

## LASER-INDUCED SPECTROCHEMICAL ASSAY FOR URANIUM ENRICHMENT (LISA-UE)

George Chan<sup>1</sup>, Kathryn Peruski<sup>2</sup> and Leigh Martin<sup>2</sup>

1. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

2. Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA.

### ABSTRACT

Uranium hexafluoride (UF<sub>6</sub>) is the uranium compound typically involved in uranium enrichment process. As the first line of defense against nuclear proliferation, accurate determinations of uranium enrichment in UF<sub>6</sub> are critical for material verification, accounting and safeguards. Shipping gaseous UF<sub>6</sub> samples off-site for analysis with mass spectrometry is time consuming and costly, and analysis results are often not available for significant lengths of time (months). Field-transportable UF<sub>6</sub> enrichment assay has the potential to substantially reduce the sample analysis time, as well as logistics and sample handling costs. Laser-Induced Spectrochemical Assay for Uranium Enrichment (LISA-UE) is an all-optical analytical technique, based on laser induced plasma emission, for the purpose of fieldable, accurate, precise and rapid UF<sub>6</sub> enrichment assay. During operation, a laser induced plasma is created directly in the gaseous UF<sub>6</sub> sample. Because different U isotopes emit light at different wavelengths, the isotopic information of the UF<sub>6</sub> sample is inherently encoded in the atomic emission spectra from the plasma. Isotope ratio information of the UF<sub>6</sub> sample can be extracted from the acquired spectrum with theoretical multivariate nonlinear spectral fitting. Advances made by the LISA-UE research team include the identification of a self-absorption-free spectral window for direct gaseous UF<sub>6</sub> enrichment assay with laser induced plasma, development of data reduction algorithms, and demonstrations of the LISA-UE technique with gaseous UF<sub>6</sub> samples. In this paper, the technical aspect of LISA-UE will be overviewed, the data reduction algorithm will be described, and performance of the technique will be discussed.

### INTRODUCTION

Uranium is a nuclear material with dual use. Because the natural abundance of <sup>235</sup>U is usually too low for nuclear-power generation, <sup>235</sup>U enrichment is a necessary major step in the production of fuel for most nuclear power plants. For enrichment, U is first transformed to UF<sub>6</sub>—the only known volatile U compound [1]—and enrichment is then performed almost exclusively by gaseous diffusion or centrifuge processes. As nuclear fuel cycle technology becomes more prevalent around the world, the need for international nuclear safeguards and UF<sub>6</sub> enrichment assay have been growing. As the first line of defense against proliferation, accurate determination of the U isotopic ratio in UF<sub>6</sub> are critical for material verification, accounting, and safeguards at enrichment plants. One role of the International Atomic Energy Agency (IAEA) is to implement safeguards measures to verify the compliance of member states with their international legal obligations to use nuclear material and technology only for peaceful purposes. Development of tools and techniques to enable timely detection of high-enriched U, HEU, production in low-enriched U, LEU, enrichment facilities is one of the IAEA long-term research and development needs [2].

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Conventionally, the IAEA monitors the production of enriched UF<sub>6</sub> at declared facilities by collecting between 1–10 g of UF<sub>6</sub> into a sample bottle, which is then transferred and tamper-sealed in an approved shipping container. The sample is shipped under a chain of custody to the IAEA laboratory for high-precision isotopic assay by mass spectrometry (MS). The logistics are cumbersome, the analysis is costly, and results are not available for some time (months) after sample collection. In addition, new shipping regulations are making it more difficult to transport UF<sub>6</sub>.

There is one field-transportable analytical system for U concentration and enrichment assays. The method, termed COMBined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA) [3], is already in use in inventory verification at LEU fuel fabrication plants [4] and is being validated by the IAEA for on-site UF<sub>6</sub> enrichment determination [5]. COMPUCEA offers excellent accuracy and precision (both routinely better than 0.5% relative), but it requires multiple steps (several hours) of on-site sample preparation and wet chemistry handling training.

