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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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In-Field Alpha Spectrometry to Assess Uranium Enrichment In Uranium Hexafluoride

D. L. Chichester[1], J. T. Johnson[1], S. M. Watson[1], T. R. Pope[2], and G. A. Fugate[3]

1. Idaho National Laboratory, Idaho Falls, Idaho
2. Pacific Northwest National Laboratory, Richland, Washington
3. Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT

A new In-Field Alpha Spectrometry (IFAS) system is being developed to allow quick turnaround measurements of uranium enrichment in uranium hexafluoride (UF_6) samples. Samples are collected using specially-designed Single-Use Destructive Assay (SUDA) wafers which have an absorptive film of zeolite deposited onto a quartz or metal substrate. The SUDA samples, along with a special holder, are designed to be attached directly to a sampling tap at a gas centrifuge enrichment plant or a uranium conversion facility, allowing gaseous UF_6 to come into direct contact with the zeolite. The zeolite absorbs this material and converts it into stable, safe UO_2F_2 within a few minutes. Once the sample has been collected it is transferred to the IFAS system where a solid-state, silicon alpha spectrometer is used to quantitatively measure the alpha emissions from ^{234}U, ^{235}U, and ^{238}U in the sample. The IFAS system is a small, light-weight device that can be quickly turned on and put into use. The SUDA samples and IFAS hardware are designed so that thin-film spectra are produced, allowing a complete measurement with a final $^{235}U:U_{total}$ determination having a precision $<\pm2\%$ to be made in less than eight hours. This short time frame will allow an inspector to get results on-site within one working shift; further innovations may reduce this to even shorter times.

INTRODUCTION

As outlined in International Atomic Energy Agency (IAEA) Information Circular 153 (INFCIRC/153), the IAEA needs to be able to verify the correctness and completeness of a State's declaration of nuclear materials (U, Pu, and Th).[1] One type of verification performed by IAEA inspectors in support of this goal is the verification of declared uranium enrichment, with the chemical form of uranium hexafluoride (UF_6), at uranium conversion and uranium enrichment facilities. Nondestructive assay methods used for uranium enrichment verification in UF_6 include in-line process monitoring of gaseous UF_6 flowing within pipes, such as the On-Line Enrichment Monitor, and bulk material analysis of solid UF_6 in containers, using x-ray and gamma-ray spectrometry.[2,3] The primary destructive assay (DA) method used for uranium enrichment verification is mass spectrometry.[4-6] In these cases samples of UF_6 are usually collected via gas transfer into a transfer container, such as a Croft 2926 UF_6 sample bottle or similarly configured stainless steel or polytetrafluoroethylene (PTFE) P-10 sampling tube, either directly as condensate or as a solid adsorbed into bulk zeolite (the "Cristallini technique" developed by the Argentine Agency for Accounting and Control of Nuclear Materials, ABACC).[7-9] Other DA measurements used for uranium enrichment verification are alpha spectrometry, a laboratory-based method, and the Combined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA), a method developed for on-site field use at nuclear facilities.[10-13]

COMPUCEA is an advanced mobile verification analytical tool deployed during physical inventory verification and design information verification inspections at fuel fabrication and uranium conversion facilities. Early work with COMPUCEA involved uranium in forms other than UF_6, such as pellets, powders, and scrap material, but more recent work has explored the extension of the COMPUCEA method for analysis of UF_6. As a general tool of uranium verification COMPUCEA is well understood and widely used by the IAEA. A challenge remains, however, with the complexity of the instrumentation that must be deployed on site; the multi-day timeline needed for set-up, start-up checks, in-field calibration, analysis, and system packing; and the training and skill level needed for an inspector to operate and execute the COMPUCEA measurements.

