

13-039 – Induction Based Fluidics Mass Spectrometry for Characterizing Radioactive Extraction Solvents

Gary Groenewold, Gracy Elias, and Bruce Mincher

Electrospray ionization (ESI) mass spectrometry (MS) is a powerful approach for the analysis of solutions employed in solvent extraction processes used to separate metal cations found in solutions of used nuclear fuel. Accordingly, there is a strong motivation to use ESI-MS to analyze solutions that may have residual radioactivity, however, this is impractical because of inefficient transfer of sample from solution into the mass spectrometer, which results in loose contamination on the exterior surfaces of the ESI instrument. New technology referred to as induction-based fluidics (IBF) was recently shown to be capable of delivering nanoliter-sized droplets onto laser desorption-MS targets that enabled measurement of minute samples without losses. It was hypothesized that an IBF device fitted to an ESI source would be capable of launching nanoliter droplets into the ESI aperture *without* losses, eliminating the problem of loose contamination of ESI-MS instrumentation. This would allow for ESI-MS analysis of a much wider range of sample types, including those that contain radioactive contamination.

The approach used in the project was to procure an IBF device from Nanoliter LLC, which was founded by the inventor of IBF, Dr. Drew Sauter. Collaborative research interfaced an IBF to two different ESI-MS instruments, one a quadrupole ion trap MS, and the other a time-of-flight MS. Demonstration experiments were conducted using both instruments that analyzed solutions containing an organic ligand used in metal solvent extraction processes, an ionic surfactant typical of an ionic liquid, and lanthanide coordination complexes.

Abundant signals were generated from droplets as small as 20 nanoliters (Figure 1), which indicated that the IBF-ESI-MS approach will function well with radioactive solutions, provided an instrument is relocated within a radiological buffer area. Instrument relocation is planned for FY 2014 as part of the scope of the project.

Summary

The IBF source was initially interfaced to a quadrupole ion trap mass spectrometer, which is an MS platform that is small, relatively inexpensive, and easily situated in a radiation buffer or contamination area. Analysis of dilute solutions of organic compounds used in solvent extraction (specifically carbamoylmethyl-phosphine oxide [CMPO] derivatives) showed facile, sensitive measurement of the solutes in droplets having volumes ranging from 20 to 100 nanoliters. CMPO concentrations in these experiments were in the micromolar range, and the droplets were delivered to the mass spectrometer without apparent losses. Subsequent experiments using the ion trap with the IBF source demonstrated detection of ionic surfactants (tetraalkylammonium salts) at very dilute concentrations (1×10^{-9} M), which corresponded to observation of an absolute mass of 35 femtograms (35×10^{-15} g) from a 30 nanoliter droplet. These results strongly suggested that the combination of the IBF source with the ion trap

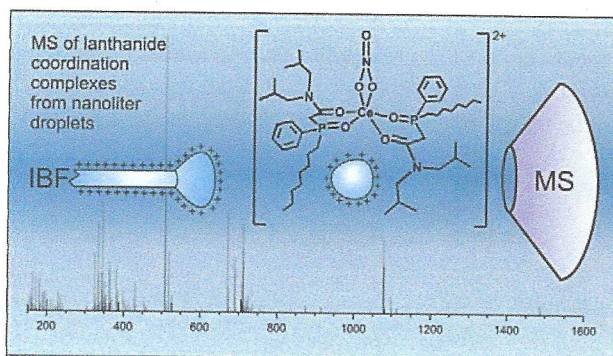


Figure 1. Schematic diagram of the IBF source, launching a nanoliter droplet toward the mass spectrometer aperture. The mass spectrum shows cerium (Ce) coordination complexes with the organic extractant ligand CMPO, for example $[\text{Ce}(\text{NO}_3)(\text{CMPO})_2]^{2+}$ at m/z 508 (shown by the chemical structure).

mass spectrometer is indeed capable of analyzing radioactive samples without seriously contaminating the ESI source.

