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Advancing Ca and Fe isotopic analysis across biological systems using MC-MICAP-MS with nitrogen plasma

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Geological, chemical, and biological processes produce significant Ca and Fe isotope fractionation, which is increasingly exploited to trace biogeochemical cycling, biomineralization, metal metabolism and homeostasis across environmental and biological systems. Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is an established technique for high-precision Ca and Fe isotope analysis, however, Ar-related spectral interferences generated by the Ar plasma limit analytical performance.

This study presents the integration of a microwave inductively coupled atmospheric-pressure plasma (MICAP) ion source sustaining an N_2 plasma with a multi-collector mass spectrometer, forming the novel MC-MICAP-MS platform for high-precision metal isotopic analysis. Replacing the conventional Ar plasma with an N_2 plasma effectively eliminates Ar-based spectral interferences.[1]

The absence of Ar-based species enables direct measurement of Ca and Fe isotopes in low mass resolution mode. Initial characterization demonstrates analytical performance comparable to conventional MC-ICP-MS. For example, $\delta^{44}Ca/^{40}Ca$ and $\delta^{56}Fe/^{54}Fe$ values show intermediate precision (external repeatability) of 0.10 ‰ and 0.07 ‰, respectively, matching the performance of Ar plasma ion source. Instrumental isotopic fractionation behavior is similar to that observed for conventional MC-ICP-MS and can be accurately corrected using established approaches. Furthermore, oxide and doubly charged ion formation are low under the tested dry plasma conditions. For example, MgO^+ and Sr^{++} interferences have negligible effects on Ca isotopic analysis when $Mg/Ca \leq 0.05$ and $Sr/Ca \leq 0.003$, respectively. The N_2 plasma also exhibits high tolerance to matrix effects. For example, Na and Mg show negligible influence on Fe isotope ratios up to a 1:1 matrix-to-Fe ratio. These features simplify sample preparation and enhance analytical robustness for complex biological matrices.[2]

Measurements of Ca and Fe isotopic compositions in biological reference materials agree with values obtained using established techniques, confirming the accuracy and reliability of the MC-MICAP-MS platform.

Overall, MICAP represents a viable alternative ion source for multi-collector mass spectrometry, maintaining high precision while removing key spectral limitations imposed by Ar plasma and advancing Ca and Fe isotope applications across environmental, biological, and health-related studies.

[1] A. Retzmann, A. Menon, M.E. Wieser (2025), *Journal of Analytical Atomic Spectrometry* 40, 2803–2815.

[2] A. Retzmann, M.E. Wieser (2026), *Analytica Chimica Acta* 1383, 344865.