Alpha spectrometric methods are well suited for the determination of uranium isotope ratios starting with material in a variety of sample matrices. Several different approaches exist in relation to sample preparation for alpha spectrometry, most commonly involving chemical purification followed by radiochemical separation and electrodeposition. A challenge exists, however, due to the rigorous and time-consuming laboratory steps required to make these samples.[14,15] Because of these challenges traditional alpha spectrometry is not well suited for use outside of laboratory settings. However, due to the excellent analytical capabilities that can be achieved using alpha spectrometry, and in acknowledgement of the aforementioned challenges with other existing in-field methods, the IAEA has expressed interest in having an alpha spectrometric method suitable for field use for the direct analysis of samples collected from UF_6.[16,17] The Agency's goals are for the method to take less than 12 hours including sample collection, preparation and measurement, to have an accuracy with a root mean square difference (RSD) $<3\%$, and to be safe, reproducible, and minimally burdensome to operators.[16] This interest was more formally expressed in 2018 when the IAEA identified a research and development (R&D) need (STR-385, R&D Need T.1.R8) to "Develop in-field alpha spectrometers (including sample preparation) for nuclear material identification and isotopic composition analysis," within their "IAEA Research and Development Plan" (STR-385), as highlighted within their report "IAEA Development and Implementation Support Programme for Nuclear Verification 2018-2019 (STR-386).[18,19]

In response to this expressed need, a research project was established by the Safeguards Technology Development Program (a part of the U.S. Department of Energy's National Nuclear Security Administration) to support work at Idaho National Laboratory (INL), Pacific Northwest National Laboratory (PNNL), and Oak Ridge National Laboratory (ORNL) to develop instrumentation and methods to allow direct, on-site alpha spectrometry of samples taken from UF_6. Prior work by the research team demonstrated the design and use of small sample coupons coated with specialized zeolite films, called "Single Use Destructive Assay" (SUDA) samplers, for the collection of UF_6.[7] Separate work by this research team also showed that robust In-Field Alpha Spectrometry (IFAS) systems could be developed to perform quantitative assays of thick-film, high-beta-activity samples.[20] This project combines the use of specially-optimized SUDA samplers with an IFAS instrument to meet the goal of developing an IFAS system for UF_6 enrichment verification.

EQUIPMENT AND METHODS

Details about the design and assembly of the SUDA sampler are provided in reference 7. The SUDA sampler is comprised of a thin, smooth substrate material (sample coupon), such as quartz or stainless steel that is coated with zeolite. This sample coupon is held within a coupon carrier, a modified version of a blank KF16 flange with a tall center pedestal that supports the coupon. Drawings of the SUDA sampler are shown in Figure 1, photographs are shown in Figure 2.

