

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

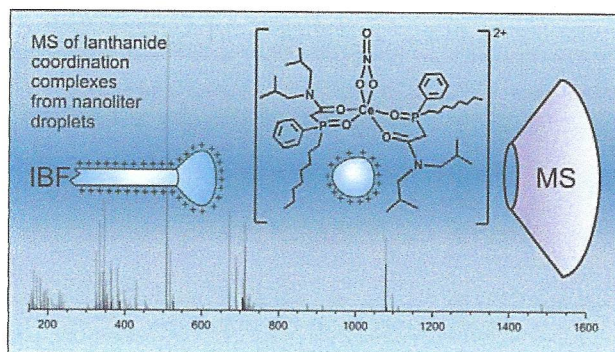


Figure 1. Schematic diagram of the IBF source, launching a nanoliter droplet toward the mass spectrometer aperture. The mass spectrum shows cerium (Ce) coordination complexes with the organic extractant ligand CMPO, for example $[Ce(NO_3)(CMPO)_2]^{2+}$ at m/z 508 (shown by the chemical structure).

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.