In-Field Collection and Analysis of Uranium Hexafluoride Cylinder Head Space Gas for the Evaluation of Fill Date

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ABSTRACT

Oak Ridge National Laboratory and Lawrence Livermore National Laboratory have developed a system that can access and collect head space samples from inside a uranium hexafluoride cylinder and perform select analysis of those samples both in the laboratory and in the field. A sample of the uranium can be collected and returned to a laboratory for high precision isotopic analysis. The system then sequentially removes reactive gases such as uranium hexafluoride, hydrogen fluoride, oxygen, and fluorine. The purified head space gas can be analyzed for its noble gas content in the field, allowing the number of helium atoms to be determined. The number of helium atoms, combined with the total mass of uranium and the uranium isotopic ratios, can be used to assess the fill date of the cylinder. Results will be shown for a series of 1S cylinders of known age and isotopic content.

INTRODUCTION

The use of uranium hexafluoride (UF_6) in commercial enrichment processes makes it the focus of many different nuclear safeguards analyses. Although other mature methods exist to determine enrichment, this work is focused on development of a method to determine the fill date of the material. The decay chains of the U isotope are well known, with examples shown below. Past work has demonstrated that application of destructive isotopic analysis of the material to quantify the presence of daughter and even granddaughter products, while effective for U metal and oxides, is less applicable to UF_6 because correctly sampling solids may be difficult and daughter behaviors in the material are poorly understood.[1] The head space of UF_6 is more attractive as it is more likely to be homogenous and gas sampling expertise on appropriate enrichment sampling methods within the nuclear safeguards community[2, 3] and can be applied to this work. This work describes the initial studies to develop a method to sample and analyze the head space gas to determine the fill date of the vessel based on the radiogenic He content.

$$^{238}_{92}U \rightarrow \beta + {}^{234}_{90}Th \rightarrow \beta + {}^{234}_{91}Pa \rightarrow \beta + {}^{234}_{92}U \rightarrow \alpha + {}^{230}_{90}Th \rightarrow \cdots$$

$$^{235}_{92}U \rightarrow \alpha + {}^{231}_{90}Th \rightarrow \beta + {}^{231}_{91}Pa \rightarrow \alpha + {}^{227}_{89}Ac \rightarrow \cdots$$

HELIUM AGE DATING METHODOLOGY

Oak Ridge National Laboratory (ORNL) and Lawrence Livermore National Laboratory (LLNL) have developed systems that can access and collect head space samples from inside a UF_6 cylinder and perform select analysis of those samples both in the laboratory and in the field. This method was developed with a few basic assumptions: daughter products (including He) are removed when U is converted to and handled as a gas during conversion to UF_6 or other gas handling operations during enrichment; daughter products (including He) will grow in with time as the purified U isotopes decay according to known decay rates; He is predominantly in the head space and is distributed homogenously within that gas; the mass of the U can be determined or provided; the enrichment (both 234 and 235) of the U can be determined or provided; the head space volume of the vessel can be determined. The detection limits for mass spectrometry (MS) measurement of He for a modest sample (50 cm^3) for a variety of standard industrial cylinder sizes (assumed 5% ullage) can be shown for a range enrichments (0.1–99 wt % 235, standard 234:235 relationships employed for natural feed enrichment) in Figure 1. Note that while the graph is shown in terms of wt % 235, but the He ingrowth is more directly proportional to the 234 enrichment.

