

REVIEW OF PORTABLE MASS SPECTROMETRIC AND ALTERNATIVE TECHNIQUES FOR FIELDABLE ENRICHMENT ASSAY OF UF₆ AND RELATED ENVIRONMENTAL SAMPLES

Brian W. Ticknor, Benjamin T. Manard; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, United States.

George C.-Y. Chan; Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.

Abstract

Instrumentation to make in-field isotopic measurements for verification of UF₆ enrichment and analysis of environmental samples without the need for complicated sample handling procedures would greatly expand the toolbox available to International Atomic Energy Agency (IAEA) inspectors. A scoping study conducted in 2017 evaluated available technologies for in-field analysis of UF₆ enrichment. The present paper updates the study and expands the scope to include:

- 1.) advances in emerging technologies for in-field UF₆ enrichment assay since 2017
- 2.) an evaluation of technologies for in-field screening of environmental samples (ES)
- 3.) a market survey of commercial off-the-shelf, (COTS), equipment currently available for in-field use, as well as some general considerations that any research efforts to develop COTS instruments for the UF₆ and ES use cases should address

The IAEA concept of operations, (CONOPS), for the UF₆ use case is the most well documented, and thus a complete evaluation of 12 emerging technologies, including the benchmark Combined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA) technique, are systematically evaluated against 11 metrics related to in-field use and performance. The evaluation led to six techniques being recommended for further study, with two additional techniques considered promising. For in-field ES analysis the CONOPS is less defined, necessitating assumptions be made about requirements and preventing a full evaluation using established metrics. Six candidate techniques were evaluated, of which three were identified that might warrant further study. The COTS survey showed that no fit-for-purpose portable mass spectrometer exists with demonstrated performance on heavy metal analysis or isotope ratio measurements.

1. Introduction

Destructive analysis of both nuclear material (NM) and environmental samples (ES) plays an extremely important role in the International Atomic Energy Agency's (IAEA) safeguards verification mission and supports conclusions regarding the confirmation of declared activities and material and the absence of undeclared activities and material. In particular, thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are widely used to analyze the amount and isotopic abundance of both uranium and plutonium in inspection samples [1, 2]. In-field measurements, however, are largely limited to non-destructive analysis techniques, which generally do not have the sensitivity or precision to make the isotopic measurements necessary for bias defect determinations or to measure the very low amount of

material typically found on environmental samples. The COMBined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA) is a destructive method approved for in-field use on certain forms of NM samples including UF₆ [3,4], but it requires extensive on-site sample preparation by a subject matter expert and requires a long measurement time. No technique for in-field analysis of ES currently exists. The ability to make in-field isotopic measurements on uranium hexafluoride (UF₆) in particular would benefit the IAEA by speeding up analysis and reducing the need to ship this corrosive gas. In-field screening of ES swipes will help inspectors to ensure that they are collecting representative samples and allow prioritization of the subsequent laboratory analysis. To this end, the authors conducted a scoping study in 2020 [5] to evaluate emerging technologies and commercial-off-the-shelf (COTS) equipment that could enable in-field analysis of UF₆ and screening of environmental swipe samples, extending and updating a scoping study completed in 2017 that focused on evaluating technologies for in-field analysis of UF₆ [6, 7]. This paper summarizes the findings of the updated scoping study [5].

The goal of the present study is to expedite the development of next-generation field-deployable instrumentation by identifying technologies that could be applied to the determination of uranium (U) enrichment in UF₆ samples or for on-site detection and characterization of nuclear particles in environmental samples. The specific objectives are described below.

The first objective—an update on emerging technologies for in-field UF₆ enrichment assay—is based on the 2017 scoping study [6, 7]. Because of continual research investment in this area, several technological advancements have been reported in the past few years. The present effort updates the performance metrics of the previously reviewed emerging analytical techniques and includes novel technologies developed since the conclusion of our previous study.

