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Single-Use Destructive Assay for Uranium Hexafluoride Sampling

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ABSTRACT

Sampling uranium hexafluoride (UF₆) for the determination of enrichments by destructive analysis (DA) is a critical component in the International Atomic Energy Agency's layered safeguards approach for uranium processing facilities. Typically, gram-quantity UF₆ samples are collected during inspections and stored under tag-and-seal until transportation to an off-site analytical laboratory. Pacific Northwest National Laboratory has developed a low-cost UF₆ sampling technology called Single-Use Destructive Assay (SUDA) that generates low amounts of waste, offers ease of shipping, and provides DA sample geometries tailored for different analytical methods, including potential on-site analyses such as in-field alpha spectrometry.[1] The SUDA samplers, along with a unique holder, are designed for direct attachment to existing taps at uranium processing facilities, allowing gaseous UF₆ to come into direct contact with a zeolite film. The SUDA technology features the ability to capture uranium in a more easily shipped and handled form as the solid, more stable, and relatively less hazardous hydrated uranyl fluoride (UO₂F₂·nH₂O), which is formed through the controlled hydrolysis of UF₆. We have recently simulated uranium collection under enrichment plant sampling conditions to further improve our understanding of SUDA sampling. Presented here is our recent work on measuring the relationship between sampling conditions and uranium collection, which includes control of the uranium-mass-to-zeolite ratio and assessing variable UF₆ gas and sampling parameters that can affect collection using the SUDA sampler.

INTRODUCTION

The IAEA conducts destructive assay (DA) sampling and analysis to provide verification of the declared uranium enrichment at gaseous centrifuge enrichment plants (GCEPs). Such safeguards measures at bulk uranium facilities involve gaseous UF₆ sampling and shipment for off-site analysis. UF₆ sample collection provides samples drawn from the cylinder population and in-process gas for off-site laboratory analysis at the IAEA's Nuclear Materials Laboratory (NML). Cylinder DA measurements are critical in the statistical analysis of the plant's material balance as they provide high-precision confirmation of a large set of cylinder measurements made through non-destructive assays (NDAs).

At present, DA samples of UF₆ are drawn from a UF₆ sampling tap at gram quantities, which results in large quantities of radioactive waste over time. The SUDA sampler technology uses a porous aluminosilicate (Al₂O₃/SiO₂) film, allowing for the controlled hydrolysis of toxic UF₆ gas into

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solid and relatively stable uranyl fluoride ($\text{UO}_2\text{F}_2 \cdot n\text{H}_2\text{O}$). This chemical conversion reduces sample sizes and could facilitate sample shipments and reduce nuclear material holdings stored at NML.

The SUDA sampler is designed to be used with existing sampling taps in facilities, such as uranium enrichment plants (UEPs). Prior and current testing was performed using samples collected using custom-built sampling taps made exclusively for UF_6 sampling technologies. The current study aims to simulate UF_6 sampling conditions that are compatible with both SUDA sampling techniques and the current sampling procedures used in UEPs. Changes in sampling time, UF_6 sampling pressures, and varying loading masses of the absorbent film will be discussed. Additionally, the ideal storage conditions of SUDA substrates will be reported.

THE SUDA SAMPLER

The SUDA sampler is designed to collect gas-phase uranium hexafluoride (UF_6) DA samples directly from a UF_6 sampling tap and is small enough to be carried on-site by an inspector. The SUDA is designed around a quick-release vacuum flange, which allows direct connection and operation with currently existing UF_6 sampling systems in enrichment facilities. During development and testing (including this work), SUDA samples were collected using custom-built sampling taps made exclusively for UF_6 sample collection technologies.