*Direct* (i.e., no sample preparation), field-deployable UF<sub>6</sub> enrichment assay substantially reduces the time and the cost of sample analysis. LISA-UE development is based on laser induced breakdown spectroscopy (LIBS), which is a demonstrated field-deployable technique for elemental analysis [6]. LISA-UE will offer direct, fieldable, accurate, precise and rapid UF<sub>6</sub> enrichment assay.

## **SCIENTIFIC PRINCIPLE OF LISA-UE**

LISA-UE is derived from LIBS, in which gaseous UF<sub>6</sub> sample is collected in a small, specially designed UF<sub>6</sub>-compatible gas cell with optical access. Through an optical port, a pulsed laser beam is focused into the UF<sub>6</sub> gas sample and the laser–gas interaction creates a transient high-temperature laser induced plasma. This high-temperature plasma breaks down the chemical bonds in the UF<sub>6</sub> sample, converts it into its constituent atoms, and promotes a portion of these U atoms into their excited states. These excited states emit photons that are characteristic of its elemental identity (U). Furthermore, atomic lines from different U isotopes emit photons at slightly different wavelengths. The isotopic shift (IS) between <sup>235</sup>U and <sup>238</sup>U is the physical basis for the enrichment assay.

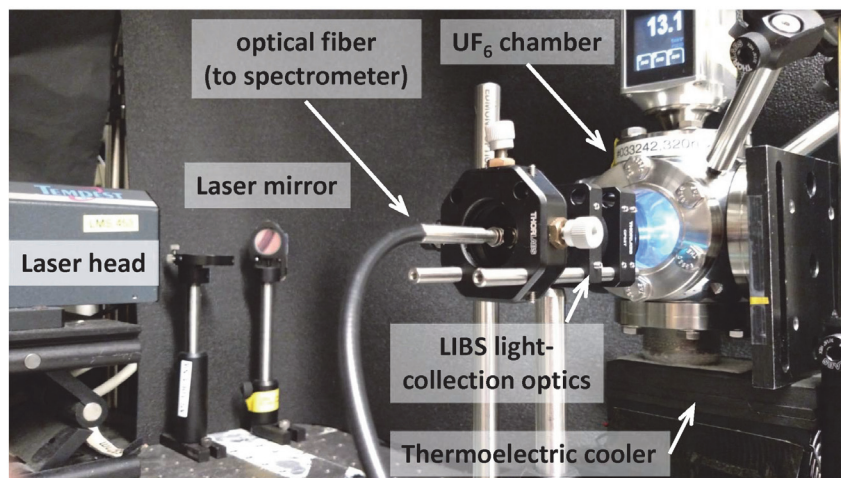
## **HARDWARE, FIELD-TRANSPORTABILITY AND CONCEPT OF OPERATION**

### General Setup

The essential hardware components of a LISA-UE system include a small, nanosecond-pulsed laser; a specially designed UF<sub>6</sub>-compatible sampling gas cell; a high-resolution optical spectrometer that is able to differentiate the emission lines from <sup>235</sup>U and <sup>238</sup>U; a sensitive, gate-able optical detector [e.g., an intensified charge coupled device (ICCD)]; and an optional UF<sub>6</sub> sampling manifold. All components are available as commercial off-the-shelf (COTS) and used as-is, even the gas cell and the UF<sub>6</sub> sampling manifold are assembled from COTS components.

Figure 1 shows a photograph of the general measurement setup. The laser was a nanosecond Nd:YAG at 1064 nm with a repetition rate at 10 Hz. Typically, laser energy of 40 mJ was used for LISA-UE measurements. Plasma emission was collected with a lens through another optical port of

the sample chamber orthogonal to the laser beam, and directed to an optical spectrometer through an optical fiber.  $\text{UF}_6$  pressure inside the gas cell was adjusted indirectly but efficiently through temperature control at the bottom surface of the chamber by means of a solid-state thermoelectric cooler (see Figure 1), which allows user-controllable setting of the  $\text{UF}_6$  vapor pressure between  $\sim 80$  Torr and 5.5 Torr within 10 minutes. Typical  $\text{UF}_6$  pressure for measurement was at 15 Torr, although we increased the pressure to 60 Torr for the simulated field test.



