https://doi.org/10.3011/ESARDA.IJNSNP.2017.5

ESARDA BULLETIN, No. 54, June 2017

Towards novel field-deployable instrumentation for UF_6 enrichment assay - an overview of existing and emerging technologies

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Abstract:

Uranium hexafluoride (UF_6) is the uranium compound typically involved in uranium enrichment processes. As the first line of defense against proliferation, accurate determinations of the uranium isotopic ratio (or enrichment) in UF_6 are critical for materials verification, accounting and safeguards. Currently, mass spectrometry (MS) is the most sensitive measurement technique for analysis of stable and long-lived isotopes. However, current MS techniques require too much infrastructure and operator expertise for field deployment and operation. In-field isotopic analysis of UF_6 has the potential to substantially reduce the time, logistics and expense of bulk sample handling by allowing for an 'informed' choice of samples to be sent to a central laboratory for further definitive analysis by standard techniques.

It is common that the next generation of analytical instruments is driven by technologies that are either currently available or just now emerging. Therefore, a comprehensive and in-depth review is conducted on state-of-the-art and emerging technologies for field enrichment analysis of UF_6. These technologies are evaluated based on their competitive advantages and current limitations for in-field UF_6 enrichment assay. The objective of the study is to identity the most promising technologies that can be used for development of the next-generation, field-deployable instrument for providing rapid, accurate, and precise UF_6 enrichment assay. In this paper, we provide an overview of instrument options, discuss their limitations, and examine the main gaps between needs and capabilities for their field use.

Keywords: uranium hexafluoride; enrichment assay; mass spectrometry; optical spectrometry

1. Introduction

Uranium hexafluoride (UF_6) is arguably the most important uranium compound in the nuclear fuel cycle, particularly for uranium isotope enrichment. The enrichment of the ^{235}U isotope in UF_6 is a necessary major step in the production of fuel for most nuclear power plants. As nuclear fuel cycle technology becomes more prevalent around the world, international nuclear safeguards and interest in UF_6 enrichment assay has been growing. As the first line of defense against proliferation, accurate analytical techniques to determine the uranium isotopic distribution in UF_6 are critical for materials verification, accounting, and safeguards at enrichment plants.

Currently, the International Atomic Energy Agency (IAEA) monitors the production of enriched UF_6 at declared facilities by collecting between 1–10 g of gaseous UF_6 into a sample bottle, which is then transferred and tamper-sealed in an approved shipping container. The sample is shipped under chain of custody to a central laboratory [e.g., IAEA's Nuclear Materials Analysis Laboratory (NMAL) in Seibersdorf] for high-precision isotopic assay by mass spectrometry (MS) [1, 2]. The logistics are cumbersome and the analysis is costly, and results are not available for some time after sample collection. In addition, new shipping regulations are making it more difficult to transport UF_6 [2]. The IAEA is challenged to develop effective safeguards approaches at enrichment plants while working within budgetary constraints [3].

There is one on-site enrichment-assay technique, termed COMbined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA), which offers exceptional analytical capabilities with typical combined (systematic and random) measurement uncertainty around 0.25% relative [4, 5]. COMPUCEA combines energy-dispersive X-ray absorption edge spectrometry and gamma-ray spectrometry to measure uranium elemental content and ^{235}U enrichment, respectively. The method is already in use in inventory verification campaigns at European LEU fuel fabrication plants [4]. Currently, the method is utilized only for solid samples and is not yet applied to UF_6 enrichment assay. IAEA is exploring extending the COMPUCEA system to in-field UF_6 enrichment determination [6]. Major shortcomings of the method are its comparatively complicated sample preparations, and its hours-long measurement time for each sample.

For off-site U-enrichment measurements, MS is currently the most sensitive analytical technique; however, current MS techniques require too much infrastructure and operator expertise for field deployment and operation. In-field UF_6 enrichment assay has the potential to substantially reduce the time, logistics and expense of bulk sample

Chan, G.C.-Y., Valentine, J.D., & Russo, R.E. (2017). Towards novel field-deployable instrumentation for UF6 enrichment assay – an overview of existing and emerging technologies. *ESARDA Bulletin - The International Journal of Nuclear Safeguards and Non-proliferation*, 54, 31-43. https://doi.org/10.3011/ ESARDA.IJNSNP.2017.5

handling by allowing for an 'informed' choice of samples to be sent to a central laboratory for definitive analysis by standard laboratory techniques.

The objective of the present study is to identify the potential, viable technologies that are likely to culminate in an expedited development of the next generation of field deployable instrumentation for rapidly determining UF_6 enrichment. One common approach to project the next generation of chemical instrumentation is to track the current trends and to extrapolate them [7]. This approach, albeit somewhat conservative, has been demonstrated with a fair degree of reliability in the fields of analytical science and chemical instrumentation [7]. Therefore, an extensive literature review on existing and emerging technologies for UF_6 enrichment assay is performed, and the competitive advantages and current limitations of different analytical techniques are compared. Based on the results of the review, requirements and recommendations for development of the next-generation field-deployable instrument for UF_6 enrichment assay are addressed.

2. Methodology

Current analytical techniques for UF_6 enrichment assay are based on one of three scientific principles: radiometry, mass spectrometry, and optical spectrometry. In this study, a comprehensive list of UF_6 enrichment-assay methods is reviewed and evaluated. COMPUCEA [4, 5] is a radiometric technique and serves as a benchmark for on-site U enrichment assay. Evaluated mass spectrometric techniques include: gas source mass spectrometry (GSMS) [8], thermal ionization mass spectrometry (TIMS) [9], inductively coupled plasma mass spectrometry (ICP-MS) [9, 10], multi-photon ionization mass spectrometry [11, 12], UF_6 molecular mass spectrometry with portable mass spectrometer [13], laser ionization mass spectrometry [14], surface-enhanced laser desorption and ionization (SELDI) [2], liquid sampling-atmospheric pressure glow discharge mass spectrometry (LS-APGD-MS) [15-18], and atmospheric-pressure solution-cathode glow-discharge mass spectrometry (AP-SCGD-MS) [19]. Techniques based on optical spectrometric principles include: optical atomic emission with argon afterglow discharge or ICP [20-22], glow discharge optogalvanic spectroscopy [23], laser-ablation laser induced fluorescence [24], laser ablation absorbance ratio spectrometry (LAARS) [25, 26], atomic beam tunable diode laser absorption [27], tunable laser infrared (IR) absorption [28, 29] and its high performance version with quantum cascade laser [30], and laser induced spectrochemical assay for uranium enrichment (LISA-UE).

GSMS, TIMS and ICP-MS are included to enable comparison with laboratory techniques. Otherwise, all other techniques should be directly compared with COMPUCEA for their potential to serve as an alternative field-based enrichment assay technique. Each technique is compared against seven assessment criteria; estimated technological maturity and instrument costs are also provided. Because of page limit, it is not feasible to describe, even briefly, all the reviewed techniques in great detail. Therefore, only those analytical techniques, according to published literature results, that so far show the highest potentials for UF_6 enrichment assay as alternatives for TIMS or multi-collector (MC)-ICP-MS will be emphasized.

2.1 Assessment criteria

The seven assessment criteria are: meeting predefined target of analytical accuracy and precision (two separate criteria), meeting relaxed target of accuracy and precision (two criteria), simultaneous ^{235}U and ^{238}U measurement, measurement time, and overall ease of operation. The IAEA published international target values (ITVs) [31] for a wide variety of measurement techniques for nuclear material accountancy and safeguards verification. The ITVs are considered to be achievable values in routine measurements and are uncertainties to be considered in judging the reliability of analytical techniques applied to the analyses of nuclear materials [31]. GSMS, TIMS and MC-ICP-MS are the only three MS systems listed under destructive analysis (DA) techniques [31]. Although more techniques (five) are listed under the category of non-destructive analysis (NDA), it is notable that measurement uncertainties from NDA techniques are much larger – typically more than an order of magnitude larger – than the three MS-based DA techniques [31].

