

ISOTOPIC ANALYSIS OF UF₆ IN THE FIELD BY LASER ABSORPTION SPECTROSCOPY

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ABSTRACT

We have developed a new method for the direct determination of UF₆ levels of enrichment in the field. The method relies on using the Single-Use Destructive Assay (SUDA) sampling protocol for collecting UF₆ gas and converting it to uranyl fluoride in a solid zeolite matrix of a SUDA sampler, which then is directly analyzed for isotope ratio determinations. A small amount of matrix is heated in a high-temperature micro-crucible where the uranyl fluoride is chemically reduced in situ by a metal reducing agent, and an atomic beam of neutral uranium is produced. A narrow linewidth diode laser interrogates the uranium atomic beam to measure the isotopic absorption spectrum. The level of enrichment is determined by comparing the ratio of the relative contributions of U-235 and U-238 to the absorption signal.

INTRODUCTION

The IAEA considers the development of instruments and associated technologies for isotopic field analysis of nuclear fuel cycle materials an important priority in their long-term R&D plan. In particular, there is a need to rapidly verify the levels of enrichment of uranium in the form of UF₆ gas at declared facilities. To this end, we have developed methods and instrumentation for the rapid isotopic analysis of UF₆ in the field based on high-resolution laser absorption spectroscopy. The Single-Use Destructive Assay (SUDA) method [1] is emerging as a viable technique for sampling UF₆ gas from uranium enrichment plant process lines and cylinders for uranium enrichment determinations. A SUDA sampler is used to collect UF₆ gas into a zeolite matrix, where it hydrolyzes into uranyl fluoride, a more stable form of uranium suitable for safe and easy storage and transport. The method presented here relies on analyzing the captured

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uranyl fluoride directly in solid form by our recently developed technique for isotopic ratio determinations by laser spectroscopy in atomic beams [2-4]. This method, being completely optical in nature, is immune to isobaric interferences, which pose a substantial problem to mass spectrometry methods. Also, the use of compact diode lasers for conducting high resolution isotopic spectroscopy makes it possible to construct portable instrumentation for analysis in the field.

EXPERIMENTAL

a. SUDA sampler for atomic beam generation

For these experiments, the modified SUDA sampler consists of a KF16 vacuum flange which holds a 2×10 mm cylindrical aluminum or nickel metal foam (Fig. 1). The metal foam holds ~ 5 mg of zeolite within. The KF flange is connected to the sampling manifold, where it is exposed to UF_6 gas at a pressure of 80 torr for 2-5 minutes. As the gas is adsorbed onto the zeolite, it hydrolyzes to form UO_2F_2 :

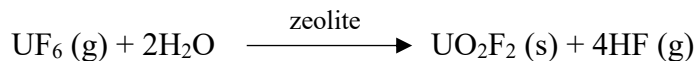
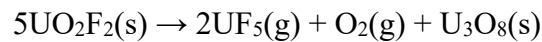


Figure 1. Standard KF-16 flange blanks used as part of the SUDA sampler to collect UF_6 gas. Right: Nickel foam support containing the collected UF_6 as uranyl fluoride adsorbed onto zeolite.

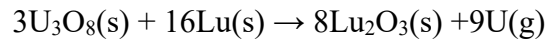
The metal foam sampler can be extracted for immediate analysis, or sealed with a mating KF16 blank cover for future use.

b. Atomic beam generation from SUDA samples

Metal foams containing uranyl fluoride are placed in a high-temperature micro-crucible (described below) and heated to 2000 °C. The chemical decomposition of uranyl fluoride at high temperatures is very well understood [5]. In addition to sublimation, the following chemical reaction occurs when solid uranyl fluoride is heated:



