Optimization of In-Field Alpha Spectrometry for Uranium Enrichment Determination in Uranium Hexafluoride

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

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

ABSTRACT

In response to needs identified by the International Atomic Energy Agency (IAEA) research is underway to develop In-Field Alpha Spectrometry (IFAS) as a method to potentially allow IAEA safeguards inspectors to collect samples of uranium hexafluoride (UF_6) at processing facilities to assess and verify uranium enrichment. For sample collection, the IFAS method uses Single-Use Destructive Assay (SUDA) samplers, which contain thin zeolite coatings that trap UF_6 gas and convert it to the safer and more stable form uranyl fluoride (UO_2F_2). For alpha spectrometry, the IFAS instrument employs a large area silicon semiconductor transducer to detect and record alpha particle energy-deposition events. Over the past year optimization work has significantly increased the diameter of useful SUDA samplers (from 12.7 mm to 48 mm), improved the manufacturability and reproducibility of SUDA samplers, increased the area of the IFAS alpha spectrometer sensor from 1.2 cm to 3.1 cm, and improved source positioning within the IFAS. This paper will report on this optimization work, its impacts on IFAS performance, and future plans for IFAS miniaturization, improvements, and testing.

INTRODUCTION

The In-Field Alpha Spectrometer (IFAS) is a modified commercial-off-the-shelf (COTS) alpha spectrometer that uses specialized collection substrates called "Single-Use Destructive Assay" (SUDA) samplers for the collection of uranium hexafluoride (UF_6).[1,2] The IFAS is designed to potentially allow International Atomic Energy Agency (IAEA) safeguards inspectors to perform direct, on-site alpha spectrometry of samples taken at UF_6 processing facilities. As outlined in IAEA Information Circular 153 (INFCIRC/153), the IAEA needs to be able to verify the correctness and completeness of a State's safeguards declaration.[3] Alpha spectrometric methods are well suited for the determination of uranium isotope ratios starting with material in a variety of sample matrices. Due to the excellent analytical capabilities that can be achieved using alpha spectrometry, 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 enrichment plants.[4,5] 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.[4] 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 "Development and Implementation Support Programme for Nuclear Verification 2020-2021 (STR-393).[6,7]

Idaho National Laboratory, Pacific Northwest National Laboratory, and Oak Ridge National Laboratory are working together on IFAS development. Prior work by the research team has demonstrated i) the design and use of SUDA coupons for the collection of UF_6; ii) that robust IFAS systems could be developed to perform quantitative assays of thick-film samples, iii) and that IFAS measurements can be used to assess uranium enrichment of UF_6.[1,2,8] This paper reports recent advances made to the modified-COTS IFAS system to improve the manufacturing and performance of the SUDA samplers, improve the ease of use of the IFAS hardware, and improve protocols for UF_6 sample collection and handling.

EQUIPMENT AND METHODS

The IFAS system is designed for safeguards inspectors at uranium processing facilities as a portable benchtop instrument. By design, it uses COTS components to facilitate training, maintenance, support, and international shipping (export control requirements). Equally important to the IFAS measurement hardware is the use of optimized SUDA samplers, an ideal sample collection medium to ensure the acquisition of high-quality alpha spectra.