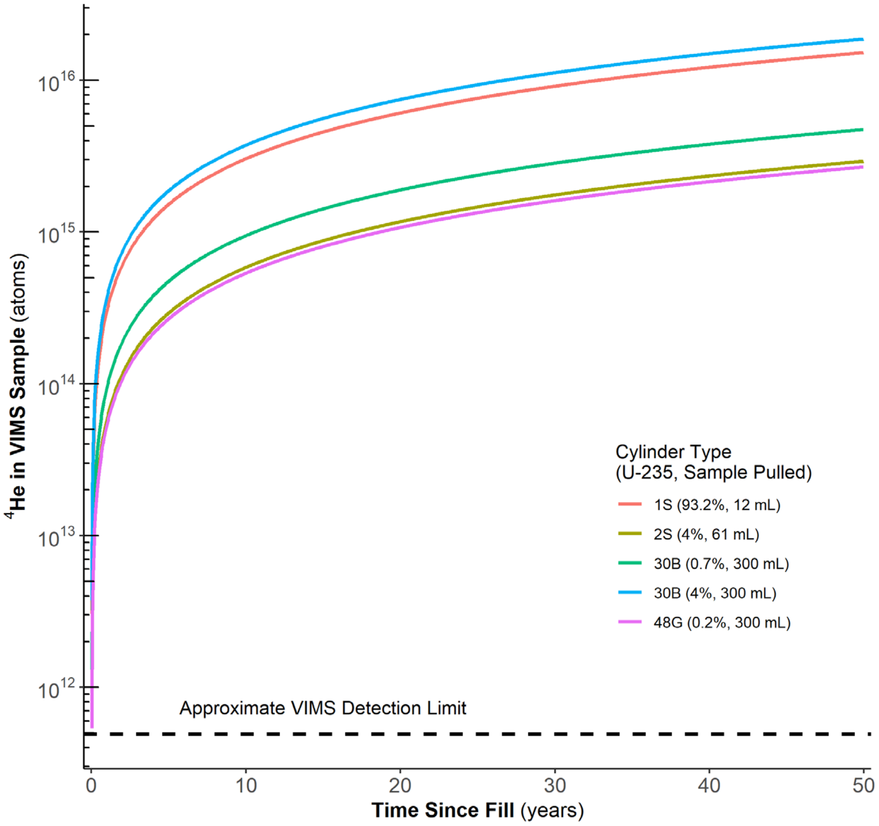

Figure 1. Samples of radiogenic He ingrowth over time from various standard sizes of industrial vessels. Typical enrichments for the vessels (wt % 235) are shown in the legend parenthesis. The number of atoms is based on the 24 cm^3 VIMS sample volume and the sample pull volume (in legend parenthesis), which depends on the vessel size.

The vessels used in this work were only used once and did not include any residual heel or wall deposits of radioactive material. The presence of such a heel or wall deposit could influence the determined age. This should be of minimal consequences because these contributions are likely a low percentage of the total radioactive decay events in larger vessels where such deposits are more common.

Accumulation of ^{4}He from the decay of U in a container of UF_6 is directly related to the time since the head space of that container was last accessed. There is no theoretical minimum or maximum limit to the ages that can be determined by this method. The challenges with applying U–He measurements as a chronometer include separating the He and other noble gases from UF_6 so that they can be measured by MS, developing an accurate understanding of the behavior of He and other noble gases in a UF_6 cylinder and relating measurements of noble gas compositions in UF_6 head space to facility operations.

After a cylinder is filled with UF_6, the accumulation of ^{4}He from the decay of U proceeds at a rate that is determined by the mass and isotopic composition of U and any other α-producers that are present. An expansion and processing manifold for separating noble gases from UF_6 and F_2 has been developed and tested at ORNL. The MS measurements are carried out onsite using a portable system developed by LLNL for this project, followed by offline analyses completed on high-precision noble gas MS at LLNL (discussed elsewhere). The following sections will describe the calculation of U–He age dates along with the collection and analysis of noble gas concentrations in a UF_6 cylinder head space.

SAMPLING AND PROCESSING GAS MANIFOLD

A specialized manifold was designed by ORNL staff to meet sampling and processing requirements for determining the fill date employing a He chronometer, which are significantly different than typical in-field pressure check or sampling equipment used within the UF_6 industry or nuclear safeguards community. Specific differences include:

- high vacuum pumps to remove residual gas from the system;
- use of ultrahigh-purity N_2 gas to reduce He and noble gas contributions;
- multiple, specific chemical traps to remove reactive gases that could damage the MS;
- advanced analytical measurements to observe chemical trap performance and monitor temperature as it affects pressures;
- metal bellows pump to circulate gas through chemical traps and analytical measurement systems;
- MS to measure He and other noble gases.

