pu content on the MEKED U assay result we can estimate the impact of the minor elements on the U and Pu. Typical Delta Mu Matrix values for U and Pu are

$$\begin{pmatrix} \Delta\mu_{1,1} & \Delta\mu_{1,2} \\ \Delta\mu_{2,1} & \Delta\mu_{2,2} \end{pmatrix} = \begin{pmatrix} 3.53665 & -0.14022 \\ -0.04662 & 3.11345 \end{pmatrix}$$

Evaluation of the 2 element matrix with these attenuation values we find that Pu in the solution begins to impact the U concentration when the Pu concentration exceeds 10 g/L. Assuming a similar impact from the presence of small amounts of Np or Am in the solutions on the U and Pu values and that these minor elements are generally only present at ≤3% of the total actinide content, we can assume that regardless of whether or not the MEKED analysis includes the minor actinides, they will have no significant impact on the reported values for U and Pu.

The attenuation matrix approach attempts to correct for the reduction in count rate across the K-edge transition of one element by the presence of the other elements relative to the reference spectrum. The general description of the method is somewhat counter-intuitive and arises simply from the historical use of the concept of delta-mu (the change in attenuation across the K-edge) and the use of a reference spectrum.

3. Minor Actinide Performance
For our evaluation only a few samples with significant minor actinides present were available for evaluation of the MEKED algorithms. However, it appears that for low concentrations of minor actinides (~<1 g/L) the minor actinide concentration reported was effectively the declaration value. For example, the spectra from a sample containing U, Pu and Np (no Am present) was analyzed three times, with the only difference being the declared Np concentration. Each assay result essentially reported the declared Np concentration. The value of the Np declaration also appears to have a slight influence on the reported Uranium concentration value.

We conclude that the MEKED analysis is not reporting a measured value for the minor actinide Np but rather the reported value is simply based on the ratio of the U and Np declarations scaled to the reported U result. A similar pattern was observed if Americium was selected as the minor element. Unfortunately, we could find no discussion of the treatment of the minor elements in the

CHKED software manual (Canberra document number 7067686 V1.0) or internal software help files.

Table 1. Impact of the minor actinide declaration value on the assay MEKED assay result (the same spectra were analyzed using different declarations).

	Declared (g/L)	Reported Concentration (g/L)	Declared (g/L)	Reported Concentration (g/L)	Declared (g/L)	Reported Concentration (g/L)
U	100.00	98.35 ± 0.86%	100.00	98.31 ± 0.86%	100.00	98.20 ± 0.86%
Pu	7.00	7.38 ± 12.64%	7.00	7.24 ± 12.88%	7.00	7.21 ± 12.94%
Np	**4.00**	**3.94 ± 11.39%**	**1.00**	**0.99 ± 11.39%**	**0.30**	**0.30 ± 20.72%**

4. Why not include a matrix (solution) term in the attenuation matrix?
   Since the attenuation matrix is a generalized approach, and for most HKED sample assays the sample density and concentrations of each actinide are included in the declaration, it may be beneficial to add another set of parameters to the attenuation matrix, the solvent attenuation parameters. The solvent (or sample matrix) concentration varies with the actinide concentrations. Although the energy dependence of the sample matrix attenuation parameters is much slower than for the actinides, the sample matrix impacts the shape of the transmitted X-ray spectrum. The potential benefit of including a correction for the solvent concentration should be examined.

Need for the Attenuation Matrix

The energy dependence of the interrogating X-ray spectrum requires that the transmission measurement be made via comparison against a reference spectrum (i.e. solution containing no actinides). The MEKED analysis defines two ROIs for each element, one above and one below the K-edge transition energy (adjacent K-edge transitions share the ROI defined between them). Each ROI from the sample spectrum is compared against the corresponding ROI in the reference spectrum. The concentration is determined by comparison of the transmission rates in the ROIs just above and below the K-edge transition energy. This is referred to as the non-extrapolated approach in the traditional KED analysis. The presence of multiple actinides within the solution increases the complexity of the energy dependence of the sample's spectrum. The MEKED analysis addresses this complexity by introduction of the attenuation matrix.

We note that if the KED extrapolated analysis were to be implemented for the multi-elemental analysis, then the attenuation matrix is not required. This is because each of the off-diagonal terms in the attenuation matrix tends to zero as the energy difference between the upper and lower ROIs approaches zero.

$$\begin{pmatrix} \Delta\mu_{1,1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \Delta\mu_{2,2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \Delta\mu_{3,3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \Delta\mu_{4,4} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Delta\mu_{5,5} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Delta\mu_{6,6} \end{pmatrix} \cdot \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \\ \rho_5 \\ \rho_6 \end{pmatrix} = \begin{pmatrix} \Delta\mu_{1,1} \cdot \rho_1 \\ \Delta\mu_{2,2} \cdot \rho_2 \\ \Delta\mu_{3,3} \cdot \rho_3 \\ \Delta\mu_{4,4} \cdot \rho_4 \\ \Delta\mu_{5,5} \cdot \rho_5 \\ \Delta\mu_{6,6} \cdot \rho_6 \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix}$$

So that simply

$$\rho_z = C_z / \Delta\mu_{z,z}$$

The traditional KED analysis provides for both an extrapolated and non-extrapolated analysis. It is puzzling why an extrapolated MEKED approach was not implemented.

Regions of Interest

The small separation in energy between the K-edge transitions of the actinides requires relatively narrow energy windows for the ROIs. Neglecting any Lorentzian broadening effects the FWHM of the observed K-edge is approximately 550 eV, the gap between left and right ROIs about a K-edge transition is less than 1 keV for most of the ROI windows. This separation is equivalent to only about 1.5 FWHM and ensures that the broadened edge will encroach into the ROI so that the observed count rates will be impacted by changes in the FWHM and any spectral drifting. More importantly, it will complicate the calculation of the attenuation matrix parameters.

