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Feasibility of a Fieldable Mass Spectrometer

FY 2015 Year-end Report

October 2015

CJ Barinaga
GJ Hager
ED Hoegg
AJ Carman
GL Hart

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99352

Summary

Currently, the International Atomic Energy Agency (IAEA) monitors the production of enriched uranium hexafluoride (UF_6) at declared facilities by collecting a few grams of product in sample tubes that are then sent to central laboratories for processing and isotope ratio analysis by thermal ionization mass spectrometry. Analysis of results may not be available for some time after collection. In addition, new shipping regulations will make it more difficult to transport this amount of UF_6 to a laboratory. The IAEA is interested in an isotope ratio technique for uranium in UF_6 that can be moved to and operated at the enrichment facility itself.

This report covers the tasks and activities of the Feasibility of a Fieldable Mass Spectrometer Project for FY 2015, which investigates the feasibility of an in-field isotope ratio technique— the forward deployment of a technique to the non-laboratory situation of a protected room with power and heat at the facility of interest.

A variety of nontraditional elemental ionization techniques were considered for testing. Of the various ionization techniques available, three were selected as viable candidates for potential in-field use:

- liquid sampling, atmospheric pressure glow discharge (LS-APGD)
- matrix assisted laser desorption ionization (MALDI)
- atmospheric pressure-laser ablation ionization (AP-LAI).

The FY 2015 work showed that of the three original techniques evaluated, only the LS-APGD-MS and AP-MALDI-MS were promising as ion sources for in-field mass spectrometer applications. They should both be moved forward for testing with the candidate in-field mass spectrometer and with the adsorbed UF_6 sample types.

With advice and consent of the sponsor, the National Nuclear Security Administration Office of Nonproliferation and Arms Control, the authors re-scoped the FY 2015 work plan and funding and ordered an MTE-50 instrument from MassTech, with an inlet type that has worked with the LS-APGD and the atmospheric pressure version of the MALDI technique that the authors evaluated for elemental/isotopic applications. Set up and testing began in late September 2015.

Acronyms and Abbreviations

AP	atmospheric pressure
APCI	atmospheric pressure chemical ionization
AP-LAI	atmospheric pressure-laser ablation ionization
CHCA	α-cyano-4-hydroxycinnamic acid
COTS	commercial-off-the-shelf
DC	direct current
ESI	electrospray ionization
GD	glow discharge
IAEA	International Atomic Energy Agency
ICP	inductively coupled plasma
LA	laser ablation
LS-APGD	liquid sampling, atmospheric pressure glow discharge
MALDI	matrix assisted laser desorption ionization
MS	mass spectrometer
MSWG	Mass Spectrometry Working Group
NPAC	Office of Nonproliferation and Arms Control
RSD	relative standard deviation
TA	tartaric acid
ToF	time of flight
UF_6	uranium hexafluoride

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1.0 Task 1: Downselect Ion Source

Currently, the International Atomic Energy Agency (IAEA) monitors the production of enriched uranium hexafluoride (UF_6) at declared facilities by collecting a few grams of product in sample tubes that are then sent to central laboratories for processing and isotope ratio analysis by thermal ionization mass spectrometry. Analysis of results may not be available for some time after collection. In addition, new shipping regulations will make it more difficult to transport this amount of UF_6 to a laboratory. Thus, the IAEA is interested in an isotope ratio technique for uranium in UF_6 that can be moved to and operated at the enrichment facility itself.

One of the major obstacles to fieldable[1] mass spectrometry—luggable, man-portable, or handheld instrumentation—for elemental and isotopic analysis is sample preparation and sample ionization. Most laboratory-based methods for solid samples involve a dissolution step followed by several purification steps before introduction to the instrument for ionization and mass analysis. The need for hazardous chemicals and processing time are significant hurdles for elemental/isotopic analysis for in-field mass spectrometer applications.

A variety of nontraditional elemental ionization techniques were considered for testing. Laser ablation/desorption-based techniques were considered important because of the potential for minimal sample preparation. Small, high-pressure glow discharge types of ion sources were also considered because of their low power requirements and the potential to operate at ambient conditions (temperature and pressure). Of the various ionization techniques available, three were selected as viable candidates for potential in-field use:

- liquid sampling, atmospheric pressure glow discharge (LS-APGD)
- matrix assisted laser desorption ionization (MALDI)
- atmospheric pressure-laser ablation ionization (AP-LAI).

LS-APGD is a small, direct current (DC) glow discharge that uses a flowing stream of electrically conducting liquid (typically dilute aqueous acids) to carry a sample, and a helium sheath gas to cool the electrodes. This ion source has been shown to produce atomic and polyatomic ions of various elements, including uranium, depending on their refractory nature (Marcus et al. 2011; Quarles et al. 2012; Carado et al. 2012; Jones et al. 2014).

