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Uniform deposition of uranium hexafluoride (UF₆): Standardized mass deposits and controlled isotopic ratios using a thermal fluorination method



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ABSTRACT

We report a convenient method for the generation of volatile uranium hexafluoride (UF₆) from solid uranium oxides and other U compounds, followed by uniform deposition of low levels of UF₆ onto sampling coupons. Under laminar flow conditions, UF₆ is shown to interact with surfaces within a fixed reactor geometry to a highly predictable degree. We demonstrate the preparation of U deposits that range between approximately 0.01 and 500 ng cm⁻². The data suggest the method can be extended to creating depositions at the sub-picogram cm⁻² level. The isotopic composition of the deposits can be customized by selection of the U source materials and we demonstrate a layering technique whereby two U solids, each with a different isotopic composition, are employed to form successive layers of UF₆ on a surface. The result is an ultra-thin deposit that bears an isotopic signature that is a composite of the two U sources. The reported deposition method has direct application to the development of unique analytical standards for nuclear safeguards and forensics. Further, the method allows access to very low atomic or molecular coverages of surfaces.

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1. Introduction

Measurement and monitoring of U enrichment activities is of significant and growing international interest due to concerns over nuclear weapons proliferation. Environmental sampling and analysis is a fundamental tool of the International Atomic Energy Agency's (IAEA's) international nuclear safeguards treaty compliance and verification efforts [1]. Validated standards are essential for any accurate analytical process and are particularly important for measurements having nuclear security and international treaty implications. Generation of standards for U enrichment measurement validation is problematic due to the tendency of UF₆ to sublime and react with moisture and substrates. Standards generation has an additional challenge of making and handling quantitative mixed U isotope standards; the ratio of ²³⁵U to ²³⁸U, for instance, is a key metric for monitoring U enrichment activities. Present IAEA analytical protocols avoid the use of unstable and unavailable UF₆ standards [2]. However, the ability to generate U standards, particularly at low mass levels and with controllable isotopic ratios, would be very useful for analytical systems calibration and validation, analytical protocol development and evaluation, as well as

supporting fundamental analytical, chemical, and physical studies of reactive chemical species at low mass coverages.

To begin to appreciate some of the controlling features of U deposition behavior, gaseous UF₆ was produced at mole concentrations ranging from an estimated 0.2–88 ppm in a carrier gas stream of ultra-high purity argon (Ar), by reaction of uranium dioxide (UO₂) with nitrogen trifluoride (NF₃), a mild fluorinating reagent [3–5]. The resulting UF₆/Ar stream was introduced into a flow geometry and deposited on sets of planar coupons along the transport path. The use of high specific activity ²³³U was used to quantify the very low masses of U deposited on the coupons, and to confirm the uniformity of depositions between coupons placed within the gaseous transport path.

In this article, the authors first discuss a simple and unique UF₆ gas generation device coupled downstream to a deposition chamber that enables the creation of U deposits of controlled mass per unit area. Next, the authors demonstrate a process whereby the device can be applied to the preparation of U depositions that contain controlled isotopic signatures. In addition to nuclear safeguards and forensics quality assurance applications, the method has applications in the controlled transport and deposition of volatile species for fundamental and applied studies in areas such as corrosion and catalysis science.

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2. Experimental

2.1. Reagents, standards, and materials

House stocks of 99.9% ^{233}U (as $^{233}\text{UO}_2$) and highly enriched uranium (HEU) (as $>90\%$ $^{235}\text{UO}_2$) were used for deposition studies. Ultra-high purity (UHP, 99.999%) Argon was purchased from Oxarc (Pasco, WA) and high purity NF_3 (99.99%) was purchased from Air Liquide (Houston, TX).

Gaseous UF_6 was generated and subsequently deposited on a variety of planar substrates (“coupons”) with surface areas of $\sim 3.8\text{ cm}^2$. These included disks of 316 stainless steel (SS), Teflon[®] (TN), cotton cloth (CL), and cellulose filter paper (FP). Additionally, coupons of high purity silicon wafers (SI) were cut into squares with the same approximate surface area.

2.2. Apparatus and method

A simultaneous thermogravimetric and differential thermal analyzer (TG/DTA) (EXSTAR6000, THASS GmbH, Friedberg, Germany) was used to obtain $\text{UO}_2 \rightarrow \text{UO}_2\text{F}_2 \rightarrow \text{UF}_6$ conversion rates as a function of temperature and NF_3 gas concentration. Additionally, the furnace from a modified Seiko Model 200 (RT Instruments, Woodland, CA) was used for the UF_6 deposition work (see Fig. 1). The modified instrument had a single sample arm that held both the reference and sample pans. The sample arm was made of nickel and was coated with a protective ceramic. A quartz furnace tube was closed over the sample arm and was isolated from ambient atmosphere by a large VCO O-ring fitting arrangement (Swagelok, Solon, OH). The sample, typically UO_2 powder, was added to a nickel sample pan as a solid or as a suspension in deionized water 1–50 μL volume addition). The furnace was closed over the sample and it was heated at $5\text{ }^\circ\text{C}/\text{min}$ to $120\text{ }^\circ\text{C}$ for an hour while the water was removed under a purge of Ar. The furnace was then ramped to a desired temperature and held isothermally. The U sample was then exposed to 5% NF_3 in Ar. The 5% NF_3/Ar was routed into the furnace through a 1.58 mm diameter nickel tube to $\sim 5\text{ cm}$ from the sample pan at a constant flow rate of $200\text{ cm}^3\text{ min}^{-1}$. UF_6 generated by the thermo-fluorination reaction was carried from the furnace by this gas mixture. Temperatures below $500\text{ }^\circ\text{C}$ were used to avoid the formation of a precipitate of $(\text{NO})_2\text{SiF}_6$ [6] which would otherwise block the passage of gas at the exit of the quartz tube. UF_6 generated by the