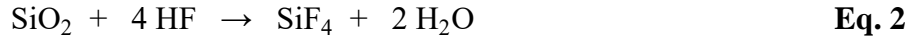
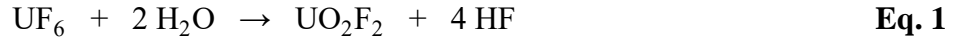
The SUDA substrate can be tailored to the desired assay technique to be used for determining uranium enrichment. For example, currently, there are three different SUDA substrates of varying sizes and chemical compositions that have been developed and tested for UF_6 sampling, including substrates (coupons) made from 0.5-inch (1.27 cm) silicon or quartz wafers, 1.75-inch (4.45 cm) quartz wafers, and 3 mm by 10 mm aluminum foam rods. For the UF_6 sampling tap study reported here, 0.5-inch silicon SUDA substrates were used. Note that after sampling, the substrate containing the collected uranium is referred to as the SUDA sample. The SUDA substrate is housed in a PTFE retainer placed in a centering ring and sealed with two blank flanges and a quick clamp (see Figure 1). By using a housing made from commercial off-the-shelf parts, the SUDA sampler can be directly connected to existing UEP sampling manifolds with or without commercial adaptors (if needed for connecting to a facility sampling manifold).



Figure 1. Typical construction of a SUDA sampler, where Left is the expanded view of a SUDA sampler; Center shows a SUDA substrate coated in UF_6 -absorbent material being loaded into the SUDA sampler (with the labeled back-side facing up); and Right is a fully assembled SUDA sampler.

THE SUDA SAMPLER'S ABSORBENT FILM

To convert gaseous UF_6 into solid uranyl fluoride, the SUDA substrate is coated with an absorbent zeolite (hydrated aluminosilicate) film. The synthesis is described in ASTM C1913-21, "Standard Practice for Sampling Gaseous Uranium Hexafluoride Using Zeolite in Single-Use Destructive Assay Sampler," as well as in reference 2.[2,3] During UF_6 sampling, uranium hexafluoride reacts with the zeolite film to produce water, hydrogen fluoride, and the non-volatile compound UO_2F_2 (see Equation 1 – Equation 3).



A Sono-Tek Exactacoat instrument was used to coat the SUDA substrates with a thin and uniform zeolite film. This auto-coating instrument uses an ultrasonic atomizing spray-nozzle combined with low-pressure air to produce a highly focused spray of micrometer-sized droplets (see inset of Figure 2). The spray of droplets containing the zeolite material has a narrow hourglass shape, where the center of the hourglass is the center focus of the spray. Below the focal point, the spray begins to spread out, and by increasing the distance between the focal point and the substrate being coated, the diameter of the coating spray area can be tuned (ranging from 0.070–1.0 inches, or 1.78–25 mm). Consequently, it is possible to focus a uniform spray area that covers the entire SUDA substrate. Ultimately, the following coating parameters were optimized and standardized for coating SUDA substrates using the Exactacoat instrument: ultrasonication (power and time) of the spray solution, solution flow rate, ultrasonic spray stall power, air pressure, spray-coating speed, spray nozzle to substrate distance, and substrate-to-substrate distance.



Figure 2. The auto-coating instrument used to coat the absorbent film onto the SUDA substrates (Left). The image on the Right shows the configuration of the instrument for coating and the inset (top right) shows the ultrasonic spray nozzle with fine spray control.

Custom coating trays were produced, which hold multiple substrates at a time (see Figure 2) to increase the number of SUDA substrates that can be fabricated at a single time. The positions of individual substrates placed on these coating trays are programmed into the instrument for the automatic coating of multiple substrates during a single coating session. Using the Exactacoat system, with optimized settings, it is possible to reproducibly coat multiple substrates at a time (typically in batches of 24) and obtain zeolite films with a standard deviation less than tens of micrograms, which is subsequently within the repeatability range of the mass balance used to weigh the SUDA substrates.

EXPERIMENTAL PARAMETERS

The study reported here can be divided into two separate investigations. The first investigation, referred to as the “Environmental” study, aims to determine the ideal storage conditions (i.e., humidity levels and heat treatment) of individual SUDA substrates coated with a fixed mass of zeolite film. The second investigation, referred to as the “Sampling Parameters” study, aims to determine ideal UF_6 sampling parameters when half-inch SUDA substrates coated with varying masses of zeolite film were exposed to different pressures of UF_6 . For both studies, the mass of uranium collected will be determined as a function of the SUDA sampler’s storage and sampling parameters. The following sub-sections outline the experimental parameters used in each study in greater detail.