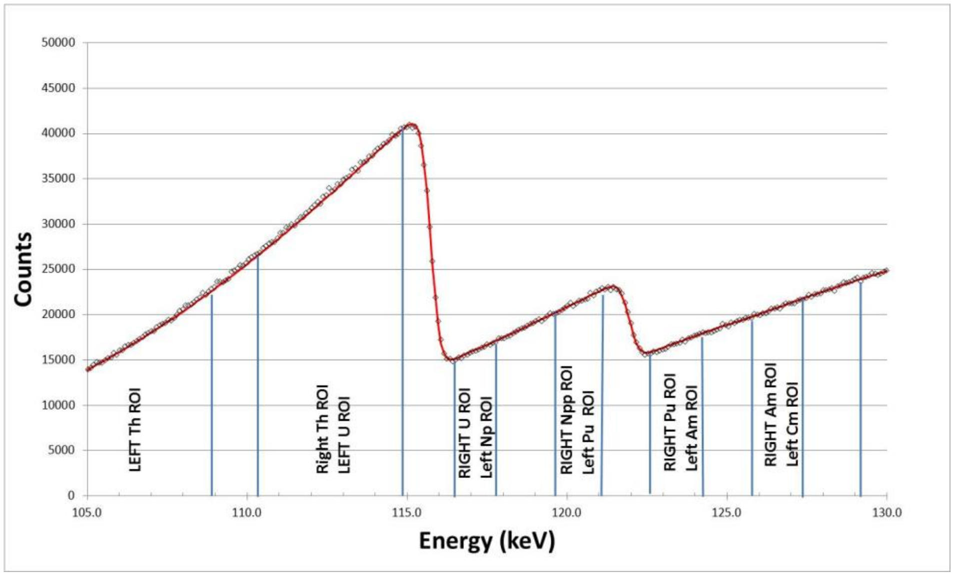
Using the CHKED MEKED default settings, most of the ROIs are only 16 or 17 channels wide. For comparison, the traditional KED ROI widths are 23 or 24 channels wide. The reduced ROI widths result in a degradation of the measurement precision by approximately 20% relative to the traditional analysis (e.g. 0.36% versus 0.3% for a single 1000s KED run).

Ideally, the separation from the K-Edge transition to the nearest ROI should be at least 2xFWHM for the typical KED HPGE detector (as was used with the traditional KED analysis) with 3xFWHM desired. Unfortunately this rule of thumb would result in widths for the ROIs of less than 1 keV. Use of the more proper settings (2xFWHM) will mitigate drift and resolution broadening effects but results in only 9 or 10 channels width for the ROI and additional degradation in the measurement precision by approximately 30%.

Table 2. K-edge Transition Energies and Regions of Interest windows for U and Pu

CHKED MEKED K-Edge Default ROI limits for multi-elemental KED analysis							
	K-edge Energy	Left ROI Limits		Width (keV)	Right ROI Limits		Width (keV)
U	115.606	110.379	114.879	4.5	116.388	117.888	1.5
Pu	121.797	119.484	120.984	1.5	122.644	124.144	1.5
Traditional KED ROI Limits							
	K-edge Energy	Left ROI Limits		Width (keV)	Right ROI Limits		Width (keV)
U	115.606	107.200	113.300	6.1	117.3	119.4	2.1
Pu	121.797	117.300	119.400	2.1	123.5	130.2	6.7

The very narrow ROIs required for the MEKED limit the measurement precision, and in general prevent a full MEKED treatment for complex spectra with 3 or more major elemental constituents.



MEKED default ROIs overlain on a portion of the KED spectrum from a U, Pu sample. The ROIs tend to encroach into the high energy portion of the Gaussian broadened K-edge transitions.

Other Concerns

Significant deficiencies common to both the VMS and CHKED analysis are the improper background correction approach and the use of incorrect temperature correction coefficients. Both of these deficiencies result in biases significant in comparison to the reported concentration uncertainties. This effects and other less well understood interferences are discussed in this section.

1. Continuum (Step Background) Correction

NOTE: A detailed discussion of this issue is attached to this report.

The CHKED analysis includes the step background correction described in Ref [1]. However, the ROIs used for determination of the step background correction include significant fraction of counts that are not representative of the background below the K-edge transitions. The result is an over subtraction of the background leading to biases in the reported actinide concentrations. The empirical calibrations used for the CHKED software effectively absorb these biases for assays performed near in time to the calibration. However, biases will begin to manifest as the ^{109}Cd source decays or the interrogating beam intensity is changed.

2. Temperature Correction

The sample's temperature and, to a lesser extent, the temperature of the assay system will have an impact on the KED assay result. As the temperature changes, the density of the solution changes as well as the diameter of the sample vial. We note that the 0.05% / °C deviation determined by Ottmar [1] is applicable to the rectangular glass cuvettes and not the polyethylene vials. The change in assay result with temperature is −0.11% °C for the cylindrical polyethylene (SGN) vial using the ORNL HKED system. Since the correction factor is not an adjustable parameter in the CHKED software, the temperature change will result in a −0.06%/ °C systematic bias.

3. Reference Spectrum

Although the KED transmission measurements rely on count rate differences across the K-edge transition to provide sensitivity and accuracy, the traditional and MEKED analyses determine the magnitude of the attenuation relative to a reference blank. However,

- The energy distribution from the X-ray generator changes as the X-ray tube ages,
- The detected spectrum is influenced by electronic effects such as dead-time and pileup effects.
- Pile-up effects vary both with count rate and energy distribution.
  Consider two spectra with the same overall count rate – one from W X-rays and one from Cd-109 The pile-up events from the W X-rays spectrum will be detected primarily in the range of 100 to 140 keV photons while for pile up events for ^{109}Cd will be detected as 176 keV photons. For the KED analysis the pile-up events from W X–rays directly interfere with the KED analysis while those from Cd-109 would not. The KED spectra consist of a few peaks such as the W X-rays but is dominated by the transmitted Bremsstrahlung X-rays. So the pile-up effect from a reference blank will have a very different shape than one obtained from 300 g U/L even for equal count rates. These differences increase with increasing complexity of the solution.

Use of the reference spectrum for analysis of simple samples (e.g. U only) provides a reliable result because the differences in energy distribution are effectively absorbed by the empirical calibration. As long as the reference blank closely matches the characteristics of the samples (e.g. dimensions, chemical composition and density) and the Cd-109 source activity of the sample measurement is not significantly different from that at calibration this approach will not result in any significant bias. However, use of the reference spectrum with complex actinide samples may introduce additional biases as the shape of the transmission spectrum becomes correspondingly complex.

4. Sample Vial Size
   The sample vial thickness can not be adjusted on a per assay basis without altering the counter configuration in the CHKED software. We note that this issue may have been already addressed by the vendor in a recent release of the software.

General Comments on the CHKED Software

SetUp\Certificates and Declarations

- Only allow definition of 3 elements
- Occasionally, definitions could not be saved – even though no errors evident.
- Round off to 2 significant digits in uncertainty entries while IDMS results may report small uncertainties to 3 decimal places (e.g. 0.115%). Given the high degree of precision of the CHKED measurements and the accuracy of the IDMS results, 3 decimal places are recommended.

SetUp\Sample Container Declaration

- Should consider entry for container wall thickness

Setup\Sample Type Processing Parameters
Only allows definition of 3 elements
Default ROIs for U, Pu and Am are not the same as noted in KfK4590 of the TT Bericht (1993)

Temperature Correction

- Parameters can not be entered from the setup screens – values used are those predefined from KfK4590
- These parameters are not representative of current generation HKED systems using the SGN vials
- The temperature correction parameters are not visible to the user.

