Improved Sensitivity in LA-ICP-MS Applications through the use of Mixed Gas Plasmas and Collisional Focusing

Julian D. Wills, Christoph Wehe and Shona McSheehy Ducos
Thermo Fisher Scientific, Bremen, Germany

Key Words
Laser Ablation, ICP-MS, iCAP Q, Collision Cell technology

Goal
To demonstrate the sensitivity improvement possible in LA-ICP-Q-MS through the use of mixed plasma gases and advanced collision cell techniques.

Introduction
Laser ablation (LA) sampling has continually taken advantage of instrument based advancements in inductively coupled plasma mass spectrometry (ICP-MS) to improve analytical performance. For example:
1. Collision and reaction cells for the reduction of spectral interferences.
2. High mass resolution (ICP-SF-MS) for the ultimate in performance.
3. Improved interface designs leading to increased robustness and reduced contamination in dry plasma applications.

For many LA-ICP-MS applications however, it’s the pursuit of higher instrumental sensitivity that’s the most interesting. When performing discrete LA-ICP-MS analyses improved instrumental sensitivity enables the use of increasingly smaller laser spots. Smaller spots are advantageous in many applications, for example in detrital zircon studies in order to maximize the number of analyzable zircons in provenance studies or to improve spatial resolution in elemental mapping analyses in both geological and biomedical studies. This paper demonstrates the sensitivity improvement possible in LA-ICP-Q-MS through the use of mixed plasma gases and advanced collision cell techniques.

The Thermo Scientific™ iCAP Q ICP-MS system was used to perform laser ablation ICP-MS (LA-ICP-MS) analyses using the standard Ar/He plasma, a N₂ doped Ar/He plasma and a N₂ doped Ar/He plasma in combination with the collision cell pressurized with He.
Results
In order to compare instrumental sensitivities in each of the three analysis modes, five replicate analyses of NIST 610 were performed using the laser parameters shown in Figure 2.

An automated tuning procedure (using NIST 610) was performed in each mode in order to maximize sensitivity while minimizing oxide formation (ThO/Th). Figures 3-5 show the gas blank subtracted intensities for NIST 610 LA-ICP-MS analyses in each of the three analysis modes tested.

Figure 3 presents the data for an Ar plasma with He from the laser cell. With a standard analysis mode that combines the particle containing He stream from the laser cell with Ar make-up gas from the iCAP Q ICP-MS, sensitivities of > 1 Mcps are achieved for elements in NIST 610 (~450 µg·g⁻¹) at a spot size of 40 µm and a fluence of 3.2 J·cm⁻².

Figure 4 presents the data for an Ar plasma with He from the laser cell and an additional flow of N₂ at 3 mL·min⁻¹ to the Ar/He stream. By adding a small flow of nitrogen to the Ar/He mixture, sensitivities across the entire mass range are improved by approximately 30%, with the largest gains made for the lighter masses.

Figure 5 presents the data for an Ar plasma with He from the laser cell, the additional flow of N₂ to the Ar/He stream and the use of collisional focusing in the iCAP Q ICP-MS collision/reaction cell (QCell). With a low He flow at 4 mL·min⁻¹ added to the iCAP Q ICP-MS QCell, sensitivities for the LA-ICP-MS analysis of NIST 610 are further improved with > 3 Mcps recorded for a spot size of 40 µm at a fluence of 3.2 J·cm⁻².

Collisional Focusing
Collisional focusing is theoretically possible with any collision cell, but works very effectively with the iCAP Q ICP-MS QCell due to the inner dimensions and volume of the cell. With collisional focusing any ions that would otherwise be lost by beam expansion in an empty (no gas) collision cell are better focused / transmitted in a (He) pressurized cell, resulting in higher instrumental sensitivities.

The sensitivity improvement possible with collisional focusing is mass dependent. Heavier masses, due to their increased numbers of collisions with He, have a lower energy in a pressurized cell. This prolongs their residence time in the cell allowing them to be better focused leading to improved transmission.
The sensitivity changes for N$_2$ doped Ar/He and N$_2$ doped Ar/He with He collisional focusing relative to a standard Ar/He plasma are shown in Figure 6.

Through a combination of mixed gas plasma and QCell flatapole collision cell technology, 3 fold sensitivity improvements can be achieved with the Thermo Scientific iCAP Q ICP-MS system.

Driven by Qtegra ISDS Software
Qtegra ISDS Software provides plug-in based support of all major laser ablation systems from ESI, TELEDYNE CETAC, and TELEDYNE PHOTON MACHINES. A dedicated data evaluation for laser ablation analyses (trQuant) with a range of integration and quantification features comes as standard in Qtegra ISDS software. Additionally, multiple export formats, including a format for export into the Iolite program are a standard part of any iCAP Q ICP-MS system running on Qtegra ISDS software.

Conclusion
Through the use of N$_2$ mixed gas plasma and He collisional focusing, sensitivity improvements of over a factor of three are possible using the Thermo Scientific iCAP Q ICP-MS system. With such a significant sensitivity improvement, smaller laser spot sizes can be routinely used opening up new LA-ICP-MS applications in geological and biomedical studies.

References