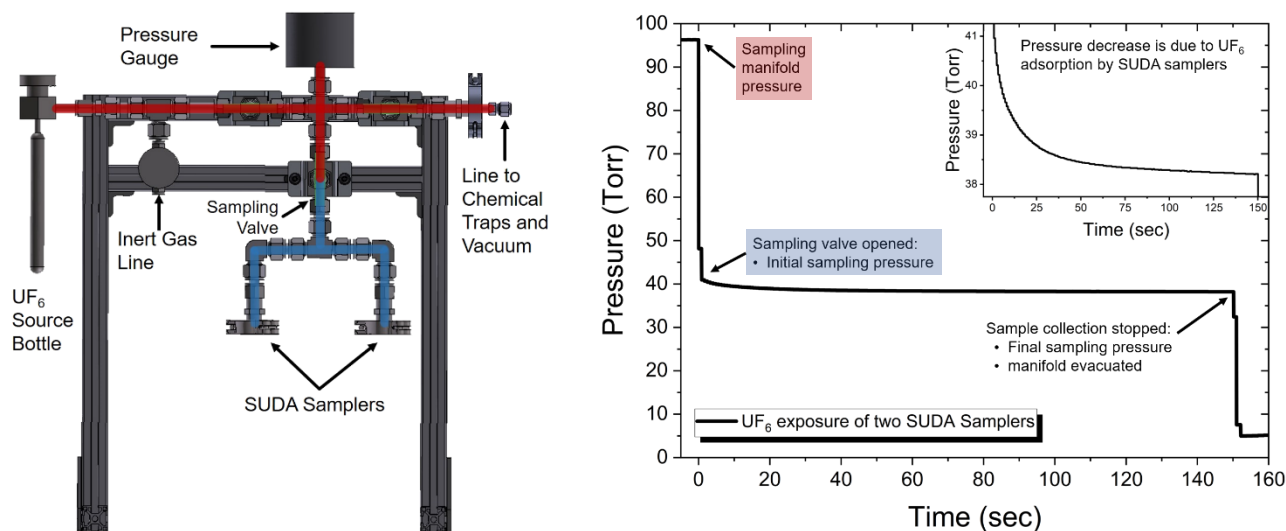


Figure 3. Left is an example schematic of the UF_6 sampling tap used in the experiment. In red is the section of the manifold that is pressurized with UF_6 prior to opening the sampling valve. After opening, UF_6 fills the blue portion of the sampling tap, and the pressure drop is recorded. An example pressure reading with corresponding sampling steps labeled is shown on the Right.

A lab-scale UF_6 sampling manifold with a connected pressure gauge (for gas pressure monitoring and data collection) was used for these studies; see schematic in Figure 3. UF_6 gas pressure data is collected over time to monitor pressure changes as the SUDA samplers collect and convert UF_6 gas to uranyl fluoride. An example pressure versus time plot collected during SUDA sampling is shown in Figure 3. As shown, the sampling manifold (the red portion of the sampling tap schematic) is pressurized to approximately 95 Torr. Once the pressure is stable, the sampling valve is opened, filling both the blue and red portions in the sampling tap schematic. Correspondingly, the UF_6 pressure drops

(due to volume expansion) to the target sampling pressure, which is approximately 40 Torr. During the extent of sampling time, the UF_6 pressure slowly decreases as the zeolite film absorbs UF_6 . When sampling is complete, the evacuation line is opened, and the sampling manifold is flushed with inert gas. For the complete sampling procedure, refer to ASTM C1913-21, “Standard Practice for Sampling Gaseous Uranium Hexafluoride Using Zeolite in Single-Use Destructive Assay Sampler.”[2]

For DA, SUDA samples are easily removed from the SUDA sampler housing by removing the bottom blank flange and allowing the SUDA sample (substrate) to fall out of the Teflon retainer into a vial or beaker containing a uranium extraction solution (either deionized water or a 2% nitric acid solution by volume) for dissolution of the sampled uranium. In previous work, we determined that 99% of the uranium is extracted in three to five minutes for SUDA samples collected within a few weeks timeframe.[4] In this work, we followed this procedure using 2% (by volume) nitric acid solution for uranium extractions.