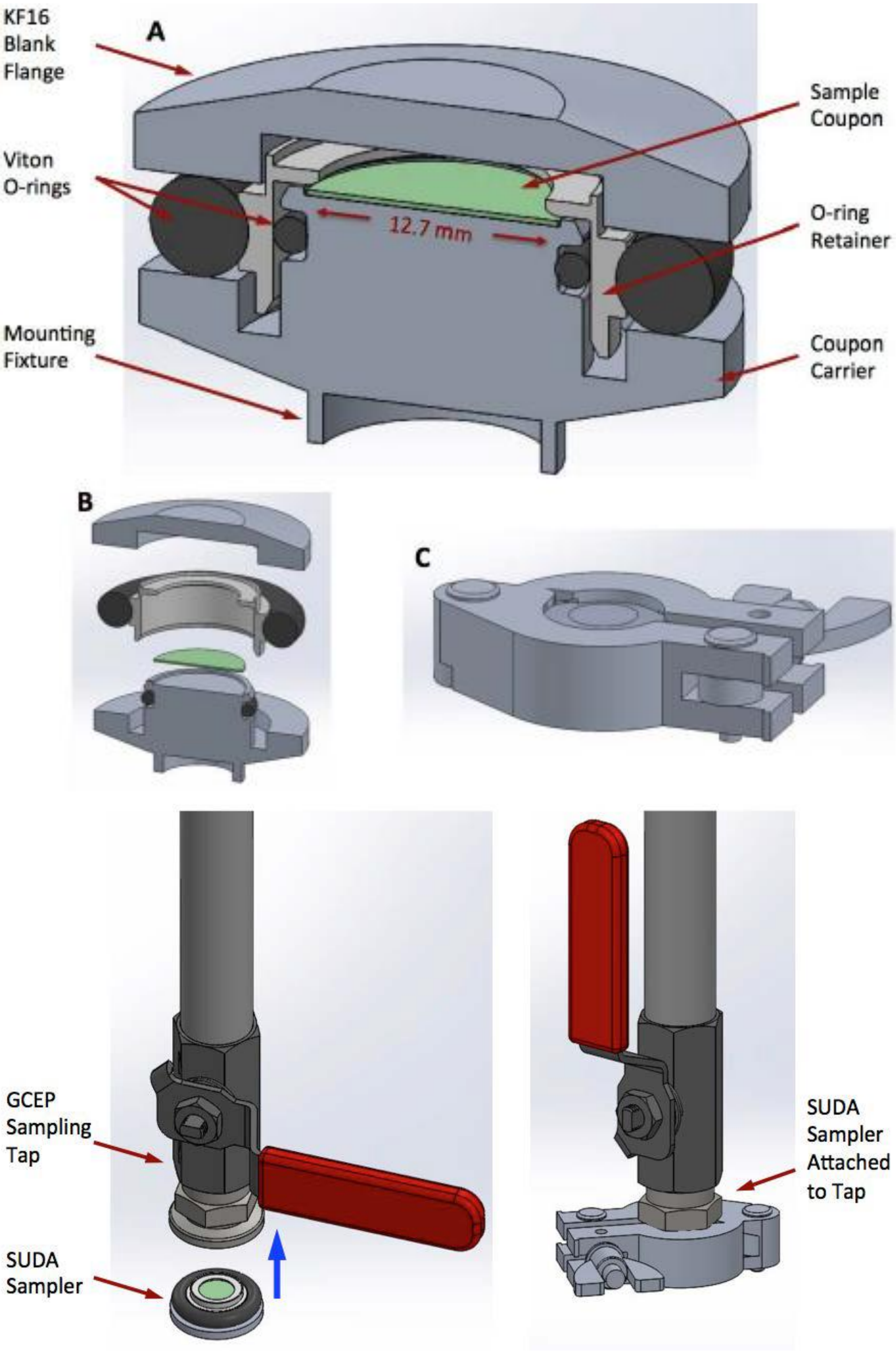

Figure 1 The top three drawings show the SUDA sampler in cross-section view (a), exploded cross-section view (b), and an external view with the hinge clamp (c). The lower left drawing shows the orientation for how the SUDA sampler would be attached to a sampling tap. The lower right drawing shows the view of the SUDA sampler attached to the tap with the hinge clamp holding it in place.[7]