**Figure 1. Photograph showing the general LISA-UE optical setup and generation of laser induced plasma directly in gaseous  $\text{UF}_6$  at a pressure of 13.1 Torr.**

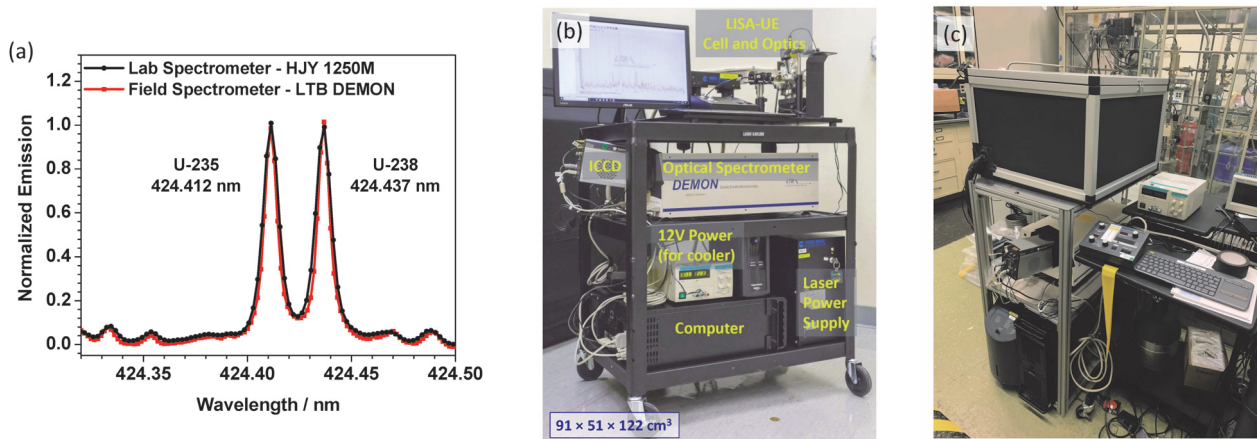
### Design, Fabrication and Testing of $\text{UF}_6$ -compatible Gas Cells

The cell design required careful attention to and testing of materials of construction not only to the chemical compatibility of highly reactive and corrosive  $\text{UF}_6$ , but also compatibility of materials with the laser and the generated LIBS plasma. Furthermore, the gas cells need to be of portable size and suitable for laser spectrometric measurements. The cell (Figure 1) consisted of a spherical cube 2.75" wide, flanges with sapphire window for optical access, a flange with gas inlet/outlet valves, a pressure sensor and a custom designed reservoir at the bottom for holding condensed solid  $\text{UF}_6$ , if needed. The internal volume of the cell is about  $270 \text{ cm}^3$ . At room temperature, it takes about 0.39 g of gaseous  $\text{UF}_6$  to fill the chamber to its saturated vapor pressure of 80 Torr. In our work,  $\text{UF}_6$  masses of 0.5 g to 1 g were loaded to the cells for long-term ( $> 1$  year) experiments.

Stainless steel was selected as the building material for the body of the gas cell because  $\text{UF}_6$  is recommended to be handled in stainless steel or other metals alloyed with nickel [7]. Sapphire was chosen as the material for the optical port because of its excellent resistance to  $\text{UF}_6$  corrosion [8] and a wide optical transmission range from vacuum ultraviolet to near-infrared wavelength [9]. Each fabricated cell underwent a series of treatments: drying of the inner cell surface, passivation by holding it under vacuum, filling with dry  $\text{N}_2$  gas, cell evacuation, and filling with fluorine gas for 72 hours. Testing of the fabricated cells revealed excellent chemical compatibility with  $\text{UF}_6$ , as well as good performance of sapphire windows under long-duration laser exposure.