MALDI is a very widely used technique for the mass spectrometric analysis of biological materials since its description by Tanaka et al. in 1988 (Nobel prize 2002) and Karas and Hillenkamp (1988). It has been rarely used for elemental analysis. The key component is that the sample is mixed with a matrix, which is what absorbs the laser energy and is thus desorbed into the gas phase and ionized. The matrix ions then ionize the sample molecules by charge exchange. The ionization is typically achieved at vacuum pressures. Mixing the sample with a matrix and placing it in a vacuum are operational complications that the authors hoped to get around. A form of MALDI at ambient pressure has been reported (Laiko et al. 2000) for biological molecules and this form is anticipated to work for elemental ions as well. MALDI mass spectrometry of uranium

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[1] For this report the authors use the terms "in-field" and "fieldable" to mean the forward deployment of a technique to the non-laboratory situation of a protected room with power and heat at the facility of interest.

has been reported using matrices of various typical organic matrices (Guerrero et al. 2001), C-60 fullerene (Havel and Soto-Guerrero 2005), pencil lead (graphite) (Black et al. 2006), and high-purity graphite (Walton and Mitchell 2013).

AP-LAI is related to laser ablation (LA) that is used to sample solid material in to the inductively coupled plasma (ICP) ion source of an ICP mass spectrometer (MS) for elemental and isotopic analysis. The high-temperature laser ablation plume is known to contain ions. At ambient pressure these are detected by optical emission, and in vacuum conditions they can be detected by mass spectrometry, typically time of flight (ToF) MS. This technique has produced biological ions at atmospheric pressure only with the aid of secondary ionization (Nemes and Vertes 2007). So, if the atomic ions that are produced at atmospheric pressure survive long enough to be sampled by an MS, it would be at very low rate. One of the possible sampling mechanisms for UF_6 in this application would be a material that would stably adsorb the UF_6 such that the surface concentration would be quite high. With this high surface concentration of uranium, it was hoped that uranium ions could be detected with the LAI technique.

The three ion sources are discussed as sub-tasks 1a, 1b, and 1c. The results of performance tests (sensitivity, detection limit, and most importantly, uranium isotope ratio precision) and other observations are reported and discussed. The comparison of results, advantages, and disadvantages of the three ion sources and a “down-selection” evaluation will be presented at the end of this section (Task 1).

1.1 Task 1a: LS-APGD

The ion source consists of a high potential DC electrode positioned perpendicular to a grounded cathode, which is made up of an inner capillary that carries the flowing, electrically conducting liquid, and an outer capillary that guides a helium sheath gas (Figure 1.1). A small glow discharge (GD) is established between the liquid stream and the DC electrode. This GD is positioned near the inlet of a metal capillary that forms the atmosphere to vacuum inlet of an atmosphere sampling MS (Figure 1.1). The atmosphere sampling MS available for this work is a Thermo Scientific™ Exactive™ model of an orbitrap-style mass spectrometer. The Orbitrap™ series of instruments is designed for mass analyzing electrospray ionization (ESI) ions from large biological molecules with a large mass range (several kDa) and very good mass accuracy in order to determine amino acid content and sequence of peptides and proteins. Although a conveniently available instrument for this work, it is not one that would be appropriate for the type of in-field work envisioned by the potential user. This instrument is rather large and heavy (although it is a benchtop instrument) and has a higher-than-ideal cost. Some of the performance of the LS-APGD on this instrument may be because of the capabilities and limitations of the MS rather than inherent with the ion source.

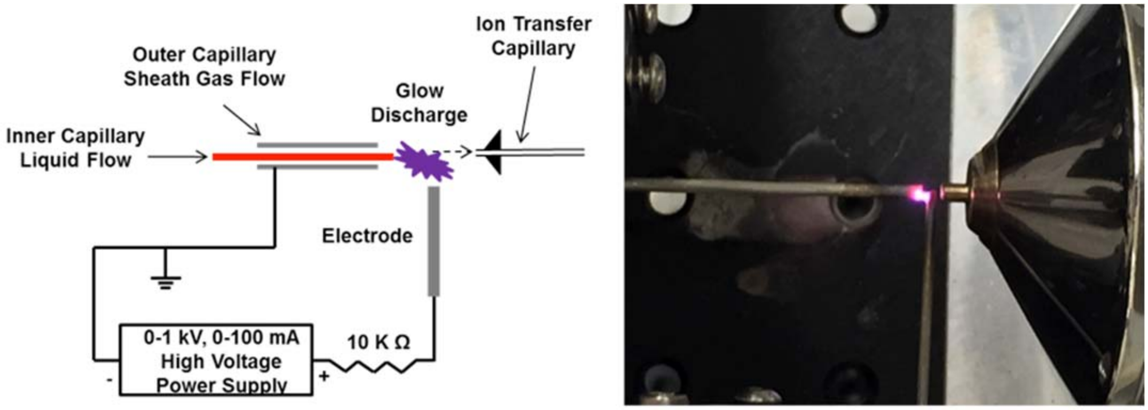

Figure 1.1. Diagram (left) Showing the Components of the LS-APGD, and Photo (right) of the LS-APGD in Operation near the Inlet Capillary of the Thermo Scientific Exactive Orbitrap Mass Spectrometer

Early work with continuous flow of cesium (1 ppm) and silver (5 ppm) in 2% nitric acid solutions showed very good detectability for cesium and less so for silver, both as atomic ions. The isotope ratio for silver (109/107 = 0.9474) determined by peak area was measured at 0.9483 with a 0.35% relative standard deviation (RSD). Even though this is for a near-ideal isotope ratio (1.0), these results were very encouraging. What was noted however was that there were times when significant memory effects occurred for both cesium and silver.