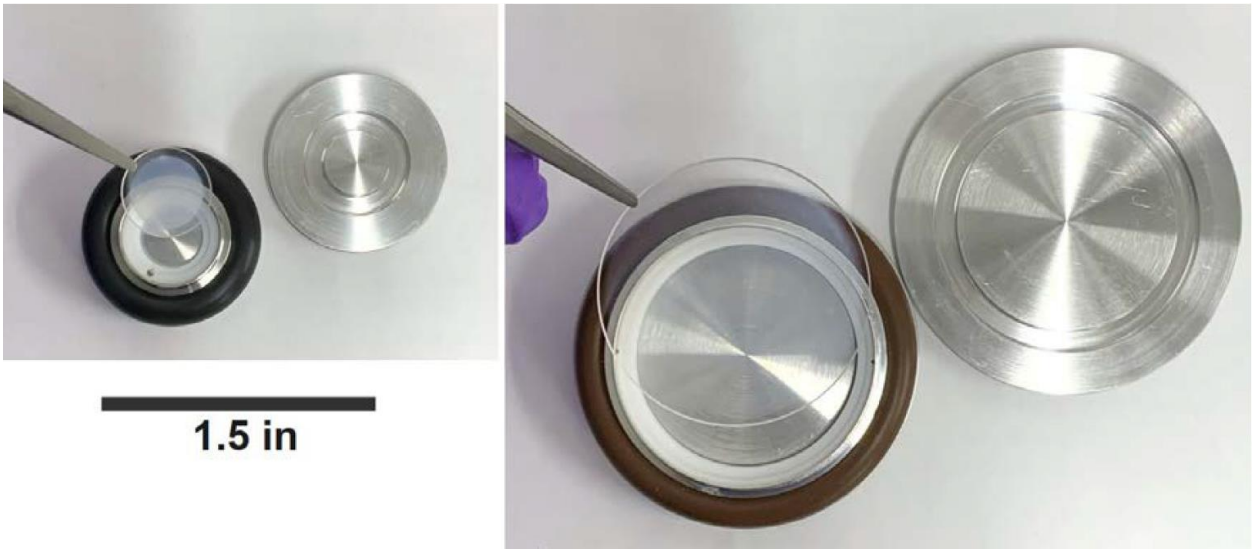

Figure 1 An original 12.7-mm diameter SUDA sampler on the left, and a new 44.4-mm diameter sampler on the right.[9]

SUDA Sampler Improvements

As has been presented previously, the SUDA coupon is comprised of a support wafer coated with an absorbent (nanocrystalline zeolite) film.[1] Original SUDA samplers used a 12.7-mm diameter silicon wafer with a roughened surface; this rough surface provided increased film surface area and film adhesion. The small diameter and rough surface of the substrate were not optimal for alpha spectrometry. Understanding that sample geometry plays an important role in alpha-spectrometry, SUDA samplers optimized for alpha spectrometry.[9] To address the issue of surface roughness, the substrates were changed to smoother optical-grade quartz (SiO_2) wafers an automated spray-coating tool was employed. For the initial SUDA sampler development, the zeolite films were applied from solutions using a simple hand-operated forced-air spray-coating tool. While an effective coating

method, this approach was insufficient for producing consistent and uniform film coatings across each wafer, and from wafer to wafer. Instead of hand application, a Sono-Tek (Milton, N.Y.) Exactacoat system was acquired which employs an ultrasonic atomizing spray-nozzle combined with low-pressure air to produce a soft, highly focused spray of micrometer-sized droplets. With this system a uniform spray area was achieved, which allowed for full coverage of the SUDA coupons. To address sample size (area), further changes were made to allow using larger diameter wafers, ultimately allowing wafers measuring up to 44.4 mm in diameter, as shown in Figure 1.[9]