## Field Transportability

One challenge of bringing optical emission spectrometry to the field for U isotopic analysis is the physical size of the optical spectrometer. Isotopic shifts are minute in magnitude and a shift of 10 pm is considered large. Therefore, the optical spectrometer to be used for LISA-UE measurement should have a resolution preferably better than 10 pm, should offer sufficient light throughput, and be of transportable size. The DEMON spectrometer (LTB Lasertechnik Berlin GmbH, Berlin, Germany), which is of fieldable size ( $60 \times 31 \times 23 \text{ cm}^3$ ) and weight (25 kg), was identified as a suitable option. Figure 2a, which shows the normalized LIBS spectra from a U-bearing solid sample with nominally 50%  $^{235}\text{U}$  and 50%  $^{238}\text{U}$ , presents a comparison of the spectral resolution between the DEMON and the laboratory bench-top based Horiba Jobin-Yvon 1250M spectrometer (which measures  $135 \times 45 \times 37 \text{ cm}^3$  and weights 97 kg). The spectral resolution of the fieldable DEMON is adequate for U isotopic analysis.



**Figure 2.** (a) Measured LIBS spectra from a U-bearing sample containing nominally 50%–50%  $^{235}\text{U}$ – $^{238}\text{U}$  with two optical spectrometers. (b) Components of LISA-UE loaded on a cart showing the transportability of the hardware. (c) LISA-UE setup (the enclosure contains the laser head and optics) at ORNL.

With the identification of a field-transportable spectrometer, the whole LISA-UE setup becomes fieldable. All necessary components (e.g., a small laser, the  $\text{UF}_6$  sampling chamber, a fieldable spectrometer, a computer with controller, and a small breadboard with mounted optics) can be fitted onto a cart which measures  $91 \times 51 \times 122 \text{ cm}^3$  (Figure 2b). The LISA-UE cell and optics are located on the top level of the cart, the spectrometer and detector sit in the middle level, and the computer and various power supplies are on the bottom level. The setup shown in Figure 2b is still a laboratory version. In the fieldable version, the laser, optics and the chamber are engineered in a light-proof enclosure equipped with interlocks for laser safety (Figure 2c). Because an operator outside the enclosure has no exposure to the laser, the whole system, by definition, is a Class-1 laser product, which is safe for the operator. Operating a Class-1 laser product does not require an operator to wear laser safety goggles or to complete laser safety training.

The breadboard LISA-UE instrument was shipped across US from Lawrence Berkeley National Laboratory (LBNL) to Oak Ridge National Laboratory (ORNL) for a simulated field test. Figure 2c shows the LISA-UE instrument in operation at ORNL; the enclosure holding the laser head and optics appears as a “black box”. The setup passed the laser-safety inspection at ORNL as a Class-1 laser system.