Although cesium, silver, and other elements were detected as atomic ions, uranium appears only as the UO_2^+ ion at 267 and 270 m/z for ^{235}U and ^{238}U respectively (Figure 1.2). The LS-APGD parameters were optimized for response and $^{235}U/^{238}U$ ratio:

- liquid flow rate ~ 30-50 µL/min
- discharge to capillary inlet distance ~ 1.5 mm
- discharge current ~ 30 mA
- helium sheath gas flow rate ~0.5 L/min.

The Exactive physical parameters that were available to optimize were:

- inlet capillary temperature 200°C
- capillary/skimmer collision energy 50 eV
- collision cell energy 70 eV.

The ion collection parameters were optimized to:

- number of microscans 10
- maximum injection time 1000 ms.

The data-handling parameters were optimized: resolution set to “enhanced” and the “collection window” set to 10 atomic mass unit (amu).

With these settings uranium isotope ratios based on peak area were determined for a depleted solution (ratio by other MS), a natural solution (ratio assumed), and a 5 ppm solution of U030 (ratio certified) (Table 1.1). The data analysis shown in Table 1.1 represents 10 data points taken within a single analytical session where the solution was continuously injected into the plasma with no interruption.

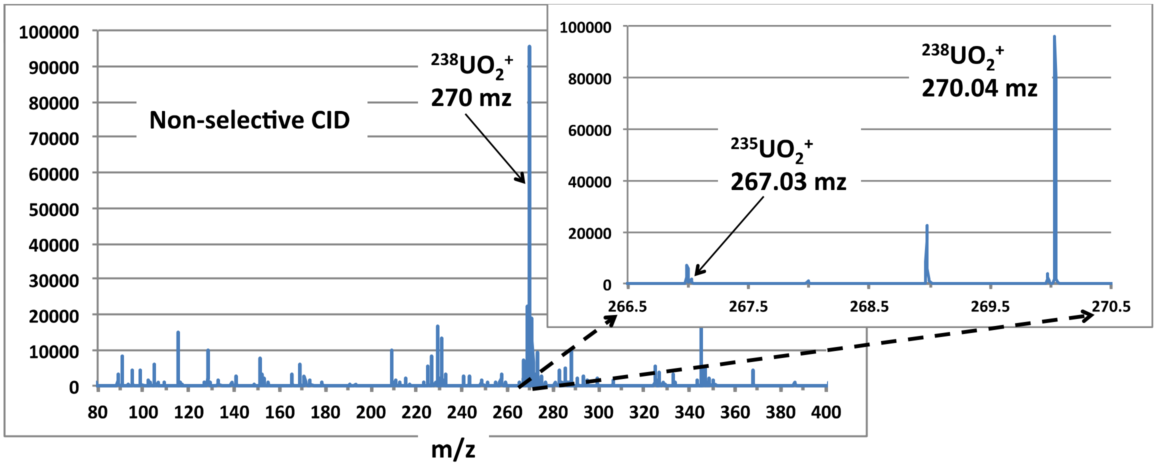

Figure 1.2. Spectra of Natural Uranium in 2% Aqueous Nitric Acid by LS-APGD and Exactive MS. Inset is an enlargement of the UO_2^+ mass region.

Table 1.1. Uranium Isotope Ratio Results for Optimized LS-APGD/Exactive MS

Uranium solution	$^{235}UO_2/^{238}UO_2$ ratio	Measured	RSD (%)
'Depleted' 10 ppm	0.00192 other MS	0.00187	0.85
'Natural' 10 ppm	0.00726 assumed	0.00703	0.40
U030-A 5 ppm	0.03040 certified	0.03137	0.34

When the uranium isotope ratios were measured across multiple analytical sessions, which involved turning off the plasma and replacing the syringe, the RSD increased to 3.05%, 1.63%, and 1.27% for the depleted, natural, and enriched samples, respectively. To better represent the analysis of an unknown and compare it to a sample, both solutions should be run during the same analytical session by continuously running the plasma with a nitric acid solution and injecting sample via an injection loop.

While there is still room for improvement and the need to develop a standard test procedure, these are considered very good, precise results and make this technique a good candidate for fieldable MS applications. In all cases it was noted that the ratio was slightly less than expected, which could be because of an under-measurement of the lighter isotope or over-measurement of the greater. However, nearly all isotope ratios are determined by measuring a standard, applying an appropriate correction factor, and then applying the same correction factor to the unknown(s). The same correction factor would be applied here to correct the measurement accuracy.