Data Review

The data review program is intended to allow review and re-analysis of HKED files to re-evaluate problematic assay results on an individual basis and to re-analyze multiple data sets with revised parameters. The Data Review tool provided with CHKED is a dramatic improvement over those available with the traditional VMS software. However, in general the data review application is difficult to navigate and certain key parameters are not readily accessible to the user. For example,

- It was not possible to select a certificate file in data review.
    - It was not possible to add a minor or major element to the declaration
    - It was not possible to add a 2nd minor element
    - It was not possible to add a minor element if a 2nd major element had been defined.

  A fairly common entry mistake is to select the wrong declaration or certificate. A drop down menu to allow selection of alternate declarations or to create a new one would be beneficial. For example, if an unexpected element were to be found in the solution, currently the only way to include this in the reanalysis is to modify the original certificate and reanalyze using the batch mode.
- MEKED only accommodates elements assigned to the sample vial in the counter definition menus.
    - This again complicates the data review since the user must back completely out of data review, and redefine the calibration.
- Help files do not define the ASF steps available or the relevant report sections.

Editing a Calibration

The CHKED software provides an option to edit an existing calibration. We note that editing a calibration does not change the “calibration date” in data review. So it is not obvious that a calibration file has been revised.

CHKED Analysis Tools

The CHKED software provides a number of utilities to assist in calibration and data review.

Calibration graphics

Graphics have been added to aid in the evaluation of the calibration process. For example, the KED calibration curve is shown in the figure below. However, given the range in concentrations and the relatively small errors associated with the KED assay it is difficult to see significant deviations from the fitted line. A more beneficial plot would be the relative difference as a function of concentration.

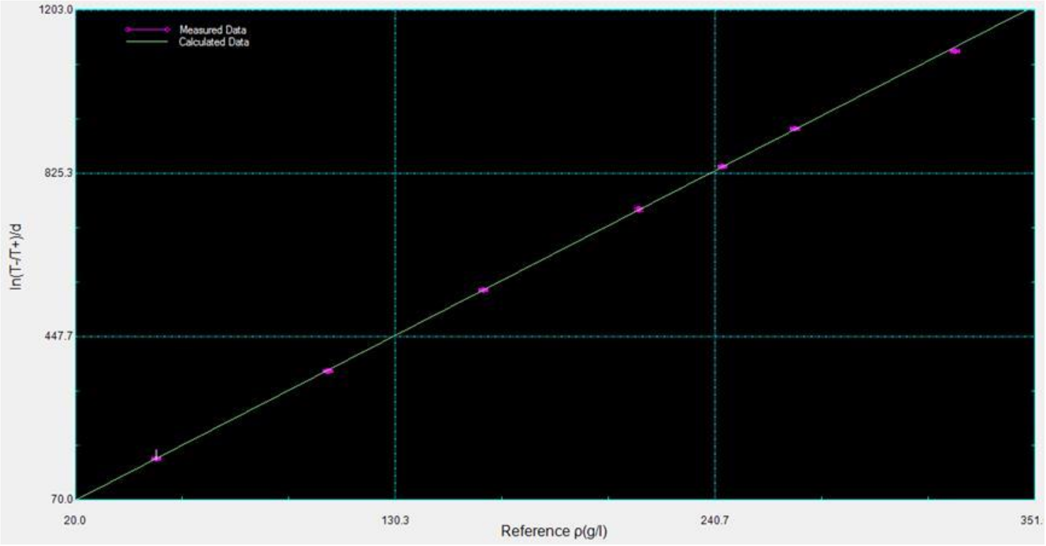


Figure 1. KED Calibration curve for uranium only solutions.

Data Analysis using the Simulator

The Genie 2k simulator tool can be used to import data files into the CHKED data base. This tool was used extensively in our evaluation of the CHKED software and while this is a useful tool, it is a simple path to enter erroneous or fictitious data into the system.

- The simulated data acquisition spectra are not the same as the imported data files. Following completion (or interruption) of the simulated assay sequence, the new data file briefly appears and is then replaced by the next data acquisition sequence. Care must be taken to ensure that the proper files are being imported.
- It is possible to import the data files with a different sample container (allowing the sample size to be altered during reanalysis).
- It is possible to "acquire" the new data file with an incorrect X-ray tube setting. While this does not appear to impact the "sample assays" it does impact the reference measurement. Since the sample spectrum is ratio'ed to the reference spectrum and adjusted for relative beam intensity, it is possible to inadvertently or deliberated affect the reported assay results.

Neither the reference manuals or help files accurately describe the necessary steps for use of the simulation tool for importing spectra.

CHKED REPORTS

The CHKED reporting templates follow fairly closely to the original VMS templates. However, both could use some improvement.

- MEKED
    - ^{109}Cd reference peak rate is actually total counts in the peak

MEKED Calibration Report

The KED calibration report is similar to that of the VMS predecessor, however, both lack relevant information for evaluation of the calibration and contain some ambiguous entries (e.g. the measured concentration values refer to the assay results calculated with the previous calibration parameters – but this is not stated in the report). Nor do the certificate values (i.e. declared concentrations) appear in the calibration report. Given that the CHKED software tags the raw data files (i.e. the .CNF files) with a sequence number and does not provide a descriptive file name, the calibration report should list the assay sequence number. Additional useful information are the HV and current settings for the X-ray generator, measurement cell temperature and sample vial diameter. It is assumed that relevant corrections are applied to each file during the calibration processing, the report should indicate this.

It is suggested that the previous (now obsolete) assay results be removed from the first section of the report and replaced with the assay sequence number, HV and current settings. The assay results using the "older" parameters should be moved to the end of the report and listed side by side with the updated values based on the new calibration parameters.

The tabulated delta-mu values in the 2nd section of the report should also provide the calculated uncertainty for the value.

Conclusions

An MEKED approach to complex actinide solutions has been implemented in the CHKED software. The method seems to work well for U and Pu solutions containing little or no minor actinides concentrations. The implementation of the MEKED algorithms allows determination of two major actinide components, typically U and Pu of a solution sample. The CHKED treatment of the minor actinides seems to be limited to a simple scaling of declared concentration ratios of the minor actinides to the measured major actinide concentration. The MEKED algorithms as implemented will result in degradation of the measurement precision in the reported major actinide concentrations (compared with the results obtained using the large ROIs associated with the traditional analysis.

The method of subtraction of the continuum or stepped background remains unchanged from the traditional analysis approach. However, we have demonstrated that this method is incorrect and can lead to biases on the order of the KED target performance values (i.e. 0.3% or greater). It is recommended that the background correction methodology be updated to reflect the true origin of the background counts.

