Designation: C1855 – 18

Standard Test Method for
Determination of Uranium and Plutonium Concentration in Aqueous Solutions Using Hybrid K-Edge Densitometry and X-Ray Fluorescence[1]

This standard is issued under the fixed designation C1855; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method specifies the determination of the volumetric uranium and plutonium concentrations, typically, in nitric acid solutions through the combination of K-Edge absorption Densitometry (KED) and K X-Ray fluorescence (XRF) using an X-Ray generator. It is known as the "Hybrid K-Edge" (HKED) technique whose original implementation is described in Ref (**1**).[2] The method is applicable to dissolver (input) solutions and product solutions. The test method also specifies the determination of low concentrations (<50 g/L) of U and Pu using XRF measurements alone (the "stand-alone XRF" mode). Using the XRF measurement in the stand-alone mode, solutions in the 0.2 g/L to 50 g/L range of Pu with or without U and solutions in the 0.2 g/L to 50 g/L range of U with or without Pu are commonly measured.

1.2 This test method is applicable to the following common-use conditions:

1.2.1 Spent nuclear fuel reprocessing and fuel production.

1.2.2 Homogeneous aqueous solutions contained in cylindrical vials or cuvettes. HKED systems may use two separate sample containers, namely a rectangular cuvette for KED and a cylindrical vial for XRF. Alternatively, there are HKED systems that use a sample contained in a single cylindrical vial, for both K-Edge and XRF.

1.2.3 The results produced by the two sample configuration (a rectangular cuvette for K-Edge densitometry and a cylindrical vial for XRF) are compliant with the International Target Values (ITV) (**1**).

1.2.4 The precision results produced by the single cylindrical vial configuration are degraded in comparison to the two container system.

1.2.5 This test method is applicable to facilities that do not adopt the ITVs, but have their own Data Quality Objectives (DQO).

1.2.6 Solutions which contain uranium and plutonium with uranium concentration of 150 to 250 g/L and a U:Pu ratio of 100:1 typically, in the presence of fission products with β, γ, activity of up to 10 TBq/L.

1.2.6.1 This test method is not applicable to samples where a minor element such as U needs to be quantified in which Pu is the major element.

1.2.6.2 This test method is applicable for common use process control applications for quantifying Pu in the 5 g/L to 30 g/L range using XRF only in the presence of up to ~10 % (~100 000 ppm) of transuranic impurities (predominantly U and Am). In this application, the impurity concentration in the Pu samples is not quantified. Additional uncertainties must be estimated and factored in the Pu concentration results.

1.2.7 Solutions containing 50 g/L to 400 g/L of uranium alone.

1.2.8 Solutions containing 50 g/L to 400 g/L of plutonium alone.

1.2.9 Solutions with low concentrations of U and Pu, typically in the 0.2 g/L to 50 g/L range.

1.2.10 The concentration ranges given in 1.2.6 – 1.2.9 are application of the HKED technique for Materials Control and Accountancy (MC&A) purposes. For process control applications where precision requirements are less stringent, KED method can be used to assay samples with lower concentrations of U or Pu (down to 30 g/L).

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.10 on Non Destructive Assay.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C859 Terminology Relating to Nuclear Materials

C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry

C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials

C1490 Guide for the Selection, Training and Qualification of Nondestructive Assay (NDA) Personnel

C1592/C1592M Guide for Making Quality Nondestructive Assay Measurements (Withdrawn 2018)[4]

C1673 Terminology of C26.10 Nondestructive Assay Methods

2.2 *ISO Standards:*[5]

ISO 13464 Simultaneous Determination of Uranium and Plutonium in Dissolver Solutions from Reprocessing Plants – Combined Method using K-absorption Edge and X-Ray Fluorescence Spectrometry

ISO/IEC 17025 General Requirements for the Competence of Testing and Calibration Laboratories

ISO 7870-2 Control Charts – Part 2: Shewhart Control Charts

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology C859 or C1673.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorption edge*—an absorption edge is the discontinuity in the mass attenuation coefficient of an element at the characteristic energy corresponding to the electron binding energy of the given atomic shell. When the energy of the incident photon exceeds the binding energy of an electron in its shell, a photo-electric interaction becomes energetically possible with this electron. This leads to an abrupt increase in the mass attenuation coefficient, and hence a discontinuity in the variation of the mass attenuation coefficient as a function of photon energy.