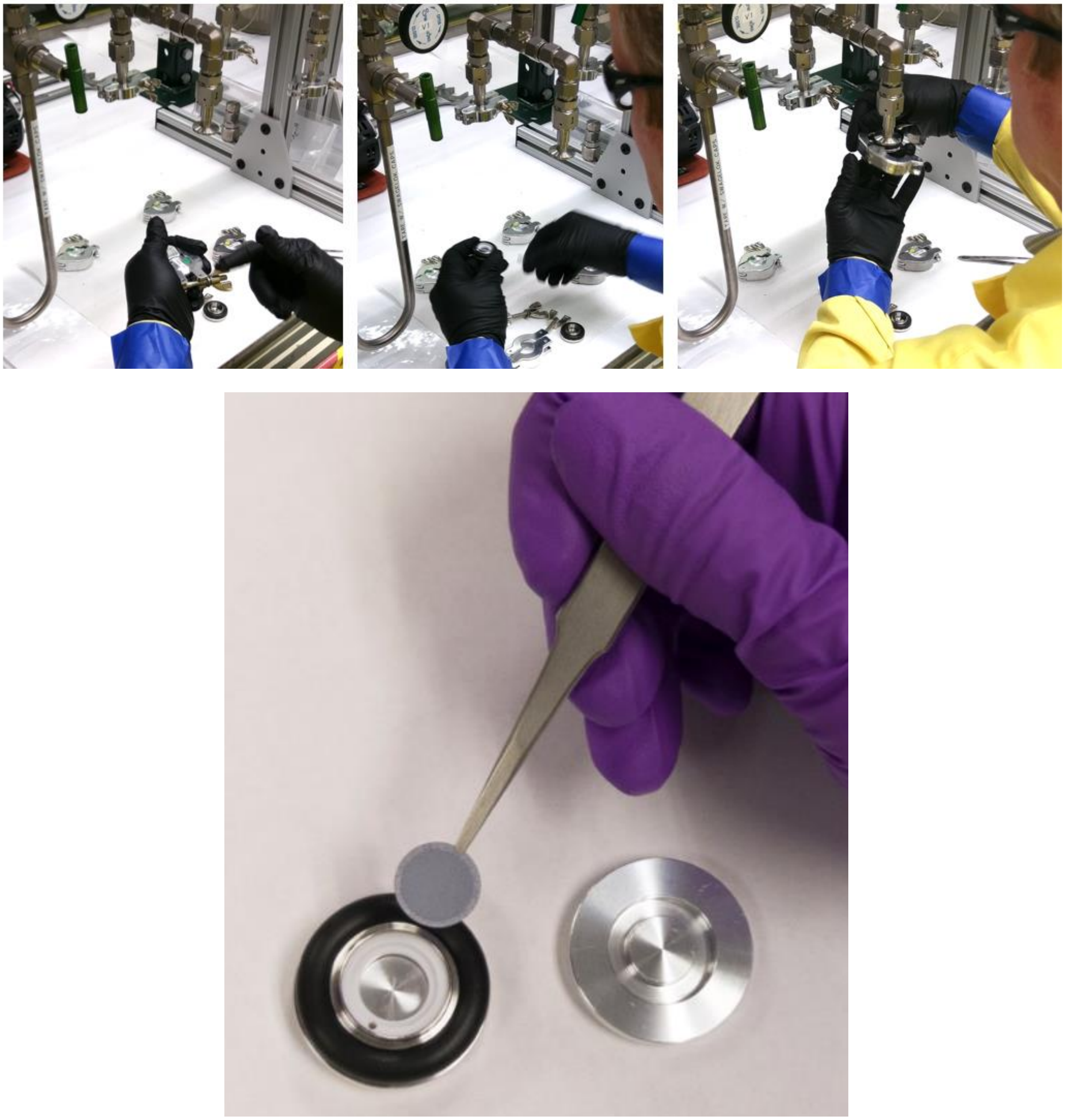

Figure 2 The top three photographs show the process for attaching a SUDA sampler to a sample tap at ORNL.[21] The photograph at the bottom shows the removal of the zeolite coupon from a SUDA sampler for inspection at INL.

Within the SUDA sampler a Teflon support ring keeps the coupon centered on the pedestal; a Viton O-ring is placed on the outside diameter of the Teflon ring. A standard blank KF16 flange is used for the upper part of the sampler (the 'lid') while a hinge-clamp is used to secure the upper and lower KF16 flange parts together for storage and transport. The zeolite is comprised of an alumina-silica structure optimized for this application. During manufacture the zeolite is 'pre-loaded' with adsorbed water in its matrix. When UF_6 is exposed to the zeolite structure at the sampling tap it adsorbs to the high-surface-area structure of the zeolite matrix.[7] Within the zeolite the UF_6 is then rapidly converted to the more chemically stable UO_2F_2 by hydrolysis with the water. The UO_2F_2 is confined within the zeolite matrix; the hydrogen fluoride produced during the hydrolysis reaction is neutralized by the alumina/silicate matrix, forming chemically stable compounds such as AlF_3 or SiF_4; any residual HF is removed from the sampling environment during a post-exposure evacuation on the sampling tap prior to removal of the SUDA sampler. Samples are meant to be kept in the closed SUDA samplers for storage and transport. Work for this project has involved multiple shipments of blank and loaded samples between INL, PNNL, and ORNL multiple times, with no noticeable degradation (e.g., no flaking of loaded zeolite) for samples exceeding one year since loading. If needed for confirmatory analysis the uranium held within the zeolite can be extracted from the sampler by soaking the coupon in water, to facilitate follow-on analyses using another DA techniques.