The ion trap experiments were limited by the need to precisely time the arrival of the solute ions from the nanodroplet with the ion trapping period; the ion trap functions by trapping ions delivered from the ion source for a short period of time and then scanning them out in a fashion that enables measurement of their mass-to-charge ratio. During the course of the initial experiments, reproducible synchronization of the ion arrival from the IBF source and ion trapping was not achieved, which resulted in droplet-to-droplet imprecision that was overcome by signal averaging. The result suggested that if synchronization were improved, even more impressive measurement results would be achieved.

An alternative solution to the synchronization problem is to utilize a mass spectrometer having a faster duty cycle. To accomplish this, the IBF source was interfaced to an ESI mass spectrometer equipped with a time-of-flight analyzer, which was operated at about 10 scans per second. Analysis of 20 nanoliter-sized droplets containing micromolar concentrations of lanthanide metals and CMPO produced highly reproducible spectra with excellent signal-to-noise. The IBF source was also operated at a fast duty cycle, delivering a drop every 0.8 seconds, which indicated that rapid analysis of multiple, nanoliter-sized samples was a viable option.

Benefits to DOE

There is an ongoing need for chemical measurement of vanishingly small sample volumes across three DOE mission areas: nuclear energy, national security, and sustainable energy. The need is especially acute for scenarios in which the sample size is small or poses risks from toxicity or radioactivity. ESI-MS provides an excellent level of information on the solution solutes but is not compatible with radioactive samples because the majority of the sample winds up deposited on the exterior surfaces of the source, where it constitutes loose contamination. The IBF project produced a high performance ESI-MS approach that provides detailed molecular information for organic and organometallic compounds from nanoliter-sized droplets, without contaminating the exterior surfaces of the ESI equipment. This opens the door for analysis of a wide range of radioactive solutions not previously compatible with ESI-MS. When the instrumentation is relocated in a radiological buffer area, it will constitute a capability that is rare in the analytical chemistry and radiochemistry communities and would significantly enhance INL's competitive position in the fuel cycle separations area. In addition, the capability would open new avenues for scientific and technological advancement, particularly in process control, since the proposed technology is capable of solution analysis using exceedingly small volumes.

Publications

Groenewold, G.S., A.D. Sauter, Jr., and A.D. Sauter III, "Rapid Analysis of Single Droplets of Lanthanide-Ligand Solutions by Electrospray Ionization Mass Spectrometry Using an Induction Based Fluidics Source," *Anal. Chem.*, Vol. 85, 6398–6404, July 2, 2013.

13-039—Induction-Based Fluidics Mass Spectrometry for Characterizing Radioactive Extraction Solvents

Gary S. Groenewold, Chris A. Zarzana, and Kristyn Johnson

Over the past several years, electrospray ionization (ESI)-mass spectrometry (MS) has been invaluable for characterizing the effects of radiation on solvent extraction systems used in fuel cycle separations. ESI functions by spraying droplets at a sampling aperture, transferring charged solutes into the gas phase where they can be analyzed by the MS. In conventional ESI-MS, the majority of the sample solution is deposited on the outside of the aperture. Usually this is inconsequential, but if the sample contains significant levels of radioactive contamination, radiological control requirements preclude the use of ESI-MS. The research objectives of this project are to minimize the volume of sample used and to improve the transfer efficiency into the mass spectrometer, thus achieving compatibility with radiological control requirements without compromising analytical quality.

Summary

Instrument development focused on interfacing a non-conductive nanoliter capillary with an ESI-MS. New technology referred to as induction-based fluidics was used to launch nanoliter-sized droplets directly into the ESI aperture, and experiments demonstrated that this could be accomplished without sample losses on the sides of the sampling aperture cone (Figure 1).

Experiments generated mass spectra of N,N-(diisobutylcarbamoyl)methyl,octyl,phenyl phosphine oxide (CMPO) derivatives (used in nuclear fuel cycle separations, Figure 2) and associated lanthanide coordination complexes. Sample volumes as small as 20 nL produced high-quality mass spectra, and not only that, the experiments could be pulsed at a rapid repetition rate, enabling very fast analyses if required to reduce dose. Experiments were then conducted that evaluated the efficacy of very low flow electrospray ionization, and similar high-quality data were generated by operating the flow as low as 4 μL per hour. Sample solutions having concentrations of 100 $\mu\text{mol/L}$ produced excellent mass spectra at this flow rate, in 30 seconds or less; this corresponds to an absolute quantity of 0.3 pmol, a significant improvement over the single droplet approach. The remarkable sensitivity achieved indicated that the nanoliter-flow ESI-MS could very likely function within radiological control requirements at the INL's Central Facilities Area, so subsequent research focused on modifying an instrument for a radiological environment.



