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# Determination of plutonium in spent nuclear fuel using high resolution X-ray

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## ARTICLE INFO

## ABSTRACT

Characterization of Pu is an essential aspect of safeguards operations at nuclear fuel reprocessing facilities. A novel analysis technique called hiRX (high resolution X-ray) has been developed for the direct measurement of Pu in spent nuclear fuel dissolver solutions. hiRX is based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF), which provides enhanced sensitivity and specificity compared with conventional XRF techniques. A breadboard setup of the hiRX instrument was calibrated using spiked surrogate spent fuel (SSF) standards prepared as dried residues. Samples of actual spent fuel were utilized to evaluate the performance of the hiRX. The direct detection of just 39 ng of Pu is demonstrated. Initial quantitative results, with error of 4–27% and precision of 2% relative standard deviation (RSD), were obtained for spent fuel samples. The limit of detection for Pu (100 s) within an excitation spot of 200 µm diameter was 375 pg. This study demonstrates the potential for the hiRX technique to be utilized for the rapid, accurate, and precise determination of Pu. The results highlight the analytical capability of hiRX for other applications requiring sensitive and selective nondestructive analyses.

## 1. Introduction

### 1.1. Determination of Pu in spent nuclear fuel

Measurement of Pu in spent nuclear fuel is important for monitoring reprocessing activities and for material control and accountancy. The use of nondestructive assay (NDA) to quantify Pu in spent fuel should provide regulators and inspectors the capability to conduct independent verification of Pu mass at sites with nuclear materials (i.e., detect misuse) and increase efficiency in reprocessing plant operations. At present, Pu assay of fuel assemblies is routinely conducted with neutron counting and gamma spectroscopy. These are indirect methods which permit calculation of expected mass of Pu and other fissionable materials based on the use of measured signatures, operator declared values, and burnup codes [1]. Knowledge of the operating history of the reactor is required along with the use of modeling, and results are thus subject to some level of uncertainty. X-ray fluorescence is one of the 13 NDA techniques for elemental Pu determination in spent fuel assemblies that have been recently evaluated by the safeguards community [2]. Specifically, self-induced (passive) XRF, in which U and Pu characteristic K X-rays are generated due to the inherent gamma flux in the sample, has been used to determine the U/Pu elemental ratio and an estimate of Pu mass [3–5]. Long counting times (>1 h) are one potential limitation of this approach [6].

For the assessment of Pu content in spent fuel dissolver solutions, more accurate and sensitive methods including controlled potential coulometry and mass spectrometry may be utilized [7,8]. Due to their extensive sample preparation requirements and complexity, these approaches may not be well suited to routine analyses. Conversely, hybrid K-Edge (HKED) is a routine method which combines K-edge densitometry with XRF for determination of U and Pu in spent nuclear fuel samples. While sample preparation is limited, volumes in excess of 2 mL are required and typical counting times are 1000 s [9,10]. Transmission-corrected K-XRF utilizing two radioactive isotopes has been demonstrated for U and Pu determination up to 300 g/L through container walls, but has not been widely adopted as an NDA approach despite on-line applicability [11]. The detection of characteristic L X-rays using conventional energy dispersive (ED)XRF has also been proposed as an approach to determine actinides in spent fuel solutions [12,13]. Berdikov et al. [14] demonstrated sensitive detection of U and Pu based on direct measurement of 3.5 mL of solution in 1982, but the authors are not aware of any more recent publications describing the use of X-ray tube excitation-based XRF for monitoring Pu in reprocessing solutions.

### 1.2. High resolution X-ray (hiRX)

hiRX is a novel technique based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF), in which doubly curved crystal (DCC) optics are utilized for both excitation and detection. Coupled with an X-ray source, the point-to-point focusing excitation optic creates a

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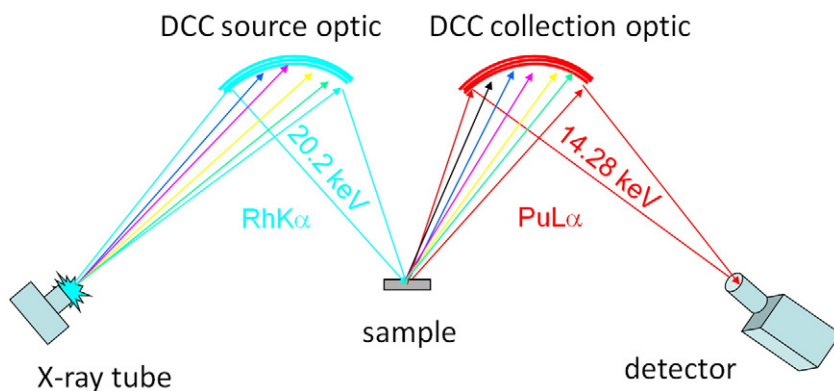  *E-mail address:* kmcintosh@lanl.gov (K.G. McIntosh).