During this work it was found that the inlet capillary to the MS had a significant carryover, or memory effect, and had to be cleaned well between different samples for good results. It is thought that ions (plasma or sample) are striking previously adsorbed ions and desorbing them into the gas stream. This could be a significant disadvantage for this technique. It should also be noted that the sensitivity of the LS-APGD and Exactive combination is not very good such that for an isotope ratio determination of a depleted sample, a uranium concentration of at least 500 ppb would be needed to detect the ^{235}U well enough for a good ratio. There is no chance of detecting ^{234}U and ^{236}U with this sensitivity. The Exactive can be a very sensitive instrument for large, multi-charged, biological ions, however it was never designed for, nor characterized by the manufacturer for atomic ions. This ion source may be able to deliver better sensitivity with a different atmosphere sampling MS.

The desorption of ions from a surface by LS-APGD has been reported for several small organic ions (Marcus et al. 2013). Preliminary work at the very end of FY 2015 indicated that ions from the GD aimed at $UO_2(NO_3)_2$ deposited and dried on a microscope slide could desorb UO_2^+ into the inlet and be detected by the Exactive MS. To the authors' knowledge, this is the first observation of desorption of small elemental polyatomic ions from a surface. This effect could be of significant importance to determining the uranium isotope ratio of UF_6 that has be adsorbed to a reactive surface such as proposed for possible future sampling of UF_6.

The advantages of this technique are the very good uranium isotope ratio precisions and that it operates at ambient conditions. The potential of LS-APGD acting as a desorption ion source is very attractive for the isotope determination of UF_6 adsorbed to reactive surface and needs to be further investigated for this sample type. Because it has been designed to fit at the atmosphere-sampling capillary of Thermo Scientific design, it should fit to and operate with the smaller, portable quadrupole ion trap MS (the MTE-50) acquired for testing as a potential MS for in-field safeguards applications.

1.2 Task 1b: MALDI-TOF

The *in vacuo* MALDI ionization technique (Figure 1.3) is widely used and a number of instruments, makes, and models (from very large to benchtop) are available. An instrument of opportunity here is a high-mass resolution MALDI-ToF MS (Daltronics Auto-Flex II, Brucker). The instrument is equipped with a nitrogen laser operating at 337.1 nm with a repetition rate of 50 Hz is operated in the reflection (higher-mass resolution) mode.

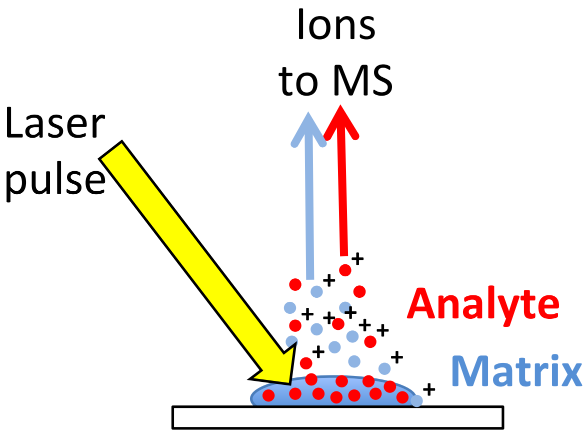

Figure 1.3. The Ion Formation Process in MALDI-MS

The substrates examined were standard stainless steel MALDI sample plates (both brushed, or roughened, and polished) to fit the Auto-Flex. The matrices examined were: colloidal graphite suspended in isopropanol (neolube), C-60 fullerene suspended in benzene, graphite from a 4b lead pencil, tartaric acid (TA) in 2% nitric acid, and α-cyano-4-hydroxycinnamic acid (CHCA). The layered matrices (neolube and C-60) were prepared by depositing 1-2 uL of solution (neolube and C60) on to the MALDI sample plate sample-circles (2 mm inner diameter) and allowed to dry. The pencil graphite was applied directly by rubbing within the boundaries of the sample spot. In most instances 1 uL of 20 ppm uranium oxide in 2% aqueous nitric acid was deposited on top of each substrate and air dried. The admixed matrices (CHCA and TA) were prepared by mixing the uranium sample and matrix solutions (50:50). A 2 µL aliquote of mixture of 100 µL of 1% CHCA solution in ACN:EtOH H_2O with 0.1% TFA and 100 uL of the 20 ppm uranium sample solution was deposited onto the ground steel sample plate and allowed to dry. Likewise, a 2µL aliquote of 100 µL of 10,000 ppm ICPMS carbon standard (TA) in 2% nitric acid and 100 uL of the 20 ppm UO_2 solution was deposited on the MALDI sample plate and allowed to air dry. Each sample spot contained 20 ng (84 pmol) of uranium.