Figure 1. Close-up view of the capillary used to generate charged droplets, aligned with the sampling aperture cone of an ESI-MS instrument.

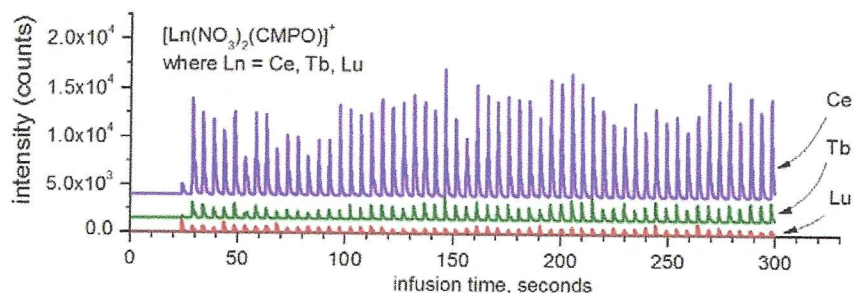


Figure 2. Temporal ion profiles generated from 50-nL droplets of a solution containing cerium, terbium, and lutetium with the nuclear fuel cycle extractant CMPO. Each peak represents a single nanodroplet, containing about 100 pmol of the metals.

Another objective is to replicate the chromatographic separation using a low-sample-volume, low-flow approach. Liquid chromatograph operations would be complicated in a radiological environment, so an electrospray capillary needle packed with a chromatographic stationary phase was developed to minimize volume and provide separation without any modification to the ESI experiment. A combined capillary column-ESI needle was specified and procured for separations experiments. Injection of 39×10^{-12} g (39 pg) of CMPO showed a defined chromatographic peak (Figure 3) sufficient for simple separations.

A benchtop mass spectrometer was prepared for operation within radiological buffer areas at INL; the instrument was subjected to extensive maintenance and thoroughly benchmarked using nonradioactive samples.

A laboratory instruction covering ESI-MS work control was written, reviewed, and approved, which enabled the instrument to be relocated to the Central Facilities Area, Building 625, Laboratory 240, within the radiological buffer area at that facility and proximate to a hood that is controlled as a radioactive contamination area.

Benefits to DOE

There is an ongoing need for the capability to chemically measure vanishingly small sample volumes of radioactive solutions in research conducted in each of the three INL mission areas: nuclear energy, national security, and sustainable energy. ESI-MS provides excellent information on the solution solutes but has not historically been compatible with radioactive samples, because the majority of the sample is deposited on the ESI source, where radioactive solutions constitute loose contamination. The induction-based fluidics project produced an ESI-MS instrument that will provide detailed molecular information for fuel-cycle separations without contaminating the exterior surfaces. The instrumentation will constitute a capability that is rare in the analytical-chemistry and radiochemistry communities and will significantly enhance INL's competitive position in the fuel cycle separations area and in process control, because the proposed technology is capable of solution analysis using exceedingly small volumes.

Publications

Groenewold, G., A. Sauter, Jr., and A. Sauter III, "Rapid Analysis of Single Droplets of Lanthanide-Ligand Solutions by Electrospray Ionization Mass Spectrometry Using an Induction Based Fluidics Source," *Analytical Chemistry*, Vol. 85, pp. 6398–6404, 2013.