The second objective is to evaluate existing and emerging technologies for in-field screening of enrichment-plant relevant ES swipes. Although the main effort is focused on U-containing particles in ES swipes, we also reviewed techniques for detection of plutonium (Pu). Completing this objective required defining the CONOPS for how fieldable technology would be utilized. The CONOPS outlined here is based on previous reports [8], as well as on assumptions by the authors. For ES, as currently no comparison benchmark is available for their in-field analysis, only potential analytical performance and analysis time are used as evaluation metrics.

The third objective of reviewing and identifying COTS options that can be directly used or readily modified for either fieldable UF₆ enrichment assay or screening of enrichment-plant-related ES updates previous surveys conducted in 2013 [9, 10] and 2015 [11]. Here, 14 instruments utilizing a variety of ionization sources and mass separators were evaluated. Despite the wide variety of COTS mass spectrometers available, no portable system currently exists with demonstrated performance for heavy metal analysis or isotope ratio measurements, both of which are requirements in the CONOPS identified for IAEA in-field analysis of nuclear safeguards samples.

2. Update of emerging technologies for in-field UF₆ enrichment assay

Because the goal of this part of the study was to update the 2017 effort [6, 7], an approach similar to that used previously was taken. Twelve candidate analytical techniques were identified (in a total of 14 different instrumental configurations). As before, the scope here extends beyond mass spectrometry; of the 12 techniques, 2 are radiometric, 6 are MS, and 4 are optical spectrometry.

2.1 Descriptions of Emerging Technologies for in-field UF₆ analysis

Only a brief description is given here for each technology, but technical details can be found in the cited references. An abridged version of the final evaluation focusing only on analytical performance and operation is provided in Table 1.

2.1.1 COMPUCEA

The COMPUCEA method has been approved by IAEA for in-field use of UF₆ and other types of uranium containing NM samples [3, 4], and has its own International Target Values (ITVs) [12]. In brief, COMPUCEA is a transportable analytical system for on-site U concentration and enrichment assays [3,4]. It combines the use of energy-dispersive x-ray absorption edge spectrometry (for U concentration measurement) and gamma-ray spectrometry (for ²³⁵U enrichment assay).

2.1.2 In-field alpha spectrometry with SUDA

Alpha spectrometry relies on the detection of alpha particles with characteristic energies from the decay of uranium isotopes in a sample [1]. In the specific formulation of the technique evaluated here, gaseous UF₆ samples are collected with a specially designed coupon termed a “single-use destructive assay” (SUDA) wafer [13, 14], which is then coupled with a COTS alpha spectrometer.

2.1.3 Molecular mass spectrometry with fieldable mass spectrometer

Molecular MS with a fieldable mass spectrometer [15] measures ions generated directly from gaseous UF₆ using electron-impact ionization for gaseous UF₆. The instrument is a retrofitted ion-trap MS (Thermo Fisher LTQ).

2.1.4 Laser Ablation ionization mass spectrometry

Laser ablation ionization mass spectrometry, (LAI-MS), is used simultaneously as the sampling, atomization, and ionization source with the ionized species directly measured with a mass spectrometer. A chemical transformation (e.g., via SUDA coupon, ABACC-Cristallini method) is needed to convert gaseous UF₆ into a solid form for laser ablation [16].

2.1.5 Surface-enhanced laser desorption and ionization

Surface-enhanced laser desorption and ionization (SELDI) [17, 18] is similar in principle to the more well-known matrix-assisted laser desorption/ionization (MALDI). In SELDI, the surface where the analyte is deposited is modified to further increase the efficiency of analyte laser desorption/ionization. In both MALDI and SELDI, the laser serves as both the desorption and the ionization source. A chemical transformation (e.g., hydrolysis) is needed to convert gaseous UF₆ into a solution form to be applied on MALDI or SELDI substrate.

2.1.6 Liquid sampling–atmospheric pressure glow discharge mass spectrometry

The liquid sampling–atmospheric pressure glow discharge mass spectrometry (LS-APGD) forms a microplasma by imposing a low direct-current potential between the surface of an electrolyte solution and a metallic counter electrode [19, 20]. The supporting electrolyte solution flows out of a small (~ 100 μm) glass capillary housed within a slightly larger metal capillary, between which cooling gas is passed. The LS-APGD ionization source is then coupled to an Orbitrap mass spectrometer for isotope ratio measurements on the dominate UO₂⁺ species. Because LS-APGD can be coupled to MS besides the Orbitrap, a separate evaluation of other configurations was included.