3.2.2 *End-point Energy*—the highest energy of the bremsstrahlung continuum, corresponding to the maximum energy of the X-Ray tube's electron beam. It can be determined by extrapolating the KED pulse height distribution measured from a blank to zero, in the vicinity of the cut-off, after the pile-up correction has been applied.

3.2.3 *K-Edge Densitometry*—technique to determine elemental concentrations in a sample by measuring the ratio of photon transmission across the energy characteristic of the actinide K-Edge cross-section of the element present in the sample.

3.2.4 *major element, n*—actinide element of highest concentration in the solution.

3.2.5 *minor element, n*—actinide element with concentrations typically 50 to 100 times lower than the concentration of the major element. Due to its low relative concentration, the minor element is typically measured using XRF.

3.2.6 *self-fluorescence, n*—X-Ray fluorescence of an actinide in the specimen due to excitation by the decay of radionuclides present in the solution; the interrogating X-Ray beam is turned off.

4. Summary of Test Method

4.1 The Hybrid K-Edge method is a highly element specific method for determining the concentration of uranium and transuranic elements. The method was developed for application to both feed and product aqueous solution generated in the process of spent fuel.

4.2 Compare to destructive analysis (DA), the HKED method is rapid. HKED method requires minimal sample preparation and handling, and generates minimal amount of radioactive waste.

4.3 The HKED instrument can be operated in three different modes: (*1*) KED densitometry only where U or Pu, or both, are measured in the 50 g/L to 400 g/L concentration range, (*2*) Hybrid mode where the concentration of U is determined using KED densitometry and the U:Pu (100:1 typically) ratio is determined using XRF measurements, (*3*) Stand-alone XRF for low U and Pu concentrations (0.2 g/L to 50 g/L).

4.4 This method relies on a fixed and controlled geometry for the K-Edge and XRF measurements.

4.5 This test method details the apparatus, calibration, measurement protocol, calculations, and the demonstrated precision and bias of the HKED technique. Also presented are suggested quality control measurements to track and maintain the performance of the HKED equipment.

4.6 HKED involves the irradiation of sample solutions by a continuous-energy X-Ray (Bremsstrahlung) beam. The concentration of the major element is determined by measuring the transmission of the incident X-Ray beam across the characteristic K-Edge energy of the element. Simultaneously, the intensities of prominent K_α X-Rays fluoresced by the incident X-Ray beam are used to determine the element ratios of actinides present in the sample. The minor element concentration is calculated from the product of densitometry value for the major element concentration and the elemental ratio of the actinides from the XRF measurement.

4.7 For the determination of U or Pu concentrations in the 50 g/L to 400 g/L range, the method uses densitometry (KED) only.

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[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

4.8 For the determination of U or Pu concentrations in the 0.2 g/L to 50 g/L, the XRF method is typically used in the stand-alone mode.

5. Significance and Use

5.1 The HKED technique is highly element specific and depends upon a well-known controlled geometry.

5.2 The HKED technique can provide concentration measurements of actinides in solutions with precision typically better than 0.3 % for uranium concentrations >50 g/L and 1 % for plutonium in typical U-Pu solutions for a typical measurement time of 3 × 1000 s (3 replicates, 1000 s live time each) (1).

5.3 For pure plutonium only product solutions, the KED technique can achieve measurement precisions better than 0.3 % for plutonium concentrations >50 g/L for a typical measurement time of 3 × 1000 s.

5.4 For pure uranium only solutions, precisions of better than 0.3 % can be achieved using the KED technique for uranium concentrations >50 g/L, for a typical measurement time of 3 × 3600 s.

5.5 For uranium only or plutonium only solutions of concentrations approximately 1 g/L, assayed using XRF, a measurement precision of 1.0 % has been achieved (1). For solutions of concentration approximately 50 g/L, assayed using XRF, measurement precisions of 0.2 % or better have been achieved. The typical measurement time for stand-alone XRF assay is 3 × 3000 s.

