ORNL/TM-2024/3298

Application of Hybrid K-Edge Densitometry in Reprocessing Facilities

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July 2024

OAK RIDGE National Laboratory

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Nuclear Nonproliferation Division

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831
managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ABBREVIATIONS

cps	counts per second
FWHM	full width at half maximum
HKED	hybrid K-edge densitometry and x-ray fluorescence
HPGe	high-purity germanium
PUREX	plutonium–uranium extraction
ROI	region of interest
XRF	x-ray fluorescence

EXECUTIVE SUMMARY

During reprocessing operations, accurately determining the elemental concentrations of uranium and plutonium is critical for nuclear security. Reprocessing facilities processes hundreds of tons of nuclear material annually, requiring accurate measurements to ensure effective nuclear material control and accountability. Hybrid K-edge densitometry (HKED) system combines K-edge absorption densitometry with x-ray fluorescence to measure actinide elemental concentrations with a low uncertainty. This system uses high-purity germanium gamma-ray detectors and advanced signal processing equipment to detect x-ray accurately. This document provides guidance on how to achieve effective performance from an HKED system for measuring uranium and plutonium concentrations in reprocessing facilities. It includes best practices for the setup and operation of an HKED system, while highlighting factors influencing uncertainties.

1. INTRODUCTION

Reprocessing used fuel allows the recovery of uranium and plutonium that would otherwise be disposed of as waste. Most of the reprocessed fuel (about 96%) is uranium, of which less than 1% is fissile ^{235}U (abundance of 0.4%–0.8%) and up to 1% is plutonium [1]. Both materials obtained from recycling can be used as fresh fuel, saving up to 30% of the natural uranium otherwise needed. Reprocessed uranium is particularly valuable for its fertile potential. Through neutron capture, it can be transformed into ^{239}Pu, a value fuel source to power the same reactor where it was formed.

The well-proven hydrometallurgical PUREX (plutonium uranium extraction) process, widely employed for uranium and plutonium separation, operates by dissolving fuel elements in concentrated nitric acid. Subsequent solvent extraction steps effectively isolate plutonium and uranium. These recovered materials can then be reintroduced into the fuel cycle: uranium returns to the conversion plant for re-enrichment, whereas plutonium is directed to MOX fuel fabrication. Additionally, neptunium, potentially used for generating ^{238}Pu for space mission thermoelectric generators, can also be recovered, depending on the intended application.

During reprocessing operations, it is necessary to accurately determine the heavy metal elemental concentrations, such as uranium and plutonium, for nuclear security. Because typically hundreds of tons of nuclear material are processed, accurate measurements are essential for effective nuclear material control and accountability. In other words, the uncertainty of measurements should be small. Hybrid K-Edge densitometry and x-ray fluorescence (HKED) is a very useful technique for determining actinide elemental concentrations with a low uncertainty. The HKED relies on x-ray detection and uses high-purity germanium gamma-ray detectors and signal processing equipment that is commonly employed in gamma spectrometry.

Application of HKED in a reprocessing facility can enhance nuclear security by:

- Providing accurate, near-real-time monitoring, and characterization of spent nuclear fuel, which allows the operator to detect irregularities or unauthorized removal, including in small quantities almost instantly
- Providing continuous process monitoring to detect unauthorized changes or theft, which enables the operator to detect unauthorized removal as well as provides indicators for any sabotage event
- Accurately characterizing nuclear wastes for storage and transportation, which may include coupling with other systems to maintain continuity of knowledge once it is established
- Integrating into the security infrastructure to diagnose and investigate abnormal or suspicious activities, serving as a valuable tool during any malicious or sabotage events

Similarly, HKED finds application in other nuclear facilities for diverse purposes, such as:

- Nuclear research laboratories, including isotope production for safety, quality assurance, and security, where fuel and isotopes would be of interest to nuclear security
- Mixed oxide fuel fabrication facilities for material accountability and quality control

2. HYBRID K-EDGE DENSITOMETRY PRINCIPLE

In the late 1970s and 1980s, Herbert Ottmar and Heinrich Eberle, working at Kernforschungszentrum Karlsruhe in Karlsruhe, Germany, developed a combined system based on the principles of continuous source K-edge absorption edge densitometry (KED) and x-ray fluorescence (XRF). This innovative system, known as HKED, offers several advantages over destructive analysis, such as delivering rapid results, requiring minimal sample preparation time, and generating a minimal amount of radioactive waste. Figure 1 shows a schematic of an HKED system that uses separate containers for KED and XRF. Since its development, the HKED method has become an important tool for diverse applications, including in-fuel fabrication, process control, quality control, material control and accountancy, and safeguards in nuclear fuel reprocessing plants.