Appendix A

Impact of Background Subtraction on the KED Transmission Result

(To be published)

The VMS HKED[2] and Windows based CHKED[3] software remove background from the KED spectra using a Region of Interest (ROI) based correction technique. In this approach, there is assumed to be a rectangular tail (step background) associated with each gamma-ray or X-ray peak (note for the continuous energy distribution from the X-ray generator, each energy bin is treated as a peak). The correction method makes use of two ROIs, one above and one below the energy region of interest, located in portions of the spectrum containing no peaks or other features. The calculated background as a function of energy in between these ROIs, is based on the average count per channel in these two ROIs scaled by the ratio of the summation of counts in the spectrum between the lower ROI and the current channel number and the total number of counts in between the ROIs.

As we will demonstrate, the ROIs are not representative of the background continuum. The lower ROI includes tailing from the tungsten X-ray peaks and a significant contribution from the tail of the ^{109}Cd peak, while the upper ROI is populated by random coincidence summing events. The contents of these ROIs have little connection to the actual background continuum. In the following sections we explain the traditional approach and, then provide a more detailed physics based description. This is used to provide a more meaningful and accurate representation.

Step Background

The traditional HKED analysis described by Ottmar and Eberle [1] applies a “stepped background” correction to the measured transmission and XRF spectra. Figure 2 shows a common representation of the response of a Ge(Li) detector to a mono-energetic photon source. The continuum background shown in the figure is generally referred to as the step background.

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[2] VMS Operating system based Hybrid K-edge Densitometry software, available from Canberra Industries

[3] Canberra Hybrid K-edge Densitometer Software, available from Canberra Industries

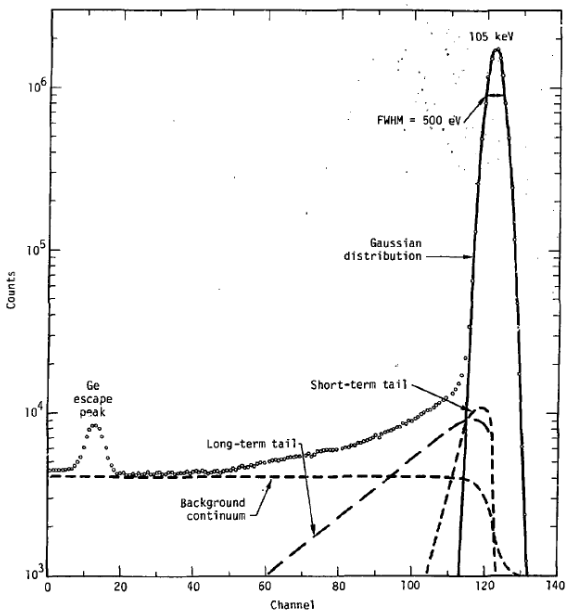

Figure 2. Peak shape from a Ge(Li) detector (from Gunnick (1975) **[2]**).

Figure 3 shows the KED step background shape for a 321.9 g U/L solution as determined following the traditional HKED analysis (described in KfK4590). In the traditional HKED treatment, the magnitude of the step background for this spectrum is equivalent to 0.6% of the spectrum height just below the K-edge transition and 2.5% of the spectrum height just above the U K-edge.

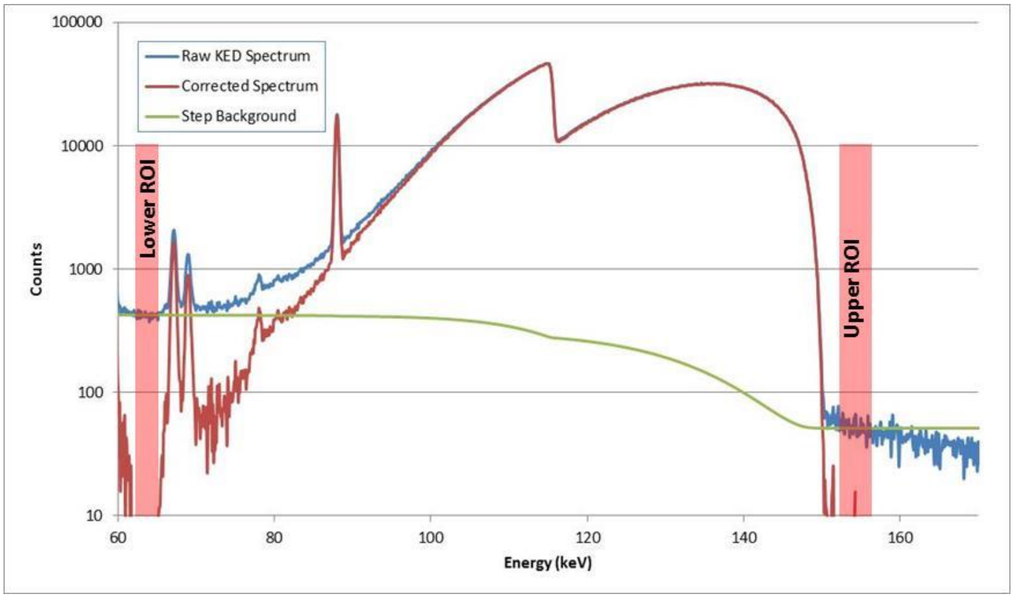

Figure 3. Step background determined for a 321.9 g U/L solution using the VMS and CHKED algorithm.

The step background, I_{BKG}, as a function of spectrum channel number shown in Figure 3 is described in Ref [1] by the following expression

$$I_{BKG}(n) = B_L + (B_R - B_L) \cdot \sum_{j=L}^{j=n} Y(j) / \sum_{k=L}^{k=R} Y(k)$$

Where Y(i) = spectra counts of channel i
B_L is the average counts in the left background ROI (Figure 3).
B_R is the average counts in the right background ROI (Figure 3).

The step background is a common feature in gamma-ray spectroscopy text books (e.g. Knoll's Radiation Detection and Measurement [3]) and scientific publications. However, there is little said about the origin of this step background or its properties. Most references eventually trace back to Gunnick's 1975, "Status of Plutonium Isotopic Measurements by Gamma-Ray Spectrometry" [5]. In this reference Gunnick attributes the step background to detector edge effects and small angle scattering by material between the detector and the source. However, the high degree of collimation used in the HKED detectors results in a pencil beam incident on a thick detector and eliminates these interferences - except for the ^{109}Cd lines and tungsten X-rays induced near the HPGe detector which occur below the energy range of interest. In other words the HKED analysis subtracts a background component that may not be present in the KED spectrum.

The following sections explore the source of counts in the Background Regions of Interest (ROIs) employed by the KED analysis.