We used Kinetic Phosphorescence Analysis (KPA) for rapid uranium concentration measurements, as we were only interested in the total uranium collected by the SUDA samplers as a function of sampling and environmental variables. KPA determines the uranium concentration in prepared DA samples (as uranyl solutions) by exploiting the phosphorescent properties of the uranyl ion (UO_2^{2+}).[5] A Chemchek™ KPA-11R instrument was used, which utilizes the phosphorescent intensity of a sample taken at selected time intervals compared against an external calibration curve to interpolate the analytical concentration within the sample. Discrimination against other light-emitting species is achieved using a laser dye with a specific excitation wavelength, interference filters for emission wavelength selectivity, and decay time for the uranyl ion. Samples are analyzed in dilute nitric acid or water with minimal sample preparation, and high selectivity and sensitivity allow for trace amounts of uranium to be detected. NIST-traceable 10 ppm uranium standard (Inorganic Ventures) was used for calibrations. A diluent blank, 2% (by vol) HNO_3 in ultra-pure deionized water, was mixed with the proprietary complexing agent, URAPLEX™, in a cuvette in the same ratio as the standards and SUDA samples. Standards and SUDA samples were prepared by adding 1 mL of sample solution and 1.5 mL of URAPLEX™ complexant to a 10 mm pathlength quartz cuvette. Each KPA analysis measurement was completed in 1-2 minutes, depending on the number of laser pulses selected in the instrument software. Accordingly, a blank and four standard/calibration solutions can be analyzed in approximately 10 minutes. Once complete, the mass of uranium collected by the SUDA samplers is inversely calculated from the measured concentration.

Environmental Parameters Study

To determine the effect of the SUDA substrates’ storage conditions prior to sample collection, we prepared 24 SUDA substrates, which were then stored under various environmental conditions prior to UF_6 sampling. Table 1 shows the average zeolite film mass and zeolite area density of the 24 substrates. The zeolite film masses were highly consistent, with a standard deviation of only 2%. A single zeolite area density was chosen to maintain a consistent uranium loading potential between samples to aid in elucidating any uranium collection variability due to storage conditions. Additionally, all substrates were coated with zeolite prepared from the same synthesis batch.

Table 1. Zeolite film data for the SUDA substrates used for the environmental study.

	Samplers Produced	Average Zeolite Film Mass (μg)	Standard Deviation of Zeolite Film Mass (μg)	Average Zeolite Area Density (mg/cm^2)
SUDA Samplers for Environmental Conditions	24	243	5	298

The storage conditions examined were high temperatures and high relative humidity, both with storage under either nitrogen or ambient air. Each condition was tested in pairs. The sampling pressure and time were held constant at 40 Torr and 2.5 minutes, respectively, to eliminate any sampling variabilities for this study. Figure 4, left, shows the UF_6 pressure decrease in the sampling tap as a function of sampling time for the SUDA samplers stored under the various conditions and the change in pressure for a blank sampling with argon gas only. Note that the initial sampling pressure (after the initial pressure drop from opening the sampling valve, approximately 40 Torr) has been scaled to zero to more easily compare the sampling pressure decrease from sample to sample. The decrease in UF_6 pressure is proportional to the amount of UF_6 taken up by the SUDA samplers.

The first set of samplers received no heat or humidity treatment and were stored under ambient air; the next set of samplers also received no treatment but were evacuated for 2 days then stored under nitrogen. The sampler stored under ambient air showed a larger initial pressure drop, but the final pressure drops of the samplers treated under the two conditions were comparable. A second set of samplers were exposed to high temperature (95 °C) for two days, after which one pair were stored under ambient conditions while the other pair were evacuated for 2 days then stored under nitrogen. The samplers stored under ambient conditions showed a similar trend and final pressure difference as the samplers not exposed to high temperatures. On the other hand, the samplers stored under nitrogen showed the largest pressure difference among all conditions tested.