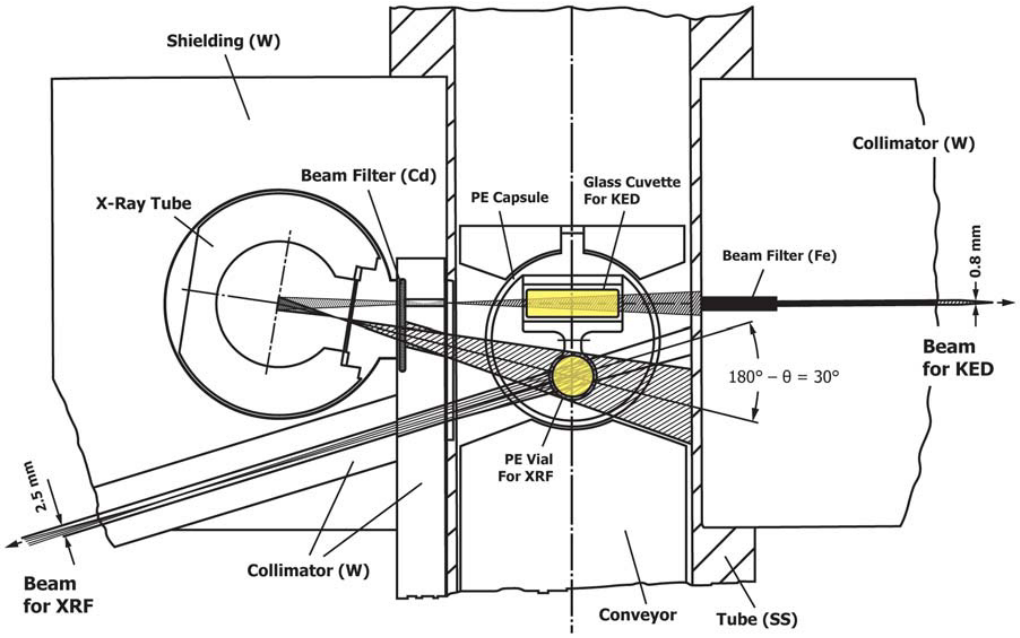

Figure 1. HKED system that uses separate sample containers for KED and XRF [2].

The bremsstrahlung continuum source functions both as a transmission source for the KED assay of uranium and as a fluorescing source for XRF assay of the uranium-to-plutonium concentration ratio. Its intensity enables researchers to realize highly restrictive sample collimation required for KED and XRF assays while significantly reducing the passive count rate from samples containing high levels of fission products.

The concentration of the major element is determined by measuring the transmission of the incident x-ray beam across the characteristic KED 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 concentration of minor elements is then calculated by multiplying the densitometry value for the major element concentration by the elemental ratio of the actinides from the XRF measurement.

The HKED instrument can be operated in three different modes:

1. **KED densitometry-only mode:** Uranium, plutonium, or both, are measured within the concentration range of 50–400 g/L

2. **Hybrid mode:** The concentration of uranium is determined using KED densitometry, whereas the uranium-to-plutonium ratio (typically 100:1) is determined using XRF measurements

3. **Stand-alone XRF mode:** Measures low uranium and plutonium concentrations ranging from 0.2 to 50 g/L

Both KED and XRF measurements are carried out using high-purity germanium (HPGe) detectors, capable of detecting low energies, coupled with digital signal processors. Three replicate measurements were performed, each with a live time of 1,000 s. The instrument is capable of assaying actinide concentrations in solutions with a precision of ±0.3% or better for the major element (usually uranium in high concentrations of 50–400 g/L) and ±1% for the minor element (typically plutonium in concentration around 1 g/L). The random and systematic uncertainties from KED and HKED techniques are listed in the 2022 International Target Values Table 4a for uranium element concentration measurements and Table 4b for Plutonium element concentration measurements [3].

2.1 K-EDGE DENSITOMETRY BRANCH

Figure 2 shows a typical KED spectrum from a uranium sample, where a distinct KED jump in count rates at the characteristic energy of the given element is observed. The ratio of the transmitted fraction of x-rays just before and after the KED is directly related to the density (concentration) of the actinide element, the path length of the x-rays, and the mass attenuation coefficients of the element.

For energy calibration and gain stabilization of the electronics, x-ray and gamma-ray peaks from the decay of a ^{109}Cd source were used. For example, the 22.1 and 25.0 keV Ag x-ray peaks, along with the 88 keV gamma-ray peak, are used for energy calibration. Similarly, the 22.1 keV Ag x-ray and the 88 keV gamma-ray are leveraged for gain stabilization. Tungsten x-rays (59.3 keV K_α and 67.2 K_β) observed in the spectrum originate from both the x-ray tube and the tungsten used for collimation and shielding.