The sample plates were inserted into the instrument and automatically pumped down and positioned at the laser focal point. The instrument parameters available for optimization were laser power (arbitrary units of 0% to 100% between an actual power of 30% and 60%), matrix ion suppression on/off, and delayed extraction (0-90 ns). Delayed extraction controls the time between the actual laser pulse hitting the sample and the time when the high potential extraction pulse is applied to send the ions through the ToF MS for mass separation. Different delay times can improve ion signals for different ion types and different matrices. Ion suppression uses a high potential pulse orthogonal to the ion path and timed to “push away” the burst of low mass ions preceding the ions of interest. Sometimes this can improve the quality of the response of the ions of interest.

The optimized instrument parameters in most cases were brushed plates, 40% laser power, delayed extraction of 0 seconds (no delay), ion suppression on, and 10,000 laser shots (pulses) per acquisition. A MALDI ToF spectrum of a U030-A solution dried on the C-60 matrix is shown in Figure 1.4. The spectrum shows that there is enough energy in the ionization process to break uranium-oxygen bonds. The ratio of the intensities of U^+, UO^+, and UO_2^+ varied with substrate and matrix.

One of the limitations with this instrument is that the analog-to-digital converter on the detector has only 8 bits of resolution, which means it has a dynamic range per elapsed time bin of only 256. With this dynamic range, if the intensity (in arbitrary units) of a particular ion approaches approximately 200×10^6 then the detector is saturating for that signal and it will be under-represented in the observed intensity. Using this value in the denominator will bias the ratio high. When the conditions are adjusted to keep the ion intensities below this value, the RSDs for the three different ions range from 2% to 5%. Similar precisions were noted in other reports (Guerrero et al. 2001).

Although *in vacuo* ultraviolet MALDI ToF has been shown capable of making reasonable uranium isotope ratio measurements, it has the disadvantage of having to transfer the samples in to the instrument vacuum. Because atmospheric pressure (AP) MALDI has been demonstrated for biomolecules (Jones et al. 2014), AP-MALDI should definitely be explored. This technique is available on the recently acquired small, portable quadrupole ion trap MS (the MTE-50) for testing as a potential MS for in-field safeguards applications.

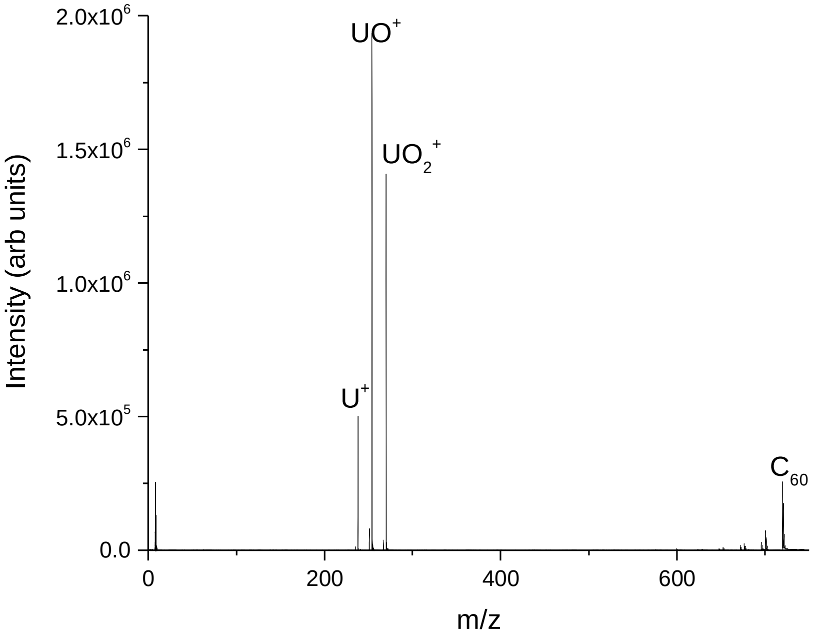

Figure 1.4. MALDI-ToF Mass Spectrum Resulting from 10,000 Laser Shots of U030 Deposited on a C60 Substrate at 40% Laser Power. The peaks above 600 m/z are due to matrix ions.

1.3 Task 1c: AP-LAI

As mentioned above, it is known that ions are produced in the laser ablation/desorption plume above the target surface. At low pressure, atomic, small polyatomic, and large biomolecular ions, including uranium, have been detected, albeit at low efficiencies. At higher pressures, including atmospheric, atomic, and small metal polyatomic ions have not been reported, but the possibility of detecting these ions suggested this approach. It would be ideal in that little to no sample preparation of a solid sample would be required (no dissolution, no matrix, etc.) and ions would be created directly.

A quadrupole ICPMS (X-Series, Thermo Scientific) was modified to operate at ambient atmosphere temperature and pressure as opposed to the more than 6000 K temperature of the typical ICP. The modification was achieved by replacing the standard sample cone (1 mm aperture) with a 0.5 mm custom-made cone or a 1 mm inner diameter stainless steel capillary similar to the one described above on the Exactive MS. High-temperature argon is more viscous than room temperature air, thus by using a smaller aperture the same flow rate of gas could be achieved in order to keep the MS operating within its design vacuum limits. The various ICP components were moved away from the sample inlet area to allow the installation of the laser optical path. An optical path was set up to focus a 1064-nm beam from a Nd:YAG laser

(Minilite, Continuum) onto a surface placed right in front of the sample cone or capillary (Figure 1.5). A sample of uranium-containing glass was positioned at this focal point and was ablated several times. No ions were detected. In fact, no ions from the LS-APGD (Section 1.1) were detected either. Since no ions were detected from an ion source known to create ions at atmospheric pressure, it could well have been that this interface did not transmit ions into the MS in this configuration.