2.1.7 Solution-cathode glow-discharge mass spectrometry

The solution-cathode glow-discharge (SCGD) is a microplasma sustained directly on the surface of a flowing liquid electrode [21]. The glow discharge is formed when a DC potential is applied to a

tungsten anode and brought within close proximity to the surface of the flowing conductive sample solution. It operates by delivering the sample solution, via pump, through a vertical glass capillary. The solution overflows from the end of the capillary onto a graphite rod surrounding the glass capillary that is held at ground potential. Ions generated in the plasma from the sample solution are drawn into the inlet of the mass spectrometer, typically an Orbitrap. Because SCGD can be coupled to MS besides the Orbitrap, a separate evaluation of other configurations was included.

2.1.8 Electrospray ionization mass spectrometry

Electrospray ionization (ESI) is a common ionization technique where analyte dissolved in an electrolyte solution is pumped through a capillary. A potential difference of ~4 kV is applied to the liquid [22] relative to a counter electrode (e.g., the mass spectrometer inlet). At some critical voltage and distance, the charged liquid surface forms a pointed cone which breaks apart yielding charged droplets. When solvent in the droplets evaporates, charge density increases and the droplet further breaks into smaller charged droplets. Ultimately, what remain are charged analyte ions with solvent or electrolyte adducts. Commercial ESI-MS and paper spray-MS instruments are available [23, 24], with many options of different MS platforms (e.g., quadrupole, TOF, and Orbitrap).

2.1.9 Laser ablation absorbance ratio spectrometry

Laser ablation absorbance ratio spectrometry, (LAARS), uses four lasers, one for ablation of a solid sample, one each for atomic absorption of ^{235}U and ^{238}U , and one for wavelength locking between the ^{235}U and ^{238}U probe lasers [25]. The technique is sensitive to the spectral shifts in the atomic transitions between the two uranium isotopes, probed as free uranium atoms created by the ablation.

2.1.10 Atomic beam tunable diode laser absorption

In atomic beam tunable diode laser absorption, 10 to 50 mg [26, 27] of solid sample is loaded in a micro-oven inside a vacuum chamber. Free atoms are formed when the oven is resistively heated. Analyte atoms expand into the vacuum chamber through a small nozzle, forming a collimated atomic beam, which crosses with a wavelength-tunable diode-laser probe beam. By tuning the laser wavelength to the absorbance peak of ^{235}U or ^{238}U , $^{235}\text{U}/^{238}\text{U}$ ratio in the sample can be determined.

2.1.11 Laser-induced spectrochemical assay for uranium enrichment

Laser-induced spectrochemical assay for uranium enrichment (LISA-UE) is an optical technique for U isotopic assay based on the isotopic shifts in emission wavelength from ^{235}U and ^{238}U atomic lines [28, 29]. The laser-induced plasma is created directly in the gaseous UF_6 , and the isotopic information of the UF_6 sample is inherently encoded in the atomic emission from the plasma.

2.1.12 High performance infrared spectroscopy with quantum cascade laser

The high-performance infrared (HPIR) spectroscopy with quantum cascade laser (QCL) [30] method directly probes the ro-vibrational states of gaseous UF_6 molecules. Because of the change of mass, isotopic shifts are present in the ro-vibrational spectra of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$. A gas cell is used to measure the UF_6 absorption signal as the QCL is scanned across the relevant wavelength range.

2.2 Assessment criteria and recommendations of in-field UF_6 analysis techniques

Based on a set of performance metrics on analytical performance and ease of field operation, each candidate technique is assessed for its suitability to operate for in-field UF_6 enrichment assay. The seven evaluation metrics used in the previous scoping study [6, 7], namely, meeting predefined targets for analytical accuracy and precision (two separate criteria); meeting relaxed targets for accuracy and precision (two criteria); simultaneous ^{235}U and ^{238}U measurements; measurement

time; and overall ease of operation and system complexity continue to be used in the present study. The definitions of these metrics have been described in detail before and thus are not included here [5-7]. One new metric on operation is added in this evaluation: form factor of the instrument.