To evaluate the analytical accuracy and precision of a candidate analytical technique, reported analytical figures of merit are compared to the ITVs of TIMS and MC-ICP-MS [31], which serve as comparison references. For these MS systems, the *u(r)* and *u(s)* (i.e., random and systematic uncertainties, respectively) ITVs are the same, and they are 0.5% (relative) for depleted U ($^{235}U < 0.3\%$ abundance), 0.2% (relative) for uranium with ^{235}U abundance between 0.3% and 1%, 0.1% (relative) for LEU ($1\% < {}^{235}U < 20\%$), and 0.05% (relative) for HEU ($^{235}U > 20\%$) [31]. The IAEA ITVs define the strict target for analytical accuracy and precision for all analytical techniques under evaluation. Because the IAEA ITVs are intended for more established techniques, to better gauge the potential of emerging techniques that are still under active development, an additional set of performance criteria is set by relaxing the target values by 10× (i.e., 5% relative for depleted U, 2% relative for samples with ^{235}U between 0.3% and 1%, and so on). In case the emerging technique is so new that experimental data are not yet available specifically for uranium, projected or extrapolated values from very similar techniques sharing the same scientific principle are used.

2.2 Importance of simultaneous measurement and signal correlation in isotope-ratio determination

Signal correlation is crucial in defining the accuracy and precision of isotope-ratio measurements, and thus, its importance needs to be stressed. So far, none of the analytical techniques ***directly*** measure the ^{235}U/^{238}U ratio. Instead, all available techniques indirectly gauge the ^{235}U/^{238}U ratio through separate measurements of the signals from ^{235}U and ^{238}U. All measurements unavoidably contain noise [32]. Noise can be further categorized as uncorrelated and correlated. Examples of uncorrelated noise include shot (also known as Poisson) noise and thermal (also known as Johnson) noise [32, 33]. Shot noise is the result of random arrival of particles [e.g., radioactive decay particles, photons for emission source, or ions for ionization source] onto the detector [33]. Thermal noise is the consequence of random movement of electrons in resistors in electronic devices [32, 33]. Correlated noise is due to flickering of the system, and examples include: variations in the sample introduction system, fluctuations in atomization, ionization or excitation efficiencies for optical and mass spectrometry, and interference noise from power supply [32, 33].

The relative error in the ratio of two signals, *x* and *y*, could be larger or smaller than those in the individual signals (i.e., a further degradation or an improvement in measurement precision); the outcome is heavily dependent on the correlation of noise in the two signals. To illustrate the importance of signal correlation, computer simulated signals with both correlated and uncorrelated noise components have been generated and are shown in Figure 1 below. Individually, the precisions of the two signals, *x* and *y* [relative standard deviations (RSD) ~ 20%] are rather unacceptable for many situations. However, because the two signals are highly correlated – that is signal dips and peaks occur at the same time for the two signals, the noise is greatly reduced in the ratio *x/y* (RSD ~ 1.5%). These highly correlated signals are usually achievable only when the two signals are acquired simultaneously, as repeatedly proven in the literature [34-36]. Signal correlation typically greatly degrades for sequential measurements (i.e., when signals *x* and *y* are measured one by one, sequentially in time).

From the foregoing discussion, not all noise sources are correlated in nature. The uncorrelated noise source that is particularly relevant to isotopic analysis is the counting statistics of shot noise. In an ideal case in which all other noise sources are eliminated, precision of isotopic analysis is then governed by counting statistics. Because radiometric techniques usually do not have other noise sources, their precisions are largely limited by counting statistics. For a truly simultaneous ICP mass spectrometer, it has been shown that isotopic-ratio precision close to counting-statistics limit is achievable [37]. Accordingly, one criterion on evaluation of a candidate analytical technique is on its capability to perform truly simultaneous measurement for ^{235}U and ^{238}U.

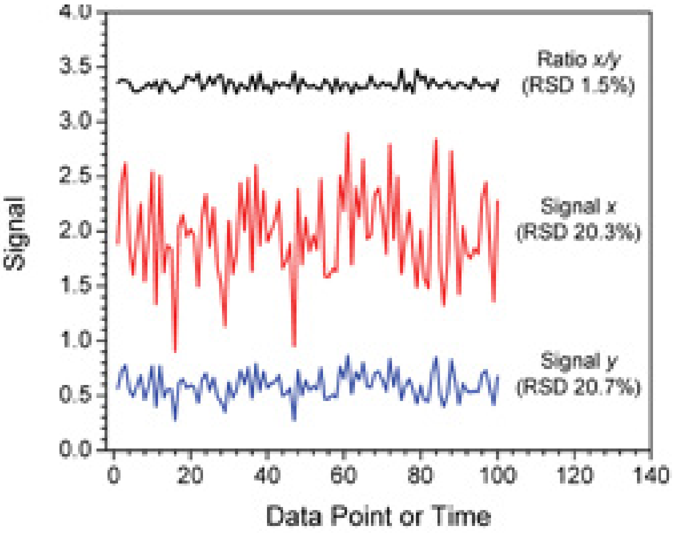

Figure 1: Two simulated signals, x and y, and the resultant signal ratios (x/y), demonstrating the importance of correlated noise and simultaneous measurement in improving the signal (isotopic) ratios.

3. Results and Discussion

3.1 Results of performance assessment

Table 1 summarizes the performance of the benchmark laboratory-based techniques (GSMS, TIMS, and MC-ICP-MS), the benchmark field technique (COMPUCEA), and the four emerging techniques that show promising potential for in-field UF$_6$ enrichment assay. There are three grades for each assessment metric. For metrics under the categories analytical performance and operation, the three grades are equivalent to pass (marked with a symbol "+"), marginal (symbol "○") and fail (symbol "–").

For analytical accuracy and precision, a "+" rating indicates meeting the stated criteria, a "○" rating represents not meeting the criteria but is within 3× the target (i.e., marginally fail), and a "–" rating denotes not meeting the criteria even if the target is relaxed by a factor of 3. The metric "simultaneous ^{235}U and ^{238}U measurements" summarizes if the ^{235}U and ^{238}U measurements are performed in truly simultaneous ("+"), quasi-simultaneous ("○") or sequential ("–") fashions. The metric "measurement time" refers to typical measurement time. Techniques rated "+" typically require less than 10 minutes for one measurement. Techniques that typically require more than 10 minutes but less than one hour are rated "○", and those requiring more than one hour are rated "–". The metric "overall ease of operation" reflects the overall complexity of the measurement procedures (including sample-preparation procedures) and instrument operation (e.g., turn-key *versus* complicated systems), as well as general robustness of the instrument and the technique.

All techniques are also compared on their "technology maturity" and "instrument cost". Unlike metrics on analytical performance and operation, which can be readily quantified and most results are available in open literature, assessments and estimations on “technology maturity” and, in particular, “instrument cost” are difficult because they depend on so many other factors (e.g., technology breakthrough or bottleneck that have not yet been recognized, research support and effort) that in general are unforeseeable. Therefore, the assessments on these two metrics reflect only our best estimation. For technology maturity, techniques rated “+” indicate that they are currently in use on routine basis for UF_6 enrichment assay. Techniques rated “○” indicate that they are not yet used routinely for UF_6 enrichment assay but should be very close to or are already available for field testing, whereas techniques rated “–” indicate further development is needed before field testing can be materialized. “Instrument cost” is compared on a relative basis with three grades of descending capital equipment cost: “$$$”, “$$” and “$”.

It should be noted that the evaluations are based solely on results that can be found in the open literature, for example: journal articles, conference proceedings, publicly accessible reports, traceable presentations in scientific meetings or conferences, and IAEA or NNSA factsheets. Although we have included the latest open literature results to the best of our knowledge, because active research is still on-going on many emerging techniques, the most updated performance of a technique could be better than what was published in the open literature. Furthermore, it is appropriate to stress that each technique is evaluated solely for its suitability to provide on-site enrichment assay specifically for UF_6. Accordingly, a technique evaluated but not listed in Table 1 should not be viewed negative as a whole because it is possible that the candidate technique could be promising for other applications (e.g., for other types of U samples, as an in-laboratory analytical method, or its ability to perform quick screening measurement that does not require the stated high accuracy or precision).