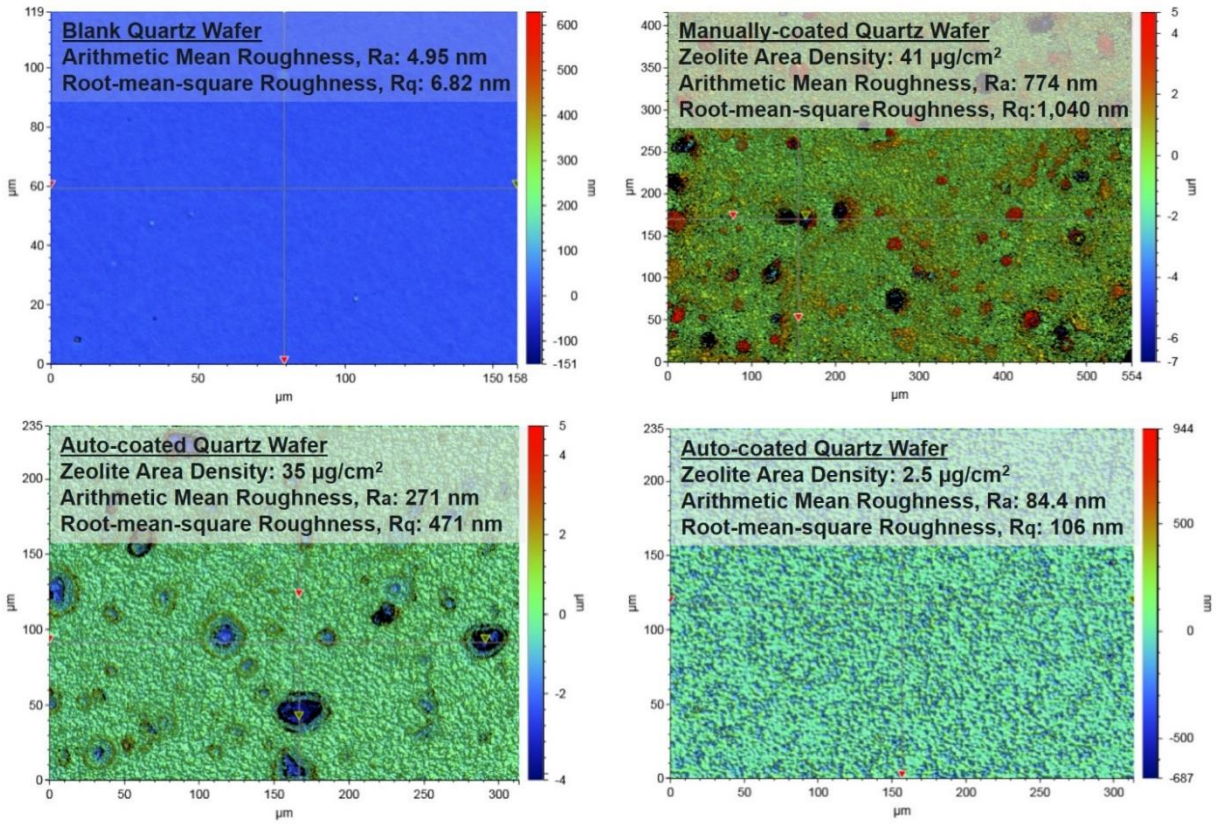

Figure 2 Profilometry data for a) an uncoated quartz wafer (top left), b) a hand-coated quartz wafer (top right), c) an auto-coated quartz wafer (bottom left), and d) an auto-coated quartz wafer (bottom right) with an IFAS-optimized zeolite area density of 2.5 µg cm^{-2}.[9]