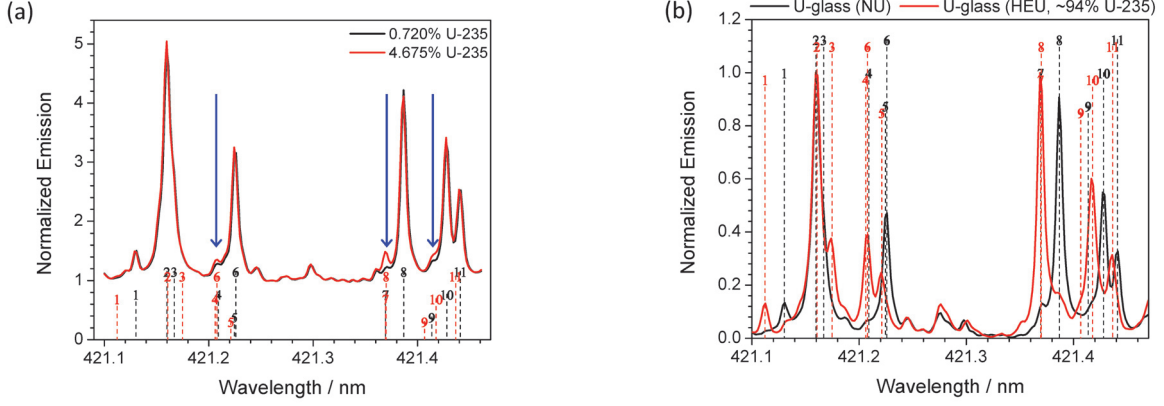
### Concept of Operation

Several operation modes, all intended for facility inspection, can be envisioned for the LISA-UE technology. In the simplest sample-and-measure operation mode, UF<sub>6</sub> is first sampled into a standard P10 tube, and transferred to the LISA-UE chamber for measurement. Alternatively, gaseous UF<sub>6</sub> can be sampled from a source (e.g., cylinder) directly into the UF<sub>6</sub>-compatible gas chamber. If a gas handling system is available in the facility, it will evacuate and then fill the cell with UF<sub>6</sub>. If a facility gas handling system is not available, a mobile, compact UF<sub>6</sub> gas-handling system, which contains a chemical trap, vacuum pump and purge gas source, will be used. In addition, the gas-handling system will provide the initial evacuation and later UF<sub>6</sub> disposal. The filled LISA-UE cell is then transported a short distance to the laser system for measurement. In any case, the LISA-UE instrument (i.e., laser, optical spectrometer and the cell) and other needed accessories are mounted on a fieldable cart.

### **DATA REDUCTION AND ANALYSIS WITH MULTIVARIATE NONLINEAR SPECTRAL FITTING**

Figure 3a shows the LISA-UE spectra from two UF<sub>6</sub> samples – one is NU with <sup>235</sup>U at 0.720% and the other is LEU with <sup>235</sup>U at 4.675%. The isotopic signatures of <sup>235</sup>U, even at LEU level, can be readily distinguished from the NU sample through visual inspection of the two spectra. Although the isotopic peaks for <sup>235</sup>U and <sup>238</sup>U are typically partially overlapped and not baseline resolved (see Figure 3a), accurate quantitative isotopic analysis can be achieved through theoretical multivariate nonlinear spectral fitting or through chemometric calibration with isotopically enriched standards. Both approaches are viable, but multivariate nonlinear spectral fitting is the preferred option for field application because it is a calibration-free method. Advantages of calibration-free method include: simpler operation procedures as in-field calibration (and re-calibration) is not needed, and no need for isotopically enriched and certified standards, which are difficult to obtain or carry to the field.

For accurate spectral fitting, the first step is the identification of spectral lines in the selected spectral window. Because the U II 424.437 nm line—a U line conventionally and commonly used for optical isotopic analysis [10, 11]—was found to suffer from self-absorption in LISA-UE [12], a new spectral window is needed for LISA-UE measurement. Through literature search, a spectral window centered on 421.3 nm is a good candidate for two reasons. First, there is no resonance emission line in this spectral window. Second, there are multiple emission lines with sufficient IS for isotopic analysis. Figure 3b shows the normalized LIBS spectra of two solid U-bearing samples, one of which contains <sup>235</sup>U at natural abundance and another at a highly enriched level at ~94%. The HEU sample highlights the IS (see Table 1 for assigned wavelengths).



**Figure 3. (a) Experimentally measured LIBS emission spectra from two  $\text{UF}_6$  samples (with 0.720% and 4.675%  $^{235}\text{U}$ ), showing the distinct isotopic peak from  $^{235}\text{U}$  (the three most distinct peaks are marked with arrows). (b) Identification of  $^{235}\text{U}$  emission lines and IS from LIBS spectra of two solid U-bearing samples with  $^{235}\text{U}$  at 0.72% (NU) and ~94% (HEU). The wavelength positions of the identified spectral peaks for  $^{235}\text{U}$  and  $^{238}\text{U}$  are marked with vertical lines (Table 1).**

**Table 1. List of  $^{235}\text{U}$  and  $^{238}\text{U}$  emission lines, and their weighting factor ( $\alpha$ ).**

Line number, $i$	$\alpha_i$	$\lambda_{238,i}^\circ$ (nm)	$\lambda_{235,i}^\circ$ (nm)	Line number, $i$	$\alpha_i$	$\lambda_{238,i}^\circ$ (nm)	$\lambda_{235,i}^\circ$ (nm)
1	2.25	421.1302	421.1122	7	0.444	421.3693	421.3693
2	0.444	421.1599	421.1607	8	2.25	421.3868	421.3699
3	1	421.1669	421.1748	9	1	421.4136	421.4067
4	0.444	421.2091	421.2061	10	2.25	421.4280	421.4176
5	0.444	421.2245	421.2211	11	0.444	421.4409	421.4365
6	2.25	421.2259	421.2078				