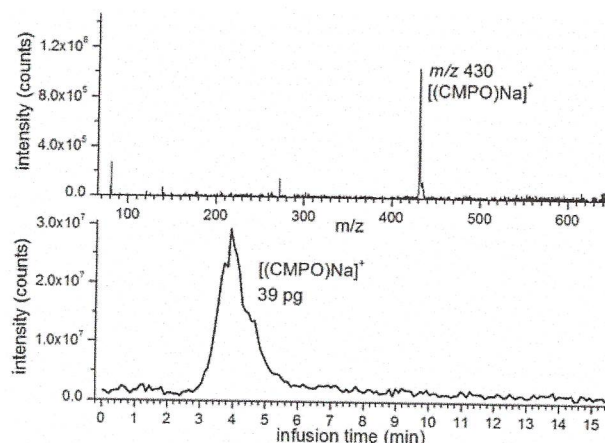


Figure 3. Top, mass spectrum, 39 pg of CMPO. Bottom, temporal ion profile of m/z 430.

13-060—Metal Fluoride Preparation for AMS Analysis

James E. Delmore, Gary S. Groenewold, and Chris A. Zarzana

INL researchers are developing new chemical approaches that will support measurements of isotope ratios that are used by U.S. and international organizations to ensure that nuclear energy facilities are operating in compliance with nonproliferation treaty commitments. The project's objective is to develop new means for converting elemental isotopes in environmental samples into negatively charged, fluorine-containing molecules called "fluoroanions" that are compatible with existing and emerging isotope ratio mass spectrometry instrumentation. If successful, the project will provide the scientific chemical basis for improved ultratrace isotope ratio measurement having better accuracy, lower detection limits, and reduced costs.

Summary

Experimental results from this research have demonstrated that unique fluoroanions of uranium, zirconium, iron, and silicon can be produced in high abundance with very low chemical background. These fluoroanions were produced by reacting oxides and salts of the metals with an ionic liquid, 1-ethyl-3-methylimidazolium fluorohydrogenate (EMF). After dilution with acetonitrile to make fluoroanion solutions, these compounds were analyzed using either electrospray ionization mass spectrometry or desorption chemical ionization mass spectrometry. The EMF sample was provided by INL collaboration with Tetsuya Tsuda (Osaka University) and Rika Hagiwara (Kyoto University).

Fluoroanions of both zirconium and iron were produced by mixing salts with the EMF ionic liquid and then diluting the resulting solution for electrospray ionization mass spectrometry analyses. The zirconyl cation ZrO^{2+} reacted to form ZrF_5^- in an efficient manner, indicating that the fluorohydrogenate anion would attack strongly bound metal-oxo species that will complicate isotope ratio measurements of actinides. Both Fe^{3+} and Fe^{2+} salts resulted in production of FeF_4^- , indicating that Fe(II) is oxidized. This theme was also observed when UO_2 and U_3O_8 were dissolved in EMF; in both instances, the resulting solution generated an exceptionally clean mass spectrum consisting principally of UF_6^- at m/z 352, which indicated oxidation of uranium from the +4 to the +5 state. The very low background seen in the mass spectra indicated sufficient dynamic range to enable measurement of the low abundance uranium isotopes.

More recent studies addressed the ability of the EMF ionic liquid to dissolve mineral particulates that are likely to be representative sample types. Treatment of a mineral glass particle resulted in dissolution, producing principally SiF_5^- , with a lower intensity AlF_4^- and much less abundant fluoroanions of iron and calcium. The results showed that the ionic liquid was highly compatible with mineral dissolution, and that it could be performed using microliter volumes on particulate samples.