	Analytical Performance					**Operation**			
	Accuracy meets target	**Precision meets target**	**Accuracy within 10× target**	**Precision within 10× target**	**Simultaneous ^{235}U & ^{238}U measurements**	**Measurement time**	**Overall ease of operation**	**Technology maturity**	**Instrument cost**
GSMS	+	+	+	+	+	–	–	+	$$$
TIMS	+	+	+	+	+	–	–	+	$$$
MC-ICP-MS	+	+	+	+	+	○	–	+	$$$
COMPUCEA	○	○	+	+	$+^{\mathrm{Note1}}$	–	–	○	$$
LS-APGD-MS (with Orbitrap MS)	?	+	?	+	+	+	○	–	$$
AP-SCGD-MS (with Orbitrap MS)	?	$+^{\mathrm{Est}}$	?	$+^{\mathrm{Est}}$	+	+	○	–	$$
LAARS	○	○	+	+	+	+	○	○	$
LISA-UE	$-^{\mathrm{Est}}$	$-^{\mathrm{Est}}$	?	$\circ^{\mathrm{Est}}$	+	+	+	–	$

Note 1: Signal correlation for measurement-noise reduction through simultaneous ^{235}U and ^{238}U measurement does not apply in COMPUCEA because the isotopic assay is performed through radiometric counting (gamma ray), in which the dominated noise source is counting statistics.

Table 1: Assessment summaries of benchmark and promising techniques for UF_6 enrichment assay. A superscript “Est” indicates estimation from scientific principle. A question mark indicates that information either is not yet available or is insufficient for estimation.

3.2 Benchmark techniques – GSMS, TIMS, MC-ICP-MS and COMPUCEA

The benchmark techniques will be briefly discussed in this section, whereas the details of each promising emerging technique will be individually discussed in the following sections. Overall, all the three benchmark, MS-based techniques offer outstanding analytical performance but demanding operation in terms of measurement time as well as expertise in instrument operation. All MS-techniques comprise two essential components – an ionization source and a mass analyzer. The mass analyzer responds only to ions (charged particles) but not neutrals; thus, an ionization source is required to convert the neutral (uncharged) sample to charged ions. The mass analyzer separates and measures the charged ^{235}U and ^{238}U atoms/molecules according to their different mass-to-charge ratios.

Gas source mass spectrometry (GSMS) accepts gaseous UF_6 samples directly for enrichment-assay measurements. Because of the homogeneity of gaseous samples, it is currently the most sensitive and precise measurement technique [38]. However, its drawback for UF_6 analyses is its long measurement time. The long measurement cycle is related to memory effects due to the corrosive and reactive nature of gaseous UF_6, which can be compensated only by multiple measurements alternating between the sample and two calibration standards. As a result, the duration for one measurement cycle is about 5 hours [38]. For TIMS measurements, samples are usually presented as a solution and deposited onto the TIMS filament for electrothermal vaporization as well as ionization. Measurement precision for TIMS is slightly lower than GSMS because the sample on a TIMS filament becomes isotopically inhomogeneous due to fractionation during the measurement process [38]. MC-ICP-MS employs a high temperature (>6000 K) inductively coupled plasma – requiring high power (~1.5 kW) – as the atomization and ionization source. The MC-designation refers to the specific type of mass analyzer, a multi-collector. The MC-mass spectrometer is a double-focusing system consisting of an electrostatic sector and a magnetic sector in which ions are separated according to their mass-to-charge ratio and focused onto a focal plane. The MC-system allows the operator to position several detectors at different positions along the focal plane of the mass spectrometer [39] for simultaneous collection and measurement of several masses.

A joint-laboratory study [40] compared U-isotopic ratio measurements by GSMS, TIMS and MC-ICP-MS. For a UF_6 sample with ^{235}U at natural abundance, the RSDs were 0.012%, 0.025% and 0.060%, respectively [40]. Sample throughput is about 1-2 samples/day for GSMS, increases to 5-10 samples/day for TIMS and further increases to around 20 samples/day for MC-ICP-MS [40].

The COMPUCEA technique, developed at the Institute for Transuranium Elements (ITU), is a transportable analytical system for on-site uranium concentration and enrichments assays [5]. Its application specifically for UF_6 enrichment assay is still under development by the IAEA [6], although its use on LEU-oxide samples is considered routine. In fact, IAEA has published an ITV for COMPUCEA – 0.4% $u(r)$ and 0.2% $u(s)$ for ^{235}U enrichment in LEU oxides [31]. ITVs for other enrichment levels (i.e., DU, NU and HEU oxides) are not published [31].

The COMPUCEA technique is based on energy-dispersive X-ray absorption edge spectrometry and gamma-ray spectrometry. Before presented to X-ray and gamma-ray measurements, the solid sample needs to undergo some laborious preparation steps. Briefly, the solid sample is quantitatively transformed into a uranyl nitrate solution, which involves sample digestion in 8 M nitric acid and subsequent dilution to 3 M acidity with a target U concentration about 190 g/L [5]. The solution is first characterized for its density and temperature [5]. During the process, standard laboratory tools (e.g., portable density meter, glass-ware, chemicals, hot plate, weighing balance) and operators' facilities (e.g., fume hood) are used [5].

The solution sample is then measured by X-ray and gamma-ray spectroscopy. Typically, for an LEU sample, three replicates of each measurement type are performed; acquisition of each X-ray and gamma-ray spectrum takes about 1000 s and 2000 s, respectively [5]. For a natural U sample, the time is increased to 5000 s for each gamma-ray counting [41]. Data treatment is not very straightforward because the two measurements are interdependent. Specifically, the X-ray measurement needs the knowledge of the enrichment to accurately convert the measured uranium concentration into mass fraction, whereas the gamma measurement needs the uranium concentration as input to correct for self-attenuation effect [41]. Therefore, data evaluation is made in an iterative manner. Furthermore, the sample parameters (including solution density, sample volume, and bottom thickness of sample container) need to be taken in account [4]. Software has been developed for automatic data acquisition and analysis for the in-field COMPUCEA measurement system [5].

The analytical performance is impressive for an on-site measurement. For LEU samples, the achievable combined uncertainty (*u(r)* and *u(s)*) is typically around 0.25% relative [4, 5] (published ITV for combined uncertainty is 0.45% [31]). According to a recent IAEA report [6], the adaptation of the chemical preparation steps for COMPUCEA determination of UF_6 enrichment is currently being studied by IAEA and with the European Commission. As chemical transformation of UF_6 to uranyl nitrate solution is comparatively simple compared with its oxide counterpart, it is anticipated that the COMPUCEA method will be available for on-site UF_6 enrichment assay in the very near future. The drawback of the method is the relatively long counting time, especially for natural (3 × 5000 s) and depleted uranium, and its labor intensive sample preparation process.