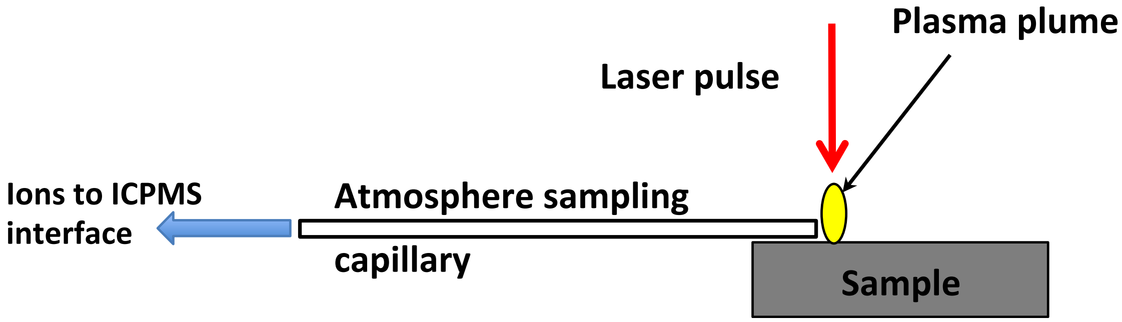

Figure 1.5. Schematic of the Atmospheric Pressure, Laser Ablation Ionization Source

1.4 Results of Performance Tests in Task 1

On further examination of the literature and discussions with others active in the laser ablation and MALDI areas, it was determined that 1) atomic ions are likely being quenched in the laser plume evolution process and 2) that atomic ions would be more likely at the higher energies of ultraviolet photons. Given these issues and the success of the MALDI and LS-APGD approaches, the LAI approach was deselected. These results only indicate that the investigators did not detect ions with this particular set-up. These results do not necessarily mean that other investigators or use of a different approach would not detect ions.

Table 1.2 summarizes the results of evaluating the ionization techniques. Clearly, within the scope of this work, AP-LAI is not currently a viable ionization technique for potential in-field MS applications; therefore it was removed from continued testing and consideration.

The LS-APGD-MS and AP-MALDI-MS both show promise as ion sources for in-field mass spectrometer applications. They should both be moved forward for testing with the candidate in-field MS and with the adsorbed UF_6 sample types.

Table 1.2. Ion Source Down-select Evaluation Criteria

Ion Source	Sensitivity [Uranium]	U isotope ratio precision RSD (%)	Advantages	Disadvantages	Potential
LS-APGD	> 500 ppb	< 1	1. Good IR precision 2. Good potential for adsorbed UF_6	1. Requires sample to be in acidic solution 2. Requires several mL of solution to obtain multiple determinations 3. Significant carryover or memory, must be cleaned between samples 4. Must monitor electrode condition 5. Must not let electrodes overheat	Atmospheric pressure desorption ionization of adsorbed UF_6
MALDI-ToF	picograms	2-5	1. Reasonable IR precision 2. Good potential for adsorbed UF_6	1. Requires sample in vacuum 2. Requires liquid samples to mix with matrices	Atmospheric pressure MALDI of adsorbed UF_6
AP-LAI	None detected	-	Least sample prep	No ions detected	May be made to work in the future with more research

AP-LAI = atmospheric pressure-laser ablation ionization
IR = Isotope Ratio
LS-APGD = liquid sampling, atmospheric pressure glow discharge
MALDI-ToF = matrix assisted laser desorption ionization - time of flight

2.0 Task 2: MS Field Instrument Evaluation

The purpose of this task was to survey and evaluate available, small MS instruments that might have the potential for in-field use for safeguards applications. The application of most interest to the IAEA is the determination of uranium isotope ratios of UF_6 at enrichment facilities and, to a lesser extent, detection of other elemental and isotopic indicators of fuel reprocessing or other nuclear activities. A similar, extensive survey of mass spectrometers was completed a few years ago by the National Nuclear Security Administration Office of Nonproliferation and Arms Control (NPAC) Mass Spectrometry Working Group (MSWG) for both elemental/isotopic and molecular (organic) analysis (Sexton and Ticknor 2013b). The conclusion of that report indicated that the commercial-off-the-shelf (COTS) MS instruments available at that time, that were relatively small (<400 lb, 180 kg) and capable of atomic ion generation and detection and of isotope ratio analysis, were essentially limited to bench-top ICPMS. Although capable instruments, ICPMS require considerable power and consumables (argon gas), sample preparation with hazardous liquids, and considerable instrumental operation training and skill. The safeguards community expressed desires to have an instrument with much lower requirements in these areas yet retaining current central laboratory-based performance capability.