The manifold use for this work is shown in Figure 2. The system was designed mainly using ¼ in. tubing to minimize the volume of the manifold as volume expansions translate into signal reduction in the He measurement. Additionally, the volume of the system must be determined as precisely as possible as the errors associated with the expansion of sample represent one of the largest contributions to the error associated with the age. The gas is first collected from the sample into a known volume that is ideally a small fraction (2–5%) of the anticipated total volume of the vessel's head space. The gas is then expanded and circulated through the section shown in orange in Figure 2, allowing the gas to homogenize and online analyses to be performed. The Fourier transform infrared (FTIR) spectrometer allows a sensitive method to specifically observe some of the key gases within the head space (UF_6, HF, and others) directly versus the pressure readings that only report the total pressure (sum of the partial pressures) of all gas components. The FTIR spectrometer can be used to measure the absorbance of specific chemical species and was used to determine the effectiveness of the specific chemical trap by watching the removal of the targeted chemicals over time. Standard operations are to pass the gas through the sodium fluoride (NaF) trap until all UF_6 and HF have been removed followed by the 280 °C copper trap to remove F_2 (monitored by pressure drop) and some organic species that may be present. Note that NaF was specifically used as it does not generate water vapor which could lead to formation of U deposits throughout the circulating manifold. At this point, the sample can be analyzed on the spot using the fieldable MS or samples can be collected to send back to the laboratory for laboratory-based measurements. This system contains more than 30 valves and requires a level of expertise to correctly operate. The full process typically requires several hours to remove all the reactive species and perform the measurement.

A system[4] was designed, fabricated and tested to collect, process, and analyze samples in the field based on the laboratory system described above. An initial field test, not described here, was performed and is being evaluated.