Upper or right Background ROI

For product materials (i.e. no fission products) the upper ROI should not have any counts in it. The observed counts are due to random coincidence summing (this has been verified by calculation and by varying the integrating X-ray beam intensity). More importantly, the HKED background subtraction model assumes that the background component is monotonically decreasing with increasing energy. The plot in Figure 4 clearly shows that this is not the case. Use of the upper ROI will lead to an over subtraction of the background under the K-edge transition.

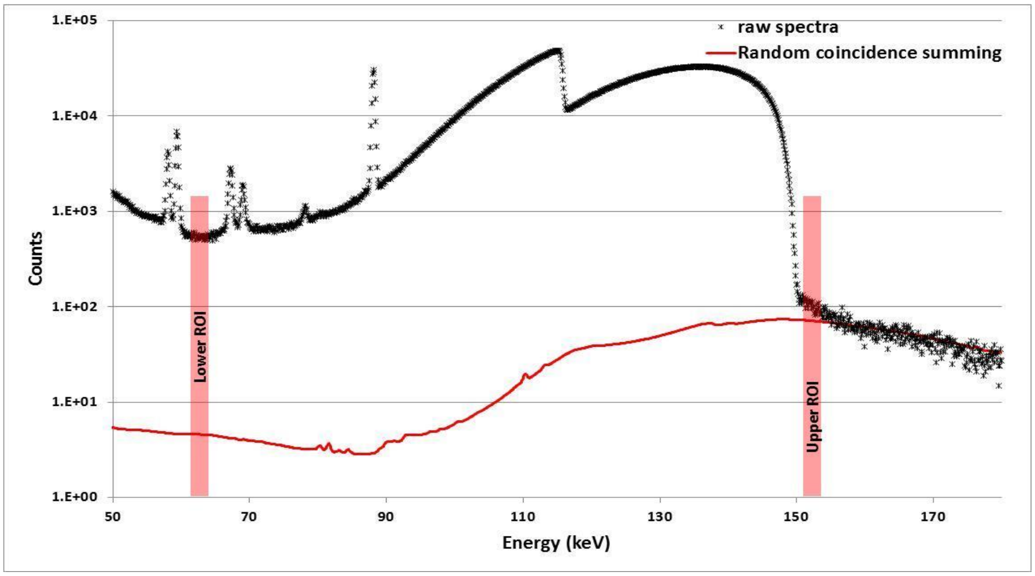

Figure 4. Plot showing the random coincidence summing contribution to the KED transmission spectrum. The ROIs (shaded area) are used in the VMS HKED and CHKED software for background correction.

Lower (left) Background ROI

The Lower Background ROI cannot be described as a simple down scatter tailing from the transmitted X-ray spectrum. The Lower Background ROI includes contributions from

- ^{109}Cd source tailing
- Tungsten X-ray peak tails
- Random Coincidence Summing

Random Coincidence Summing: From Figure 4 above, we note that there is a small contribution to the lower ROI from random coincidence summing. Random coincidence summing contributes 1 to 2% of the lower “background” ROI counts

^{109}Cd Source Tailing: To examine the contributors to the lower ROI count rate we acquired KED transmission spectra for the U300 uranium solution standard (321.9 g U/L) with and without the ^{109}Cd energy stabilization source (Figure 5). Due to the location of the ^{109}Cd source within the tungsten shield, in close proximity to, but significantly off center from, the detector centerline, there is a very large tail associated with the ^{109}Cd peak. Due to the location of the source, the peak shape of the 88.034 keV line is not representative of the transmitted X-rays incident on the detector face in tight collimation. This is because the energy is deposited over a different region of charge collection electric field. As can be seen in Figure 5 the tail extends through the lower background ROI.

Tungsten X-ray Peak Tails: We can also see in Figure 5 that due to the Voigt shape associated with the X-ray peaks, the tungsten X-ray peaks contribute to the lower background ROI. These peaks contribute only about 1% of background ROI. We note that the majority of the tungsten X-rays detected in this spectrum were induced by the decay of the ^{109}Cd source so that the contribution to the background will change as the source decays (^{109}Cd half-life ~ 1.267 years).

For the spectrum shown in Figure 5, the X-ray generator was operating at 15mA and 150kV, the ^{109}Cd peak count rate was 153cps and contributed 25% of the counts in the lower background ROI. Random coincidence summing contributed 1% and the tailing from the tungsten X-ray peaks contributed an additional 1% to the counts in the ROI. We estimate that in a typical assay the ^{109}Cd source contributes from 20 to 60% of the counts in the lower ROI depending upon the Cd source activity, X-ray tube current, and sample concentration. This contributor to the background ROI is time dependent with the decay of the ^{109}Cd source.

Back Scatter: For the 10 mm thick HPGe detector backscatter (from the copper cold finger) does not produce any significant count rate below 70 keV and is not expected to impact the Lower Background ROI.

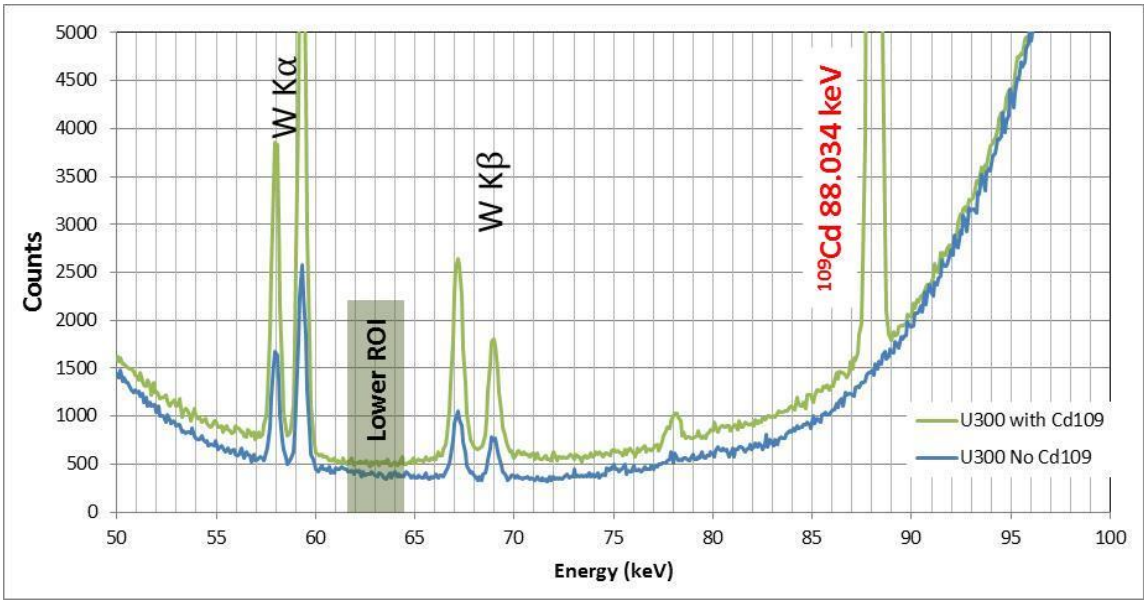

Figure 5. Measured KED transmission spectra illustrating the impact of the ^{109}Cd peak exponential tail on the lower background ROI. The large exponential tail from ^{109}Cd is due to its off axis location in close proximity to the detector and surrounded by the tungsten shield. Count rate in the 88.034 keV peak from ^{109}Cd was 153.5 cps. Note: without the ^{109}Cd source, the count rate minimum is at 70 keV confirming that the Lower ROI includes counts other than from the background.