Depicted in Table 1 below, there are three grades for each assessment metric with symbols “+,” “o,” and “-” corresponding, respectively, to pass, marginal, and fail. For metrics for which there is insufficient information for a reliable estimation, a question mark is indicated in the table. Techniques are grouped into one of the three categories: “Recommended,” “Promising,” or “Not Recommended”. In addition, because the focus of this evaluation is on *fieldable* enrichment assay of UF₆, the field deployability of a candidate technique is of prime importance. Thus, if the team noted that a technique would need to overcome a particularly challenging engineering hurdle before a robust and fieldable instrument can be realized, its overall classification was reduced by one level (e.g., from “Recommended” to “Promising”). This is particularly relevant to LS-APGD and SCGD, where the ionization methods rank highly, but to date have mainly been coupled to an Orbitrap MS. As explained in the previous scoping study, Orbitraps as currently available on the commercial market are not considered fieldable under the use case defined here. Thus they are flagged as having significant engineering challenges for in-field use. Likewise LAARS, which requires 3 or more lasers, was evaluated as “Promising” as well. In summary, the techniques rated as “Recommended” are listed below with a brief description of their pros and cons.

Recommended techniques:

- In-field alpha spectrometry with single-use destructive assay (SUDA) sampling coupon
 - Pros: ability to measure all U isotopes; signals of the minor isotopes (i.e., ²³⁴U and ²³⁶U) are “amplified” owing to their orders-of-magnitude higher radioactive decay rates; offers a simple procedure for UF₆ sampling with coupon; sampling coupon can serve as archive
 - Cons: long measurement time; unlikely to quantitatively measure U concentration
- Liquid sampling-atmospheric pressure glow discharge (LS-APGD) with fieldable MS
 - Pros: low detection limit [requires parts per million (ppm) U concentration]; can detect minor U isotopes; potential to measure U concentration; demonstrates capability to meet ITVs of laboratory-based MS with Orbitrap; performance characterization reported from depleted uranium (DU) to high-enriched uranium (HEU).
 - Cons: U isotopic analysis coupled with MS other than Orbitrap is yet to be shown.
- Atmospheric-pressure solution-cathode glow-discharge (AP-SCGD) with fieldable MS
 - Pros: low detection limit (requires ppm U concentration); can detect minor U isotopes; has potential to measure U concentration; demonstrates capability to meet the ITVs of laboratory-based mass spectrometry with Orbitrap.
 - Cons: U isotopic analysis coupled with MS other than the Orbitrap is yet to be shown.
- Laser-induced spectrochemical assay for uranium enrichment (LISA-UE)
 - Pros: no sample preparation (direct measurement on gaseous UF₆); simultaneous isotopic measurements; adaptable to various sample forms; short measurement time.
 - Cons: unlikely to measure U concentration; currently limited to ²³⁵U/²³⁸U measurement.

- High-performance infrared (HPIR) spectroscopy
 - Pros: no sample preparation (direct measurement on gaseous UF₆); small instrument form factor; short measurement time; demonstrated performance from DU to HEU; fieldable prototype equipped with automated sampling manifold already has been built.
 - Cons: applicable only to gaseous UF₆; unlikely to measure U concentration; limited to ²³⁵U/²³⁸U ratio measurement.
- Atomic beam tunable diode laser absorption
 - Pros: has high immunity to spectral interference (potential for other sample types); small instrument form factor; potential to measure minor U isotopes with optical means
 - Cons: provides sequential ²³⁵U and ²³⁸U isotopic measurement; requires in situ thermo-reduction of uranium compounds to free uranium atoms.