3.3 Emerging mass-spectrometric techniques

3.3.1 Liquid sampling-atmospheric pressure glow discharge mass spectrometry

Liquid sampling-atmospheric pressure glow discharge mass spectrometry (LS-APGD-MS), under joint development from Clemson University and Pacific Northwest National Laboratory (PNNL) [15-18], is the most well characterized emerging mass-spectrometric technique, especially for the determination of uranium isotopic ratio. Figure 2 shows a schematic diagram of the LS-APGD-MS setup. The glow discharge is a microplasma (volume ~ 1 mm^3) formed by imposing a low direct-current potential (typically several hundred volts) between the surface of

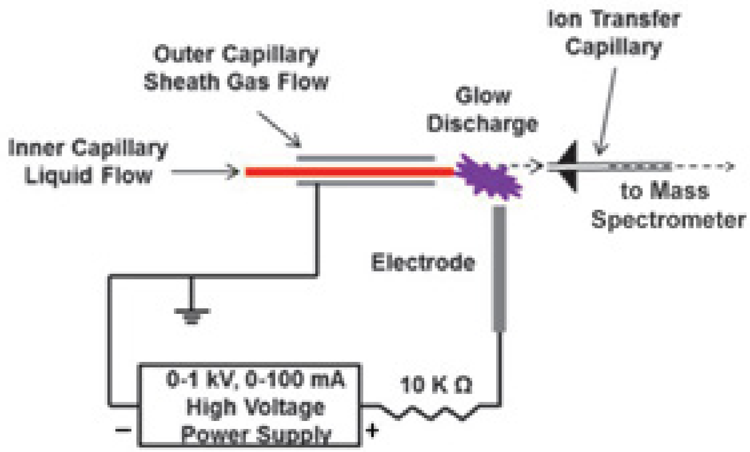

Figure 2: Schematic diagram of LS-APGD-MS. Adapted with permission from reference [2], published by Pacific Northwest National Laboratory, US Department of Energy.

an electrolyte solution (e.g., 2% nitric acid) and a metallic counter electrode [42, 43]. The supporting electrolyte solution flows at atmospheric pressure out of a small (~ 100 µm) glass capillary housed within a slightly larger metal capillary, between which cooling gas is passed [43]. The normal operating parameters include liquid electrolyte flow rates of 5–100 µL/min, cooling gas (typically helium or argon) flow rate of < 1 L/min, and power consumption of < 40 W [16].

Currently, the researchers coupled this LS-APGD ionization source to a high-resolution mass spectrometer (the Orbitrap). Hoegg *et al.* [15, 16] recently discussed various aspects of the LS-APGD and Orbitrap combination for uranium isotopic analyses, including optimization of various operating parameters (both for the discharge and the Orbitrap), preliminary analytical figures of merit, and known limitations. U-containing sample was introduced in a solution form and mixed with the supporting electrolyte. The researchers reported that the dominant U-species in the mass spectra was UO_2^+, and little U^+ or UO^+ were detected [15].

Based on published results [16, 18], the reported analytical precision is encouraging, and is, so far, the best in all the emerging techniques reviewed. In a recent published work [18], which the effort was primarily focused on factors affecting the precision of isotope ratio measurements, reported precisions (in terms of RSD of measured $^{235}U/^{238}U$ ratios from 1 µg/mL natural-U solutions, before correction of scaling factor) were in the range of 0.05% to 0.13% and met the ITV target for precision (i.e., 0.2% RSD for ^{235}U at natural abundance).

At present, the researchers evaluated the analytical accuracy through a correction scaling factor [15, 18]. In their latest report [18], the researchers determined this scaling factor through a certified reference material of natural U, and measured the $^{235}U/^{238}U$ ratios of three unknown natural-U samples. However, it has been stated that this correction scaling factor depends on the $^{235}U/^{238}U$ ratio, as well as a change every time that the system is restarted [18]. At this point, it would be difficult to estimate or project the accuracy of the LS-APGD-MS technique in the field for a sample with unknown ^{235}U abundance.

Although the LS-APGD, in its present form, would not directly accept gaseous UF_6 for analysis, a two-step reaction to transform UF_6 to a uranium solution is well established and regarded as a somewhat standard procedure [8]. The two-step reaction involves hydrolysis of UF_6 to UO_2F_2 ($UF_6 + 2\ H_2O \rightarrow UO_2F_2 + 4\ HF$), followed by conversion to nitrate salt with nitric acid ($UO_2F_2 + 2\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2\ HF$).

One potential drawback of the LS-APGD-MS technique for UF_6 enrichment assay is memory effect, which has been documented in several reports [2, 16, 44]. The cause(s) for the memory effect is not well characterized, but it was suggested that material deposited on the capillary counter-electrode and/or the mass spectrometer capillary interface could be the source [2, 44].

3.3.2 Atmospheric-pressure solution-cathode glow-discharge mass spectrometry

Atmospheric-pressure solution-cathode glow-discharge mass spectrometry (AP-SCGD-MS), currently under development jointly at Rensselaer Polytechnic Institute and Indiana University [19], is identical in scientific principle to the LS-APGD-MS reviewed in the last section but different in design for the generation of the microplasma discharge (cf. Figure 3). The AP-SCGD is a direct-current plasma sustained directly on the surface of a flowing liquid electrode (typically at a rate of 1–2 mL/min), supported in ambient air without the need for a cooling gas or other gas flows [19]. Power of AP-SCGD is ~ 70 W (normally < 100 W) [45], and is generally slightly higher than that of the LS-APGD. A distinct difference between AP-SCGD and LS-APGD is that AP-SCGD sustains on a flowing liquid cathode, with the liquid in excess, whereas LS-APGD operates in a total consumption mode in which all the electrolyte solution is consumed [15]. An advantage of the total consumption in LS-APGD is that no chemical waste solution is generated. Although the excessive flow of electrolyte generates chemical waste for AP-SCGD, the continuously self-renewing liquid surface of the flowing solution cathode potentially minimizes memory effects. In terms of instrument setup, footprint and operation requirements, AP-SCGD shares many similarities with LS-APGD.

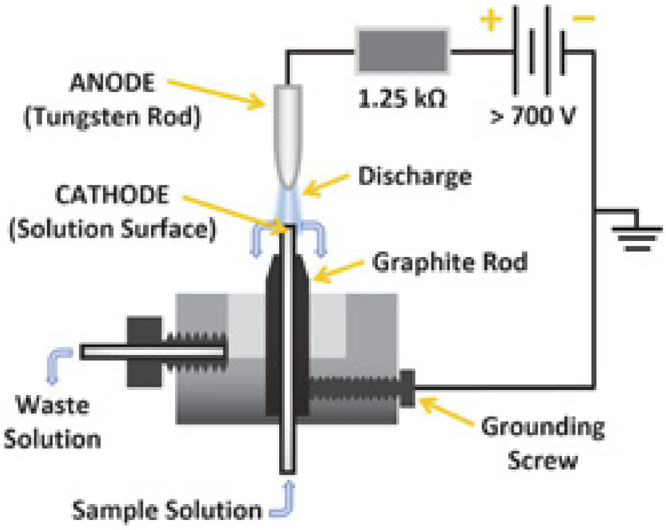

Figure 3: Schematic diagram of AP-SCGD cell utilized for mass spectrometry. Adapted with permission from reference [46], published by The Royal Society of Chemistry. Original figure is published under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Although not yet characterized for its performance on isotopic analysis, the AP-SCGD demonstrated a notably better detection limit than the LS-APGD as an ionization source for atomic mass spectrometry [19]. The latest work on AP-SCGD [19], reported the analytical performance of this source coupled to an Orbitrap mass spectrometer for atomic and molecular mass spectrometry. Specific for uranium solution samples, the reported detection limit in AP-SCGD was 0.8 ng/mL (parts per billion, ppb) with UO_2^+ as the measuring ion [19]. As detection limit is related directly to sensitivity and/or background noise, a better (lower) detection limit for the AP-SCGD implies that it offers higher sensitivity and/or lower background noise. As both factors are important for isotopic ratio measurements, the AP-SCGD should be considered as a candidate emerging technology meriting further evaluation of its full potential for uranium isotopic assay.

3.3.3 Is Orbitrap suitable as field-deployable mass spectrometer?

In the two emerging mass-spectrometric techniques covered above, both research teams employed Orbitrap mass spectrometer. Given the impressive isotopic-ratio precisions and detection limits achievable by the two techniques, one might think that the problem of looking for the next generation of field-deployable instrument for UF_6 enrichment assay is solved. Unfortunately, the current technology of the Orbitrap mass spectrometer makes it inappropriate to serve as a field-deployable instrument [2]. A comment from the LS-APGD-MS research team [2] is that *"Although a conveniently available instrument for this work* (the LS-APGD-MS)*, it* (the Orbitrap) *is not one that would be appropriate for the type of in-field work envisioned by the potential user."* To elaborate, although the Orbitrap is a benchtop instrument, it is rather large and heavy (490 pounds [47]). Also, the requirement for environmental conditions for the Orbitrap mass spectrometer is quite demanding. For instance, according to the pre-installation manual of the Orbitrap [47], the optimum operation temperature is between 18°C to 21°C and temperature fluctuations of 1°C or more over a 10 minute period can affect performance. There are also rather strict requirements for humidity and vibration controls [47].