An iterative, multivariate, nonlinear spectral-fitting algorithm is developed to extract the U isotopic information of the sample from the measured spectrum. The spectral fitting takes the general form:

$$I^{expt}(\lambda) = \sum_{i=1}^n \left\{ \frac{R H_i \omega^2}{\left[4(\lambda - \lambda_s - \lambda_{235,i}^0)^2 + \omega^2\right]} + \frac{(1-R) H_i \omega^2}{\left[4(\lambda - \lambda_s - \lambda_{238,i}^0)^2 + \omega^2\right]} \right\} + c_0 + \varepsilon(\lambda) \quad (1)$$

The first and second terms inside the summation bracket represent the spectral profiles from  $^{235}\text{U}$  and  $^{238}\text{U}$ , respectively.  $I^{expt}(\lambda)$  is the experimental spectrum;  $\lambda$  and  $\lambda_s$  are respectively the measured wavelength and a correction term for wavelength shifts between wavelength calibration

and measurement;  $\lambda^0$  denotes the center wavelength of the atomic emission line;  $H$  is the spectral-peak height;  $\omega$  is the linewidth;  $c_0$  represents the plasma continuum background;  $R$  is the [ $^{235}\text{U} / (^{235}\text{U} + ^{238}\text{U})$ ] atom ratio; and  $\varepsilon(\lambda)$  is the fitting residual. In this work, eleven spectral lines are fitted to the measured spectrum, and variables denoted with a subscript  $i$  refer to spectral-line specific parameters (see Table 1). The fitting algorithm searches the optimal combination of the variables for the minimization of the sum of the weighted residual square ( $S^2$ , Equation 2), which is the product of the wavelength-dependent weighting factors,  $\text{wt}(\lambda)$ , and  $\varepsilon(\lambda)$ .

$$S^2 = \sum \text{wt}(\lambda) \times [\varepsilon(\lambda)]^2 \quad (2)$$

The fitting is performed in an iterative fashion. Several factors, such as (i) spectral line positions, (ii) determined isotopic ratio ( $R$ ), and (iii) isotopic shift ( $\alpha_i$ ), are taken into consideration in the form of weighting factor (Equation 3) for spectral-fitting. Because of the presence of wavelength shifts between wavelength calibration and measurement (i.e.,  $\lambda_s$  in Equation 1), an iterative approach is used. The calibrated wavelength is corrected for wavelength shift through the value of determined  $\lambda_s$  from the previous iteration. The array of wavelength-dependent weighting factors is then recalculated with the re-calibrated wavelength, and the fitting is performed again until the determined U isotopic ratio of the sample,  $R$ , converges.

$$\text{wt}(\lambda) = \sum_{vi} \left\{ \frac{\alpha_i 0.0075^2}{R [4(\lambda - \lambda_{235,i}^0)^2 + 0.0075^2]} + \frac{\alpha_i 0.0075^2}{(1-R) [4(\lambda - \lambda_{238,i}^0)^2 + 0.0075^2]} \right\} \quad (3)$$

As shown in Equation 3, the weighting factor takes the form of Lorentzian spectral profiles, with a half width of 0.0075 nm, of the  $^{235}\text{U}$  and  $^{238}\text{U}$  spectral lines that are present in the spectral-fitting database (Table 1). This arrangement forces the fitting to focus only on the spectral features that are present in the database and not interfered by outliers (i.e., any spectral peaks that are not included in the fitting database). To account for uneven uncertainty distribution (i.e., heteroscedasticity) in data points, the weighting is set to be *inversely* proportional to the variance ( $\sigma^2$ ) of the data point [13]. Under photon shot-noise limit, the ratio of the variance of the two isotopic spectral peaks is directly proportional to their emission intensities (and hence to the ratio of their respective isotopic contents,  $R$ ). Thus, the weighting is set to be *inversely* proportional to  $R$  and  $(1-R)$ , respectively, for  $^{235}\text{U}$  and  $^{238}\text{U}$ . Furthermore, for line pairs with IS significantly larger than the measured line width ( $\sim 7.5$  pm), an additional weighting factor ( $\alpha_i$ ) of 2.25 is assigned. In contrast, for IS that is significantly less than 7.5 pm, a reduced weight of 0.444 (the reciprocal of 2.25) is appointed. The numerical value of 2.25 for  $\alpha_i$  was experimentally determined with a set of testing data.