Table 1. Recommendation summaries of existing and emerging techniques for in-field UF₆ enrichment assay. Symbols “+,” “O,” and “-” indicate “pass,” “marginal,” and “fail,” respectively. A superscript “Est” indicates estimation from scientific principle. A question mark indicates that information either is not yet available or is insufficient for estimation.

	Analytical Performance					Operation			Remarks	
	Accuracy meets IAEA ITV u(s) for TMS	Precision meets IAEA ITV u(l) for TMS	ITV u(s) for TMS	ITV u(l) for TMS	Simultaneous ²³⁵ U & ²³⁸ U measurements	Measurement time	Overall ease of operation	Instrument form factor		Notable challenging engineering issue for field use
COMPUCEA	o	o	+	+	+ ^a	-	-	+		Benchmark
In-field alpha spectrometry (w/ SUDA)	-	-	+	+	+	-	o	o		Recommended
LS-APGD-Orbitrap	+	+	+	+	+	+	o	-	Y	Promising
LS-APGD-MS (other than Orbitrap MS)	?	?	?	?	o	+	o	o		Recommended
SCGD-Orbitrap	+ ^{Est}	+	+ ^{Est}	+	+	+	o	-	Y	Promising
SCGD-MS (other than Orbitrap MS)	?	?	?	?	o	+	o	o		Recommended
Molecular MS w/ fieldable mass spectrometer	-	-	o	o	o	+	+	o		Promising
MALDI or SELDI (non-Orbitrap)	- ^{Est}	-	o ^{Est}	o	o	+	o	-		NR*
Laser ablation ionization (LAI)-MS	-	-	o	o	o	+	o	o		NR*
Electrospray ionization (ESI)-MS	-	-	o	o	o	+	o	-		NR*
LAARS	o	o	+	+	+	+	o	-	Y	Promising
LISA-UE	-	-	o	o	+	+	+	-		Recommended
HPIR spectroscopy	-	-	+	o	-	+	+	+		Recommended
Atomic beam tunable diode laser absorption	-	-	o	o	-	+	o	+		Recommended

^aSignal correlation for measurement-noise reduction through simultaneous ²³⁵U and ²³⁸U 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. *NR = not recommended

It should be noted that labeling a technique as “Recommended” does not mean that it is already mature enough to be used in the field for routine UF₆ enrichment assay. It loosely means that relatively short-term development of a few years is needed before in-field use could be realized. Likewise, techniques labeled as “Promising” and “Not Recommended” require projected development or engineering with mid-term efforts of roughly between 5 and 10 years and long-term efforts that could be more than 10 years, respectively.

3. Detection and Characterization of Materials Contained in Environmental Samples and Emerging Technologies for in-field ES analysis

As part of IAEA safeguards activities inside of nuclear facilities, environmental sampling is a process by which inspectors collect samples that may contain trace amounts of NM and then transfer them to specialized laboratories where they are analyzed by sensitive analytical methods [1, 2, 31]. While the term technically covers many sample types (e.g., air, water, vegetation, soil), it often refers specifically to swipe sampling, in which a cotton swipe matrix is used as the collection media. ES remains one of the key safeguards measures for the detection of undeclared material or activities [1, 2, 31]. A scenario for IAEA use of in-field measurements would be to provide inspectors in the field with the ability to detect and possibly characterize NM contained in ES. Inspectors could determine whether particles of NM were present on the swipe samples they had just collected and take more targeted swipes if material of interest was detected.

3.1 Concept of operations (CONOPS) for in-field analysis of environmental samples

Because there is no current method approved and employed for the in-field analysis of ES swipes, specific performance metrics could not be defined in the manner done for UF₆. A working CONOPS was developed to generally define the problem space, with assumptions coming from the current understanding of the use case and previous reports [6, 8].