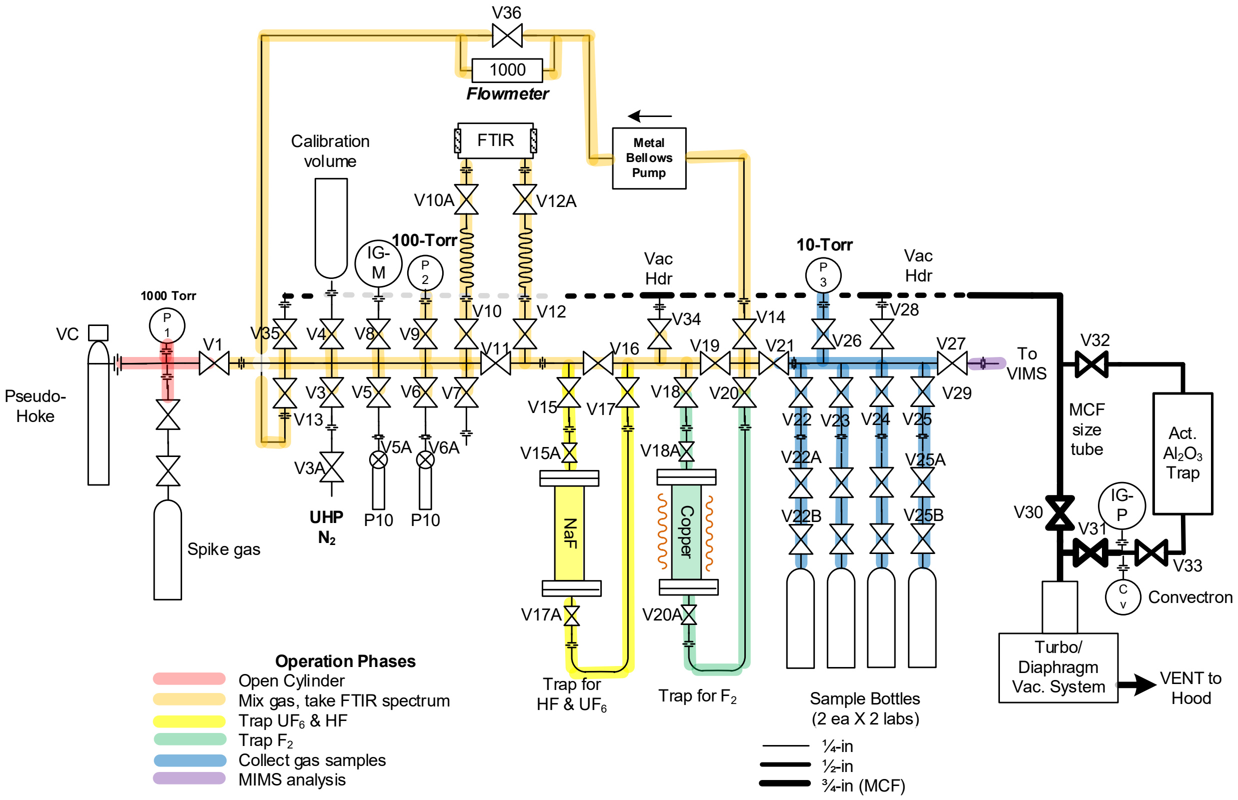

Figure 2. Sampling and process manifold design to support He chronometry measurements.

HEAD SPACE VOLUME DETERMINATION

Several approaches can be used to determine the volume of the head space. The most direct would be to accept cylinder name plate volumes (if available) and the mass of the UF_6 to calculate a volume of solid (assuming a density such as 5.09 g/cm^3). This value can be confirmed by a direct measurement of the volume using one of two methods employed in this work.

The serial dilution method entails making two measurements from separate samples of the head space. Ideally, these samples should represent a reasonable fraction of the expected head space (2–5%). This can also be achieved by the collecting and discarding UF_6 head space gas of known volumes between the collection of the samples. Measurement of the He from both samples combined with the volume of head space gas removed can be employed to determine the total volume.

The volume can be confirmed from a single sample if a calibrated spike is added and allowed to homogenize inside the UF_6 vessel. In this work, a sample of ^{3}He of known pressure, volume, and purity was injected and allowed to equilibrate for 4 to 12 hours, depending on the size of the UF_6 cylinder. The headspace volume can then be calculated directly using pressure dilution comparing the known spike sample and the measured MS result. Alternatively, the spike can be used to directly calculate the amount of ^{4}He in the head space, based on the known amount of ^{3}He added and the measured ^{3}He/^{4}He ratio.

HELIUM MEASUREMENT SYSTEM

Staff at LLNL have modified a commercial variable inlet system, and a quadruple residual gas analyzer (RGA) and associated turbo pump that is contained within a Pfeiffer Omnistar system. The system, shown in Figure 3, receives a sample of known volume from the process and sampling manifold and performs a final gas preparation using a reactive getter (SAES st707 getter pellets) at 300 °C to remove N_2, O_2, and other reactive gases from the sample. The resulting gas, now consisting almost entirely of noble gas components, is introduced into the variable inlet MS (VIMS) for measurement. Measurements are typically completed within minutes for a sample.