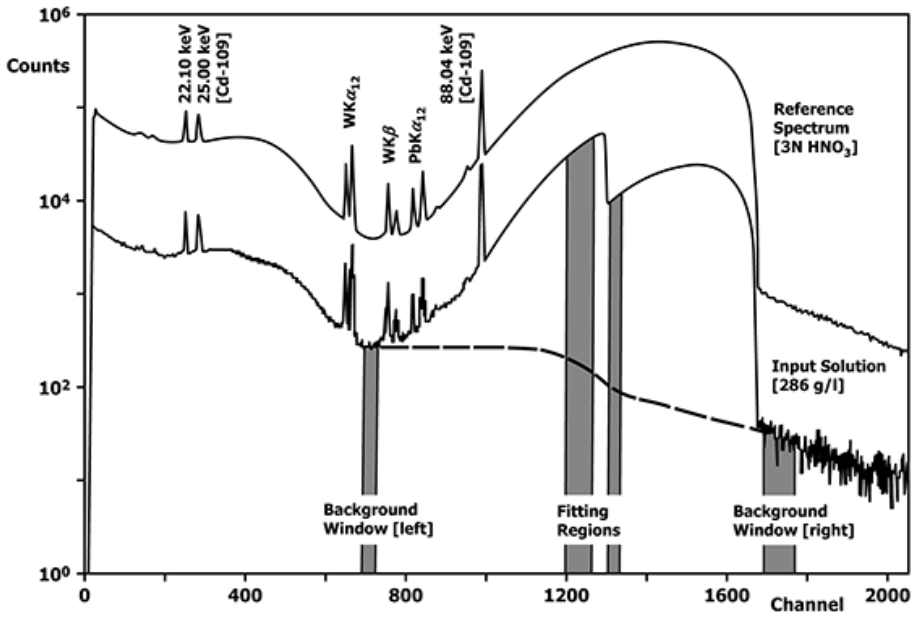

Figure 2. Typical KED spectrum from the uranium sample with region of interests [2].

2.2 X-RAY FLUORESCENCE BRANCH

The x-rays fluoresced by the heavy elements in the sample are detected using a second HPGe detector, which is optimized for low energy and coupled to a multichannel analyzer. The net peak areas of the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks from major and minor actinide elements are quantified, allowing for the determination of the major and minor element concentrations. In HKED measurements, uranium is typically the major element, and plutonium is the minor element. In the current implementation of the hybrid analysis, the x-ray peak areas are determined using a region of interest (ROI) approach.

Figure 3 shows an XRF spectrum from the bremsstrahlung irradiation of a dissolver solution sample with uranium and plutonium concentrations of 276 and 1.85 g/L, respectively [2]. In this spectrum, the K_{α} and K_{β} x-ray peaks are evident as well as the tungsten x-rays. Additionally, the passive spectrum measured with the bremsstrahlung source turned off is shown in this figure, where the gamma-ray peaks from fission products are evident.

Guidance for setting up the apparatus, conducting calibration, and performing measurements are provided in Section 3.

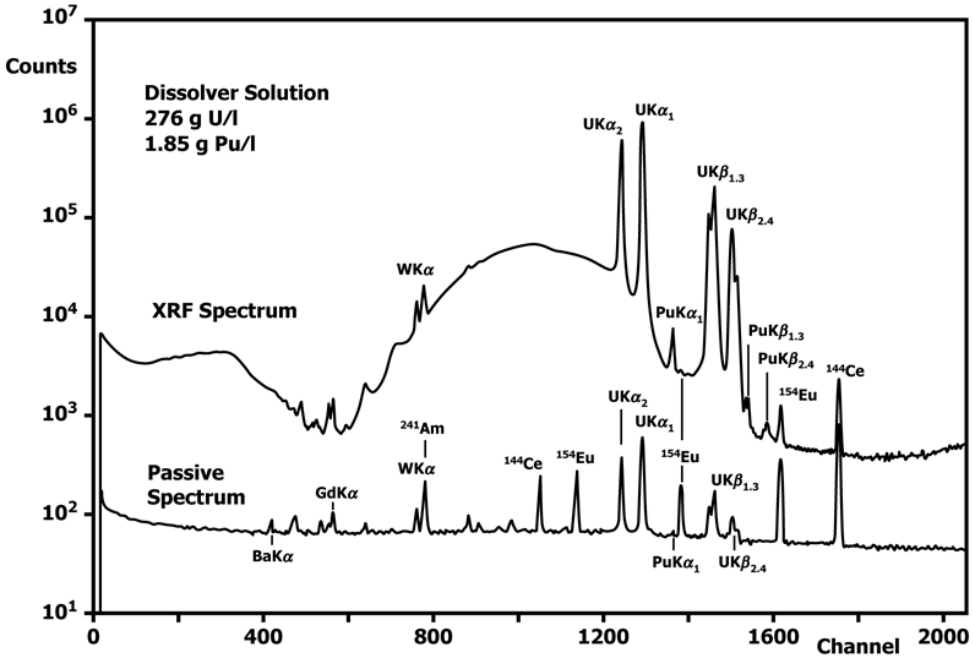

Figure 3. An example of an XRF spectrum from a uranium–plutonium dissolver solution sample [2].

3. SAFETY PRECAUTIONS

The following safety precautions should be considered when using an HKED system:

- The high-voltage supply for the x-ray generator has sufficient power to be a lethal hazard. Appropriate precautions should be taken during maintenance or initial system setup. Additionally, proper grounding of the high-voltage generator is essential.

- When energized, the x-ray generator emits high levels of ionizing radiation, which can deliver a lethal dose within a short time frame (in a matter of minutes). Cautions must be exercised during maintenance or initial system setup.

- The system typically incorporates a red lamp that lights up when the x-ray generator is energized. Establishing a radiological boundary based on a dose rate map around the system is important, and the area must be cordoned off. Access to the marked area should be avoided when the x-ray generator is energized, adhering to the as low as reasonably achievable principle.

- The x-ray system is connected to a three-phase external power supply of 220-230-240 V. The procedure must be followed correctly when energizing or de-energizing the x-ray tube to prevent arcing.