The truly small instruments were all designed for electron or chemical ionization of gas-phase organic compounds, i.e., incapable of elemental analysis. One or more of them might have been capable of analyzing UF_6 as a gas, albeit the materials of construction would likely not withstand the corrosive gas. At that time, an experimental (non-COTS) quadrupole ion trap instrument that had been applied to UF_6 was identified (Whitten et al. 2004). Those investigators have since been included in the MSWG and development of a similar instrument has been restarted.

In addition, the MSWG also produced a concept of operations document (Sexton and Ticknor 2013a), envisioning how the safeguards community might use such capability, and a gap analysis document (Yoshida et al. 2013) discussing the gaps existing between current COTS instrumentation and the desired capability and the areas of research recommended to close these gaps. One of the significant gaps is a technique combining sample preparation and sample ionization that would be compatible with one of the smaller instruments.

Although some advancements have occurred in the small (luggable, man-portable, and handheld) MS arena, the conclusion is essentially the same as it was in 2013 in the MSWG survey (Sexton and Ticknor 2013b), namely there are no instruments of this type specifically designed for the elemental/isotopic analysis applications. The small MS vendors presented in the survey are still present and since 2013 there is at least one new vendor (908devices 2015) that offers a high-pressure (near atmospheric pressure thus less vacuum pumping required), handheld MS. All of these small instruments are directed toward volatile and semi-volatile organic compounds (drugs, explosives, chemical threats, environment, oil and gas, etc.). Other than UF_6, nearly all other uranium and other actinide compounds are solids and these small instruments all “inhale” neutral gases (atmosphere, gas chromatographic effluent, etc.) and ionization occurs *in vacuo*. The sample preparation and sample ionization process is still a significant gap for the small-size, low-power instruments.

2.1 Task 2a: Initial Specifications and Requirements

Thus, in the evaluation of a potential, fieldable MS for elemental/isotopic applications, the major criterion was that a viable instrument had to have an inlet system that inhaled atmospheric pressure gas in which ions had been generated prior to the MS. The investigators believe that ion formation at atmospheric pressure provides the most amenable approach to minimize and simplify sample processing and ionization. Atmosphere sampling vacuum interfaces are typically found on two types of instruments: ICPMS and ESI MS. In the case of ICPMS, the very high temperature argon plasma at atmospheric pressure atomizes and ionizes the liquid or laser ablated sample particles. The plasma is drawn into the instrument through water-cooled apertures and the ions are mass analyzed. Even though the COTS, benchtop ICPMSs were the only instruments meeting the performance criteria, their high-power requirements, cooling water needs, and argon gas consumption render them less-than-desirable for a fieldable instrument. In the case of ESI, ions are generated and released from a liquid stream at ambient temperature and pressure by a large potential gradient and then inhaled through a stainless steel capillary, ~0.3 mm inner diameter, into the mass analysis section. A similar ion source, atmospheric pressure chemical ionization (APCI), generates ions at ambient conditions by chemical reaction of gas-phase sample ions with reagent ions formed by a corona discharge. Atomic and small polyatomic ions related to elemental solutions generated by a LS-APGD ion source have been detected using this type of capillary interface Havel and Soto-Guerrero 2005; Black et al. 2006; Walton and Mitchell 2013; Nemes and Vertes 2007).

2.2 Task 2b: Small MS – List and Evaluation

The only small, portable instrument with this atmospheric pressure sampling, capillary inlet of which the authors are aware is the MTE-50 from MassTech (Figure 2.1). It is one of the instruments identified in the survey report (Sexton and Ticknor 2013b), however there is no literature indicating that it could analyze atomic ions. However, one of the ion sources that it is designed to accept is an ESI/APCI source from Thermo Scientific that is used on a variety of larger Thermo instruments for biological and pharmaceutical applications. In addition MassTech has a license to use and develop a technique called AP-MALDI that generates ions at atmospheric pressure and that are then drawn into the MS via the capillary inlet (Figure 2.2). Thus, this instrument has an inlet type that has worked with the LS-APGD and the atmospheric pressure version of the MALDI technique that the authors were also evaluating for elemental/isotopic applications.

Because there is only one known COTS version of this type of instrument and it has never been evaluated for elemental and isotopic application, developing a set of performance specifications was moot. Given this situation, it made sense to push the acquisition of this instrument into FY 2015 rather than the original plan of decision and acquisition in FY 2016. With advice and consent of NPAC, the authors re-scoped the FY 2015 work plan and funding and ordered the instrument. It was delivered in early September 2015 and the installation and training occurred the last week of September 2015.

The first experiments using the MTE-50 will include AP-MALDI using the matrices and samples from the earlier vacuum-MALDI work. The authors expect significant difference between AP and vacuum MALDI. After the initial AP-MALDI work is completed, the LS-APGD ion source will be mounted and its performance will be evaluated.