5.6 Quality Control (QC) samples are assayed for a typical measurement time of 3 × 3000 s.

5.7 It is applicable when solutions to be measured are homogeneous with respect to chemical composition.

5.8 Results are typically used for fuel fabrication, process control, quality control, material control and accountancy, and safeguards in nuclear fuel reprocessing plants. Each application can have its own data quality objectives (Guide C1068).

5.9 The HKED instrument may use a single cylindrical vial for both the KED and XRF measurements, or separate sample containers for KED and XRF. The typical values for the path length of the rectangular cuvette and the inner diameter of the cylindrical vial are given in 7.8.

5.10 The transfer of the sample into the HKED system can be accomplished either horizontally by means of a suitably designed sample conveyor system coupled to a shielded glovebox or hot cell facility or vertically through a pneumatic sample transfer system.

5.11 The U and Pu concentrations measured by HKED are dependent on the sample temperature. The analysis software includes a normalization of the measured concentration at the ambient room temperature to a reference temperature of 25 °C. The ambient room temperature is input into the analysis software. HKED has been employed as a rapid alternative to destructive chemical analyses, such as Isotope Dilution Mass Spectroscopy (IDMS) or titration, because there is minimal sample preparation, and precision of HKED is comparable to the precision of such chemical analyses. This is especially useful when high sample throughput is important.

5.12 For the three modes of operation that are possibly, namely, K-Edge only, Hybrid K-Edge/XRF, and Stand-alone XRF, the uncertainty levels that can be achieved for U and U/Pu samples have been established for routine safeguards measurements are described in the ITV (2).

6. Interferences

6.1 *K-Edge Measurement*—In the energy region of interest, the intensity of the transmitted X-Ray beam for KED is about three orders of magnitude higher than that obtained from the self-radiation of typical input solutions. In view of this, the KED measurement is insensitive to self-radiation from input solutions. This is true for fuels with relatively short cooling times (1).

6.2 If the system is calibrated for samples in a limited range of U:Pu ratios, for example 100:1, in a given mass range, (50 g/L to 400 g/L), but a sample with a much higher U:Pu ratio is measured, the attenuation of the bremsstrahlung by the minor actinide (Pu) will cause a bias on the KED results from the major actinide (U). The hybrid XRF measurement of samples with U and Pu may be subject to the following types of interferences.

6.2.1 The $UK_{\alpha1}$ and the $PuK_{\alpha2}$ peaks overlap and interfere with each other. In the current region of interest (ROI) based approach, a correction is applied for this interference.

6.2.2 The $UK_{\alpha2}$ and $UK_{\alpha3}$ peaks overlap, and so do $UK_{\beta1}$ and $UK_{\beta3}$. An ROI that includes $UK_{\alpha2}$ and $UK_{\alpha3}$, and another ROI that includes $UK_{\beta1}$ and $UK_{\beta3}$ are set up and used during calibration as well as sample analysis. Therefore no bias results from interferences in these cases.

6.2.3 The $AmK_{\alpha1}$ ROI is used to provide a correction for the presence of $AmK_{\alpha2}$ X-Rays in the $PuK_{\alpha1}$ background ROI.

6.2.4 Dissolver solutions (or "input" solutions) from spent nuclear fuels are chemically complex and highly radioactive. The spectrum from a dissolver solution is dominated by gamma rays from a few longer lived fission products such as ^{137}Cs, ^{144}Ce, ^{154}Eu, and ^{155}Eu. The gamma rays from fission products cause the excitation of uranium and plutonium in the sample and result in the emission of their characteristic X-Rays. This is termed "self-radiation."

6.2.4.1 To correct for self-radiation effects, a separate passive spectrum can be acquired by turning off the X-Rays. Alternatively, an empirical derived correction factor can be used by relating the additional counts due to fission products in the energy range 125 keV to 131 keV, to the passive count rates in the ROIs for the evaluation of the net X-Ray peak counts (1).

6.2.5 Besides self-radiation, the downscattering of the fission product gamma rays increases the continuum levels, degrading the precision of the measurements.