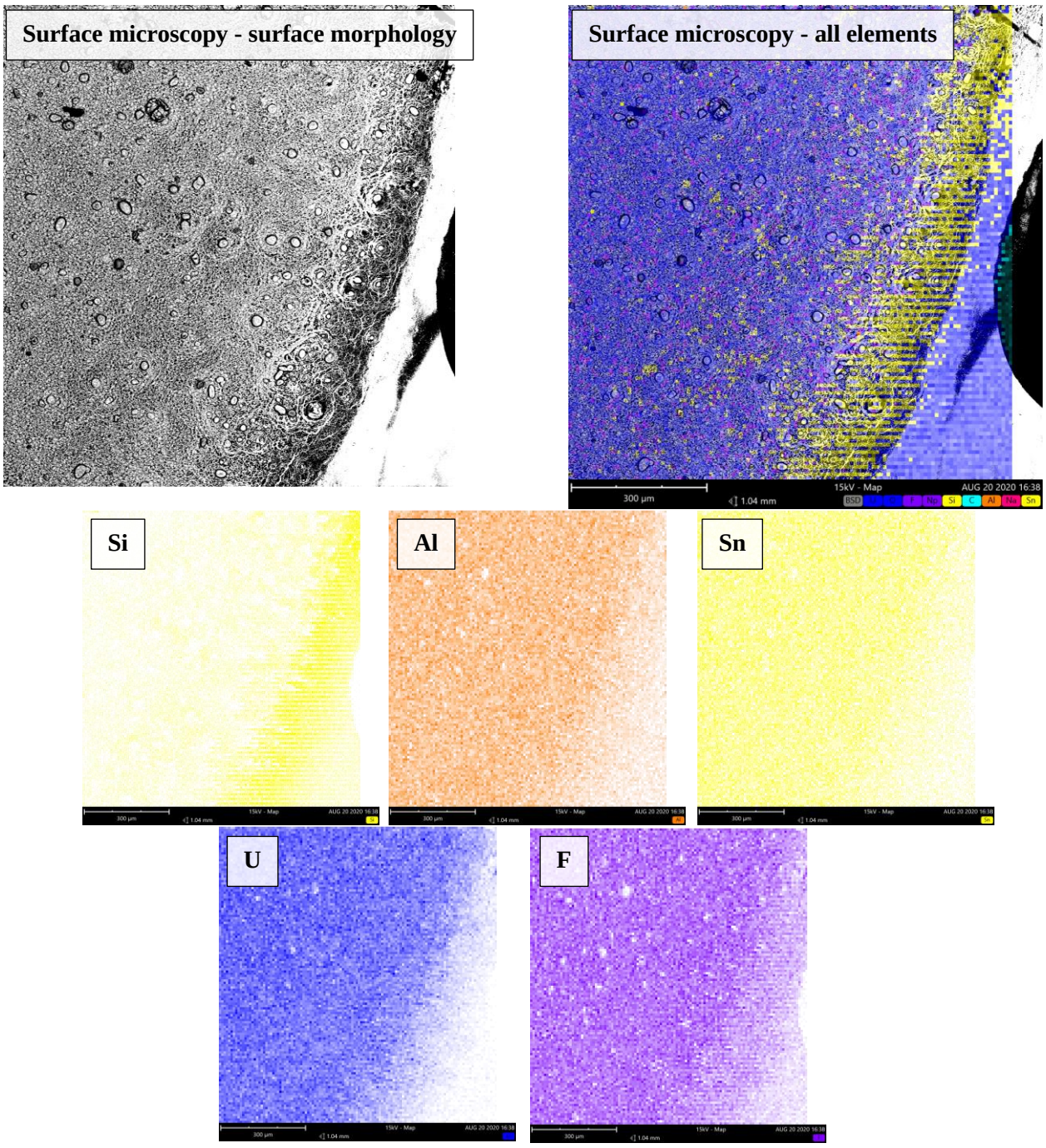

Figure 3 Surface morphology and elemental presence of Si, Al, Sn, U, and F in a newly made, UF_6 loaded SUDA sample. The AL and Sn are from the zeolite coating. Silicon may be from the zeolite coating or the glass substrate. Uranium and fluorine are from the deposited uranyl fluoride.

Figure 4 Photograph of the improved SUDA sampler wafer (left), and the new markings on the SUDA sampler's KF flange (right).

With these new methods for SUDA sampler production, materials science studies were performed to better understand the structure and performance of the zeolite coatings.[9] White light interferometry, with a height resolution on the nanometer scale, was used to measure surface profiles of coatings. These analyses included comparisons of the surface roughness of an uncoated quartz wafer, a manually spray-coated quartz wafer, an auto-coated quartz wafer, and an auto-coated quartz wafer with a lighter zeolite coating. The root-mean square (RMS) roughness of the films was 6.82 nm for the uncoated quartz wafer, 1,040 nm for the manually coated film, 471 nm for the auto-coated film, and 106 nm for the auto-coated film with a lighter zeolite coating. Two-dimensional surface plots of the films are shown in Figure 2 for these four cases.[9] Scanning electron microscopy and energy dispersive spectroscopy were used to look for uniformity of U uptake in the SUDA film surfaces and to understand elemental distributions within the films. Results from this analysis are shown in Figure 3. As expected, the U and F composition in the films is correlated and reasonably uniform across the film. It can be noted that the SUDA produced with the new coating system are much more uniform and show near homogenous loading of uranium.

In addition to technical improvements to the SUDA samplers, improvements were made to make them user friendly and easier to inventory. A CO_2 laser etching system (Epilog Laser Mini, Golden, Colo.) was used for etching of quartz wafers and aluminum KF flanges so that each sample bears a unique serialized identification code. To further aid operators to ensure the samplers are oriented correctly during connection to a manifold and during measurements, the SUDA samplers are now also labelled on the back side of the quartz wafer with the word “SUDA” and "This Side Up". Laser etching is also used to mark the metal surfaces of the outer KF flanges. This marking includes the sampler ID, sampler fabrication date, fabrication lab, zeolite batch number, zeolite mass loading, estimated uranyl fluoride mass (fully loaded), and estimated uranium mass after sampling (when fully loaded). Also included on the flange is a quick response (QR) code which is encoded with the summary of the unique sample information for ease of laboratory inventory management.