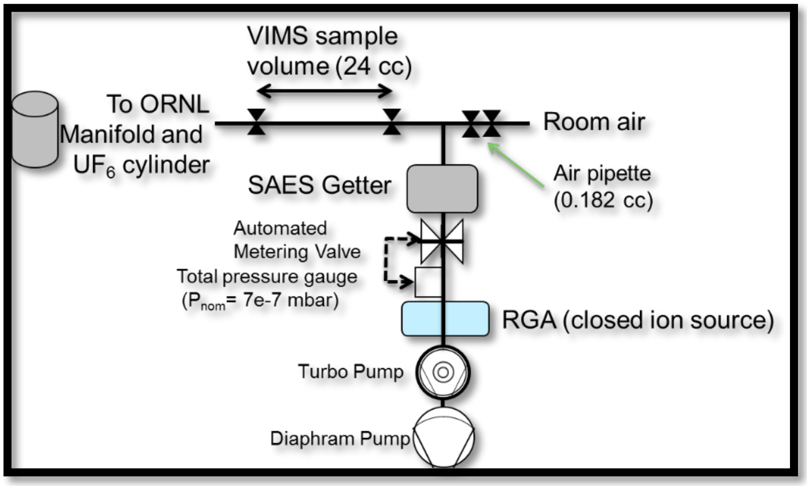

Figure 3. Schematic diagram of the VIMS system.

Calibration is carried out using a 0.182 cm^3 air pipette that is open on one end to room air. The air is processed through the getter and the analyzed. Typically, several aliquots of air from the pipette are analyzed with the VIMS to establish the sensitivity of the detector to the gases of interest. The area under these air pipette spikes peaks is calculated, and the average area divided by the known concentration of that noble gas in air becomes the sensitivity factor for the unknown gas. The standard deviation of multiple air pipette spikes is used in the calculation of measurement precision. VIMS precision is better than 2%, and the detection limit is approximately 5×10^{11} atoms, which is several orders of magnitude below typical He concentrations in samples from UF_6 cylinders.

When analyzing a sample, an aliquot of head space gas is admitted to the (24 cm^3) VIMS sample volume from the sampling and processing manifold. The gas pressure is then allowed to reach a stable value before closing the valve to the processing manifold and proceeding with the gas measurement. An air pipette spike is added to the sample gas before admitting the sample gas to the VIMS. The average area of the air pipette peaks for each noble gas are then subtracted from the combined sample and air pipette to calculate the noble gas compositions of the head space gas sample. Typically, we will analyze three aliquots of the processed UF_6 head space gas from the ORNL field manifold for each extraction. A typical measurement of both the air pipette and the combined sample and air pipette are shown in Figure 4.