OTHER CONTRIBUTIONS

It is not clear that the remaining counts in the lower background ROI are attributable to a traditional stepped background. Figure 6 provides a comparison of a measured and MCNP [6] simulated KED spectrum. Comparison of the energy region between 70 and 75 keV with the lower background ROI suggest that an additional 5% of the lower background ROI is not related to a step background. We note that in the energy region of 60 to 75 keV the MCNP simulation severely underestimates the continuum underneath the tungsten X-ray peaks. This difference is in part attributable to the limitations of MCNP for the modeling of X-ray interactions, however, the very noticeable difference in the modeled and measured spectra suggests an additional contributor of unknown origin may exist. (Also note that because coincidence summing is not incorporated into the model, the tungsten K_{β} line intensities are underestimated).

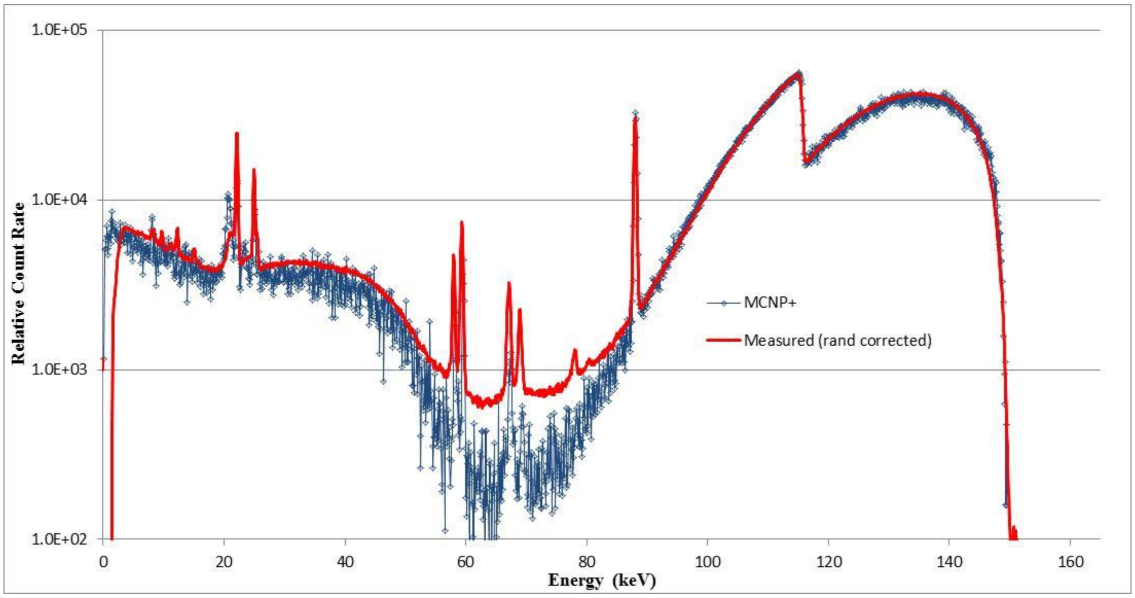

Figure 6. Comparison of the MCNP6 simulation of a KED transmission measurement for a 270 g U/L aqueous sample using corrected uranium photon cross-section libraries with a measured spectrum of the same concentration.

Because the scattering and tailing features of the ^{109}Cd peak are exaggerated compared to the transmitted X-ray characteristic response, we conclude that current use of the Lower Background ROI significantly over estimates the background below the K-edge transmission edge. We also note that the magnitude of the overestimate will change with time as the ^{109}Cd source decays.

As will be discussed, the empirical calibration of the KED measurement "hides" this bias to a large extent at time of calibration, however, as the ^{109}Cd source decays a bias in the reported concentrations will develop.

Representation of the Lower Background ROI Counts – Under development

We are presently investigating a more realistic representation of the background for the KED transmission measurement. Preliminary results based on a semi-empirical model of the low energy portion of the KED spectrum are shown in Figure 7. Although the representation of the background is still under development, the results appear to confirm that almost all of the counts in the lower background ROI used in the existing CHKED analysis are due to tailing from the low energy scattering events unrelated to the step background.

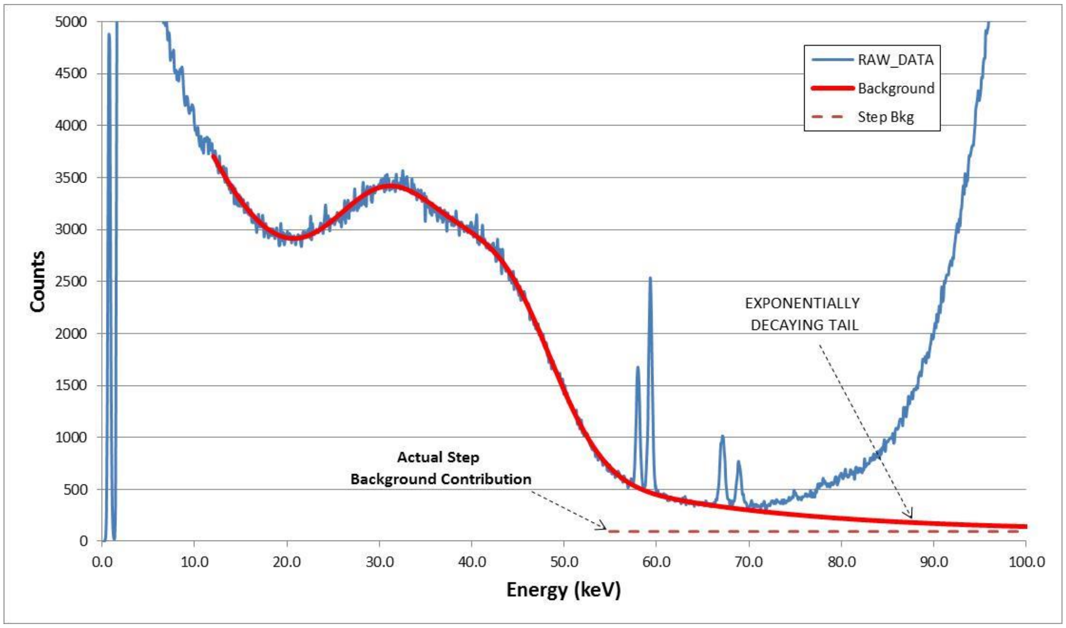

Figure 7. Low energy portion of the KED spectrum from a 321 g U/L sample without the ^{109}Cd source. The solid red line represents a semi-empirical fit to the data.