IFAS Hardware Improvements

The IFAS system consists of a modified COTS alpha spectrometer (ORTEC Alpha Mega spectrometer, Oak Ridge, Tenn.), a small vacuum pump, a laptop computer, cables, and tubing. A photograph of the IFAS system, assembled on a lab bench, is shown in Figure 5. The modification to the COTS system consists of a specialized drawer insert that goes inside the Alpha Mega measurement cavity, which holds and positions different-sized KF-flanges that, in-turn, hold correspondingly different-sized SUDA samplers. A photograph of the open Alpha Mega door is shown in Figure 6, along with an image showing the sample positioning tray swiveled to the open position, holding a KF flange and a SUDA sample. The drawer insert and swivel tray were specifically designed to allow an operator, while wearing gloves, to easily and reproducibly position samples under a large-area (3000 mm^2) silicon semiconductor alpha spectrometer held in the ceiling of the Alpha Mega measurement cavity (not shown). The sample geometry, using a large-area SUDA sampler and correspondingly large-area silicon detector, optimizes the measurement time while still allowing for an alpha spectrum with sufficient energy resolution for uranium assay. An example of an alpha spectrum collected using this hardware configuration and a 44.4-m diameter SUDA sampler that contains low-enriched uranium (LEU) (4.62 wt.% ^{235}U) is shown in Figure 7.

Figure 5 Photograph of the IFAS on a lab bench.

Figure 6 Photograph of the open Alpha Mega drawer (left) and the insert tray in the open position, holding a small-sized KF flange and SDUA sample (right).

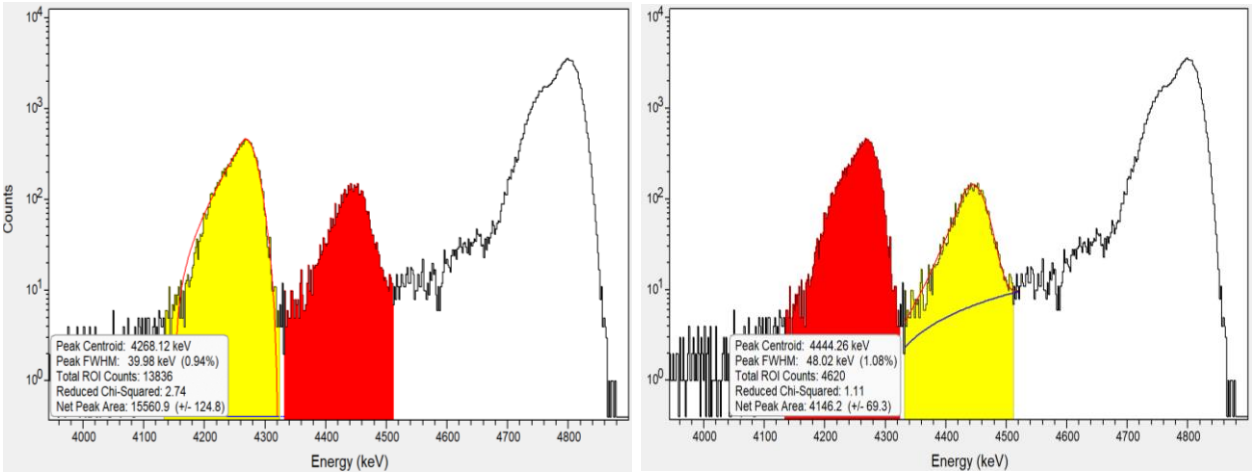

Figure 7 Alpha spectrum measured with the IFAS for an LEU UF_6 sample (4.62 wt.% ^{235}U). The left panel shows a simple asymmetric Gaussian fit for the ^{238}U alpha particles (yellow) and the right panel shows a fit for the ^{235}U alpha particles (yellow).