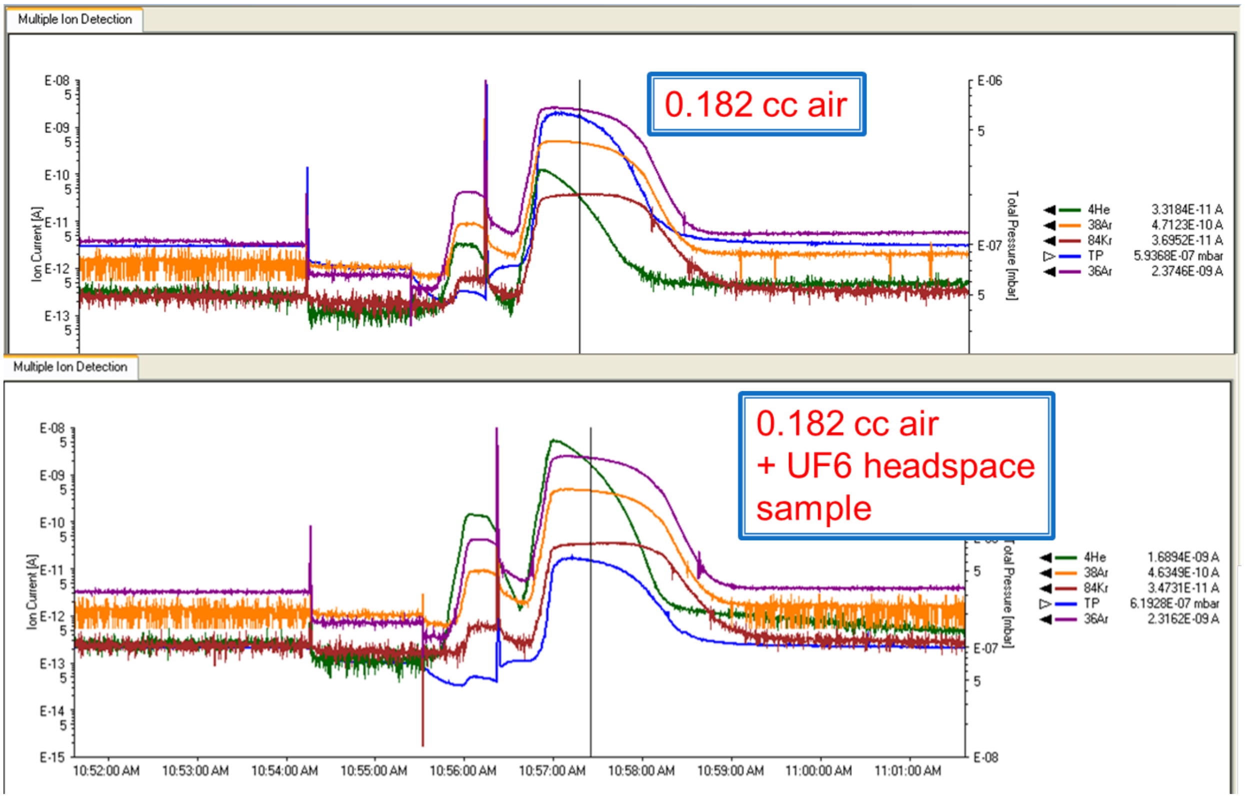

Figure 4. Ion current with time measured for an air pipette spike alone (top) and an aliquot of UF_6 head space gas that has been spiked with the air pipette (bottom). The areas of each gas peak are used to calculate the gas concentrations. Note that He (green) is the only gas that shows significant difference between the two measurements.

The VIMS has a mass resolution of 1 AMU. This mass resolution is not high enough to completely resolve the peaks for ^{3}He and ^{4}He. As a result, a small fraction of these peaks overlap each other. This overlap causes a small excess of measured ^{4}He when a ^{3}He spike is added to the sample gas. In order to correct for this effect, we have established a preliminary correction factor based on the correlation between measured ^{3}He and the difference between the VIMS and laboratory-based noble gas MS ^{4}He measurements. This approach indicates that a correction factor of 1.43% of the ^{3}He peak is needed to account for the overlap into the ^{4}He peak in our system. The results shown below have been corrected for this effect by subtracting the excess ^{4}He due to ^{3}He overlap. This correction factor may be improved in the future using a direct calibration of a ^{3}He spike on the VIMS manifold.

ATMOSPHERIC CORRECTIONS

There may be air within the UF$_6$ sample at the time of filling due to industrial practices or from other processes. This contribution of He, if not accounted for, can skew the apparent age toward older values compared to the true age of the cylinder. This can be corrected during the VIMS analysis by determining the ^{36}Ar along with ^{3}He and ^{4}He. The volume of ^{36}Ar measured in the analysis was divided by its volume fraction in air to determine the total volume of air in the sample gas. The total volume of air was multiplied by the volume fraction of ^{4}He, yielding the amount of atmospheric ^{4}He in the sample gas. The volume of atmospheric ^{4}He was subtracted from the total measured volume of ^{4}He, resulting in the corrected volume of ^{4}He.

AGE CALCULATIONS

The decay of ^{238}U, ^{236}U, ^{235}U, and ^{234}U and several of their respective daughters produces α particles (^{4}He nuclei). By making the following assumptions, the number of ^{4}He atoms in a sample of the cylinder head space gas can be used to calculate the age of the cylinder:

- The cylinder was initially filled with UF$_6$ containing only 67.618 wt% U and 32.382 wt% fluorine, with no U daughters or other α-producing nuclei.
- The cylinder has remained closed to the environment since it was filled.
- The isotopic composition of the initial fill of U is known.
- The net weight of UF$_6$ in the cylinder is known.
- All ^{4}He produced by α decay is present in the cylinder head space, without any trapped in closed voids.
- The number of ^{3}He atoms from the spike added to the cylinder is known.
- The ^{3}He spike has been homogenously distributed within the head space.
- No isotopic fractionation of He or atmospheric gases takes place during the extraction, purification, and measurement of the sample gas.