It should also be noted that the high resolution offered by the Orbitrap likely contributes to the impressive analytical figures of merit reported for the LS-APGD-MS, as it is documented that several low-intensity, non-uranium ions remain after collision-induced dissociation (CID, a process to dissociate and reduce background ions in the mass spectrometer) and require the high-resolution capability of the Orbitrap to resolve them [17]. If the Orbitrap is replaced by a more fieldable (and very likely lower resolution) mass spectrometer, it is currently unknown how such replacement would affect the analytical accuracy and precision. Clearly, there is a need to couple, characterize and evaluate the LS-APGD and AP-SCGD (and possibly other similar glow-discharge variants) to a mass spectrometer that is more field-deployable and preferably capable of performing truly simultaneous measurements.

3.4 Emerging optical-spectrometric techniques

3.4.1 Laser ablation absorbance ratio spectrometry

Laser ablation absorbance ratio spectrometry (LAARS), developed at PNNL, is an all-optical technique for uranium isotopic assay. Its working principle is based on the isotopic shifts in atomic transitions between ^{235}U and ^{238}U atoms, and employs atomic absorption as the measurement means. The technique employs three lasers at a minimum – one for ablation sampling and two for simultaneous measurements of the relative abundances of ^{235}U and ^{238}U [25], as depicted in Figure 4. Laser ablation creates free uranium atoms from a solid sample, and these atoms are then probed by diode laser through atomic absorption. Measurements are conducted in a reduced-pressure environment to reduce spectral-line broadening. The current LAARS setup employs four lasers for better wavelength stability.

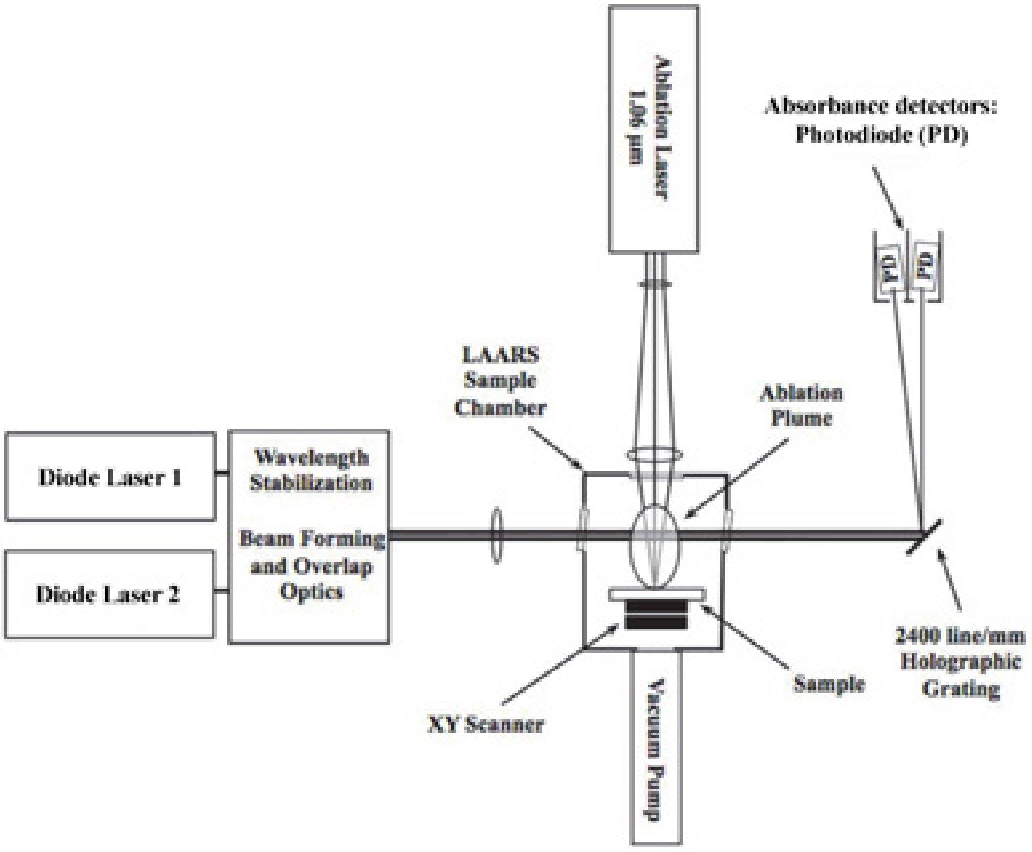

Figure 4: Schematic diagram of LAARS. Adapted with permission from reference [25], published by Los Alamos National Laboratory, US Department of Energy.

The Niemax research group in 2002 [48] is probably the first to report measurements of uranium isotope ratios in solid samples through combination of laser-ablation sampling and diode-laser atomic absorption (before the technique was coined as LAARS). With a two-diode-lasers approach, which allows *simultaneous* measurements of the two U isotopes, Liu *et al.* [48] reported a measurement precision of 1.1% RSD for a pure uranium-oxide sample with ^{235}U at natural abundance [48]. Reported accuracy for the ^{235}U/^{238}U ratio was within 5% (relative) for a uranium mineral sample (i.e., an impure sample) at natural isotopic abundance. In this predecessor to LAARS, the two diode lasers need to be tightly aligned with each other so that the two laser beams are probing identical volumes of the laser plume generated by the ablation laser. The absorption of the two beams is directly related to the number density of ^{235}U and ^{238}U atoms along their optical path, which directly translates to ^{235}U/^{238}U ratio of the sample if an identical plasma volume is probed. Because the number densities of atoms inside laser induced plasma are spatially dependent, a slight misalignment of the two measurement beams (which then probe different volumes of the plasma) could lead to analytical bias on the measured ^{235}U/^{238}U ratios.

The initial LAARS setup [25, 26] was somewhat similar to that reported by Liu *et al.* [48]. The LAARS system was evolved in the last few years and several sophisticated advancements are in place in the current version [49]. For instance, the two probe laser beams are directed into a single-mode optical fiber, in which the two beams overlap and are directed to the laser plume with a single achromatic focusing lens. This single optical fiber approach largely reduces the difficulty of optical alignment and warrants that identical laser-plume volumes are probed by the two lasers. Wavelength stability of the ^{235}U probe beam was also improved through Zeeman splitting method and offset locking [49], although at the expenses of an additional diode laser.

Specific for UF$_6$ enrichment assay, LAARS employs a tailored solid thin-film sorbent to convert gaseous UF$_6$ to uranyl fluoride through a hydrolysis reaction [49]. Data from a presentation dated October 2014 [49] showed that accuracy and precision can achieve 0.1% in ^{235}U enrichment levels for natural U and LEU. Specifically, for three UF$_6$ samples with ^{235}U abundances at 0.725%, 3.982% and 5.119%, the reported *relative* bias with frequency-locked probe lasers were 10%, 0.8% and 0.3%, respectively [49]. Reported relative precisions for these three UF$_6$ samples were 8.3%, 1.5% and 1.5%, respectively [49]. The latest result [50, 51] demonstrated significant improvements in both accuracy and precision, especially for natural-U samples. For a sample with ^{235}U abundance at 5.119%, the relative bias and precision were about 0.1% and 0.6%, respectively. For a natural-U sample, the relative bias and precision were about 0.3% and 0.5%, respectively. Because the ITVs for relative random and systematic uncertainties [i.e., $u(r)$ and $u(s)$] are both 0.1% for LEU and 0.2% for natural-U samples [31], the precision of LAARS is currently within 3× to 6× from the target as a replacement for laboratory-based mass spectrometry. Accuracies are close (within a factor of 2) to the target.