- Technology should not replace current sample collection methods.
- The method should preserve a portion of the sample for future laboratory analysis.
- U analysis is the primary objective. Pu analysis is a secondary objective.
- Elemental detection of U is not sufficient.
 - Important to distinguish DU, NU, and LEU
 - Detection of minor U isotopes (²³⁴U and ²³⁶U) is desirable.
 - Elemental detection of Pu without an isotope ratio measurement may be sufficient.
- A high degree of automation is desired; technology should be useable by a trained non-expert.
- Must be “deployable” to an on-site laboratory, but not necessarily “portable”.
- Should operate in a setting with temperature 15–25°C and relative humidity below 80%.
- Access to AC main power and compressed N₂ gas are assumed.
- Should have a lifetime of 10 years. Major refurbishment required no less than every 2 years.
- A total cost of less than €100,000 per unit is required, with €50,000 preferred.

3.2 Emerging Technologies for in-field screening of ES

With these considerations from the CONOPS in mind, six emerging technologies were considered: particle imaging with an autoradiographic camera, X-ray fluorescence, micro-Raman spectroscopy, laser induced breakdown spectroscopy (LIBS), optical fluorescence spectroscopy, and ion mobility spectroscopy. None has yet demonstrated the capability to perform isotopic analysis of ES in the

field, and more research is needed to fully understand capabilities and limitations. Nevertheless, three techniques show potential for some scenarios; they are briefly summarized as follows:

3.2.1 Alpha-particle imaging with an autoradiographic camera system

The autoradiographic camera depends on emission of alpha particles from radionuclides in the sample to generate photons after impacting a scintillator. For example, the alpha particles emitted by the individual PuO₂ particles of 10s of μm in size cause a scintillator to blink intermittently, which is then captured by the electron multiplying CCD operating in movie-capture mode [32]. The pixels that show the blink locate the particles, and the blink frequency is related to the activity of the particle. Due to the detection limits, count times, and the inability to identify uranium particles, this method is unlikely to find widespread safeguards use. Nevertheless, the technique is of a small, fieldable size and could be potentially useful in other scenarios (e.g., contamination screening).

3.2.2 Micro-Raman spectroscopy

Raman spectroscopy is an optical technique to probe identities of chemical bonds through inelastic light-scattering (Raman scattering) of vibrational modes of molecules. Light from a low-power laser is directed to the sample, and the scattered laser light is collected [33]. The wavelength difference between the incident and scattered laser light records the energy change during the scattering, which is related to the vibrational mode of a chemical bond in the sample. Measurement of Raman scattering with a microscope objective (micro-Raman) makes the technique amenable to individual 1-μm sized particles, and it is sensitive to elemental detection of both U and Pu [34].

3.2.3 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is a highly field-deployable technique [35] based on atomic emission in a laser-induced plasma. Atomic emission wavelengths are characteristic of the chemical elements present in the sample. Under certain carefully controlled conditions it has demonstrated sensitivity for some elements down to femtogram levels; but in the conventional approach it likely does not have the sensitivity to detect individual 1-μm particles of U. However, unique amongst other techniques evaluated here, LIBS does offer the possibility of U isotopic analysis through isotopic shifts in the detected U emission lines [28].

3.3 Recommendations for emerging technologies for in-field analysis of ES samples

Recommended technique:

- Laser-induced breakdown spectroscopy (LIBS)
 - Application scenario: in-field isotopic analysis of U particles on ES samples
 - Pros: working principle and form factor are applicable to in-field isotopic U analysis; no sample preparation required; isotopic analysis is demonstrated at the scale of micro-analysis.
 - Cons: further sensitivity improvement needed for single-particle analysis.

Promising techniques:

- Micro-Raman spectroscopy
 - Application scenario: surveys and screening for the presence of U-particles without a need for isotopic information on-site
 - Pros: demonstrates capability for the identification of single particles with high U-content; amenable to detection of Pu; commercially available; nondestructive
 - Cons: no isotopic information; cellulose substrate not suitable for Raman spectroscopy so sample transfer to another substrate is needed; measurement time is relatively slow.