The effect of exposure to humidity before sampling was then examined. Eight samplers were prepared with no heat treatment and stored under ambient conditions, and eight additional samplers were prepared with high heat treatment (95 °C) and evacuation for 2 days, followed by storage under nitrogen. Pairs of these samplers were then exposed to 25%, 50%, 75%, or 90% relative humidity for 1 day directly before sampling. All humidity conditions led to similar final pressure differences, with the exception of the untreated sample sealed under 25% relative humidity which showed a lower final pressure difference. KPA was then performed on all of the samplers after collection. The average ratio of the collected uranium mass to zeolite mass per SUDA sample was 2.0 (with a 0.3 standard deviation). No apparent trends were found in the sampled U mass with relative humidity between the heat-treated and non-heat treated samples (right plot in Figure 4). These data indicate that storage conditions do not significantly impact the collected U mass when the zeolite area density is constant. Moreover, these data suggest that opening the sampler under humid conditions prior to sampling does not significantly impact the collected U mass. Another observation for these data is that the pressure decrease for the majority of the samples begins to plateau near the end of the sampling (at two and a half minutes), except for the samples heat-treated, evacuated, and stored under nitrogen, which had the largest pressure decrease and, additionally, never fully reached a steady pressure state. This result

suggests that there is potential for further UF_6 capture for samples stored under these conditions if sampling times were increased. Thus, heat and evacuation treatment followed by storage under nitrogen will be used for future sample storage procedures.

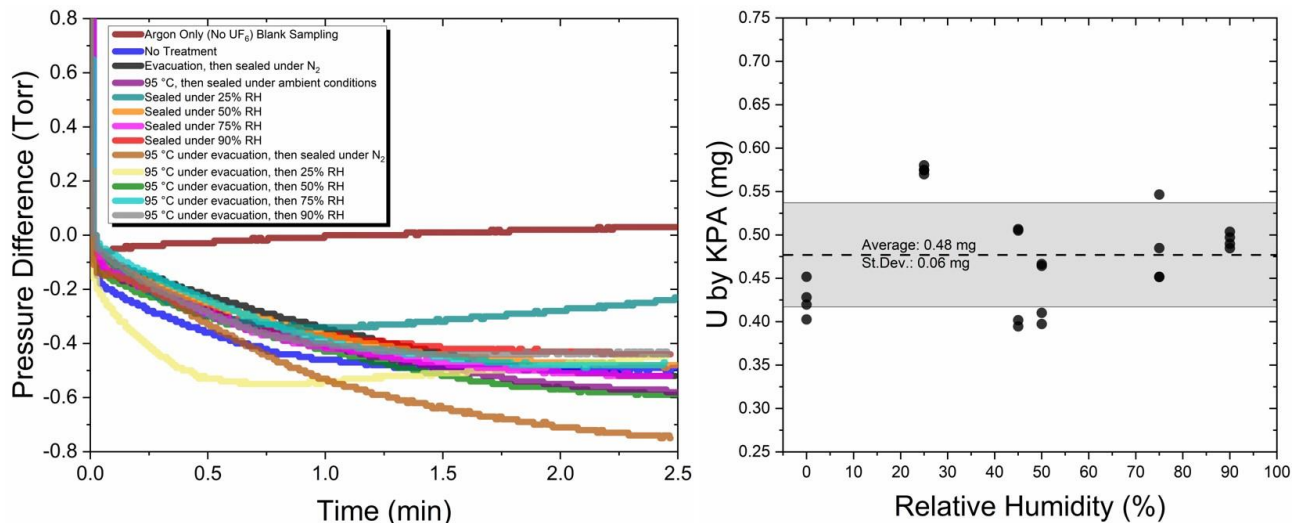


Figure 4. The normalized pressure drop over time for SUDA substrates stored under varying conditions (Left) and the total uranium mass collected as a function of the relative humidity of the SUDA substrates. Note that the 0% RH data points are the samples stored under dry nitrogen and the 45% RH data points are for the samples stored under ambient air.