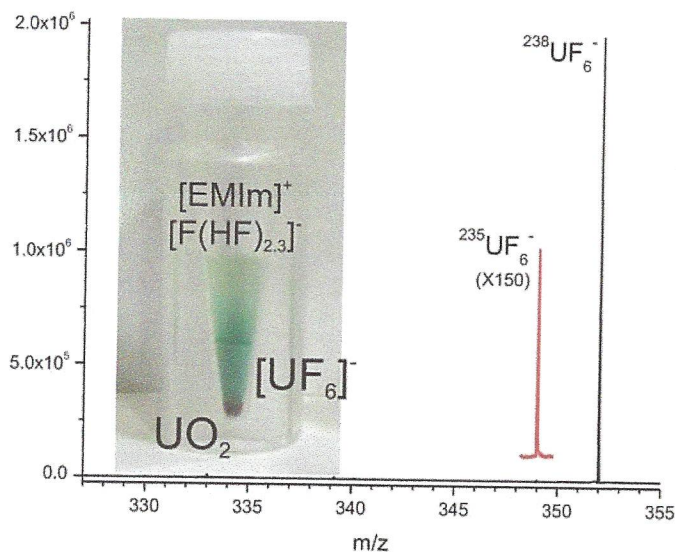


Figure 1. Photograph of an EMF- UO_2 solution; the green color indicates U(V) . The mass spectrum of the solution shows the intense $^{238}\text{UF}_6^-$ and a much lower U-235 isotopic ion (left).

Benefits to DOE

The project developed a new approach for generating metal fluoroanions that may be highly compatible with making ultratrace isotope ratio measurements. Transitioning the fluoroanion formation chemistry into an accurate analytical isotope-ratio measurement method will enable the United States to make more informed nonproliferation policy decisions regarding the nonproliferation status of international nuclear energy programs at a substantially reduced cost compared with current methods. Improved measurement of isotope ratios at the ultratrace level will advance the DOE nonproliferation mission and elevate the global recognition of DOE's leadership position in nuclear and radiological science and measurement technologies.

Publications

- Groenewold, Gary S., James E. Delmore, Michael T. Benson, Tetsuya Tsuda, and Rika Hagiwara, "Fluorohydrogenate Cluster Ions in the Gas Phase: Electrospray Ionization Mass Spectrometry of the [1-ethyl-3-methylimidazolium⁺][F(HF)_{2,3}]⁻ Ionic Liquid," *Journal of Physical Chemistry A*, Vol. 117, pp. 14191-14199, 2013.
- Groenewold, Gary S., James E. Delmore, Michael T. Benson, Tetsuya Tsuda, and Rika Hagiwara, "Generation of gas phase zirconium fluoroanions by electrospray of an ionic liquid," *Rapid Communications in Mass Spectrometry*, Vol. 26, pp. 1233-1242, 2014.
- Zarzana, Chris A., Gary S. Groenewold, Michael T. Benson, James Delmore, Tetsuya Tsuda, and Rika Hagiwara, "Iron Fluoroanions and Their Clusters by Electrospray Ionization of a Fluorinating Ionic Liquid," *Journal of the American Society for Mass Spectrometry*, Vol. 26, pp. 1559-1569, 2015.

14-095—In Situ Measurement of Electrolyte Chemistry in Battery Cells during Operation

Gary S. Groenewold, David Jamison, Cathy Rae, Kristyn Johnson, Chris A. Zarzana, and Kevin Gering

Lithium-ion batteries are remarkable power storage devices capable of delivering power over repeated discharge/recharge cycles and a range of environmental conditions. Nevertheless, lithium-ion battery performance is eventually degraded as a result of chemical and physical changes within the cells. If time- and use-dependent behavior were known, it is likely that informed approaches to mitigate deterioration and improve performance would emerge. Unfortunately, battery cells are sealed to prevent reaction with the ambient atmosphere, so it is difficult to measure quantitative chemical changes occurring within the cell. The objective of this research is to develop lithium-ion battery cells that will enable chemical interrogation in the form of sub-microliter sampling and analysis, and in situ vibrational spectroscopy, without compromising the integrity or function of the cell as it undergoes discharge/recharge cycling. It is hypothesized that diagnostic changes in the chemical composition of the electrolyte mixtures can be measured as the battery ages and progresses toward eventual failure.

Achieving this objective is challenging because the total quantity of electrolyte present in a typical cell is small. However, the project leverages the recent development of mass spectrometry analysis strategies that require only a small fraction of a microliter, so a salient challenge is to manufacture a cell with ports that support periodic sample collection.