Measurement time for LAARS is fast and is typically around 10 minutes [25]. The overhead for sample preparation is also minimal; the reaction time for the conversion of gaseous UF$_6$ onto the solid thin-film sorbent is several minutes [25]. Because wavelength selectivity for the two isotopes comes from the narrow-bandwidth diode laser, a small optical spectrometer/grating is sufficient to separate the two signals [in this case, different atomic transitions (i.e., wavelengths) can be used for ^{235}U and ^{238}U], which further reduces the footprint of the instrument.

3.4.2 Laser induced spectrochemical assay for uranium enrichment

Laser induced spectrochemical assay for uranium enrichment (LISA-UE) is in a very early stage of development (starting October 2016), and is a joint effort between Lawrence Berkeley National Laboratory (LBNL) and Oak Ridge National Laboratory (ORNL). It is an all-optical technique for uranium isotopic assay and, in fact, is an extension of the well-known laser induced breakdown spectroscopy (LIBS) technique to low-pressure gaseous UF$_6$ samples. Like LAARS, its principle is based on the isotopic shifts in ^{235}U and ^{238}U atomic transitions. Instead of utilizing atomic absorption, LISA-UE employs atomic emission as the measurement means. It is known that isotopic shifts for some uranium atomic emission lines can reach tens of picometers and are large enough to be readily measured with an optical spectrometer even under ambient pressure and comparatively high temperature (e.g., 5000 K) [52]. In fact, atomic emission spectrometry has a long history of being utilized for uranium isotopic analysis [53, 54]. Recently, Krachler *et al.* [20, 21] validated isotopic analysis of ^{235}U and ^{238}U in depleted, natural and enriched uranium with ICP-atomic emission spectrometry, and further extended the analysis to other U-isotopes like ^{233}U.

The LISA-UE system is targeted for direct analysis of gaseous UF$_6$ samples, although a solid sample (e.g., UF$_6$ absorbed on a solid substrate) also can be used. Specifically for gaseous UF$_6$ samples, a small gas chamber with optical access couples directly to a UF$_6$ cylinder/pipeline valve for sampling (cf. Figure 5). Through the optical port, a

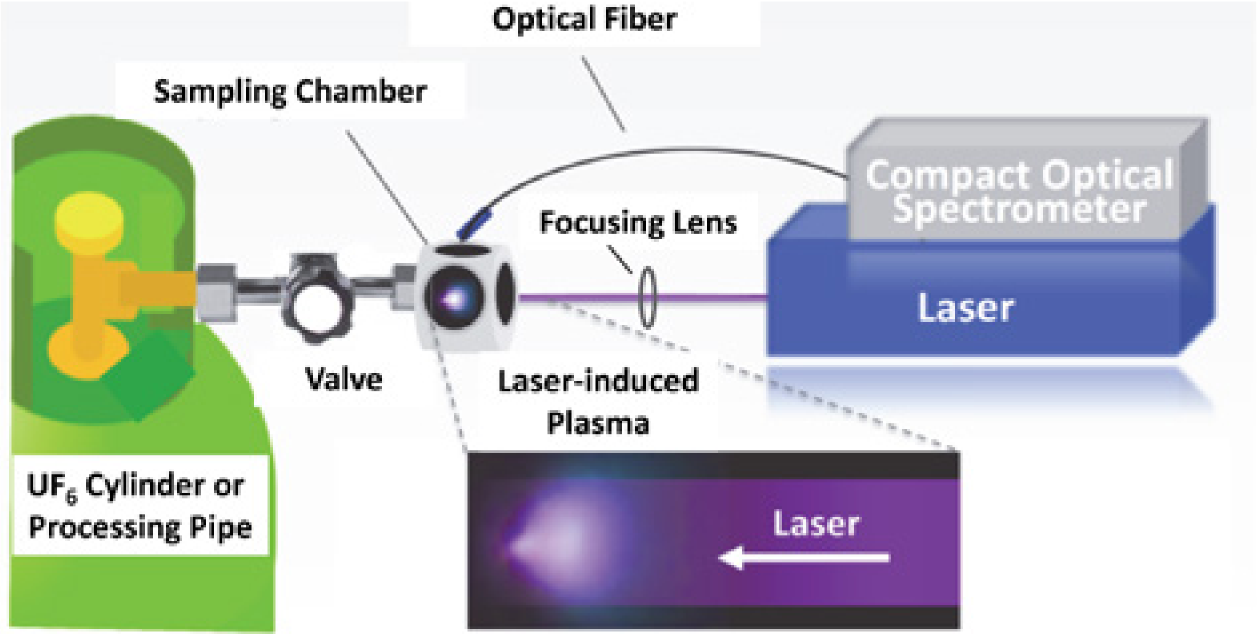

Figure 5: Schematic diagram of LISA-UE.

pulsed laser beam is focused into the UF_6 gas sample and the laser–gas interaction then creates a transient high temperature plasma excitation source. This high-temperature plasma is capable of breaking down the chemical bonds in the sample, converts it into its constituent atoms, and promotes a portion of these atoms into their excited states. These excited states, through radiative decay, emit photons that are characteristic of its elemental and isotopic identities. When this transient plasma starts to cool (typically after several microseconds), molecules form through recombination. It has recently been reported that resulting molecular emissions also carry isotopic information [55]. The technique is potentially applicable to both off-line and on-line measurements.

There are some marked contrasts between LAARS and LISA-UE. Only one ablation laser is required in LISA-UE whereas LAARS needs three/four lasers [25]. Similar to the LAARS ablation laser, there are no constraints on the LISA-UE laser wavelength, and a laser with nanosecond (or shorter) pulse width is required in both cases. Plasma emissions in LISA-UE are collected by single set of light-collection optics for simultaneous ^{235}U and ^{238}U measurement, which also inherently guarantee that an identical plasma emission volume is probed. Furthermore, one potential advantage of employing emission over laser absorption is that a large collection of spectral lines (atomic) and bands (molecular) are emitted from the laser induced plasma, which can be simultaneously measured with a multi-channel optical spectrometer. As many of these spectral features carry the isotopic information of the sample, multiple emission-line/band measurement has been shown through simulations to improve analytical precision [55].

As LISA-UE is in a very early stage of development, its analytical capabilities are not yet known. However, it is anticipated that emission measurements on a collection of spectral features likely offers advantage over single line-pairs commonly employed in absorption measurements. For example, it has been shown through computer simulation that the use of a chemometric algorithm from a collection of spectral features provides several times improvement in the precision of ^{235}U abundance compared to those measurements utilizing only a single pair of emission lines [56]. In simulation, the ultimate precision was about 0.11% in absolute ^{235}U abundance for multiple line analysis [56], with signals accumulated from 10 laser pulses. Clearly, further improvement in precision can be achieved through more signal accumulation (i.e., accumulating signal from more than 10 laser pulses), although it is also anticipated that computer simulation probably offers the best-case scenario. The anticipated measurement time is a few minutes for each UF_6 sample. Commercial, field-deployable LIBS instruments for direct solid-sample analysis are readily available. Although these commercial systems are not specifically designed for gaseous samples, modification for handling gaseous samples is feasible. The size, as well as power requirements, of the components can be readily fit into a field-deployable instrument. While it is extremely early in the development cycle, the LISA-UE instrumentation set up – with a single laser excitation source and a single set of light-collection optics – is likely to be the simplest among all the techniques discussed above, which is advantageous as an in-field instrument.

4. Outlook

To summarize, a comprehensive and in-depth review was conducted on state-of-the-art and emerging technologies for field enrichment analysis of UF_6. All techniques were assessed for their potential to serve as an alternative for laboratory-based mass spectrometry. The evaluation was comprised of seven criteria, broadly defined: measurement characteristics and analytical capability, measurement time, and overall ease of operation and system complexity.

In terms of both analytical performance and sample throughput, the LS-APGD-MS is currently the best in all the emerging techniques reviewed, and is already shown to offer analytical precisions meeting the ITVs of TIMS and MC-ICP-MS. The AP-SCGD-MS, although currently utilized only for elemental analysis and not yet for isotopic measurements, already exhibits its pronounced sensitivity advantage for uranium detection. Unlike the ICP, these glow-discharge ion sources use microplasmas which allow operation under low power and low gas flow (if a plasma gas is ever needed) — and, thus, are highly field deployable. The technical challenge to transform them into the next generation field-deployable UF_6 enrichment-assay instrument, perhaps, relates to identifying and coupling to a multi-channel field-deployable mass spectrometer that, through simultaneous measurement, can maintain the current achievable analytical figures of merit.