Bias in the KED Measurement due to the Step Background Correction

From the information available we can't definitively state whether or not the step background contributes at all to the KED transmission spectrum, however, from the above discussions it is evident that the current HKED analysis (VMS and CHKED) over corrects for this effect. In this section we examine the potential impact on the KED transmission results. The KED transmission analysis has historically only been applied to solutions with concentrations exceeding 50 g /L. To examine the potential bias from the step background correction, we examined the KED transmission spectra for a series of uranium solutions with concentrations from 50 g U/L to 322 g U/L.

A KED calibration based on this data set was performed using the traditional KED analysis with step background correction. The step background correction was then adjusted to vary the low background ROIs, a revised calibration was performed and the spectra reanalyzed (Figure 8). The summary results of the various calibrations are presented in Table 1 (no step background is applied for the x0 multiplier while x2 corresponds to subtraction of twice the standard step background values). From these results, we conclude that the impact of the erroneous step background is effectively absorbed by the empirical calibration. Each modification of the step background correction yields a valid calibration even for obviously inappropriate background corrections. This can be seen in Table 1 as the value of the calibration parameter delta-μ can be seen to vary with the background correction. However, although at the time of calibration the approach yields a satisfactory assay result, an increasing bias in the reported concentrations will develop over time as the ^{109}Cd source decays.

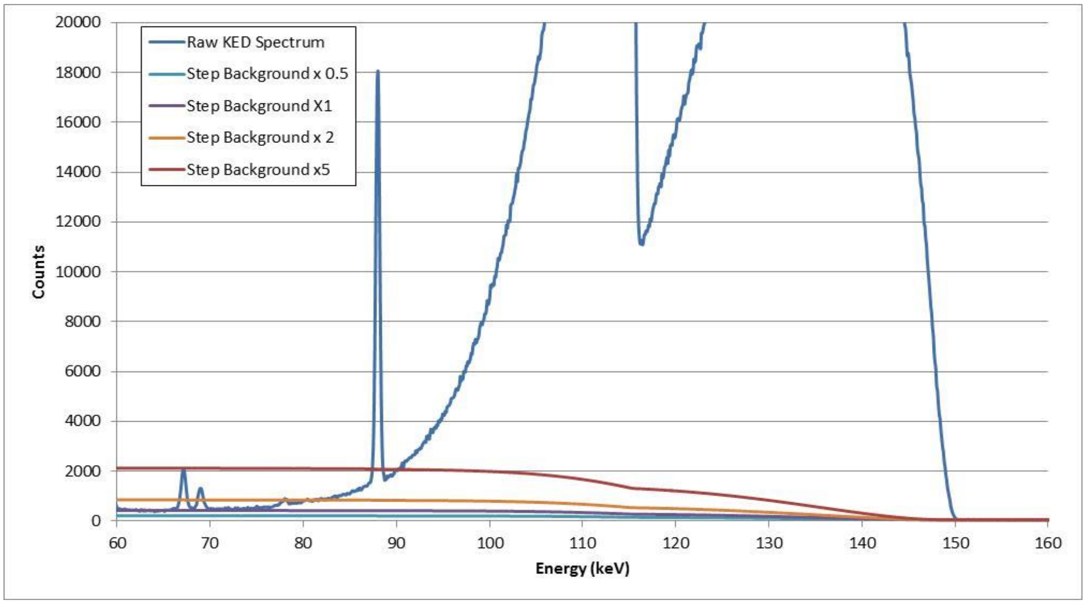

Figure 8. Plot showing the step background corrections applied to the uranium solution data set to generate each calibration.

Table 1. Impact of the Lower Region of Interest on the KED transmission calibration (^{109}Cd peak count rate = 168 cps).

Declared Concentration (g U/L)	Measured Concentration (g U/L)					
	Lower ROI x 0	Lower ROI x 0.5	Lower ROI x 1	Lower ROI x 1.5	Lower ROI x 2	Lower ROI x 5
48.27 ±0.24	47.99 ±0.16	48.08 ±0.16	48.18 ± 0.16	48.28 ± 0.16	48.39 ± 0.16	49.06 ± 0.16
107.30 ±0.54	107.37 ±0.23	107.45 ±0.23	107.53± 0.23	107.60± 0.23	107.68± 0.23	108.19± 0.23
160.90 ± 0.8	159.90 ±0.40	159.95 ±0.40	160.00±0.40	160.04± 0.40	160.09± 0.40	160.37± 0.40
214.60 ±1.07	215.71 ±0.47	215.62 ±0.47	215.53± 0.47	215.44± 0.47	215.34± 0.47	214.72± 0.48
268.21 ±1.34	268.25 ±0.65	268.17 ±0.65	268.08± 0.66	267.99± 0.66	267.9 ± 0.67	267.3 ± 0.70
321.90 ±1.61	321.72 ±0.94	321.61 ±0.94	321.51± 0.95	321.40± 0.96	321.28± 0.97	320.54± 1.03
Average Bias	-0.11%	-0.08%	-0.04%	-0.01%	0.02%	0.24%
St.Dev.	0.43%	0.38%	0.34%	0.33%	0.35%	0.83%
Delta-μ (cm^2/g)	**3.398**	**3.429**	**3.460**	**3.491**	**3.523**	**3.732**

* St. Dev. refers to the standard deviation of the relative difference between the declared and measured concentrations for a given calibration.

Impact of the ^{109}Cd source decay on the Assay Result

As the ^{109}Cd source decays, the ratio of counts in the lower background ROI to the main body of the spectrum changes relative to the count rate ratios obtained during calibration. A smaller background correction is applied making the relative reduction in count rates across the K-edge transition appear smaller and a subsequent under reporting of the solution concentration.

To examine the effect, a ^{109}Cd spectrum was added to the measured spectra to simulate a higher emission rate from the ^{109}Cd source. The simulated count rate in the 88 keV peak was 325 cps at the nominal time of calibration. A ^{109}Cd source that produces a count rate of 325 cps in the 88 keV peak will produce approximately 60% of the counts in the Lower Background ROI. The spectra were then adjusted to simulate the decay of the ^{109}Cd source after 6 months, 1 year and 2 years from calibration. The results from the reanalysis are provided in Table 2 and depicted graphically in Figure 9.