Improved Protocols for Loading SUDA Samplers

During laboratory testing there were some instances when measured alpha spectra were observed to exhibit unusually significant low-energy tailing. This work occurred using laboratory-based UF_6 manifolds. While it is unclear if these effects would manifest at a commercial UF_6 processing facility, research was performed to examine the effects and develop improved loading protocols. To do this, a parametric study was performed to assess if environmental conditions present during sample storage and loading could affect the samples. As a result of this analysis, optimized conditions were established for pre-drying the samples, shipping and storing the samples, and loading the samples. The single largest improvement was found by pre-drying the SUDA samplers after fabrication. This was done in a 100 °C vacuum for several hours to remove excess water content. It appears that excessive moisture within the zeolite may lead to low-energy alpha tailing in some cases. The vacuum oven was back filled with a dry inert gas to prevent excess wetting while each sample was sealed

using a KF blank flange and clamp for shipping and storage. As an additional precautionary, our team now also takes an extra step of storing and shipping SUDA samplers inside a resealable mylar bag with a desiccant capsule (Figure 8). It should be emphasized that this is an advised 'best practice', to address the possibility that samplers may be stored or shipped in unknown conditions that are worse than we have encountered so far. In our current efforts, SUDA samplers in excess of three years since loading have been repeatedly opened, measured, and resealed under laboratory conditions, without the mylar bag and desiccant, with no observable quality degradation in alpha spectral.

Figure 8 Photograph of a large SUDA sampler being placed in a mylar resealable bag (left) and a close-up image of a laser-etched marking in a mylar bag (right).

The SUDA samplers were loaded using a two- or four-station sampling port that has previously been used to load SUDA and other samples, as described previously.[10] Typically, 2 or 4 samples are collected simultaneously on the system. The SUDA samplers are removed from their mylar bags and attached to the sample taps using the KF clamp and the blank flange. The samplers are then evacuated and back flushed with dry inert gas twice, and then evacuated once more. The submanifold, including the samples, is then isolated to verify the system is leak tight. The samples are then isolated under vacuum before filling the submanifold with the desired pressure of uranium hexafluoride from a source bottle. Typically, a pressure of 80 torr was used for most studies, although testing at other loading pressures has been performed. The UF_6 source was isolated before opening the valves to the sample taps and exposing the SUDA sample. Typical pressure changes are shown in Figure 9; a quick, initial drop is observed as the gas expands into the vacuum around the SUDA samplers followed by a slow decrease in pressure as the UF_6 sorbs onto the SUDA substrate. Typical experiments allow 2 minutes for the SUDA substrate to react with the gas before the system is evacuated into the main manifold. The system is then evacuated and back-filled with dry, inert gas three times to remove any residual UF_6. The system is then brought to ambient pressure with dry, inert gas to disconnect the SUDA samplers. The UF_6-loaded SUDA are then sealed with KF flanges and clamps, placed inside the original resealable mylar bag with a desiccant capsule, and were ready for shipping. Typically it took 30 minutes from installation to removal of the samplers.