From this equation, we observe that 60% of the uranium atoms in the uranyl sample are contained in the resulting oxide product. As part of our efforts to demonstrate a fieldable system for the determination of uranium enrichment by laser absorption spectroscopy, we have developed chemical reduction methods for the production of neutral uranium atomic beams from oxides using lutetium as reducing agent [4]. Thus, after the initial decomposition of uranyl fluoride into the oxide, atomic beams of uranium can be generated using lutetium reduction according to the following reaction:



c. Isotopic ratio determinations by laser spectroscopy in atomic beams

Collimated atomic beams of uranium are generated from SUDA samples effusing from a high-temperature micro-crucible as described above. Disposable micro-crucibles are fashioned from tantalum foil, which can be resistively-heated to temperatures up to 2500 °C [2]. The micro-crucible is placed inside a chamber (Fig. 2) where rough vacuum is applied. A laser beam from a compact, tunable, external-cavity diode laser (ECDL), with a center wavelength at 861 nm is intersected with the atomic beam through the vacuum chamber windows (Fig. 3). By detecting the photon absorption through the atomic beam while rapidly tuning the laser frequency across the uranium isotopes atomic transition bands, a spectrum showing the relative isotope abundance is obtained. The isotope shift, which depends on a specific atomic transition (typically a few

GHz) is much larger than the sub-MHz ECDL linewidth. The total analysis time from sample loading to enrichment determination takes less than 10 minutes.