Summary

The approach adopted for cell fabrication has been to design pouch cells for use in a chemical-characterization test bed. In fact, coin cells were originally considered based on their widespread application. However, coin cells have exceedingly small volumes and steel walls that cannot be easily penetrated. The pouch-cell design that was adopted at the end of FY 2014 circumvents these impediments and contains identical chemistry. The pouch cells employ an aluminized polymer housing that can be easily fitted with a sampling port (Figure 1) or with a port that holds a miniature infrared probe used for making vibrational spectroscopy. The initial prototypes displayed reproducible discharge/recharge cycling from $V_{\max} = 4.7$ to $V_{\min} = 2.7$, so a production run was initiated to manufacture 15 cells for an experimental campaign that would evaluate cell performance (a) with and without the sampling valves, (b) operated at 30 and 50°C, and (c) operated with and without a fire-retardant compound added to reduce flammability and improve cycling reproducibility.

The initial production run was slowed by premature cell failures, which were initially caused by leaking seals in the pouch polymer and cathode delamination. Modification of the thermal sealing procedure and cathode adhesive solved these problems. Later cell failures were attributed to voltage cycling too close to the V_{\max} and V_{\min} levels, which has led to a change in the test plan. As of September 2015, a total of eight cells were being cycled in temperature-controlled chambers made from gas-chromatograph ovens.

A gas-chromatography/mass-spectrometry approach was adopted for measuring the relative concentrations of the electrolyte components. Dilution of a sub-microliter sample by >5 orders of magnitude resulted in analytical signals that were at the upper end of the instrumental linearity response. Analysis of head space was also demonstrated, and this is likely to be the best path forward: exposure of a solid-phase microextraction tip to the

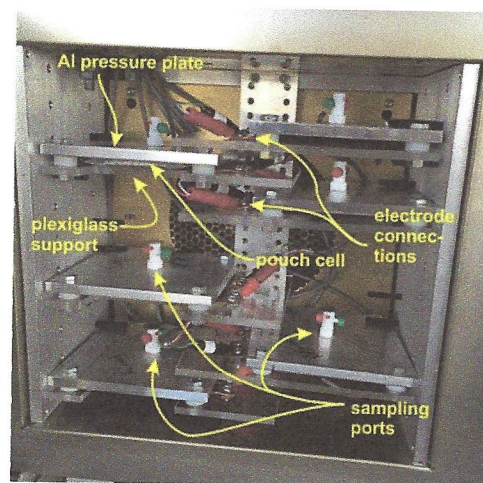


Figure 1. Six pouch cells (fitted with sampling ports) situated in a test oven.

residual vapor in the microsampling valve also produced abundant signal. In addition to detecting the carbonate electrolytes, degradation impurities were also seen; this was significant because it showed that indicators of solvent breakdown could be detected and suggested mechanistic pathways, specifically ester hydrolysis. Surprisingly, electrospray ionization mass spectrometry did not work well for the carbonate analysis, but the technique was excellent for analysis of the fire-retardant additives. These phosphazene ring compounds have anywhere from one to four trifluoromethyl groups, all of which were readily measured using a submicroliter sample. The measurements also revealed the affinity of the additives for lithium ions, which is a key feature of their function and has only been theoretically calculated so far.

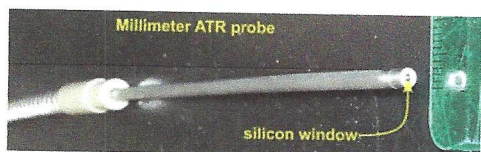


Figure 2. Photograph of the miniature attenuated total reflectance infrared probe.

Attenuated total reflectance infrared spectroscopy provides molecular structure information for the carbonates, and an exceptionally small attenuated total reflectance probe was fabricated in 2015. The diameter of the probe is 3 mm (Figure 2), and an interfacing flange for the pouch cells has been developed. The probe is capped with a silicon window that protects an AgCl-AgBr fiber, which has high transmission over the salient range of infrared frequencies characteristic of the carbonates. Initial measurement tests were under way in September 2015.

Benefits to DOE

This project holds excellent potential for providing a much improved understanding of electrolyte chemistry that impacts battery performance and ultimate lifetime. The range of DOE and government functions that would benefit from improved battery performance would be vast and would include applications in national security, energy storage, and environmental remediation. Consequent improvements in battery technology would have wide-reaching effects benefitting virtually all government agencies.