Some emerging techniques based on optical spectrometric techniques are also promising. LAARS shows its promise with demonstrated precisions within 3× to 6× and accuracies within a factor of 2 [50, 51] from the target as a replacement for laboratory-based mass spectrometry for natural-U and LEU samples. LISA-UE is a new development and is based on well-established atomic emissions (LIBS). All of these emerging technologies show potential to be the next generation of rapid, field deployable instrumentation for UF_6 enrichment assay.

5. Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231. The project was funded by the U.S. Department of Energy/National Nuclear Security Administration's (DOE/NNSA's) Office of Nonproliferation and Arms Control (NPAC) in the Safeguards Technology Development Program.

6. References

[1] Anheier N., Cannon B., Martinez A., Barrett C., Taubman M., Anderson K., and Smith L.E.; *A new approach to enrichment plant UF_6 destructive assay sample collection and analysis;* PNNL-SA-112353, Pacific Northwest National Laboratory, 2015.

[2] Barinaga C.J., Hager G.J., Hoegg E.D., Carman A.J., and Hart G.L.; *Feasibility of a fieldable mass spectrometer FY 2015 year-end report;* PNNL-24842, Pacific Northwest National Laboratory, 2015.

[3] Smith L.E., and Lebrun A.R.; *Design, modeling and viability analysis of an online uranium enrichment monitor; in 2011 IEEE Nuclear Science Symposium Conference Record;* 2011; Paper 1030-1037

[4] Erdmann N., Amador P., Arboré P., Eberle H., Lutzenkirchen K., Ottmar H., Schorlé H., van Belle P., Lipcsei F., and Schwalbach P.; *COMPUCEA: A high performance analysis procedure for timely on-site uranium accountancy verification in leu fuel fabrication plants; ESARDA Bulletin;* 43; 2009; 30-39

[5] Berlizov A., Schachinger A., Roetsch K., Erdmann N., Schorlé H., Vargas M., Zsigrai J., Kulko A., Keselica M., Caillou F., Unsal V., and Walczak-Typke A.; *Feedback from operational experience of on-site deployment of bias defect analysis with COMPUCEA; J. Radioanal. Nucl. Chem.;* 307; 2016; 1901-1909

[6] International Atomic Energy Agency; *Development and implementation support programme for nuclear verification 2016-2017;* STR-382, International Atomic Energy Agency (IAEA), 2016.

[7] Hieftje G.M.; *The future of plasma spectrochemical instrumentation. Plenary lecture; J. Anal. At. Spectrom.;* 11; 1996; 613-621

[8] Mialle S., Richter S., Hennessy C., Truyens J., Jacobsson U., and Aregbe Y.; *Certification of uranium hexafluoride reference materials for isotopic composition; J. Radioanal. Nucl. Chem.;* 305; 2015; 255-266

[9] Boulyga S., Konegger-Kappel S., Richter S., and Sangely L.; *Mass spectrometric analysis for nuclear safeguards; J. Anal. At. Spectrom.;* 30; 2015; 1469-1489

[10] Ardelt D., Polatajko A., Primm O., and Reijnen M.; *Isotope ratio measurements with a fully simultaneous Mattauch-Herzog ICP-MS; Anal. Bioanal. Chem.;* 405; 2013; 2987-2994

[11] Okada Y., Kato S., Satooka S., and Takeuchi K.; *Measurements of U-235/U-238 isotopic ratio in the photoproduct UF_5 by multiphoton ionization and time-of-flight mass spectrometry; Appl. Phys. B;* 62; 1996; 515-519

[12] Armstrong D.P., Harkins D.A., Compton R.N., and Ding D.; *Multiphoton ionization of uranium hexafluoride; J. Chem. Phys.;* 100; 1994; 28-43

[13] Whitten W.B., Reilly P.T.A., Verbeck G., and Ramsey J.M.; *Mass spectrometry of UF_6 in a micro ion trap; in 7th International Conference on Facility Operations: Safeguards Interface;* Charleston, SC; 2004; Paper 345-349

[14] NNSA Office of Nonproliferation and Arm Control; *Safeguards technology factsheet - portable mass spectrometry working group (MSWG);* 2016.

[15] Hoegg E.D., Barinaga C.J., Hager G.J., Hart G.L., Koppenaal D.W., and Marcus R.K.; *Preliminary figures of merit for isotope ratio measurements: The liquid sampling-atmospheric pressure glow discharge microplasma ionization source coupled to an Orbitrap mass analyzer; J. Am. Soc. Mass Spectrom.;* 27; 2016; 1393-1403

[16] Hoegg E.D., Barinaga C.J., Hager G.J., Hart G.L., Koppenaal D.W., and Marcus R.K.; *Isotope ratio characteristics and sensitivity for uranium determinations using a liquid sampling-atmospheric pressure glow discharge ion source coupled to an Orbitrap mass analyzer; J. Anal. At. Spectrom.;* 31; 2016; 2355-2362

[17] Barinaga C.J., Hager G.J., Hart G.L., Koppenaal D.W., Marcus R.K., Jones S.M., and Manard B.T.; *Toward a fieldable atomic mass spectrometer for safeguards applications: Sample preparation and ionization; in 12th Symposium on International Safeguards: Linking Strategy, Implementation and People (IAEA-CN-220);* Vienna, Austria; 2014; Paper S08-08

[18] Hoegg E.D., Marcus R.K., Koppenaal D.W., Irvahn J., Hager G.J., and Hart G.L.; *Determination of uranium isotope ratios using a liquid sampling-atmospheric pressure glow discharge - Orbitrap mass spectrometer system; Rapid Commun. Mass Spectrom.;* 31; 2017; 1534-1540

[19] Schwartz A.J., Williams K.L., Hieftje G.M., and Shelley J.T.; *Atmospheric-pressure solution-cathode glow discharge: A versatile ion source for atomic and molecular mass spectrometry; Anal. Chim. Acta;* 950; 2017; 119-128

[20] Krachler M., and Carbol P.; *Validation of isotopic analysis of depleted, natural and enriched uranium using high resolution ICP-OES; J. Anal. At. Spectrom.;* 26; 2011; 293-299

[21] Krachler M., and Wegen D.H.; *Promises and pitfalls in the reliable determination of U-233 using high resolution ICP-OES; J. Anal. At. Spectrom.;* 27; 2012; 335-339

[22] Zamzow D., Murray G.M., Dsilva A.P., and Edelson M.C.; *High-resolution optical-emission spectroscopy of uranium hexafluoride in the argon afterglow discharge; Appl. Spectrosc.;* 45; 1991; 1318-1321

[23] Barshick C.M., Shaw R.W., Young J.P., and Ramsey J.M.; *Evaluation of the precision and accuracy of a uranium isotopic analysis using glow-discharge optogalvanic spectroscopy; Anal. Chem.;* 67; 1995; 3814-3818

[24] Smith B.W., Quentmeier A., Bolshov M., and Niemax K.; *Measurement of uranium isotope ratios in solid samples using laser ablation and diode laser-excited atomic fluorescence spectrometry; Spectrochim. Acta Part B;* 54; 1999; 943-958

[25] Boyer B.D., Anheier N., Cable-Dunlop P., and Sexton L.; *Incorporation of new, automated environmental sampling systems into safeguards approaches;* LA-UR-13-28412, Los Alamos National Laboratory, 2013.

[26] Bushaw B.A., and Anheier Jr N.C.; *Isotope ratio analysis on micron-sized particles in complex matrices by laser ablation-absorption ratio spectrometry; Spectrochim. Acta Part B;* 64; 2009; 1259-1265

[27] NNSA Fact Sheet; *Fieldable atomic beam laser spectrometer for isotopic analysis;* 2016.