Initial development of the SUDA sampler technology focused on the development of thick zeolite matrices >500 $\mu g\ cm^{-2}$ (>5-10 μm). Thick in this case relates to the maximum zeolite thickness possible to still allow high-resolution alpha spectrometry (the ability to individually resolve the alpha-particles from ^{234}U, ^{235}U, and ^{238}U (Table 1). As illustrated below, the zeolite thickness needs to be ~0.1 μm or less to allow high-resolution alpha spectrometry. Thicker samples can still be used to produce high-quality alpha spectra. However, in such cases it becomes difficult to discriminate the alpha emissions from ^{235}U from the other U isotopes since, in terms of energy, they fall in-between those of ^{238}U (lower in energy) and ^{234}U (higher in energy). Prior work has shown it is possible to fit the alpha peaks in thick-film spectra and extract quantitative results.[22,23] However, for thick samples of natural or depleted uranium the low concentration and low specific activity of ^{235}U generally rules out peak fitting for these cases. In principle it would be possible to perform an analysis of the ^{234}U:^{238}U atom ratio, and then extrapolate this to estimate the ^{235}U:U_{total} ratio, and thus still perform assays with thick spectra. Analysis using thick-film samples is much faster than those using thin films, and thus may be adequate for use in rapid screening measurements. However, prior work shows that while the ratio of ^{234}U to ^{235}U in enriched and depleted samples follows general trends, those trends are not consistent to a level that would allow safeguards enrichment verification for safeguards applications.[24]

Table 1 Key nuclear data for the alpha decay of uranium isotopes.

Isotope	Specific activity, Bq g^{-1}	Alpha energy, keV	Alpha particle yield, %
^{234}U	7.31×10^4	4774.6	71.4
		4772.4	28.4
^{235}U	3.89×10^3	4397.8	55.0
		4336.1	17.0
		4214.7	5.7
		4596.4	5.0
		4556.0	4.2
^{238}U	1.16×10^4	4198	79.0
		4151	20.9

The first prototype for the IFAS system was centered on the use of a single-crystal (sc), chemical vapor deposited (CVD) semiconductor sensor made using industrial diamond.[20] This was chosen because initial information suggested the beta-decay radiation signal from thick-film SUDA samples might be too intense to allow the use of more traditional, silicon-based surface-barrier semiconductor detectors. Following initial testing that showed this concern was unwarranted, and that Si semiconductors regularly used in high-resolution alpha spectrometer would work with thin-film SUDA samplers, work then shifted to the temporary use of small-scale commercial packages, using the ORTEC (Oak Ridge, Tenn.) DUO and MEGA detector housings with ORTEC ULTRA-AS ion-implanted, circular Si surface barrier detectors at different sizes including Ø 23.9 mm (450 mm^2) and Ø 61.8 mm (3000 mm^2). A photograph of a SUDA sampler resting on a tray below a 450-mm^2 ULTRA-AS alpha detector in the left-side counting drawer of a DUO detector housing is shown in Figure 3.

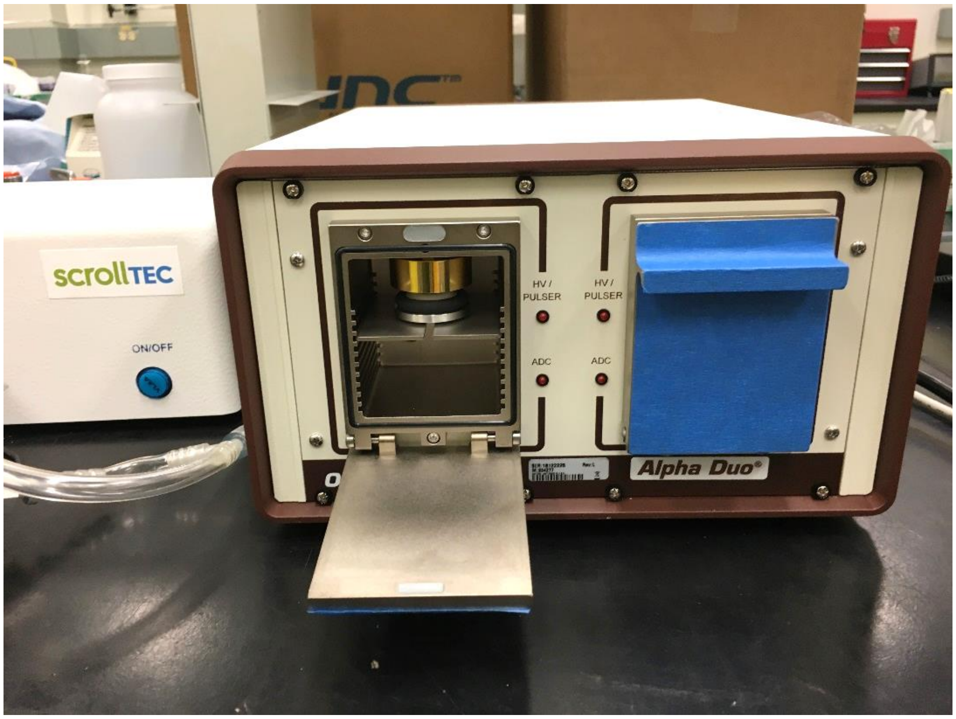

Figure 3 Photograph of a SUDA sampler resting on a tray below an ULTRA-AS alpha detector in the left-side counting drawer of a DUO detector housing.