7. Apparatus

7.1 Standard equipment for high resolution gamma ray spectroscopy, including two high resolution high-purity germanium detectors each with electronics for fast pulse processing, a multichannel analyzer and a dedicated software package are used for spectrum acquisition and evaluation. Electronics should be capable of handling a count rate of at least 50 000 counts per second (cps).

7.2 Planar HPGe detectors with an active area of 100 mm^2 to 200 mm^2 and a thickness of 10 mm are generally used.

7.3 The energy resolution is demonstrated using ^{109}Cd and ^{57}Co by measurement of the FWHM of the gamma ray peaks for these two isotopes with the same electronics configuration as used under routine measurement conditions. During system installation and set up, the energy resolution (FWHM) of the KED and XRF detectors is demonstrated using a ^{57}Co source and is typically 570 eV or better at 122 keV at a shaping time of 2.0 microseconds. During operation, the energy resolution is monitored using the FWHM at the 88 keV gamma ray peak from ^{109}Cd and is typically 520 eV or better at a count rate of approximately 50 000 cps.

7.4 Some instruments use a sample changer. The position of the samples must be controlled to within 0.3 mm to control the misalignment from causing more than 0.1 % bias.

7.5 ^{109}Cd source is typically affixed near the detectors for energy calibration and gain stabilization. The typical count rates from the ^{109}Cd source are 2000 cps (peak/background ratio of 2:1).

7.6 X-Ray equipment consisting of a cooled X-Ray tube, high voltage power supply, and operation console. An X-Ray tube with a window diameter not exceeding 50 mm is recommended.

7.7 The X-Ray tube is nominally run at 150 kV and 5 mA to 15 mA. Stability of the high voltage supply should be less than 0.1 % with adjustable high-voltage and current controls.

7.8 *Sample Containers:*

7.8.1 Either a single cylindrical vial or a combination of rectangular cuvette and cylindrical vial are typical. In a system that uses two sample containers (see Fig. A1.1, Annex A1), the typical path length of the X-Rays through the rectangular cuvette is 2.0 cm, and the typical inner diameter of the cylindrical vial is 0.9 cm. In a system where the sample contained in a single cylindrical vial is used for KED and XRF, the typical inner diameter of the vial is 1.4 cm. These path lengths are dependent on the areal density of the samples and must be selected appropriately. For example, a measurement precision of 0.23 % can be achieved in a KED assay of a 150 g/L uranium solution contained in a cuvette of path length equal to 2.0 cm (**1**). This corresponds to an areal density of 0.3 g/cm^2. To achieve a similar precision for a 100 g/L uranium solution, one will need to use a cuvette of path length equal to 3.0 cm (areal density = 0.3 g/cm^2). Refer to 13.3 for additional guidelines on areal densities of samples.

7.9 The K-Edge measurement depends on the effective path length of the X-Ray beam through the solution. For meeting the ITVs this geometrical parameter must be carefully controlled, because its fractional uncertainty propagates directly into the fractional uncertainty of the uranium or plutonium concentration measurement. The uncertainty on the path length in this case must be small compared to other sources of uncertainty (0.01 % typically). The preferred type of sample vials are spectroscopy cells whose thickness is known to a precision less than 0.01 %.

7.10 In HKED systems that use a single cylindrical vial for both KED and XRF, the uncertainty in the KED measurements due to uncertainty in the pathlength is ~0.07 % typically. The poorer uncertainty is because of the curvature of the cylindrical container. The uncertainty in sample positioning is typically <0.1 %.

7.11 The vial wall thickness should be as acceptably thin as possible in order to manage the intensity of scattered radiation from the X-Ray beam while maintaining structural integrity and safe containment of the solutions.

7.12 If secondary containment is required for the sample container (for example, to prevent contamination of the system), it should allow for transmission of the X-Rays from the generator and the sample with minimal interference. A schematic drawing of the HKED system geometry is shown in Fig. A1.2 in Annex A1. The drawing shows the configuration with a composite sample container consisting of a quartz cuvette for the KED measurement and a polyethylene vial for XRF.