The α production rate (Table 1) for n = 238, 236, 235, and 234 is calculated using an implementation of the Bateman equation that accounts for all decays from the parent nuclei to the terminal stable isotope for each decay chain. Half-lives in seconds for each nuclide are taken from the International Atomic Energy Agency's Live Chart of the Nuclides. The calculation assumes that one year contains 365 days of 86,400 seconds each for a total of 31,536,000 seconds per year.

Table 1. The α production rate, in number of α-particles per initial gram of an individual isotope of U per year.

Isotope (^{n}U)	P_n (α/g ^{n}U/y)
238	3.9224×10^{11}
236	7.5474×10^{13}
235	2.5231×10^{12}
234	7.2585×10^{15}

The production rate per gram of a sample of known U isotopic composition is calculated by multiplying the production rate for each isotope by the weight percent of that isotope in the material, then summing the results,

$$P_{\text{total}} = (P_{238} \cdot \text{wt\% } 238) + (P_{236} \cdot \text{wt\% } 236) + (P_{235} \cdot \text{wt\% } 235) + (P_{234} \cdot \text{wt\% } 234)$$

That production rate is multiplied by the net weight of U in grams in the cylinder (assuming UF_6 is 67.618% U) to yield the total number of ^{4}He atoms produced per year in the cylinder,

$$\left(\frac{^{4}\text{He}}{\text{y}}\right)_{\text{rad}} = P_{\text{total}} \times m_{\text{UF}_6} \times 67.618\%$$

If using the ^{3}He method to calculate the head space volume, the number of ^{3}He atoms in each spike pipette and the fraction of the spike added to the cylinder are multiplied to find the number of ^{3}He atoms added to the cylinder. Assuming the ^{3}He is well-mixed in the cylinder head space, the number of ^{4}He atoms in the cylinder is found by dividing the number of ^{3}He atoms added to the head space by the measured ^{3}He/^{4}He ratio,

$$^{4}\text{He}_{\text{total}} = \frac{^{3}\text{He}_{\text{added}}}{\left(\frac{^{3}\text{He}}{^{4}\text{He}}\right)_{\text{measured}}}$$

After subtracting any atmospheric ^{4}He, the remaining number of radiogenic ^{4}He atoms is divided by the production rate to yield the apparent age of the sample,

$$\text{Age (y)} = \frac{\left(^{4}\text{He}_{\text{total}} - {}^{4}\text{He}_{\text{atm}}\right)}{\left(\frac{^{4}\text{He}}{\text{y}}\right)_{\text{rad}}}$$

RESULTS

Testing the systems and methods requires access to appropriate UF_6 vessels. Only metal vessels were considered as He can permeate into and out of plastics such as P10 samples. The vessel must hold a reasonable combination of mass and enrichment U to produce a measurable signal.

Preferably, the vessels are of a size that will allow multiple measurements without depleting all the headspace gas volume and have not been access for months to years with well documented use history. Unfortunately, the number of samples meeting these criteria on hand within various sources are limited. The project was able to identify a small number of UF_6 cylinders (Table 2) that met the project needs and were available for use at ORNL.

The 1S samples were the most ideal samples as they were filled for this project and held in reserve until sampled. Their head space was sampled periodically for several years. After the initial sample, the apparent ages are much younger than the fill age, since the He clock of the 1S have been partially reset during each measurement event. This is consistent with the fact that a significant fraction of the total head space is removed during each sampling event. We have corrected for the amount of He removed in each subsequent extraction in in Figure 5.

Note, the 2S and Hoke-like samples have two known ages reported in Table 2. The following assumptions have been made on the ages of these samples. The process knowledge of these 2S samples is known with much lower fidelity. The older age corresponds to the reported fill date, and the younger age is related to the last date that the vessel was accessed. Because of the results observed for removing head space gas in the 1S, the age has been assumed to be the average between these two points with error bars encompassing the fill and last known accessed dates. The Hoke-like samples have a certificate of analysis date. It is assumed that the transfer date would have been 2–6 months before this date. An age of 2.5 years was employed with an error large enough to accommodate the potential range in true ages.