Sampling Parameters Study

To determine whether the amount zeolite film coated on an individual SUDA sampler influenced the total amount of uranium that could be captured by a single SUDA substrate, three different zeolite film mass-loadings were investigated. The first set of SUDA samplers, referred to as low-mass (Group A) SUDA samplers, were coated with an average of 36 μg of zeolite; the second set, referred to as mid-mass (Group B) SUDA samplers, were coated with an average of 235 μg of zeolite; and the third set, referred to as high-mass (Group C) SUDA samplers, were coated with an average of 1133 μg of zeolite. Table 2 summarizes the zeolite mass loadings for the three groups used in this study.

Table 2. Zeolite film data for the SUDA samplers described in the sampling parameters study.

	Samplers Produced	Average Zeolite Film Mass (μg)	Standard Deviation of Zeolite Film Mass (μg)	Average Zeolite Area Density (mg/cm^2)
Low-mass SUDA sampler data (Group A)	4	36	2	73
Mid-mass SUDA sampler data (Group B)	4	235	3	498
High-mass SUDA sampler data (Group C)	4	1133	14	1282

In a previous SUDA report, the UF_6 sampling pressures used were 50 Torr and higher.[4] To simulate lower sampling pressures that may be present in facilities, we conducted UF_6 samplings from the three SUDA sampler groups (A-C) at 40 and 15 Torr. The normalized pressure decrease, where the starting pressure after opening the sampling valve is normalized to zero, is shown in the top left of Figure 5. A clear trend is visible where the pressure decrease during sampling increased with the corresponding mass group of the SUDA samplers, i.e., the low-mass samplers show the lowest pressure drop, the mid-mass samplers show the median pressure drop, and the high-mass samplers show the highest pressure drop. Interestingly, the change in UF_6 pressure over sampling time was consistent for both 15 and 40 Torr. KPA assay showed a direct relationship between the final UF_6 pressure difference of the groups to the collected uranium mass (top right in Figure 5).

Also shown in Figure 5 (bottom) is the relationship between the final UF_6 pressure difference and the collected uranium mass to the zeolite area density of the samples. A correlation between increasing zeolite area density and uranium collection is observed; however, the trend is nonlinear. This nonlinearity for the Group C samples is due to them not fully reaching UF_6 saturation. This can be observed in the pressure decrease versus sampling time in Figure 5, where Groups A and B have reached a steady pressure by the end of the sampling time (ten minutes), yet the pressure decrease for the Group C samples is continuing to drop. This indicates the full sample saturation for low-pressure SUDA sampling will require longer sampling times (likely 30 minutes) if milligram-scale uranium collection is desired.