8. Hazards

8.1 *Safety Hazards:*

8.1.1 The high voltage supply for the X-Ray generator has sufficient power to be a lethal hazard. Appropriate precautions should be taken when performing maintenance or during initial system set up. The HV generator must be properly grounded.

8.1.2 The X-Ray generator creates a high level of ionizing radiation when energized, that can result in a lethal dose in a short period of time (on the order of minutes). Appropriate precautions should be taken when performing maintenance or during initial system set up.

8.1.3 High resolution gamma-ray detectors operate at voltages as high as 5 kV. Appropriate precautions should be taken when using, assembling, and disassembling these systems.

8.1.4 Some detectors have beryllium windows which are fragile and considered hazardous due to oxidation and inhalation hazard due to BeO.

8.1.5 Collimators and shielding may use materials (for example, lead and cadmium) which are considered toxic, and can be physically heavy and difficult to maneuver. Proper care in their use and disposal are required.

8.1.6 Uranium-, plutonium-, and fission-product-bearing materials present both chemical and radiological hazards. The analyst should be aware of these hazards and take appropriate precautions.

8.1.7 The solutions are typically highly acidic (for example, nitric or hydrofluoric acid). Proper care must be taken in the preparation and handling of these solutions.

8.1.8 The X-Ray system is connected to a three phase external power supply of 220/230/240 volts. Proper procedure must be followed in energizing or de-energizing the X-Ray tube to prevent arcing.

8.1.9 The operator must be cognizant of the possibility of liquid leaking from the cooler or the generator, leading to a slippery condition or electrocution.

8.1.10 Proper maintenance of high voltage cable in the X-Ray system is necessary to prevent arcing in the X-Ray system.

8.1.11 The high voltage generator must be grounded to the earth to minimize the potential for arcing of the system.

8.1.12 Sealed calibration standards stored for an extended period of time pose a hazard due to build-up of pressure which could result in the seals cracking, leading to spread of contamination.

8.2 *Technical Hazards:*

8.2.1 Personnel operating the HKED system must have the appropriate qualifications and training, in accordance with recommendations found in Guides C1297 and C1490.

8.2.2 The detector and the signal processing electronics must be properly grounded to eliminate ground loops.

8.2.3 Electromagnetic interference, vibrations, and coupling to a hot cell (mechanical or electrical, or both) can also introduce noise artifacts and must be mitigated.

8.2.4 Inhomogeneity of the sample solution due to residues/sedimentation or precipitation will impact the correlation of the transmission of the X-Rays to the concentration of U and Pu in the solution.

8.2.5 If the sample contained in the vial is not used immediately after being prepared, and instead stored, evaporation will occur. The evaporation rate could be as much as 0.2 % per hour and will result in an overestimation of the U or Pu concentration in the container the sample was drawn from. The rate of evaporation depends on the temperature, humidity and the fill height of the solution in the vial.

8.2.6 The fill height of the solution inside the container must be high enough in order to envelope the X-Ray beam passing through it.

8.2.7 The activity of the ^{109}Cd source must be high enough to ensure that the 88 keV peak is detected above the continuum and can be reliably used for gain stabilization and small enough to avoid random coincidence summing between the 22 keV X-Ray and the 88 keV gamma ray lines.

8.2.8 The matrix of the reference (blank) solution must be the same as the matrix of the sample.

8.2.9 The high voltage generator and the X-Ray tube must be cooled to a consistent temperature; otherwise the output could vary.

8.2.10 Solutions with high concentrations of uranium or plutonium can cause radiolysis in the matrix, leading to the formation of bubbles. The rate of radiolysis on the HKED results depends on the isotopic composition of uranium or plutonium in the sample. The impact on the results is not predictable. Shorter lived isotopes can cause higher radiolysis (^{241}Pu, ^{238}Pu, ^{240}Pu) than longer lived isotopes such as ^{239}Pu.

8.2.11 Partial warm-up of Ge detectors can lead to gain shift and degradation in energy resolution, and resulting in incorrect results.

8.2.12 Sample temperature is required as an operator input for the normalization of the final result. The appropriate reference temperature must be indicated in the software set up. Entering an incorrect temperature leads to a bias in the result (see Table 1).