Over the concentration range of 50 to 322 g U/L we expect an average bias of 0.25% to develop after 2 years. However, from these results we can see that the impact is greater for more highly concentrated (self filtering) solutions and the bias introduced will exceed the ITV for the HKED system within the 2 years.

Table 2. Predicted change in assay results based on decay of the ^{109}Cd source ($\tau_{½}$ =1.267 y).

Results at Calibration		Results at 6 months		Results at 1 year		Results at 2 years	
48.2	± 0.16	48.2	± 0.16	48.21	± 0.16	48.21	± 0.16
107.64	± 0.23	107.69	± 0.23	107.73	± 0.23	107.77	± 0.23
215.52	± 0.47	215.73	± 0.47	215.89	± 0.47	216.11	± 0.47
268.07	± 0.65	268.41	± 0.66	268.66	± 0.66	269.01	± 0.66
321.3	± 0.94	321.84	± 0.95	322.25	± 0.95	322.8	± 0.95
Average Bias		-0.09%		-0.16%		-0.25%	
Standard Deviation		0.06%		0.11%		0.18%	

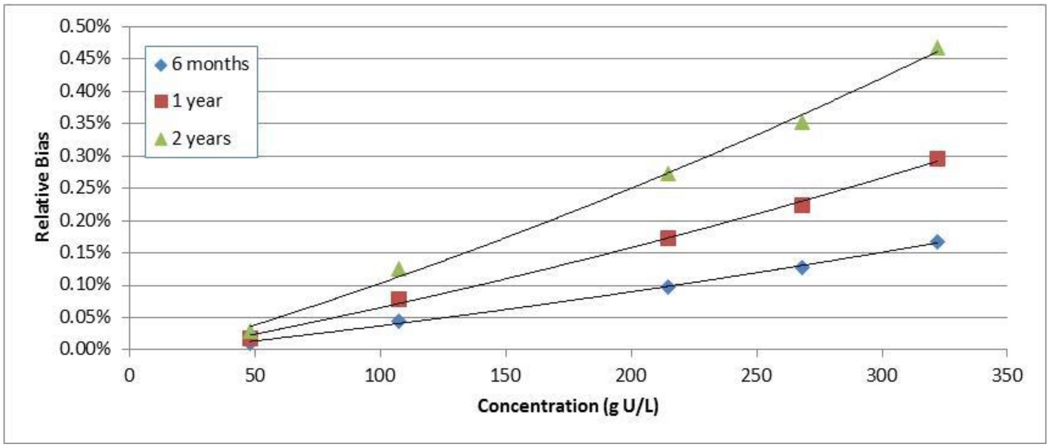

Figure 9. Relative change in response as a function of time for the uranium solutions due to the decay of the ^{109}Cd source – where the reference spectra acquired using a 5 mA current setting.

Impact of Reference Spectrum Current Setting.

It is common practice to acquire the reference spectrum for the KED analysis with the X-ray generator at a reduced setting (i.e. 5 mA vs 15mA) to limit the impact of the dead-time, pile-up and spectral shape on the analysis. While the rationale behind that approach will be the subject of another paper, here we limit the discussion to the impact on the correction for the step background. If we reapply the above analysis approach using a 15mA based reference spectrum, we find that using a reference spectrum acquired with reduced X-ray generator current exaggerates the impact of the decay of the ^{109}Cd source. Figure 10 shows the relative bias as a function of concentration and decay time, where the reference spectra was obtained with a 15mA setting of the X-ray generator, while in Figure 10 the reference spectrum was acquired with

5mA current setting (note in both instances the solution spectra were acquired at 15mA). In the case of the ORNL system (the source of the data) the biases are reduced by a factor of two if the reference spectrum is obtained with the higher current setting. This is simply because the ^{109}Cd source has a lesser impact on the lower background ROI.

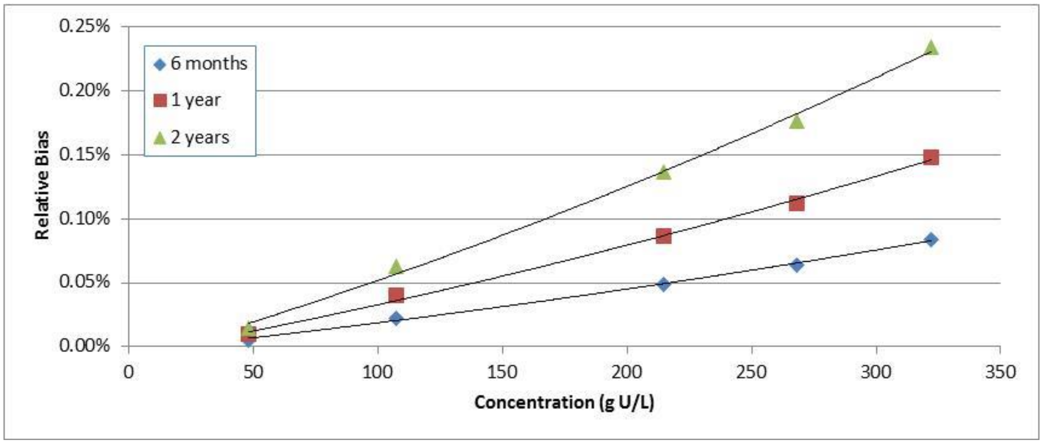

Figure 10. Relative change in response as a function of time for the uranium solutions due to the decay of the ^{109}Cd source – where the reference spectra acquired using a 15 mA current setting.

SUMMARY

The traditional correction based on the step background assumption in the case of the KED transmission analysis does not accurately represent the properties of the KED background and over estimates the background that is subtracted from the KED spectrum. The KED transmission analysis implemented in the VMS and CHKED software accommodates this effect over the calibration range and at the time of calibration, biases will not be evident. However, as the ^{109}Cd source decays, the fractional count rate in the lower background ROI changes relative to the transmitted spectrum resulting in a bias that increases with both time and concentration. These biases, although small (~0.2 to 0.5%) are significant compared to the KED measurement precision, accuracy, and performance target values. To minimize this effect, the KED transmission measurement must be recalibrated on a 6 to 12 month interval.

We have not yet evaluated the impact of the background correction on plutonium assay or mixed actinide (e.g. U=Pu solutions). Although the impact on the plutonium assay is expected to be less severe because the background decreases at higher energies.

As shown in Figure 4, the count rate reaches a minimum at approximately 70 keV so that the current 61.75 to 64.75 keV window, without any contribution from ^{109}Cd, overstates the background correction. This is in part due to the higher energy Compton scattered events extending into the background ROI and due to the lower energy tail of the transmitted Bremsstrahlung spectrum through the stainless steel filter. We have not, in this discussion, addressed the “correct” description of the background, only that the description used by the commercial software packages is wrong and will introduce biases in the assay result in the absence of frequent recalibrations.

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