- Alpha-particle imaging with autoradiographic camera system
 - Application scenario: contamination screening of relatively pure, μm -sized Pu particles
 - Pros: demonstrated technique for analysis of Pu particles; nondestructive
 - Cons: not applicable to the analysis of U particles; no isotopic information

4. Survey of portable COTS MS instrumentation, other laboratory and non-COTS techniques

The final section of the scoping study summarizes COTS options that can be directly used or potentially modified for either fieldable UF_6 enrichment assay or screening of ES. 14 COTS instruments were included, using a variety of ionization sources and mass separators. A detailed list of these instruments is included in the full scoping study [5]. In general, these instruments have been developed for detection of volatile or semi-volatile organic species or for chemical process monitoring. Inorganic analysis has not been a traditional focus of the commercial market. No identified COTS instrument has demonstrated performance for heavy metal analysis or isotope ratio measurements, which are requirements in the CONOPS identified for IAEA in field analysis.

The laboratory mass spectrometric techniques are utilized for analysis of ES swipes, particularly TIMS and MC-ICP-MS, are not easily amenable to miniaturization. However, literature does exist showing ionization sources, similar to those that have been successfully miniaturized, coupled to laboratory-based COTS mass spectrometers and used to make safeguards relevant measurements, especially on uranium. In particular, several derivatives of ESI-MS [23, 24], LS-APGD-MS [20], and LA-MS [36] have been applied in the laboratory to ES-type sample analysis. These studies show that the availability of the ionization sources on portable instruments do not by themselves present physical limitations on actinide analysis in ES swipes and that the current range of available COTS instrumentation presents some opportunities for more detailed studies.

Without definitive laboratory testing documenting capability, only broad conclusions may be made. Some general considerations and remarks from the COTS survey are summarized below:

- Most portable COTS instruments have a useable mass range suitable for analysis of U and Pu.
- Mass resolution, where information is available, ranges from 0.5–0.7 m/z . This will likely make the determination of minor isotopes (^{234}U , ^{236}U) unfeasible, and may impact the ability to measure the major $^{235}\text{U}/^{238}\text{U}$ ratio at suitably high precision.
- Sensitivity will prove challenging for all instruments, especially for Pu. Pu content of ES can be sub-pg on the entire swipe, below the stated sensitivity of any of the instruments identified.
- The detector dynamic range limits the detection capability of the minor U isotopes. A dynamic range better than 10^6 will be required. Some COTS instruments claimed meeting this requirement.
- Because isotope ratio measurements have not been a target of the portable COTS MS market, essentially no information is available on achievable precision on those measurements.
- Cost may prove prohibitive. The cost of the instruments described here ranges from \$50k–350k per unit, and if customization is required the cost may be expected to increase.

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 and by Oak Ridge National

Laboratory under contract DE-AC05-00OR22725. The work presented in this paper was funded by the National Nuclear Security Administration of the Department of Energy, Office of International Nuclear Safeguards.