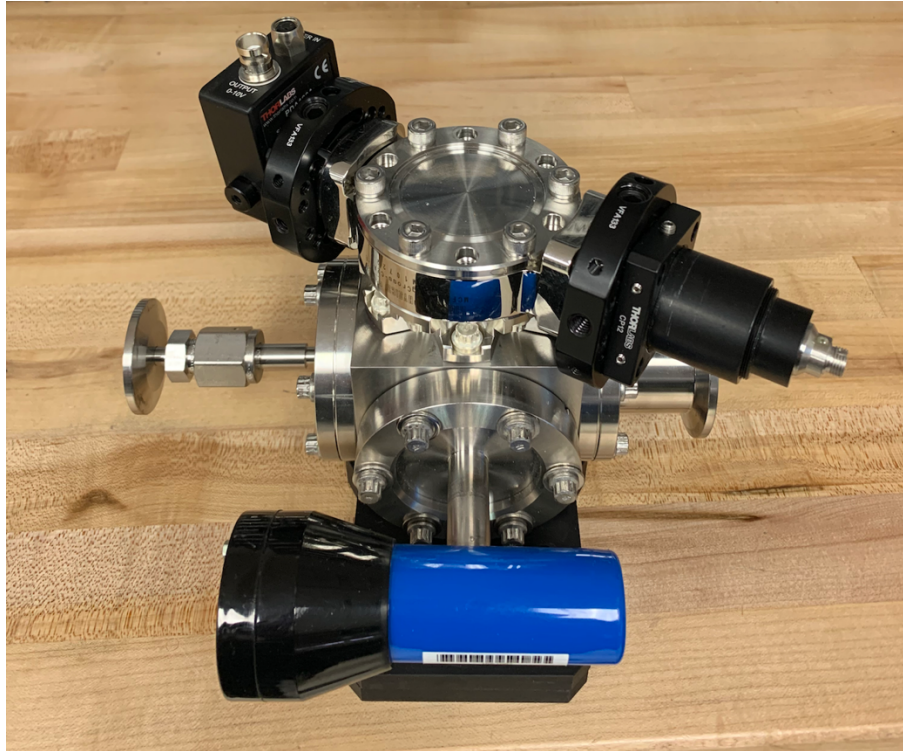


Figure 2. Compact vacuum chamber for the isotopic analysis of SUDA samples

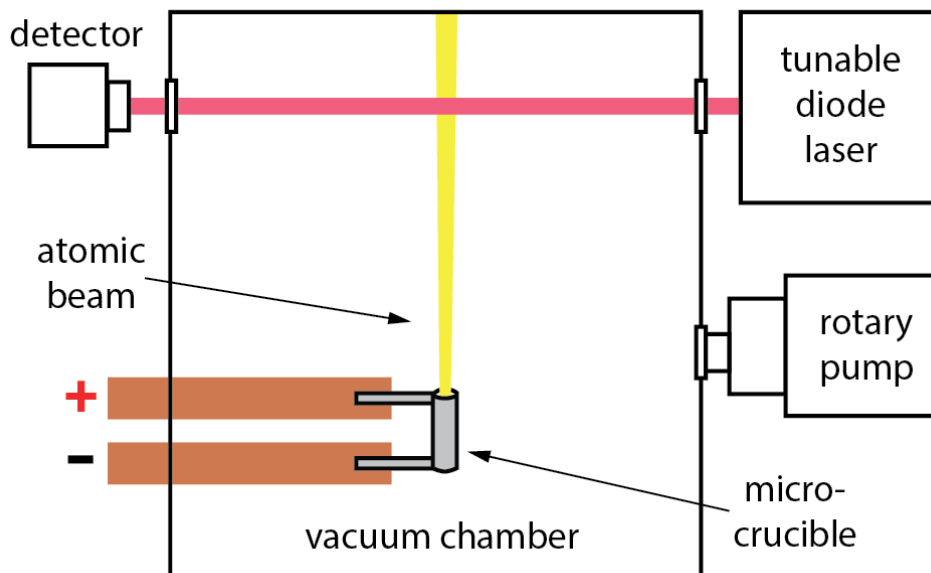


Figure 3. Schematic diagram of the atomic beam laser absorption spectroscopy technique.

RESULTS

We analyzed SUDA samples at various levels of enrichment: 4.7%, 9.2%, and 92.2% (expressed as $^{235}\text{U}/(^{235}\text{U} + ^{238}\text{U})$ atom percentage). The collected uranium mass in each SUDA sample was 7 to 8 mg. Fig. 4 shows typical spectra obtained for the three levels of enrichment. The multiplet to the left originates from the ^{235}U isotope, and consists of a superposition of 21 hyperfine transitions due to its non-zero nuclear spin. The single peak on the right originates from the ^{238}U isotope. By measuring the relative areas of these two features, the isotope ratio can be determined. A comparison of the measured values to those obtained by thermal ionization mass spectrometry (TIMS) reveals a measurement accuracy of 0.5%, and a precision of 1%, in the worst cases. Fig. 5 shows this comparison.