With the above caveats, the results for these measurements are shown in Figure 5. Each point represents an average of two or three measurements performed on subsequent days for the sample. Samples are color coded based on the size of the vessel. Note that the errors on the actual ages are sometimes large and have been discussed above. The errors associated with the measured age are propagated from dilution factors and measurements and are reported at 2σ. In general, there is reasonably good agreement between the known ages and then ages determined using the He chronometer. Most points are within error of the line of unity slope. Only one point (from a 1S) showed significant deviation.

Table 2. Table of UF_6 vessels analyzed during this work.

Vessel size	wt% 235	Age (y)	Age details
2S	2.3	23.9, 47.3	Last access and true ages
2S	4.6	24.9, 32.5	Last access and true ages
Hoke-like	90	2.1, 2.5	Certificate age and assumed true age
Hoke-like	90	2.1, 2.5	Certificate age and assumed true age
1S	4.6	< 3, < 1	True and separation ages

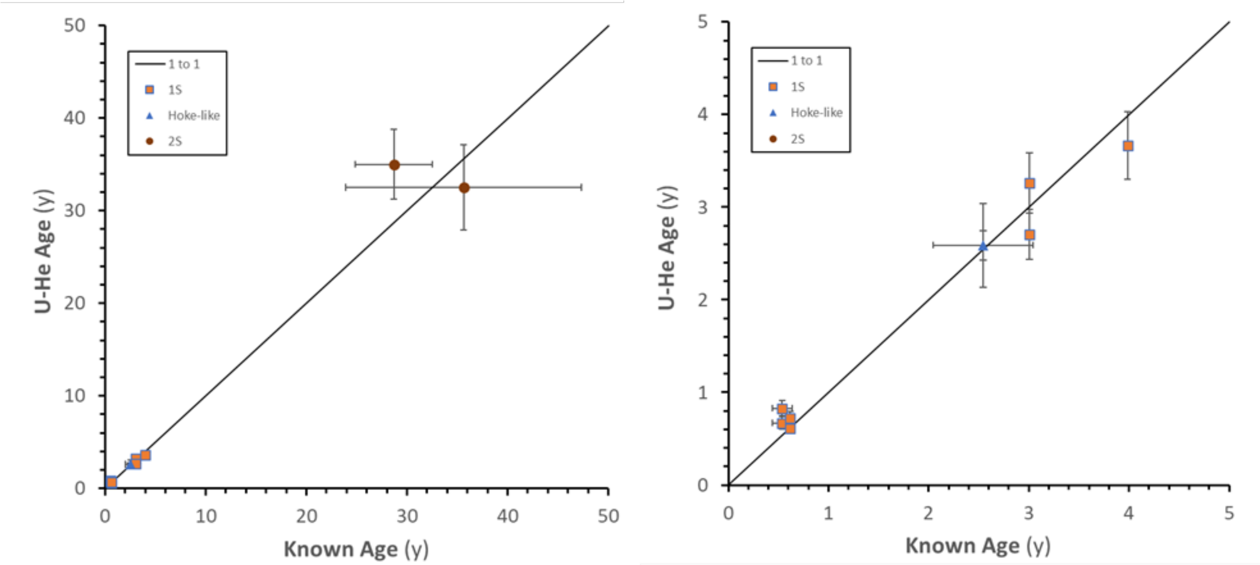

Figure 5. Comparison of age determined by the He chronometer for different UF$_6$ samples.

SUMMARY

This work has shown the initial development of a method for determining the fill date of UF$_6$ cylinder by employing He chronology on headspace gas samples. Initial testing the method is promising, but additional studies are required to understand material property and process impacts on the measurements.

ACKNOWLEDGMENTS

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