[28] Berezin A.G., Malyugin S.L., Nadezhdinskii A.I., Namestnikov D.Y., Ponurovskii Y.Y., Stavrovskii D.B., Shapovalov Y.P., Vyazov I.E., Zaslavskii V.Y., Selivanov Y.G., Gorshunov N.M., Grigoriev G.Y., and Nabiev S.S.; *UF_6 enrichment measurements using TDLS techniques; Spectrochim. Acta Part A;* 66; 2007; 796-802

[29] Grigor'ev G.Y., Lebedeva A.S., Malyugin S.L., Nabiev S.S., Nadezhdinskii A.I., and Ponurovskii Y.Y.; *Investigation of $^{235}UF_6$ and $^{238}UF_6$ spectra in the mid-IR range; Atomic Energy;* 104; 2008; 398-403

[30] NNSA Fact Sheet; *Spectroscopic methods for ultra-low isotopic analysis of proliferant material;* SRNL-STI-2016-00217, 2016.

[31] Zhao K., Penkin M., Norman C., Balsley S., Mayer K., Peerani P., Pietri C., Tapodi S., Tsutaki Y., Boella M., Renha Jr. G., and Kuhn E.; *International target values 2010 for measurement uncertainties in safeguarding nuclear materials;* STR-368, International Atomic Energy Agency (IAEA), 2010.

[32] Hieftje G.M.; *Signal-to-noise enhancement through instrumental techniques. 1. Signals, noise, and S/N enhancement in the frequency domain; Anal. Chem.;* 44; 1972; 81A-88A

[33] Derks E.P.P.A., Pauly B.A., Jonkers J., Timmermans E.A.H., and Buydens L.M.C.; *Adaptive noise cancellation on inductively coupled plasma spectroscopy; Chemometrics and Intelligent Laboratory Systems;* 39; 1997; 143-159

[34] Hieftje G.M.; *Emergence and impact of alternative sources and mass analyzers in plasma source mass spectrometry; J. Anal. At. Spectrom.;* 23; 2008; 661-672

[35] Meija J., and Mester Z.; *Signal correlation in isotope ratio measurements with mass spectrometry: Effects on uncertainty propagation; Spectrochim. Acta Part B;* 62; 2007; 1278-1284

[36] Grotti M., Todoli J.L., and Mermet J.M.; *Influence of the operating parameters and of the sample introduction system on time correlation of line intensities using an axially viewed CCD-based ICP-AES system; Spectrochim. Acta Part B;* 65; 2010; 137-146

[37] Schilling G.D., Ray S.J., Sperline R.P., Denton M.B., Barinaga C.J., Koppenaal D.W., and Hieftje G.M.; *Optimization of Ag isotope-ratio precision with a 128-channel array detector coupled to a Mattauch-Herzog mass spectrograph; J. Anal. At. Spectrom.;* 25; 2010; 322-327

[38] Richter S., Kuhn H., Truyens J., Kraiem M., and Aregbe Y.; *Uranium hexafluoride (UF_6) gas source mass spectrometry for certification of reference materials and nuclear safeguard measurements at IRMM; J. Anal. At. Spectrom.;* 28; 2013; 536-548

[39] Wieser M., Schwieters J., and Douthitt C.; Multi-collector inductively coupled plasma mass spectrometry, in Isotopic analysis - fundamentals and applications using ICP-MS, 1st ed., Wiley-VCH Verlag, (2012) p 77-91

[40] de Oliveira O.P., de Bolle W., Alonso A., Richter S., Wellum R., Ponzevera E., Sarkis J.E.S., and Kessel R.; *Demonstrating the metrological compatibility of uranium isotope amount ratio measurement results obtained by GSMS, TIMS and MC-ICPMS techniques; Int. J. Mass Spectrom.;* 291; 2010; 48-54

[41] Erdmann N., Albert N., Amador P., Arboré P., Eberle H., Lutzenkirchen K., Ottmar H., Schorlé H., van Belle P., Lipcsei F., Schwalbach P., Jung S., and Lafolie R.; *COMPUCEA 2nd generation performance evaluation;* IAEA-CN-184/316, International Atomic Energy Agency, 2010.

[42] Quarles C.D., Carado A.J., Barinaga C.J., Koppenaal D.W., and Marcus R.K.; *Liquid sampling-atmospheric*

pressure glow discharge (LS-APGD) ionization source for elemental mass spectrometry: Preliminary parametric evaluation and figures of merit; Anal. Bioanal. Chem.; 402; 2012; 261-268

[43] Marcus R.K., Quarles C.D., Barinaga C.J., Carado A.J., and Koppenaal D.W.; *Liquid sampling-atmospheric pressure glow discharge ionization source for elemental mass spectrometry; Anal. Chem.;* 83; 2011; 2425-2429

[44] Carado A.J., Quarles C.D., Duffin A.M., Barinaga C.J., Russo R.E., Marcus R.K., Eiden G.C., and Koppenaal D.W.; *Femtosecond laser ablation particle introduction to a liquid sampling-atmospheric pressure glow discharge ionization source; J. Anal. At. Spectrom.;* 27; 2012; 385-389

[45] Schwartz A.J., Ray S.J., and Hieftje G.M.; *Evaluation of interference filters for spectral discrimination in solution-cathode glow discharge optical emission spectrometry; J. Anal. At. Spectrom.;* 31; 2016; 1278-1286

[46] Schwartz A.J., Shelley J.T., Walton C.L., Williams K.L., and Hieftje G.M.; *Atmospheric-pressure ionization and fragmentation of peptides by solution-cathode glow discharge; Chemical Science;* 7; 2016; 6440-6449

[47] Thermo Fisher Scientific; *Exactive^{TM} series: Exactive^{TM} and Q Exactive^{TM} preinstallation requirements guide;* Revision A - 1288110, 2011.

[48] Liu H., Quentmeier A., and Niemax K.; *Diode laser absorption measurement of uranium isotope ratios in solid samples using laser ablation; Spectrochim. Acta Part B;* 57; 2002; 1611-1623

[49] Anheier N., Cannon B., Martinez A., Barrett C., Taubman M., Anderson K., and Smith L.E.; *A laser-based method for onsite analysis of UF_6 at enrichment plant;* PNNL-SA-105776, Pacific Northwest National Laboratory, 2014.

[50] NNSA Safeguards Technology Factsheet; *Laser ablation absorption ratio spectroscopy (LAARS);* PNNL-SA-123926, 2017.

[51] Barrett C.A., Cannon B.D., Martinez A., Chen C.S., Guerrero R., and Anheier Jr N.C.; *Destructive assay safeguards technology for sample collection and assay (presentation); in STM Workshop on Analytical Developments, Reference Materials, and Statistical Applications in the Nuclear Fuel Cycle;* Vienna, Austria 2016; Paper PNNL-SA-118821

[52] Chan G.C.Y., Choi I., Mao X., Zorba V., Lam O.P., Shuh D.K., and Russo R.E.; *Isotopic determination of uranium in soil by laser induced breakdown spectroscopy; Spectrochim. Acta Part B;* 122; 2016; 31-39

[53] Burkhart L.E., Stukenbroeker G., and Adams S.; *Isotope shifts in uranium spectra; Phys. Rev.;* 75; 1949; 83-85

[54] Edelson M.C., and Fassel V.A.; *Isotopic abundance determinations by inductively coupled plasma atomic emission spectroscopy; Anal. Chem.;* 53; 1981; 2345-2347

[55] Mao X., Chan G.C.-Y., Choi I., Zorba V., and Russo R.E.; *Combination of atomic lines and molecular bands for uranium optical isotopic analysis in laser induced plasma spectrometry; J. Radioanal. Nucl. Chem.;* 312; 2017; 121-131

[56] Chan G.C.Y., Mao X., Choi I., Sarkar A., Lam O.P., Shuh D.K., and Russo R.E.; *Multiple emission line analysis for improved isotopic determination of uranium – a computer simulation study; Spectrochim. Acta Part B;* 89; 2013; 40-49