- Regular maintenance of high-voltage cable in the x-ray system is necessary to prevent arcing in the x-ray system.

- Proper grounding of the high-voltage generator to the earth minimizes the potential for arcing in the system.

- Calibration solution standards must be used shortly after preparation. Extended storage of calibration standards may lead to pressure buildup, which results in seals cracking and potential contamination spread.

- Uranium, plutonium, and fission product–bearing materials present both chemical and radiological hazards. Wearing gloves and safety glasses is mandatory, and minimizing exposure by staying outside of the radiological boundary is advised.

- The sample conveyor, along with the sample vial, must be correctly positioned and centered about the path of the collimated x-ray beam. Upon positioning, the sample conveyor engages a magnetic switch, prompting closure of a steel door at the entrance to the sample loading station as a safety measure. If the sample conveyor does not engage the magnetic switch, then it has not been pushed all the way in and, if the steel door is not closed, the x-ray generator cannot be energized. This is a built-in safety mechanism, preventing accidental exposure to x-rays.

4. MEASUREMENT SETUP

Figure 4 shows a schematic of the measurement setup within the HKED system.

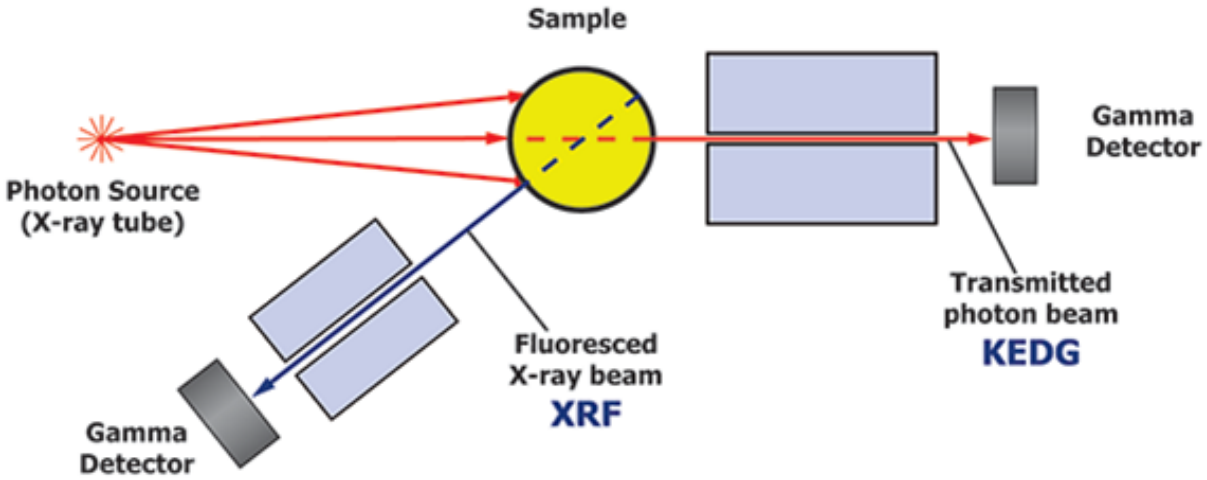

Figure 4. Schematic of the measurement setup using a single vial in the HKED system.

The following steps describe the measurement setup for the HKED system:

1. The standard equipment for high-resolution gamma-ray spectrometry comprises two high-resolution HPGe detectors, each with electronics for fast-pulse processing, a multichannel analyzer, and a dedicated software package used for spectrum acquisition and evaluation. The electronics should be capable of handling a count rate of at least 50,000 counts per second (cps).

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

3. The energy resolution is assessed using ^{109}Cd and ^{57}Co by measurement of the full width at half maximum (FWHM) of the gamma-ray peaks for these two isotopes with the same electronics configuration used during routine measurements. During installation and setup, 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 with a shaping time of 2 µs. During operation, 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.

4. Some instruments incorporate a sample changer. Sample positions must be controlled within 0.3 mm to prevent misalignment causing more than 0.1% bias.

5. A ^{109}Cd source is typically positioned near the detectors for energy calibration and gain stabilization, with representative count rates of 2,000 cps (peak-to-background ratio of 2:1).

6. X-ray equipment consists 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. The x-ray tube is nominally run at 150 kV and 5–15 mA. High-voltage supply stability should be less than 0.1% with adjustable high-voltage and current controls.

8. Sample containers:

    a. A single cylindrical vial or a combination of rectangular cuvette and a cylindrical vial are typical. The path length of x-rays through the rectangular cuvette is 2 cm, and the 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 depend on the areal density of 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 with a path length equal to 2 cm. This corresponds to an areal density of 0.3 g/cm^2. To achieve a similar precision for a 100 g/L uranium solution, a cuvette with a path length equal to 3 cm (areal density: 0.3 g/cm^2) is needed.

    b. The KED measurement accuracy depends on the effective path length of the x-ray beam through the solution. Geometrical parameters must be carefully controlled to meet the International Target Values criteria as 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 with other sources of uncertainty (typically 0.01%). The preferred type of sample vials are spectroscopy cells whose thickness is known to a precision of less than 0.01%.

c. 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 path length is about 0.07%. The poorer uncertainty is because of the curvature of the cylindrical container. The uncertainty in sample positioning is typically <0.1%.

d. The vial wall thickness should be as acceptably thin as possible to manage the intensity of scattered radiation from the x-ray beam while maintaining structural integrity and safe containment of the solutions.