It should be mentioned that although the developed spectral-fitting algorithm does not require the use of calibration standards, it does not preclude the use of isotopically enriched standards for calibration for further improvement in the analytical accuracy. For example, a hydride calibration model, in which either the spectral fitting-determined isotopic ratio is re-calibrated with the reference values of a set of calibration standards, or a correction factor could be applied to fine-tune the determined isotopic ratio, can be envisioned.

## RESULTS

### Measurements in Laboratory Environment

LISA-UE measurements were performed on three UF<sub>6</sub> samples under three sets of slightly different experimental conditions. The use of slightly different detector delay times for the three sets of measurement was intentional. Because the IS-based weight factor,  $\alpha_i$  (and its reciprocal, see Table 1), was optimized with a testing data set (Data Set A in Table 2), an intentional slight change in the experimental parameters ensures that the training and validation data sets are not identical so as to check for overfitting. To elaborate, overfitting occurs when a modeling function follows too closely to the training data set, including the specific noise therein [14]. The best practice to avoid overfitting is to verify the model with an independent data set [14].

Table 2 shows the comparison of the LISA-UE results of the three UF<sub>6</sub> samples measured by multi-collector inductively coupled plasma MS: the [<sup>235</sup>U / (<sup>235</sup>U + <sup>238</sup>U)] atom ratios of 0.720% for the NU, 4.675% for the LEU #1, and 9.157% for LEU #2. In addition, Data Set C was taken months apart from that of Data Sets A and B, so that the medium-term reproducibility of the method also could be estimated. In terms of analytical accuracy, although one measurement gave an absolute bias of 0.83% <sup>235</sup>U, other measurement biases were contained within  $\pm 0.5\%$  in *absolute* <sup>235</sup>U (Table 2). Measurement precision (standard deviations from twelve replicate measurements) ranged between 0.2% and 0.5% in absolute <sup>235</sup>U content. In relative scale, relative standard deviations (RSDs) were in the range of 2% to 5% for the two LEU samples; RSD for the NU sample was much larger because of the small value of <sup>235</sup>U in the denominator of the RSD calculation.

**Table 2. Calculated [<sup>235</sup>U / (<sup>235</sup>U + <sup>238</sup>U)] ratios of the three tested UF<sub>6</sub> samples. Twelve spectra, each with accumulated LIBS signals from 3000 laser shots, were measured for each sample.**

Data Set	A (ICCD delay = 4.0 $\mu$ s)			B (ICCD delay = 3.9 $\mu$ s)			C (ICCD delay = 4.14 $\mu$ s)		
	NU	LEU #1	LEU #2	NU	LEU #1	LEU #2	NU	LEU #1	LEU #2
Average	0.26%	5.06%	9.38%	0.35%	5.10%	9.21%	0.84%	5.51%	9.22%
SD ( $n = 12$ )	0.16%	0.16%	0.27%	0.16%	0.12%	0.20%	0.23%	0.14%	0.48%
RSD	63%	3.1%	2.9%	46%	2.4%	2.1%	27%	2.6%	5.2%
Reference <sup>235</sup> U	0.720%	4.675%	9.157%	0.720%	4.675%	9.157%	0.720%	4.675%	9.157%
Bias (absolute)	-0.46%	0.39%	0.22%	-0.37%	0.43%	0.05%	0.12%	0.83%	0.07%
Bias (relative)	-64%	8.3%	2.4%	-51%	9.1%	0.58%	16%	18%	0.72%

### Simulated Field Test at ORNL

A simulated field test was performed at ORNL. The main objective for the simulated field test was to test system transportability and to gain experience on the relevant procedures for on-site LISA-UE measurements. This simulated field test was performed solely by ORNL researchers, who were not involved in the spectroscopy part of the LISA-UE development. This arrangement allowed us to



better test the ease and also the weakness on the system operation not from the viewpoint of a spectroscopist but from that of trained operators. The simulated field test also provides an opportunity to benchmark and validate the functionality and performance of the breadboard system under a simulated but relevant operating environment.