**Fig. 1.** Schematic of hiRX prototype components.

monochromatic, high flux source to excite characteristic X-ray fluorescence from the sample, while the collection optic passes X-rays of a specific energy and focuses them onto the detector. The use of two DCCs makes hiRX highly sensitive and selective, as background due to scatter and peaks outside the specified collection energy are removed from detection. MWDXRF technology is currently used in commercial instrumentation for the determination of S, Cl, Si, and P in petroleum products, and a limit of detection (LOD) of 0.36 mg/kg has been reported for S in a fuel matrix (4 mL, 300 s) [15]. The hiRX instrument is designed specifically for detection of actinide elements in spent nuclear fuel. A schematic of the single channel hiRX configuration for Pu detection is shown in Fig. 1.

hiRX offers a new approach for the rapid and accurate determination of Pu. Low sample volumes (<10 μL) and simple sample preparation reduce safety risks and costs associated with handling and disposing of radioactive materials. This low sample volume may also permit more frequent sampling of a spent nuclear fuel reprocessing stream, allowing more complete characterization of the dissolver tank composition. The use of MWDXRF permits direct, nondestructive measurement of Pu at sub-ng levels, much lower than other XRF approaches. The development of the hiRX prototype and its preliminary applications to detection of Pu, U, and Cm in various surrogate matrices has been described previously [16–20]. This is the first work in which hiRX is utilized to detect Pu in an actual spent fuel matrix. Dried residues of Pu-spiked surrogate spent fuel (SSF) are used to calibrate the hiRX for determination of Pu in the spent nuclear fuel residues. While dried residues are utilized in this preliminary study, the future aim is to use hiRX technology to measure Pu in liquid fuel dissolver samples. The low Pu content of the successfully measured samples relative to the nominally 1 g/L levels (typical range 0.1 to 3 g/L) expected in reprocessing streams highlights the sensitivity of the hiRX technique.

## 2. Experimental

### 2.1. Instrumentation

The hiRX breadboard setup is shown in Fig. 2. A 50 W Rh anode X-Beam (XOS, East Greenbush, NY) X-ray source is coupled with the excitation DCC optic which transmits the Rh Kα line at 20.2 keV. The optic is Si <200> crystal in Johann geometry with 1.2° b\y 51.2° solid angle and source to optic distance of 181.5 mm. The reflection efficiency is estimated at 5%, flux is $4 \times 10^8$ photons/s, and focal spot size is 190 by 250 μm. The 360° collection DCC optic passes the Pu Lα line at 14.279 keV, with a bandwidth of approximately 200 eV. This optic is Si <400> crystal in log spiral geometry with 0.22 steradian solid angle and sample to optic distance of 144 mm. The reflection efficiency is 2% and focal spot size on the detector is 1000 by 1350 μm. The Vortex-90EX silicon drift detector (SDD) (Hitachi High-Technologies Science

America Inc., Northridge, CA) has 50 mm$^2$ active area, 300 μm thick Si layer, and energy resolution of approximately 130 eV at the Mn Kα line (5.9 keV).

The components of the hiRX breadboard system including the source with DCC, sample mount, and detector are mounted on translation stages (Newport URS100BCC and 443 Series, Newport Corporation, Irvine, CA) which permit precise alignment and provide the mapping capability of the instrument. Stages are controlled with a Newport XPS 8 channel motion controller and the X-Beam is controlled with an XOS PCS50 power control system; both are connected to a PC via Ethernet interface. Detector data collection is done using in-house developed acquisition software based on LabView (National Instruments, Austin, TX).

All hiRX measurements were completed with 50 kV, 1 mA operating conditions. Pu elemental maps were obtained for each of the samples and standards using a 200 μm step size and 10 s dwell per point. For the standards, the mapped area was 3 × 3 mm, while the larger size of the sample deposits necessitated maps up to 6 × 6 mm. Additional spectra from selected regions of the maps were collected for 100 s or 600 s. Data were processed using a custom MATLAB (Version 7.1, The MathWorks, Inc., Natick, MA) script. An integrated intensity for the Pu region of interest (ROI) was generated for each of the maps and a filter was utilized to remove noise, i.e., pixels with <1.5 counts were recorded as 0.

The commercial micro-EDXRF instrument (Eagle III, EDAX Inc., Mahwah, NJ) utilized in this study has an Rh anode, operating at
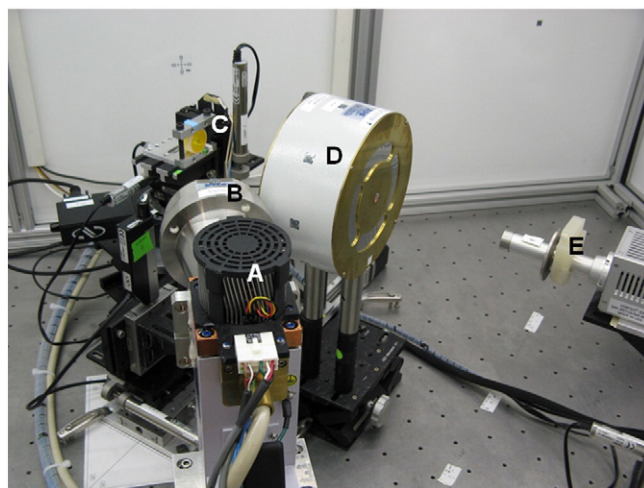


**Fig. 2.** Image of hiRX breadboard setup (A: X-Beam, B: Excitation DCC, C: Sample mounted on stage, D: Collection DCC, E: SDD).