9. Ensure proper set up of the HPGe detectors and signal processing modules (e.g., amplifier, analog to digital converters, stabilizer) following the operations manual.

10. The shaping time of the amplifier should be optimized to achieve maximum throughput without compromising spectroscopic quality, such as energy resolution. A typical shaping time parameter for an analog amplifier is 1 μs (Gaussian shape) or a digital equivalent with a rise time of 1.8 μs and flat-top of 0.6 μs (trapezoidal shape).

11. The amplifier gain and pole-zero should be adjusted.

12. For optimal performance, the dead time should be less than 30%. Adjust the x-ray tube current, if necessary, to reduce the dead time to desired levels.

13. The energy range of the spectra for the HPGe detectors in the KED and XRF subsystems is about 0–170 keV and a minimum of 2,048 channels. To achieve near optimal performance, ensure that the energy resolution (FWHM) is less than 520 eV at the 88 keV gamma line from ^{109}Cd with a total count rate of 50,000 cps. Investigate if the energy resolution is worse than 520 eV.

14. The pile-up rejection should be enabled.

15. The sources of ^{109}Cd should be mounted in front of the detectors (away from the x-ray beam path) for energy and shape calibration and gain stabilization. Gain stabilization should be 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.

16. The high-voltage setting should correspond to the intended value using the endpoint energy of the KED spectrum. Set up the acquisition and analysis software.

17. Of critical importance are parameters such as the x-ray tube voltage and current, source certificates and declarations, region of interest before (left) and after (right) the uranium and plutonium K-edges for the KED analysis, peak analysis parameters for the uranium, plutonium K_α, and plutonium K_β x-ray peaks for the XRF analysis, and ROIs for continuum subtraction.

18. Table 1 shows typical KED ROI bounds.

Table 1. Typical bounds for KED ROIs.

KED ROI	ROI Bounds (keV)	
	Lower	Upper
Left background	61.8	64.8
Right background	151.9	158.4
Uranium KED lower window	107.2	113.3
Uranium KED upper and plutonium KED lower window	117.3	119.4
Plutonium KED upper window	123.5	130.2

19. The KED ROIs are illustrated in Figure 5.

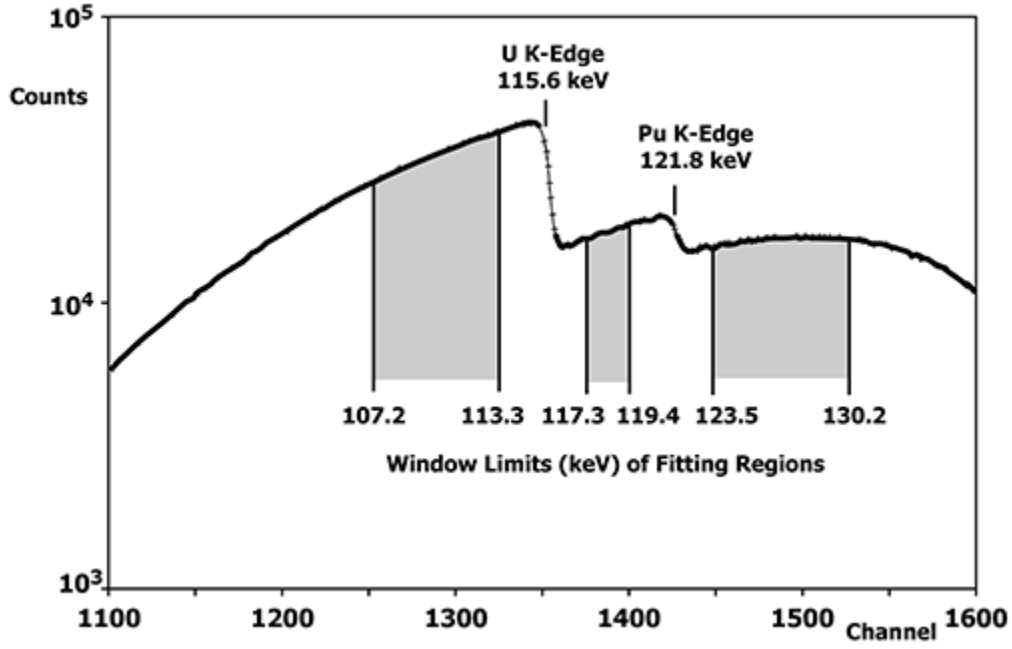

Figure 5. ROI window limits for KED analysis [2].

20. XRF ROIs—generally, the ROIs for the XRF analysis are set according to the following rules:

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

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

    c. The exception is the uranium $K_{\beta 1,3}$ double-peak complex. Peak ROI is from uranium $K_{\beta 3}$ − 1.1 FWHM to uranium $K_{\beta 1}$ + FWHM.

    d. Three other ROIs are also included beyond those for the uranium $K_{\alpha 2}$, uranium $K_{\alpha 1}$, uranium $K_{\beta 1}$, and plutonium $K_{\alpha 1}$, as described in item 20e.

    e. The americium $K_{\alpha 1}$ ROI is available to provide a correction for the presence of americium $K_{\alpha 2}$ x-rays in the plutonium $K_{\alpha 1}$ background ROI. The ROI is also used to quantify americium in the solution, if present.

i. A background window between ^{154}Eu (123.07 keV) and ^{144}Ce (133.54 keV) is used to account for passive self-fluorescence.

ii. Europium-154 (123.07 keV) is used for bias correction.