TABLE 1 Summary of Uncertainties for K-Edge Densitometry Measurement for a Two Sample Container System (Rectangular Cuvette for KED and Cylindrical Vial for XRF)

Uncertainty Component	Magnitude of Uncertainty (%)	Comment
Counting precision (3 times 1000 s live time)	0.15 %	Concentration range: 150 – 300 g/L
Cell length	0.01 % <0.1 %	For individual cuvette Variation for a production batch of cuvettes
Cell positioning	<0.1 %	Determined by dimensional tolerances for sample holder
Sample matrix	<0.2 %	Can be taken into account in calibration
Uranium isotopic composition	0.013 %	Per % change of ^{235}U enrichment
Sample temperature	0.05 %	Per degree centigrade of sample temperature
Calibration	0.2 %	Uncertainty in reference concentration from chemical analysis
Non-linearity	<0.2 %	Concentration range: 150 – 300 g/L
Instrument variability	<0.3 %	Monitored from control charts
Total	0.5 %	Summed in quadrature

8.2.13 Sample vials from different batches or vendors may have varying dimensions and tolerances, which can introduce bias in the result if not accounted for.

9. Preparation of Apparatus

9.1 Ensure that the high-purity germanium detectors and signal processing modules (for example, Amplifier, Analog to Digital Converters, Stabilizer) are set up properly according to the Operations Manual.

9.2 Optimize the shaping time of the amplifier so that it provides the highest throughput without degrading spectroscopic quality of the data, for example, the energy resolution. The typical shaping time parameter for an analog amplifier is 1 µs (Gaussian shape), or digital equivalent with a Rise-time of 1.8 µs and Flat-top of 0.6 µs (trapezoidal shape). Adjust the amplifier gain and pole-zero. For optimum performance the system dead time should not exceed 30 %. The X-Ray tube current can be adjusted if necessary to reduce the dead time to desired levels. The energy range of the spectra for the HPGe detectors in the K-Edge and XRF sub-systems is 0 to about 170 keV and a minimum of 2048 channels. When set up in this way and in order to achieve near optimal performance, the energy resolution (FWHM) should be less than about 520 eV at the 88 keV gamma line from ^{109}Cd, when the total count rate is 50 000 cps. If the energy resolution is worse than 520 eV, investigate.

9.3 Enable pile-up-rejection.

9.4 Sources of ^{109}Cd are mounted in front of the detectors (away from the X-Ray beam path) for performing energy and shape calibration, and gain stabilization. Gain stabilization is set up around the 88 keV gamma ray peak from ^{109}Cd. The 22 keV X-Ray peak can be used in addition to the 88 keV gamma peak.

9.5 Monitor that the HV setting corresponds to the intended value using the end-point energy of K-Edge spectrum. Set up the acquisition and analysis software.

9.6 Of critical importance are parameters such as the X-Ray voltage and current, source certificates and declarations, Regions of Interest (ROI) before (left) and after (right) the U and Pu K-Edges for the K-Edge analysis, peak analysis parameters for the U and Pu K_α and K_β X-Ray peaks for the XRF analysis, and ROIs for continuum subtraction.

9.7 Typical KED ROIs bounds are shown in Table 2. Figs. 1 and 2 show a spectrum of the K-Edge spectrum with the ROI limits.

9.8 *XRF ROIs*—Typically the ROIs for the XRF analysis are set according to the following rules:

9.8.1 Bounds of ROIs are set ±1.1 FWHM from the peak centroid.

9.8.2 Background windows are centered 1.7 keV below and 3.7 keV above the peak centroid.

9.8.3 Exception is $U_{k\beta 1,3}$ double peak complex; peak ROI is from $U_{K\beta 3} - 1.1$ FWHM to $U_{K\beta 1} +$ FWHM.

9.8.4 Three other ROIs are included beyond those for the $U_{k\alpha 2}$, $U_{k\alpha 1}$, $U_{k\beta 1}$, and $Pu_{K\alpha 1}$. These are:

9.8.4.1 The Am_{Ka1} ROI is available to provide a correction for the presence of Am_{Ka2} X-Rays in the Pu_{Ka1} background ROI. The ROI is also used to quantify Am in the solution if present.