MEASUREMENTS AND SIMULATIONS

Examples of alpha spectra from two SUDA samples loaded with natural uranium, with zeolite matrices with thicknesses of ~0.1 μm and ~0.04 μm, are shown in Figure 4. The major alpha emission energies from ^{234}U, ^{235}U, and ^{238}U are also shown in the figure. In terms of energy resolution and noise, these spectra are on par with what would be expected from uranium produced using traditional radiochemical separation and electrodeposition methods. In order to better understand the performance of the SUDA samplers when used for alpha spectrometry, computer simulations were performed to estimate the counting time needed to achieve different levels of precision, as a function of sample thickness and diameter, sample-to-detector spacing, and detector diameter.[25] An example of a simulated spectrum ('measured' time of 12 hours) is shown in Figure 5 together with a measured spectrum (5.5 hours). In the simulation the sample diameter was increased from 12.7 mm to 39 mm, the sample thickness was decreased from ~0.1 µm to 0.07 µm, the sample-to-detector spacing was decreased from 15 mm to 10 mm, and the detector diameter was increased from 9.8 mm to 40 mm. Overall, with these optimizations the general spectral shape remains comparable and still acceptable for direct ^{235}U determination. The 'counting time' for the simulated spectrum was 12 hours vs. 5.5 hours for the measured spectrum; however, the signal rate has increased by a factor of 60.