21. Table 2 shows examples of ROI limits used in the XRF analysis.

Table 2. ROI bounds for an XRF analysis.

XRF ROI	ROI Limits		Left Background		Right Background	
	Lower	Upper	Lower	Upper	Lower	Upper
Uranium $K_{\alpha 2}$	94.053	95.263	92.353	93.563	97.753	98.963
Uranium $K_{\alpha 1}$	97.831	99.041	96.131	97.341	101.531	102.741
Plutonium $K_{\alpha 1}$	103.129	104.339	101.429	102.639	106.829	108.039
Americium $K_{\alpha 1}$	105.918	107.128	—	—	—	—
Uranium $K_{\beta 1,3}$	109.82	111.907	108.12	110.207	113.52	115.607
Europium-154	122.465	123.675	—	—	—	—
Self-radiation background	125	131	—	—	—	—

22. Additional setup parameters include defining count times, determining the number of replicate counts for each assay, configuring the sample changer (if there is an automated sample changer), establishing the counting protocol (e.g., KED-only, XRF-only, hybrid), implementing quality control, and setting up reporting.

23. A warm-up procedure of the x-ray tube should be performed according to the x-ray tube manufacturer's recommendations.

5. CALIBRATION

Calibration is essential for establishing the relationship between concentration and the instrument response. The KED measurement is the ratio of transmissions across the K-absorption edge, and the XRF measurement is the count rate from the fluoresced x-rays in the sample. Section 5 describes a representative calibration procedure for uranium, plutonium, or both contained in aqueous solutions, in which the calibration should remain valid as long as the quality assurance and quality control checks permit:

1. Prepare reference materials shortly (within a few days), before the calibration measurement campaign, to avoid changes in concentration values due to evaporation or degradation.

2. Obtain a blank nitric acid solution that does not contain uranium or plutonium, similar in concentration to that of the sample solutions (typically 3 or 4 mol/L), as required for the calibration in the three operating modes.

3. Prepare a set of three or more synthetic uranium–plutonium solutions that simulate the characteristics of feed solutions relating to the uranium concentration (50–400 g/L), uranium-to-plutonium ratio (typically 100:1–150:1), spanning the expected measurement range, and nitrate concentration (typically 3 or 4 mol/L). Specify uncertainty on calibration standards to meet data quality objectives.

4. For a uranium- or plutonium-only calibration using stand-alone KED measurements, measure a set of three or more calibration solutions spanning the expected uranium or plutonium concentration range (e.g., 50–400 g/L) and nitric acid concentration range (typically 3 or 4 mol/L). Specify uncertainty on calibration standards to meet the data quality objectives.

5. For XRF-only calibration (for measuring low uranium or plutonium concentrations), measure a set of three or more uranium- or plutonium-only calibration solutions that simulate process solutions containing uranium or plutonium concentrations of 0.2–50 g/L and nitric acid concentration of 3 or 4 mol/L. Specify uncertainty on calibration standards to meet the data quality objectives.

6. Set the x-ray tube high-voltage to 150 kV. Set the current to an appropriate value (a few milliamperes) to achieve the desired counting statistics and dead time.

7. For measuring the blank KED reference (e.g., nitric acid solution), reduce the x-ray tube current to avoid the excessive count rate in the KED detector.

8. Deposit 5 mL aliquots of solution (whether a blank or calibration standard) in a polyethylene vial and position the aliquots within the sample conveyor to ensure proper alignment with the collimated x-ray beam. Push the sample conveyor in until it engages a magnetic switch and close the steel door for safety. If the sample conveyor does not engage the magnetic switch, it has not been pushed all the way in; if the steel door is not closed, the x-ray generator cannot be energized. These are built-in safety mechanisms that prevent accidental exposure to x-rays.

9. Measure the blank solution with the XRF detector using the same current that was used during sample measurement.

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

11. Acquire XRF spectra using synthetic uranium- or plutonium-only solutions under the same measurement conditions as the unknowns.

12. After calibration, conduct verification measurements using reference solutions that were not used for calibration (a typical practice for safeguards measurements).

13. For calibration solutions containing fission products, turn off the x-ray tube and acquire passive spectra for background subtraction.

6. MEASUREMENT PROCEDURE

The following steps describes the measurement procedure for the HKED system:

1. If the x-ray system has been inactive for more than 24 hours, perform the x-ray tube warm-up procedure following the manufacturer’s instructions.

2. Set the x-ray tube voltage to 150 kV, with an appropriate current value based on expected precision and system dead time characteristics.