thermo-fluorination reaction was carried from the furnace by this gas mixture. Planar coupons were fixed to an aluminum foil tray with double-sided tape. The tray was placed inside the deposition chamber and the chamber was closed with 6.4 cm quick flanges for air and moisture-tight sealing of the flow path. The deposition chamber was a 5 cm diameter 316 stainless steel tube, with a length of about 17.1 cm (internal surface area $\sim 308\text{ cm}^2$). The deposition chamber was connected to the output of the furnace with stainless steel tubing about 15.2 cm in length and 1.9 cm in diameter. The length of the connections provided good thermal equilibration of emitted gases from the center of the furnace ($400\text{--}500\text{ }^\circ\text{C}$) to the deposition chamber, which maintained an internal temperature of $\sim 20\text{ }^\circ\text{C}$. The deposition chamber and connections to the furnace were not corroded by room temperature exposure to the fluorinating gas [3,7] and were inexpensive to replace, as they eventually became contaminated with U. The gases were routed out of the deposition chamber to a water bubbler to control U emissions and then were routed to the plenum of the fume hood.

Following a UF_6 deposition experiment, the back flange of the deposition chamber was detached and the coupons removed. Upon removal from the chamber, the U deposit was exposed to ambient air, thus permitting hydrolysis reactions to occur. The coupons were counted directly by alpha spectroscopy (described later). In order to maximize the sensitivity of the measurement, high specific activity (SA) $^{233}\text{UO}_2$ ($^{233}\text{U SA} = 0.357\text{ Bq ng}^{-1}$) was utilized as the source U to provide for quantifiable measurements on the sample coupons down to $\sim 10\text{ pg cm}^{-2}$ ($\sim 3.6\text{ mBq cm}^{-2}$).

For each $^{233}\text{UO}_2$ fluorination experiment, samples were exposed at a given temperature to the 5% NF_3/Ar mixture for 1 h prior to their removal from the chamber for subsequent U deposit analysis. In several trials, new coupons were then added to the deposition chamber and the reaction was continued for an additional 5 h without refreshing the source $^{233}\text{UO}_2$. These experiments were run to understand the nature of residual U that might remain in or near the sample pan or on the furnace walls adjacent to the sample pan. Because 5% NF_3/Ar is a mild fluorinating reagent, U volatilization would require temperatures near $500\text{ }^\circ\text{C}$ for efficient UF_6 production to occur [12]. The experimental apparatus had a steeply diminishing temperature gradient between the sample pan in the center of the furnace (near $500\text{ }^\circ\text{C}$) and the deposition chamber ($20\text{ }^\circ\text{C}$). Potential U residues in and around the sample pan may or may not have been pure UF_6 but plausibly

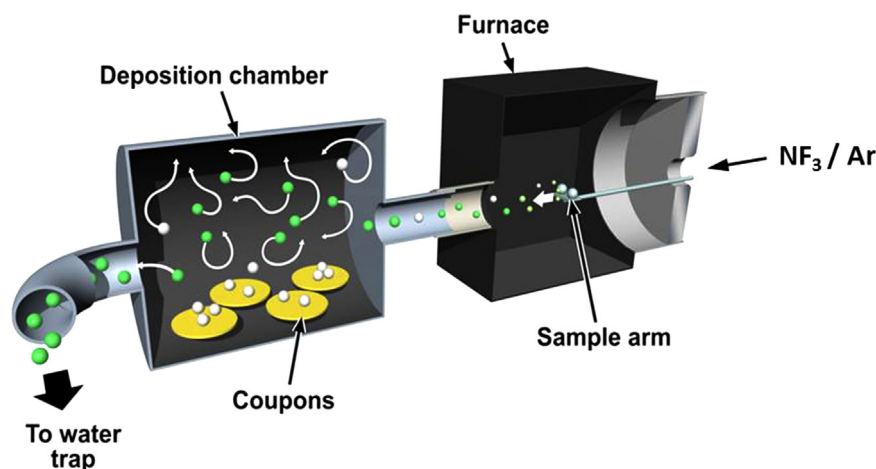


Fig. 1. Experimental apparatus for deposition of UF_6 onto coupons. The U source material is added to a pan at the end of the sample arm. An influent mixture of NF_3 and Ar converts UO_2 to UF_6 (white molecules). The UF_6 is transported through a conduit by the Ar carrier gas flow (green atoms). Next, the $\text{UF}_6/\text{NF}_3/\text{Ar}$ stream enters the deposition chamber. UF_6 is deposited on the surfaces of the deposition chamber. This includes deposition onto the sample coupons placed on a sample tray (tray not shown). Residual UF_6 flows from the deposition chamber and is captured by a water trap. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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