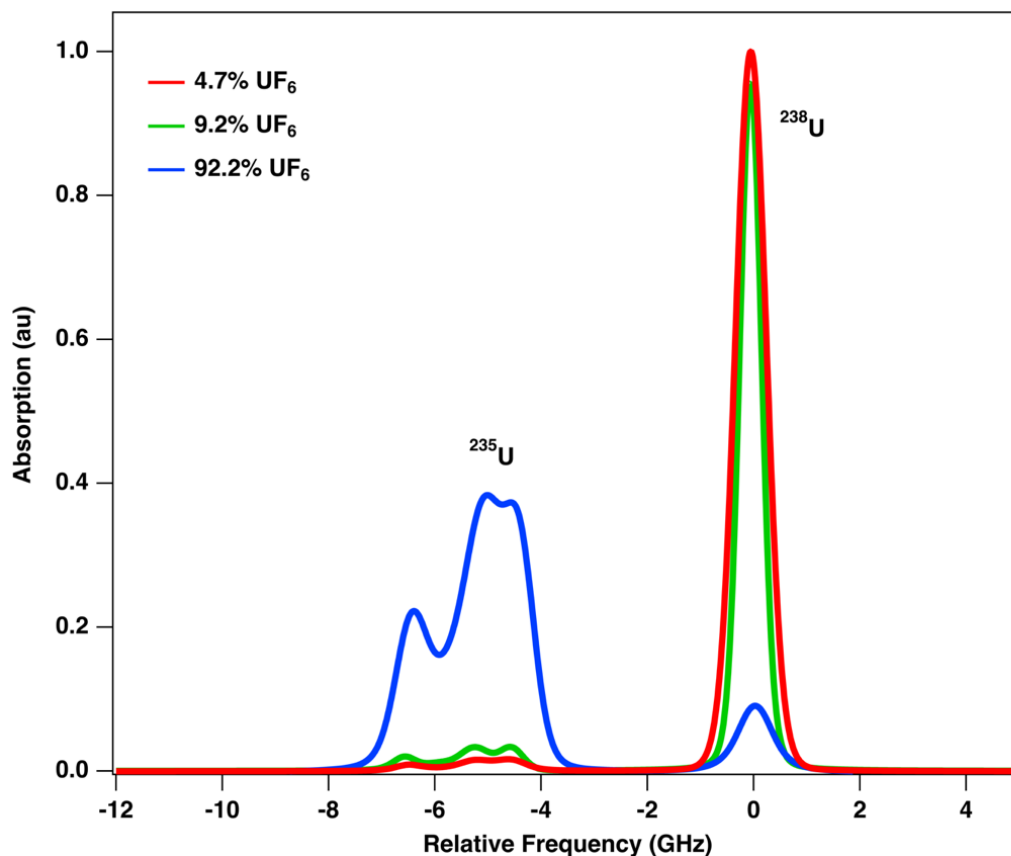


Figure 4. Typical absorption spectra of uranium SUDA samples around the 861 nm transition of neutral uranium.

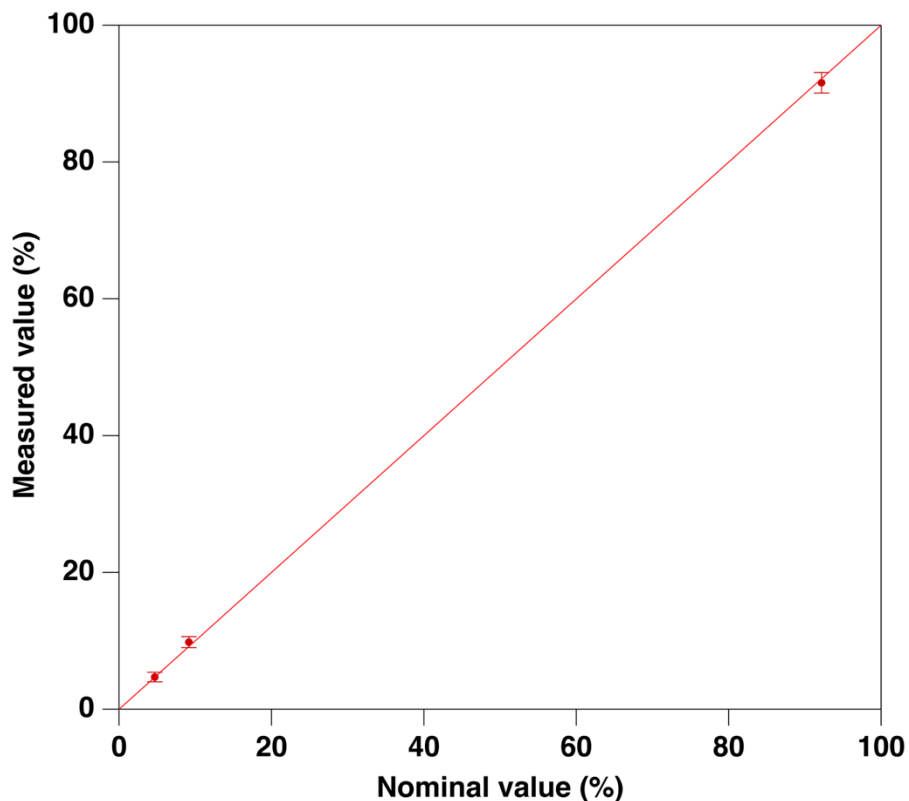


Figure 5. Comparison of the measured values to those obtained by thermal ionization mass spectrometry.

CONCLUSIONS

We have demonstrated a new technique for in the field UF_6 enrichment determination based on SUDA sampling and analysis by high-resolution isotopic laser spectroscopy. SUDA samplers are used to collect UF_6 gas and solidify it in a zeolite matrix, which can be transferred directly to our instrument without further preparation. Total analysis time, including chamber evacuation, sample heating and data collection, takes less than 10 min. The measured isotopic compositions were in agreement with the TIMS values. High atomic absorption SNRs allowed the determination of isotope ratios with an accuracy of 0.5% and a precision of 1% or better. We expect that the method presented here will lead to the development of instrumentation capable of deployment in the field, as desired for nuclear safeguards applications. We are currently building a fieldable prototype based on this technique, which is estimated to weigh less than 25 kg, occupy a volume of 0.06 m^3 , and require 1000 W of electrical power.

ACKNOWLEDGEMENT

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