3. Deposit 5 mL aliquots of solution (whether a blank or calibration standard) in a polyethylene vial and position them within the sample conveyor to ensure proper alignment with the collimated x-ray beam. Push the sample conveyor in until it engages a magnetic switch, and close the steel door for safety. If the sample conveyor does not engage the magnetic switch, it has not been pushed all the way in; if the steel door is not closed, the x-ray generator cannot be energized. These are built-in safety mechanisms that prevent accidental exposure to x-rays.

4. Use the blank solution spectrum collected during calibration for sample (or standard) analysis unless a new sample matrix is used or any of the system components have been serviced and reinstalled. Verify all hardware and software setup parameters before starting the sample measurement campaign, which must be the same as it was during the calibration.

5. Acquire KED and XRF spectra simultaneously (or XRF-only spectra for low concentrations of uranium and plutonium) using the unknown solutions under the same measurement conditions (tube voltage and measurement geometry) during calibration. Perform several repeat (cycle) measurements on each sample to reduce uncertainty and demonstrate repeatability. Performing three counting trials for 1,000 s per sample is the common practice.

6. Turn off the x-ray tube and acquire passive spectra for background subtractions from unknown solutions that contain fission products. This step is especially necessary for high burnup spent fuel dissolver solutions because of the presence of high fission product activity in the samples.

7. Analyze the KED and XRF spectra using the methods outlined in the International Organization for Standardization [4] and ASTM International standards documents [5]-[7] and determine the concentrations of uranium, plutonium, or both. These analysis methods have been implemented in commercially available software packages, including one by Mirion Technologies [8].

8. For cases when uranium and plutonium are present in ratios such as 50:1 and 100:1, determine the uranium concentration using KED, plutonium-to-uranium ratio using XRF, and plutonium concentration by multiplying the uranium concentration with the plutonium-to-uranium ratio.

9. Review the results to ensure that random and systematic uncertainties for uranium and plutonium concentrations are within the values prescribed by the 2022 International Target Values.

7. HYBRID K-EDGE DENSITOMETRY AND X-RAY FLUORESCENCE APPLICATION EXAMPLES

Section 7 highlights two examples of HKED applications: one at La Hague, France, and another at Oak Ridge National Laboratory (ORNL), United States. In La Hague, HKED systems serve a process control purpose, whereas the HKED system at ORNL is for validating new analysis methods and applications (e.g., determination of neptunium concentrations, crucial for producing ^{238}Pu, which are used in thermoelectric generators for space missions).

7.1 UP3 ROUTINE CONTROL LABORATORY IN LA HAGUE

Located within the UP3 central building at La Hague, the UP3 routine control laboratory performs analyses following the process control programs for UP3 and UP2-800 reprocessing plants, focusing on safety, security, quality, and environmental concerns while adhering to budgetary constraints. The laboratory includes the following key features:

- Capable of performing 150,000 analyses annually

- Conducts 12,000 KED analyses per year in automated mode
- Performs 4,000 KED analyses per year in manual mode

The laboratory is equipped with four fully automated KED systems (see Figure 6), facilitating direct measurements in liquid solutions within sampling jugs (see Figure 7) without the need for reagent and effluent. Moreover, the system has a fully interfaced sample management and results reporting network.

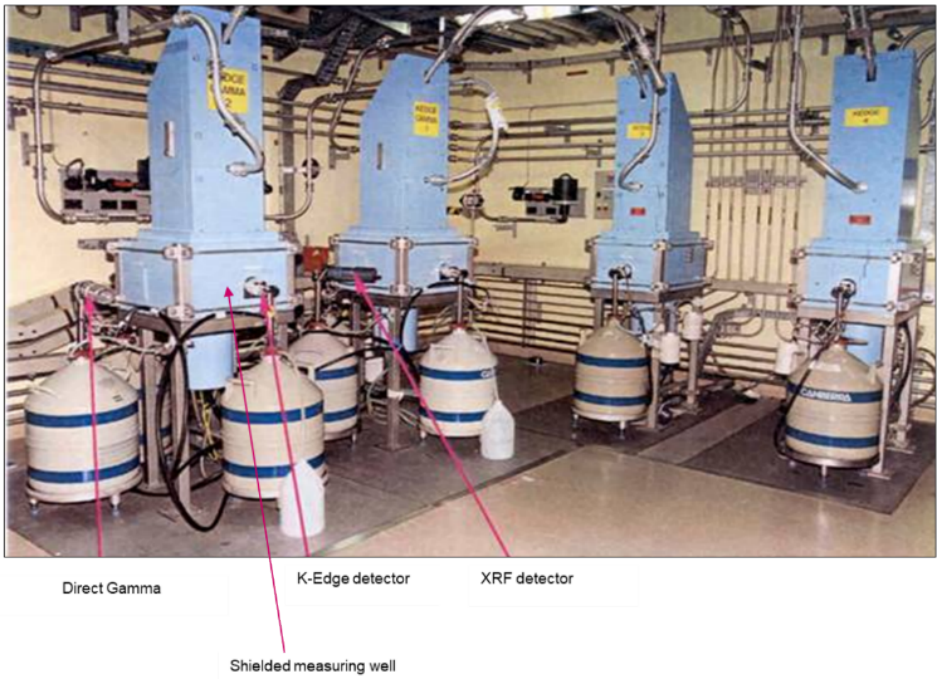

Figure 6. HKED systems at La Hague [9].