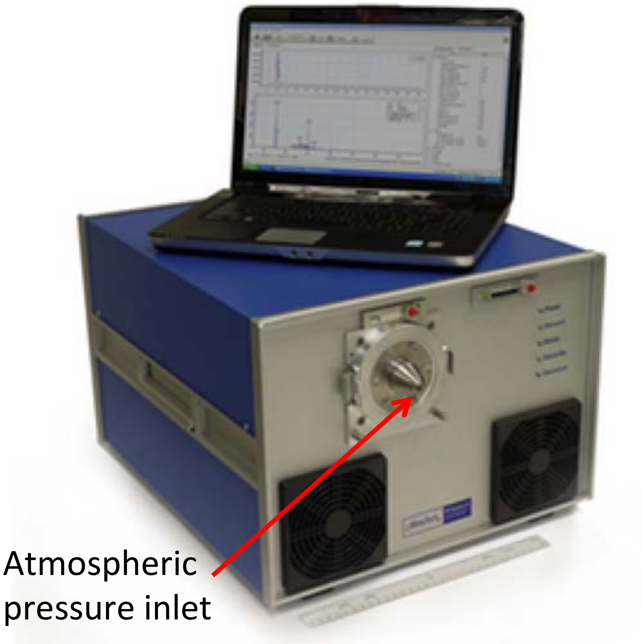

Figure 2.1. The MassTech MTE-50 Atmospheric Pressure Inlet, Quadrupole Ion Trap MS. Note the 12-inch scale for size.

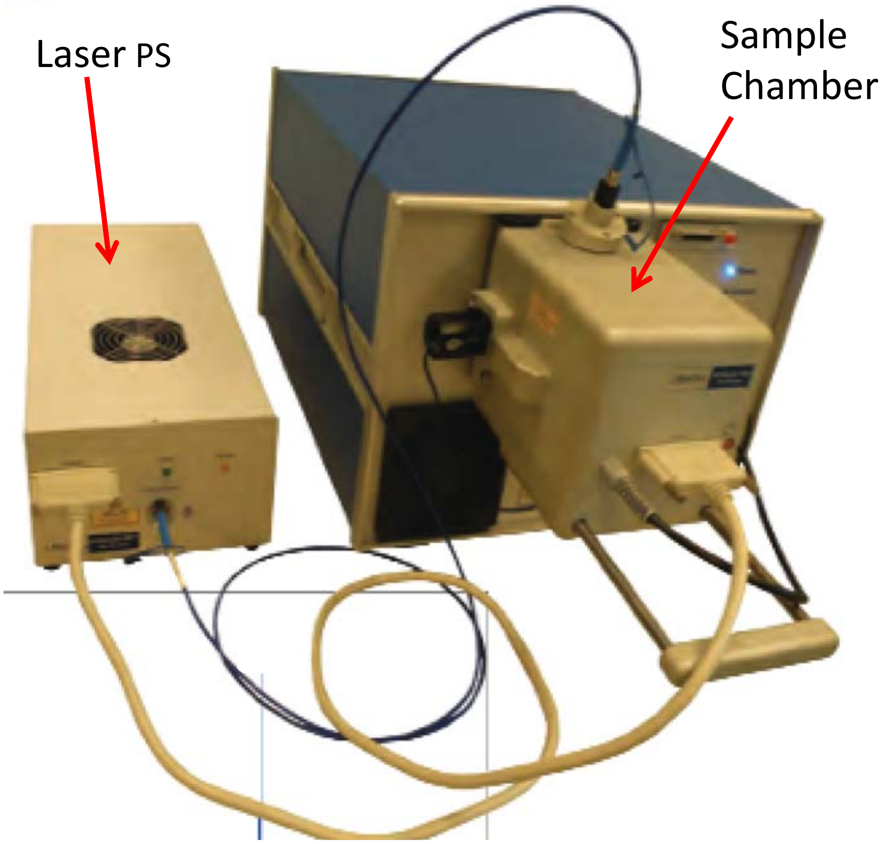

Figure 2.2. MTE-50 with Atmospheric Pressure MALDI Ion Source Composed of the Laser, Laser Optical Fiber, and Sample Chamber

3.0 Task 3: Mass Spectrometry Working Group Technical Exchange

The MSWG was designed to keep the members from Los Alamos, Oak Ridge, Savannah River and Pacific Northwest national laboratories and NPAC current on their various activities and to sponsor a better sense of cross-fertilization and cooperation. The coordination and meeting scheduling for the MSWG (also known as the Portable MSWG [PMSWG]) was originally a PNNL task. NPAC decided to operate it separately and agreed to the funds for this task to be reassigned to acquisition of the small, portable AP-MS in FY 2015.

PNNL MSWG members participated in and presented at the PMSWG meeting in Washington DC (June, 2015). At the invitation of Eleanor Dixon, NPAC, PNNL also presented a briefing on the goals and activities of the MSWG in regard to in-field MS for safeguards applications.

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