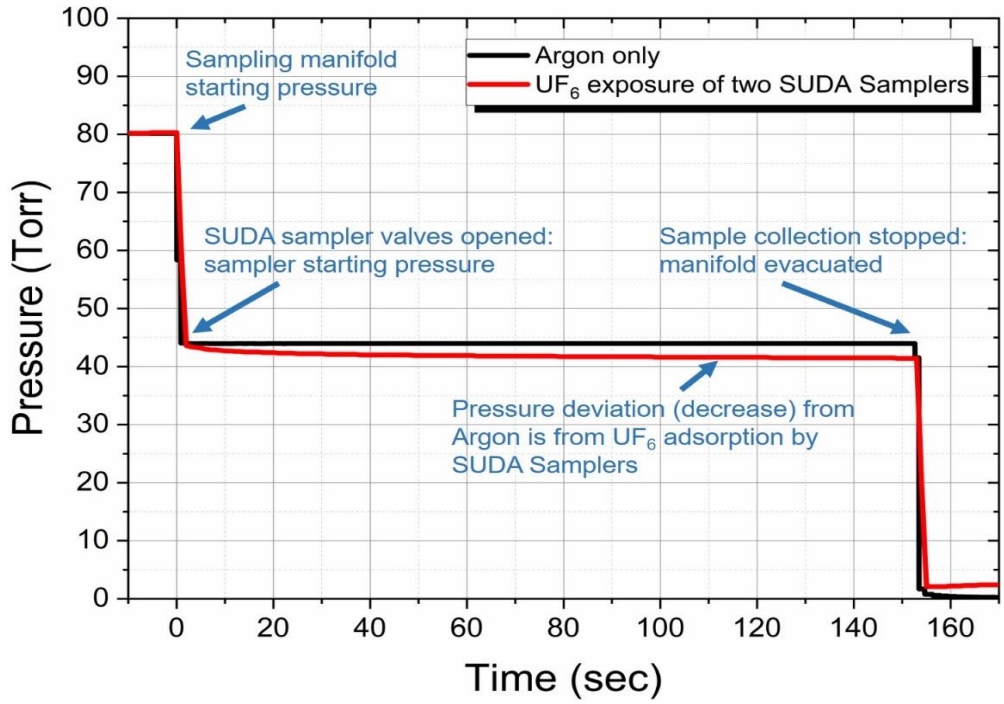

Figure 9 Example showing typical pressure readings for loading SUDA samplers with UF_6.

SUMMARY AND FUTURE WORK

Many practical aspects of the IFAS system have improved and optimized over the past year. Improved methods for manufacturing SUDA samplers now allow for using much larger surface-area samples while still supporting high-quality alpha spectrometry. Improved SUDA sampler packaging now aids in laboratory sample tracking and inventory management. The development of a modified COTS measurement system now makes sample handling, insertion, and removal easier and safer for a field operator. Research has led to improved knowledge of how process conditions can impact the final alpha spectrum quality of SUDA samplers and has led to an optimized loading procedure for these samples. New concepts for sampled handling and packaging now also improve the resilience of the packages for transport and longer-term storage too. The complete IFAS system has been packaged into one, medium-sized shipping box that can be handheld by one person. Laboratory exercises show that the IFAS can be unpacked, assembled, and ready for use by one person in fewer than ten minutes.

Work is now underway to perform studies to assess overall method uncertainty and reproducibility. A large number of SUDA samplers has been loaded at a variety of different uranium enrichment levels, these will be assayed and analyzed to assess the combined standard uncertainty for using the IFAS system to perform uranium enrichment determination in low-enriched uranium samples. Further work is also anticipated to collect and analyze SUDA samplers at real-world facilities, beyond the laboratory-type work done so far, to assess practical aspects related to its deployment and use.

ACKNOWLEDGEMENTS
Work described here was funded by the Safeguards Technology Development Program within the U.S. Department of Energy / National Nuclear Security Administration / Office of Defense Nuclear Nonproliferation / Office of International Nuclear Safeguards.

REFERENCES

1. Chichester, D. L., et al., "In-Field Alpha Spectrometry to Assess Uranium Enrichment in Uranium Hexafluoride," Conf. Proc., INMM Annual Meeting, Baltimore, Md. (2020).
2. Anheier, N. C., Barrett, C. A., and Guerrero, R., "PNNL Single Use Destructive Assay Sampler," Report PNNL-25123, Pacific Northwest National Laboratory, Richland, Washington. (2016).
3. Circular INFCIRC/153, IAEA, Vienna, Austria (1972).
4. Berlizov, A, "Towards Field Alpha Spectrometry of UF_6," A Presentation given at the Meeting on UF_6 Analysis for IAEA Safeguards, EC JRC IRMM, Geel, Belgium, May 10 (2016).
5. "In-Field Analysis of UF_6 for Nuclear Safeguards," minutes prepared by Aregbe, Y., Minutes of Meeting with EC-JRC-IRMM, Geel, Belgium, May 10 (2016).
6. "IAEA Research and Development Plan, Enhancing Capabilities for Nuclear Verification," Report STR-385, IAEA, Vienna, Austria, January (2018).
7. " Development and Implementation Support Programme for Nuclear Verification 2020-2021," Report STR-393, IAEA, Vienna, Austria, January (2020).
8. Chichester, D. L., Johnson, J. T., and Miller, B. D., "Direct Alpha Spectrometry as a Screening Method for Assaying Thick, Highly-Radioactive Materials," J. Radioanal. Nucl. Chem. 318 (2018) 553-560.
9. Pope, T., "SUDA Sampler Production Methods and Improvements for Uranium Enrichment Assay via In-Field Alpha Spectrometry," Report PNNL-30605, Pacific Northwest National Laboratory, Richland, Wash. (2020).
10. Anheier, N. C. et al., "New Samplers for UF_6 Destructive Assay: Field Testing and Demonstration, Conf. Proc., INMM Annual Meeting, Baltimore, Md. (2018).