6. References

1. M. Zendel, D.L. Donohue, E. Kuhn, *et al.* (eds), *Handbook of nuclear chemistry, 2nd ed.*, Springer US, Boston, MA (2011) pp. 2893-3015.
2. S. Boulyga, S. Konegger-Kappel, S. Richter, L. Sangely, *J. Anal. At. Spectrom.* 30 (2015) 1469-1489.
3. A. Berlizov, A. Schachinger, K. Roetsch, *et al.*, *J. Radioanal. Nucl. Chem.* 307 (2016) 1901-1909
4. E. Zuleger, "Experience of UF₆ sampling preparation and analysis", presented at the *Technical Meeting on the IAEA 2019 Nuclear Material Round Robin: Workshop on UF₆ sampling method (ABACC-Cristallini)*, Vienna, Austria, June 2019.
5. G. Chan, B. Ticknor, B. Manard, *ORNL/LTR-2021/1905*, Oak Ridge National Laboratory, (2021).
6. G.C.Y. Chan, J.D. Valentine, R.E. Russo, *LBL-2001050*, Lawrence Berkeley National Laboratory, (2017).
7. G.C.Y. Chan, J.D. Valentine, R.E. Russo, *ESARDA Bulletin 54* (2017) 31-43.
8. L.T. Sexton, B.W. Ticknor, *SRNL-STI-2013-00062*, Savannah River National Laboratory, (2013).
9. G. Hart, C. Barinaga, G. Hager, D. Duckworth, *PNNL-22237*, Pacific Northwest National Laboratory, (2013).
10. L.T. Sexton, B.W. Ticknor, *SRNL-STI-2013-00119*, Savannah River National Laboratory, (2013).
11. T.M. Yoshida, C.P. Leibman, P.C. Stark, *LA-UR-15-28831*, Los Alamos National Laboratory, (2015).
12. International Atomic Energy Agency (IAEA), *STR-368*, IAEA, (2010).
13. D. Chichester, J. Johnson, S. Watson, G. Fugate, *INL-CON-20-57162*, Idaho National Laboratory, (2020).
14. N. Anheier, T. Pope, C. Padilla-Cintrón, *et al.*, *PNNL-28426*, Pacific Northwest National Laboratory, (2019).
15. C.V. Thompson, W.B. Whitten, *ORNL/TM-2017/70*, Oak Ridge National Laboratory, (2017).
16. M. Dirmyer, B. Judge, *LA-UR-16-25370*, Los Alamos National Laboratory, (2016).
17. G.H. Hager, E.D. Hoegg, G.L. Hart, R.K. Marcus, "Towards a fieldable, atomic mass spectrometer for safeguards applications", presented in *DOE NNSA MS Working Group Meeting 2016*, (2016).
18. P.A. Kuzema, *J. Anal. Chem.* 66 (2011) 1227-1242.
19. E.D. Hoegg, R.K. Marcus, D.W. Koppelaar, *et al.*, *Rapid Commun. Mass Spectrom.* 31 (2017) 1534-1540.
20. H.W. Paing, B.T. Manard, B.W. Ticknor, *et al.*, *Anal. Chem.* 92 (2020) 8591-859.
21. G.M. MacLean, G.C.Y. Chan, J.T. Shelley, "Uranium isotope-ratio analysis with solution-cathode glow discharge mass spectrometry (SCGD-MS)", in *66th ASMS Conference on Mass Spectrometry and Allied Topics*, San Diego, (2018), Paper MP 202 (Citation ID 295432).
22. H. Hotta, K.I. Tsunoda, *Anal. Sci.* 31 (2015) 7-14.
23. T.P. Forbes, C. Szakal, *Analyst* 144 (2019) 317-323.
24. K. Coopersmith, R.B. Cody, J.M. Mannion, *et al.*, *Rapid Commun. Mass Spectrom.* 33 (2019) 1695-1702.
25. B.A. Bushaw and N.C. Anheier Jr, *Spectrochim. Acta Part B*; 64; 2009; 1259-1265
26. V. Lebedev, J.H. Bartlett, A. Castro, *J. Anal. At. Spectrom.* 33 (2018) 1862-1866.
27. J.H. Bartlett, A. Castro, *Spectrochim. Acta Part B* 155 (2019) 61-66.
28. J. Song, G.C.Y. Chan, X. Mao, *et al.*, *Spectrochim. Acta Part B* 150 (2018) 67-76.
29. G.C.Y. Chan, L.R. Martin, L.D. Trowbridge, *et al.*, *Spectrochim. Acta Part B* 176 (2021) 106036.
30. K.A. Strange Fessler, P. O'Rourke, N. DeRoller, *et al.*, *Proc. SPIE, Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XXI* 11416 (2020) 114160R.
31. International Atomic Energy Agency (IAEA), *STR-348*, IAEA, (2005).
32. Y. Morishita, *Nucl. Instr. and Meth. in Phys. Rev. A* 954 (2020) 161708.
33. F. Pointurier, O. Marie, *J. Raman Spectrosc.* 44 (2013) 1753-1759.
34. M.J. Sarsfield, R.J. Taylor, C. Puxley, H.M. Steele, *J. Nucl. Mater.* 427 (2012) 333-342.
35. R.S. Harmon, R.E. Russo, R.R. Hark, *Spectrochim. Acta Part B* 87 (2013) 11-26.
36. A.-L. Ronzani, F. Pointurier, M. Rittner, *et al.*, *J. Anal. At. Spectrom.* 33 (2018) 1892-1902.