

TANDEM ICP – MASS SPECTROMETRY WITH CHEMICAL RESOLUTION: AN IDEAL TOOL FOR THE DETERMINATION OF ULTRA-TRACE CONCENTRATIONS OF METALS AND METALLOIDS IN ENVIRONMENTAL SAMPLES

Eduardo Bolea-Fernandez,¹ L. Balcaen,¹ M. Resano² and F. Vanhaecke¹

¹*Ghent University, Department of Analytical Chemistry, Ghent, Belgium*

²*University of Zaragoza, Department of Analytical Chemistry, Zaragoza, Spain*

Eduardo.BoleaFernandez@UGent.be

Keywords: ICP-MS/MS; Chemical resolution; Methyl fluoride; Arsenic; Selenium

Introduction

Nowadays, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is widely used for the quantitative determination of trace elements in a large variety of sample types, including environmental samples. However, with conventional ICP-MS systems, the determination of ultra-trace concentrations of many elements may be seriously hampered by the occurrence of spectral overlap, i.e. overlap of the signals of the target analyte ions with those of interfering ions with the same nominal mass-to-charge (m/z) ratio.

Over the years, different approaches have been developed to cope with the problem of spectral interferences (e.g., high resolution sector field ICP-MS (HR-SF-ICP-MS) and quadrupole based ICP-MS equipped with collision-reaction cell systems (Q-ICP-CRC-MS)). While HR-SF-ICP-MS comes at a much higher cost than Q-ICP-MS systems, and an increase of the mass resolution is accompanied with a significant drop in sensitivity, the use of Q-ICP-CRC-MS is often limited by the lack of control over the cell chemistry.

Recently, the introduction of a novel Q-based ICP-MS technique, tandem ICP – mass spectrometry (ICP-MS/MS), has brought the concept of chemical resolution in CRC systems to a higher level, and the application range of ICP-MS/MS for the determination of ultra-trace amounts of highly interfered elements is growing fast (Balcaen et al., 2015).

The aim of this work is to demonstrate the capabilities of ICP-MS/MS with chemical resolution from a general point of view, but also in the context of the determination of ultra-trace concentrations of As and Se in various samples of environmental relevance (Bolea-Fernandez et al., 2015).

Methods

An ICP-MS/MS system consists of a quadrupole based ICP-MS instrument, equipped with an octopole collision/reaction cell (CRC) and an additional quadrupole in front of the CRC. By using the first quadrupole as a mass filter, only those ions with the m/z ratio of interest reach the CRC (MS/MS mode). This allows for an enhanced control over the reactions taking place in the reaction cell, thus improving the possibilities of the use of chemical resolution to avoid spectral overlap by means of conventional, but also highly reactive gases (e.g., NH_3 (Balcaen et al., 2014) and CH_3F (Bolea-Fernandez et al., 2014)).

The possibility of using highly reactive gases improves both the efficiency of the reactions taking place in the CRC and the selectivity of such reactions. The use of mass-shift approaches i.e., the reaction gas reacts

with the analyte ions and converts them into reaction product ions that can be measured under interference-free conditions, is often an elegant and very efficient approach to overcome spectral overlap.

For the application described in this work, the performance of the reaction gas mixture CH₃F/He (1:9) was evaluated for an accurate and precise determination of As and Se in a variety of sample types.

Results

The quantification of Arsenic and Selenium is hindered by spectral overlap with Ar-based polyatomic interferences (⁴⁰Ar³⁵Cl⁺ for ⁷⁵As⁺ and ⁴⁰Ar³⁷Cl⁺ and ^{76,78,80}Ar₂⁺ for Se⁺).

Via product ion scanning, i.e. a scan over the entire mass spectrum with the second quadrupole (Q2) with the first quadrupole (Q1) is fixed at the m/z ratio of interest, while the CRC is pressurized with the reaction gas mixture, the most suited reaction product ions were found to be AsCH₂⁺ and SeCH₂⁺. Table 1 shows the instrumental LODs and LOQs obtained for As and different isotopes of Se, determined as AsCH₂⁺ and SeCH₂⁺, respectively, using CH₃F/He in MS/MS mode.

Table 1. Instrumental limits of detection (LODs) and of quantification (LOQs) obtained for As and Se using chemical resolution (CH₃F/He gas) in ICP-MS/MS.

Nuclide	CH ₃ F/He flow (mL min ⁻¹)	Q1 (amu)	Q2 (amu)	LOD (µg L ⁻¹)	LOQ (µg L ⁻¹)
⁷⁵ As	0.75	75	89	0.0002	0.0007
⁷⁷ Se		77	91	0.01	0.04
⁷⁸ Se	1.00	78	92	0.007	0.02
⁸⁰ Se		80	94	0.004	0.01

The method developed was applied for the determination of As and Se in environmentally relevant samples with different matrices (and consequently, also in the potential presence of other interfering ions), and covering a wide range of concentrations. For all samples, accurate results were obtained.

Conclusion

The use of tandem ICP - mass spectrometry opens new possibilities to deal with spectral overlap by means of enhanced control over the cell chemistry compared to single quadrupole ICP-CRC-MS systems. This approach enables the use of highly reactive gases (e.g., CH₃F), resulting in an improvement of both the efficiency and selectivity of the reactions, permitting one to overcome strong spectral interferences often encountered with the more traditional ICP-MS systems. This approach can be used for the successful determination of ultra-trace concentrations of environmentally relevant elements like As and Se in the most diverse and complex matrices.

References

- Balcaen, L; Bolea-Fernandez, E; Resano, M; Vanhaecke, F. (2015). Inductively coupled plasma – Tandem mass spectrometry (ICP-MS/MS): A powerful and universal tool for the interference-free determination of (ultra)trace elements – A tutorial review. *Anal Chim Acta.*, 894, 7-19.
- Bolea-Fernandez, E; Balcaen, L; Resano, M; Vanhaecke, F. (2015). Interference-free determination of ultra-trace concentrations of arsenic and selenium using methyl fluoride as a reaction gas in ICP-MS/MS. *Anal Bioanal Chem.*, 407, 919-929.
- Balcaen, L; Bolea-Fernandez, E; Resano, M; Vanhaecke, F. (2014). Accurate determination of ultra-trace levels of Ti in blood serum using ICP-MS/MS. *Anal Chim Acta.*, 809, 1-8.
- Bolea-Fernandez, E; Balcaen, L; Resano, M; Vanhaecke, F. (2014). Potential of methyl fluoride as a universal reaction gas to overcome spectral interferences in the determination of ultra-trace concentrations of metals in biofluids using ICP-MS/MS. *Anal Chem.*, 86, 7969-7977.