With an increased UF<sub>6</sub> pressure of 60 Torr, a pseudo-field measurement was conducted on an HEU sample with a reference [<sup>235</sup>U / (<sup>235</sup>U + <sup>238</sup>U)] atom ratio of 94.71%. In this measurement, no cooling was applied to the cell and approximately 0.2 g of HEU UF<sub>6</sub> was loaded into the cell (i.e., an amount lower than filling the cell to its saturated vapor pressure at room temperature). Three cycles, with each cycle containing six replicated measurements, were used to study repeatability (see Table 3). The determined [<sup>235</sup>U / (<sup>235</sup>U + <sup>238</sup>U)] atom ratios compared favorably with the reference value of 94.71%. Because of the increased <sup>235</sup>U content, the RSD improved to within 0.4%, whereas the *absolute* bias was about 5%. It is interesting to note that the *absolute* standard deviations were around 0.1 to 0.3% and were similar to NU and LEU measurements (Table 2).

**Table 3. Calculated [<sup>235</sup>U / (<sup>235</sup>U + <sup>238</sup>U)] ratios of a HEU UF<sub>6</sub> sample. Six spectra, each with accumulated LISA-UE signals from 3000 laser shots, were measured for each sample. The sample was measured three times.**

	Average	SD ( <i>n</i> = 6)	RSD	Reference <sup>235</sup> U	Bias (absolute)	Bias (relative)
Measurement #1	89.35%	0.18%	0.21%	94.71%	-5.36%	-5.66%
Measurement #2	89.53%	0.33%	0.37%		-5.18%	-5.47%
Measurement #3	89.66%	0.10%	0.11%		-5.05%	-5.33%

## ON-GOING AND FUTURE WORK

The simulated field test provided valuable experience on areas that need improvement to ready the LISA-UE technology for field-deployable use. Several differences in LISA-UE measurements performed in the pseudo-field environment compared with those from a laboratory were noted. Further development of the system should include engineering efforts to increase robustness and user friendliness for field use. Several identified subjects require assessment and modification: (a) investigation of the feasibility of precise loading of gaseous UF<sub>6</sub> into the LISA-UE cell, to eliminate the use of a thermoelectric cooler, which is known to be a heat source inside the enclosure; (b) testing on the ease of use of a miniaturized LISA-UE cell; and (c) chemical identification of the white precipitate found inside some of the gas sampling cells after LISA-UE measurements, and better understanding of the photochemical interactions of gaseous UF<sub>6</sub> with the laser and the plasma.

Further optimization of analytical performance, specifically an optimization of the spectral window for the spectral-fitting calibration approach, is currently underway. Uranium emits thousands of emission lines and many of them show measurable isotopic shifts. A scanning of U emission lines in the whole UV-visible region would allow us to pick the best, optimized spectral window for U

isotopic analysis. An optimized spectral window would be beneficial not only to the development of LISA-UE, but also other atomic emission techniques for U enrichment assay (e.g., LIBS).

## CONCLUSION

This work represents advances in the development of field-deployable analytical tool and methodology for U enrichment assay using optical spectrometry. The current status and advances of the technique include: design, fabrication, and extensive testing of UF<sub>6</sub>-compatible sampling gas cells of portable size for laser spectrometric measurements; design and testing of a computer algorithm, based on theoretical multivariate nonlinear spectral fitting, to extract isotopic information from LISA-UE spectra; identification, characterization, and testing of all necessary components for a field-deployable LISA-UE; and demonstration of direct enrichment assay on gaseous UF<sub>6</sub> samples, in both laboratory and simulated field environments. The developed LISA-UE technique is field-deployable, and provides rapid (minutes), simple and direct (no sample preparation) UF<sub>6</sub> enrichment assay. With additional development, more rapid and accurate field-deployable U enrichment assay, for UF<sub>6</sub> and other sample types, will be possible for nuclear material verification and other applications. Further, results from our work on optical U isotopic analysis also benefit other similar atomic spectrometric techniques for other sample types (e.g., U enrichment assay on solid samples with LIBS).

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