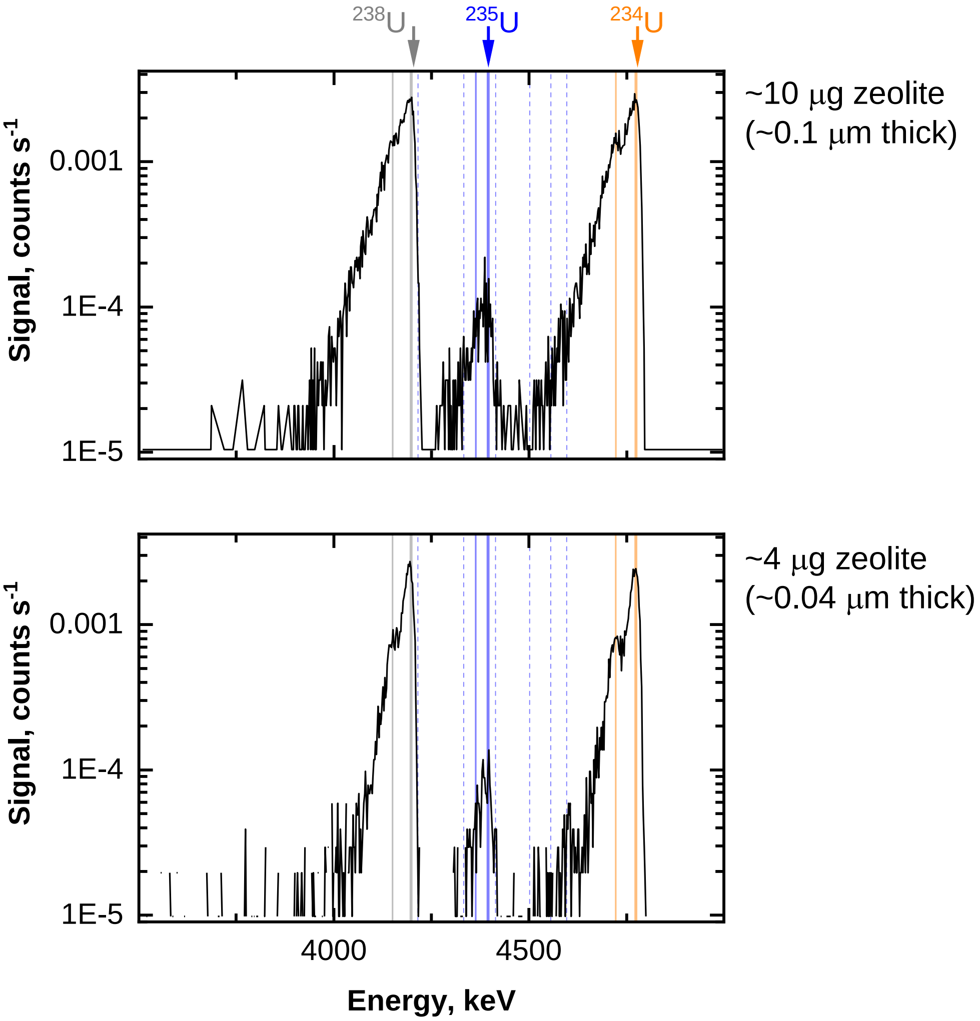

Figure 4 Measured alpha spectra, using a Ø 23.9-mm detector, from two SUDA samples loaded with natural uranium with zeolite matrices with thicknesses of ~0.1 µm (top), and ~0.04 µm (bottom).

Using the optimized detection parameters presented above, an analysis was performed to assess the measurement times that will be expected from an IFAS system to achieve different levels of precision for the ^{235}U:^{238}U determination. These simulations used larger-diameter SUDA samples along with larger-diameter detectors than were available for recent laboratory testing. The results from this analysis are shown graphically in Figure 6. For depleted uranium, alpha-spectrometry in the field using these IFAS system parameters and larger SUDA samples is expected to reach a precision of ±3% (1-σ) after a 9-h counting period. For natural uranium, alpha-spectrometry in the field with these

IFAS system parameters and larger SUDA samples is expected to reach a precision of ±3% (1-σ) after a 2.8-h counting period.

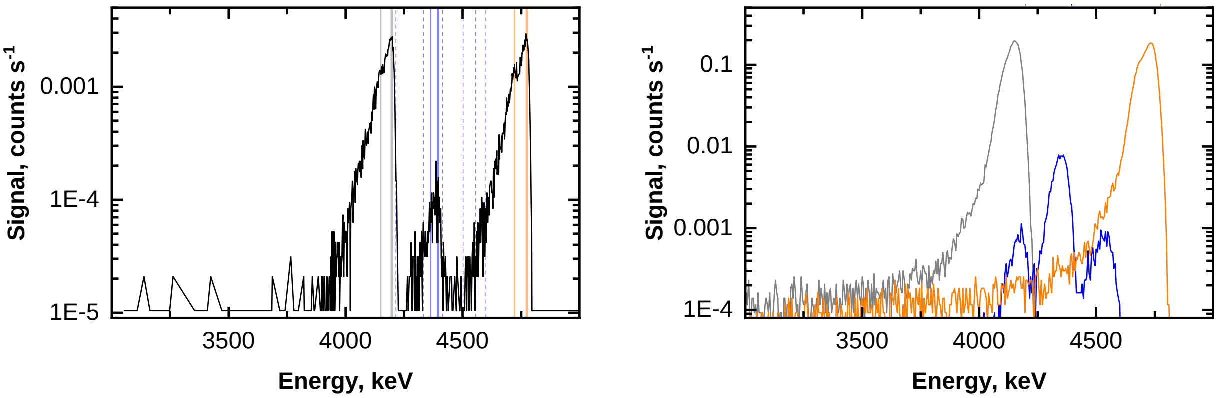

Figure 5 Measured (left) and simulated (right) alpha spectra for analysis of a SUDA sample loaded with natural uranium. The measured spectrum was for a ~0.04-µm thick sample measured with a Ø 23.9-mm detector, the simulated spectrum used a ~0.07-µm thick sample and a Ø 39-mm detector.