9.8.4.2 Background window between ^{154}Eu (123.07 keV) and ^{144}Ce (133.54 keV) to account for passive self-fluorescence.

9.8.4.3 ^{154}Eu (123.07 keV) for bias correction.

9.8.5 Table 3 shows example ROI limits used in XRF analysis. Fig. 3 illustrates the XRF spectrum with the ROI window limits.

9.9 Other set-ups include count times, number of replicate counts for each assay, sample changer set up (if there is an automated sample changer), counting protocol set up (K-Edge only or XRF only or Hybrid), quality control, and reporting.

9.10 Perform a warm-up procedure of the X-Ray tube following the X-Ray tube manufacturer's recommendations.

10. Calibration

10.1 The purpose of calibration is to establish the relationship between concentration and the instrument response. In case of the KED measurement it is the ratio of transmissions across the K-absorption edge and in the case of XRF it is the count rate from the fluoresced X-Rays in the sample. This section describes a typical calibration procedure for U or Pu, or both, contained in aqueous solutions. The calibration should remain valid as long as the QA/QC permits.

TABLE 2 Typical Bounds for KED Regions of Interest

KED ROI	ROI Bounds, keV	
	Lower	Upper
Left Background	61.8	64.8
Right Background	151.9	158.4
U K-Edge Lower Window	107.2	113.3
U K-Edge Upper & Pu K-Edge Lower Window	117.3	119.4
Pu K-Edge Upper Window	123.5	130.2

10.2 The calibration in the three operating modes requires reference materials that are prepared in accordance with Guide C1128 and Practice C1168 or any other international consensus standard (ISO/IEC 17025). These materials must be prepared shortly (within a few days) before the calibration measurement campaign is begun. This is to avoid any changes in the concentration values because of evaporation and other degradation mechanisms.

10.3 A blank nitric acid solution not containing U or Pu, similar in concentration to that of the sample solutions (typically 3 or 4 mol/L).

10.4 A set of three or more synthetic U-Pu solutions simulating the characteristics of feed solutions with respect to uranium concentration (~50 g/L to 400 g/L), U/Pu ratio (typically 100 to 150) spanning the expected measurement range, and nitrate concentration (typically 3 or 4 mol/L). The uncertainty on the calibration standards must be specified to meet the data quality objectives (DQO).

10.5 To perform uranium or plutonium only calibration using stand-alone KED measurements, measure a set of three or more uranium or plutonium only calibration solutions ideally spanning the range of expected uranium or plutonium concentrations (for example, 50 g/L to 400 g/L), and nitric acid concentration (typically 3 or 4 mol/L). The uncertainty on the calibration standards must be specified to meet the data quality objectives (DQO).

10.6 To perform XRF only calibration for measuring low uranium or plutonium concentrations, measure a set of three or more U or Pu only calibration solutions simulating the characteristics of process solutions with respect to uranium or plutonium concentration (0.2 g/L to 50 g/L), and nitric acid concentration (typically 3 or 4 mol/L). The uncertainty on the calibration standards must be specified to meet the data quality objectives (DQO).

10.7 The high voltage is routinely set to 150 kV. The current is set to an appropriate value (a few milli-amperes) in order to achieve the desired counting statistics and dead time.

10.8 For measuring the blank KED reference (for example, nitric acid solution), the current is set to a reduced value in order to avoid the excessive count rate in the KED detector.

10.9 Measure the blank solution with the XRF detector at the same current as that set during sample measurement.

10.10 Acquire simultaneous K-Edge and XRF spectra from the calibration solutions under the same measurement conditions (tube current, voltage, and measurement geometry) as for the unknowns. It is recommended to perform several repeat measurements on each standard, based on the envisioned measurement conditions to reduce the uncertainty and to demonstrate repeatability. This is to achieve a calibration uncertainty (precision) that is less than the targeted uncertainty in the sample measurement.

10.11 Acquire XRF spectra using synthetic U or Pu only solutions under the same measurement conditions as for the unknowns.