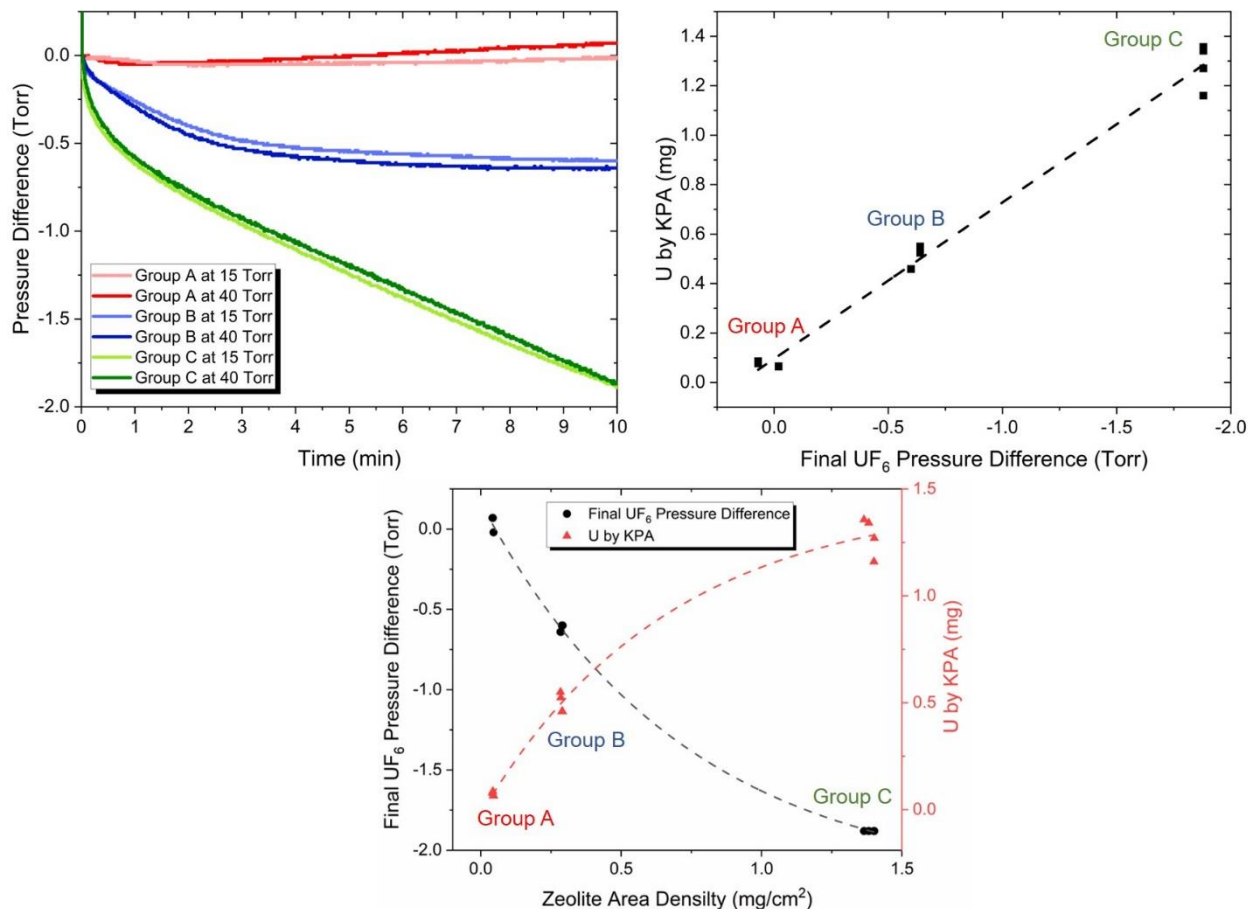


Figure 5. The normalized pressure drop over time for SUDA sampler Groups A-C for sampling pressure of 15 and 40 Torr (Top Left), the total uranium mass collected as a function of final sampling pressure difference (Top Right), and the total uranium mass collected and final sampling pressure difference as a function of the zeolite area density of the SUDA samples (Bottom).

CONCLUSIONS

SUDA samplers, designed for direct attachment to UF₆ sampling taps at uranium processing facilities, allow for uranium collection in the form of a solid, less hazardous hydrated uranyl fluoride, based on the controlled hydrolysis of UF₆ on a zeolite film. In this work, we simulated uranium collection under low-pressure UF₆ sampling conditions to examine the relationship between sampling conditions and uranium collection. We examined the control of the uranium-mass-to-zeolite ratio and assessed various SUDA sampler treatment and storage conditions that might affect uranium collection using SUDA samplers. We found that heat treatment, storage under nitrogen, and high relative humidity have limited effect on uranium mass collection, indicating that the SUDA sampler is robust to storage and sampling under various environments. We also found the zeolite area density correlated to the collected uranium mass determined by KPA; therefore, increasing the zeolite area density in the SUDA sampler will allow higher uranium collection. However, sampling at low pressures (less than 15 Torr) of UF₆ would require longer sampling times (greater than 10 minutes) for milligram quantity sample collection.

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