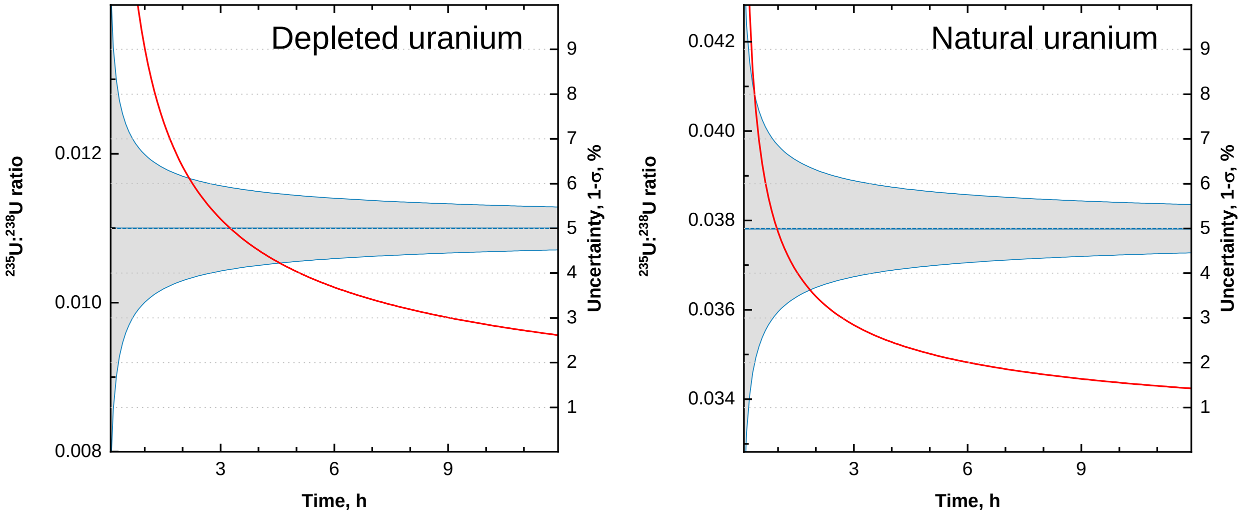

Figure 6 Simulated IFAS signal evolution for depleted uranium (left) and natural uranium (right). The grey areas denote the ±1-σ bounds on the ^{235}U/^{238}U activity ratio (left axes) vs counting time while the red curves show the trend in uncertainty in the determination of the activity ratio (right axes) vs. counting time.

SUMMARY AND FUTURE WORK

Initial work has shown that SUDA samples made using especially-designed thin, zeolite films can safely capture uranium following exposure to gaseous UF_6 and produce stable, thin-film substrates suitable for high-resolution alpha spectrometry. Further, these samples have been shown to be stable and robust to allow shipment via commercial carrier, as well as having the ability to endure long-term storage, in excess of a year following collection, while still being able to produce non-degraded alpha spectra. Simulations were performed to analyze an IFAS system with some optimized parameters in order to estimate the measurement time that would be needed to achieve different levels of analytical precision on the determination of ^{235}U:^{238}U (based only on counting statistics) for the analysis of depleted uranium and natural uranium. This work showed that depleted uranium analysis might extend to 9 h to reach a 3% (1-σ) uncertainty level while analysis of natural uranium (with more ^{235}U) might be done in as little as 2.8 h. For the analysis of natural uranium or low-enriched uranium, the IFAS system should be able to produce results with a precision of better than ±2% (1-σ) in under eight hours. This measurement method is more sensitive for U at higher ^{235}U enrichment levels. The IFAS concept seems like a promising analytical method for field use to support uranium enrichment verification as a screening method for regular inspection of gas centrifuge enrichment plant (GCEP) cascade conditions, and unannounced inspections of GCEP facilities or unannounced inspections of feed-stock, product, or by-product cylinders.

Additional work is needed to examine factors that may influence degradation of the zeolite coupons and an associated degradation in measured alpha spectral quality, which manifests as a decreased apparent energy resolution and peak smearing. Some initial works suggest, for example, that humidity in the sample handling environment can affect the quality of measured spectra. Similarly, work is also underway to decrease the size and footprint of the IFAS system. Included in this is the development of a custom-designed sensor housing that will provide for the electrical feedthrough and vacuum connections but which will attach directly to the SUDA sample, using the SUDA sampler's hinge bracket to attach the sample directly to the IFAS. Also, work is underway to produce a miniature digital data readout and integrated voltage supply, so that the entire IFAS unit (exclusive of vacuum pump) will have a total volume of under 1,000 cm^3.

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