Figure 7. Sample jug [9].

Uranium and plutonium elements were measured in UOX1, UOX2, UOX3, MOX, Muka, research and test reactor nuclear fuels, and Uranium Recovery Program solutions. The following is a range of measurements:

- KED: uranium (30–400 g/L); plutonium (30–150 g/L)

- XRF: uranium (40–100 g/L); plutonium (40–100 mg/L)
- Combined uranium–plutonium: uranium (30–250 g/L), with the uranium-to-plutonium ratio between 5:1 and 200:1 (simultaneous KED and XRF measurement)
- Global uncertainty for process samples: better than ±5% (K = 2, 95% confidence level)

Table 3 lists the sample types that are analyzed using the KED densitometry and XRF.

Table 3. Hybrid KED analyses at La Hague.

Method number	Type of measurement	Remarks
1	Automatic method KED or XRF	After XRF precounting, this is the best method choice according to the estimated concentration in the sample
2	KED rapid uranium	Uranium correction for the automated H^+ measurement by conductimetry
3	KED uranium	Only uranium solution between 30 and 400 g/L
4	XRF uranium	Only uranium solution between 100 and 40 g/L
5	KED plutonium	Only plutonium solution between 30 and 140 g/L without americium
6	XRF plutonium	Only plutonium solution between 40 and 100 g/L with or without americium
7	KED uranium and XRF plutonium	Mixed uranium–plutonium solution with 30 g/L < uranium < 400 g/L and a uranium-to-plutonium ratio between 80 and 200
8	KED uranium and XRF plutonium	Mixed uranium–plutonium solution with 30 g/L < uranium < 400 g/L and a uranium-to-plutonium ratio between 5.5 and 80
9	XRF plutonium	Only plutonium solution <40 g/L with neptunium

7.2 RADIOLOGICAL ENGINEERING DEVELOPMENT CENTER AT OAK RIDGE NATIONAL LABORATORY

The evolution of the nuclear fuel cycle has resulted in an expansion of the list of actinides of interest and a need for algorithm enhancements for HKED analysis. With new material processing methods and evolving fuel cycles, there is demand for accommodating higher levels of plutonium in the solutions, sometimes even in equal proportion to uranium (i.e., uranium-to-plutonium ratio = 1:1). These changes also result in higher concentrations of minor actinides like americium and neptunium. Because of the increased focus on measuring americium and neptunium along with the rising plutonium-to-uranium ratio in proposed processing solutions, the HKED software requires validation for these applications. To support this development, a commercial HKED system was installed at the ORNL Radiological Engineering Development Center. This multipurpose Category II radiochemical processing facility at ORNL can produce a wide range of mixed actinide solution standards for testing and advancing HKED techniques. The ORNL HKED system, shown in Figure 8, is a single cylindrical sample vial measurement system.

Figure 8. HKED system installed at the Radiological Engineering Development Center facility in ORNL. (Photo courtesy of R. D. Mcelroy, ORNL.)

REFERENCES

1. World Nuclear Association. Processing of Used Nuclear Fuel. https://world-nuclear.org/information-library/nuclear-fuel-cycle/fuel-recycling/processing-of-used-nuclear-fuel.aspx (last accessed on March 18, 2024).
2. Ottmar, H., and Eberie., H., 1991. *The Hybrid K-Edge/K-XRF Densitometer: Principles – Design – Performance*. KfK 4590. Germany: Kernforschungszentrum Karlsruhe.
3. IAEA (International Atomic Energy Agency). 2022. *International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials*. Vienna, IAEA. https://nucleus.iaea.org/sites/connect/ITVpublic/Resources/International%20Target%20Values%20for%20Measurement%20Uncertainties%20in%20Safeguarding%20Nuclear%20Materials.pdf.
4. ISO. 1998. *Simultaneous Determination of Uranium and Plutonium in Dissolver Solutions from Reprocessing Plants*. ISO 13464:1998.
5. ASTM International. 2018. *Standard Test Method for Determination of Uranium and Plutonium Concentration in Aqueous Solutions Using Hybrid K-Edge Densitometry and X-Ray Fluorescence*. ASTM C1855-18. https://www.astm.org/c1855-18.html.
6. ASTM International. 2022. *Standard Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry*. E1621-21. West Conshohocken: ASTM International.
7. ASTM International. 2018. *Standard Test Method for Determination of Uranium and Plutonium Concentration in Aqueous Solutions using Hybrid K-Edge Densitometry and X-Ray Fluorescence*. C1855-18. West Conshohocken:ASTM International. https://img.antpedia.com/standard/files/pdfs_ora/20230612/astm/C/C%201855%20-%2018.pdf.
8. Mirion Technologies. n.d. “Hybdrid K-Edge Densitometry Software.” Accessed February 28, 2024. https://www.mirion.com/products/technologies/measurement-systems-for-fuel-cycle-safeguards-and-

d-d/nda-safeguards-applied-systems/nda-systems-software/hked-hybrid-k-edge-densitometry-software.

9. D. Colombo. 2007. “La Hague Laboratory Experience in Routine Control Analysis.” Paper presented at the International Workshop on X-Ray Techniques for Nuclear Materials Assay.