



New approach to measure isotopic ratios in species using MC-ICP-MS coupled with chromatography

Vladimir N. Epov (1), Sylvain Beraïl (1), Vincent Perrot (1), Maria Jimenez-Moreno (1,2), Christophe Pecheyran (1), David Amouroux (1), and Olivier F.X. Donard (1)

(1) CNRS UMR 5254, Université de Pau et des Pays de l'Adour, Hélioparc Pau Pyrénées, Laboratoire de Chimie Bio-Inorganique et Environnement, IPREM, Pau, France (vladimir.epov@univ-pau.fr, +33 559 407781), (2) Faculty of Environmental Sciences, University of Castilla-La Mancha, Toledo, Spain

Isotopic composition in different elemental species is relatively new field in analytical chemistry. It can be used for interdisciplinary purposes in geo-sciences, biological sciences, ecology, environmental sciences etc. Recently, several new methods to measure species-specific isotopic ratios in some real-world samples using on-line chromatographic separation coupled with multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) have been developed.

The coupling of a chromatographic technique to MC-ICP-MS provides a transient signal within a specific time window in which the isotope ratios must be accurately measured. Depending on the introduction technique applied, the duration of the transient signal will be different and consequently the precision and accuracy of the isotope ratio measurement will change.

The aim of this study was to improve precision and accuracy of the determination of isotopic ratios in species using new methodology of calculation strategy. This new methodology was adopted from Fietzke et al (Sr isotope ratio using LA-MC-ICP-MS) and applied for Hg isotopic ratios for four mercury species using gas chromatography (GC) coupled to MC-ICP-MS. Briefly describing this new approach: isotopic ratios for two Hg isotopes are calculated using slopes of the lines obtained by the raw data intensities of these isotopes. Thallium is used for the mass-bias correction using Russell correlation. Precision and accuracy of the new method was found to be similar to the continuous signal sample introduction. For example, precision of $\delta^{202}\text{Hg}$ measurements was found to be 0.1-0.5‰, calculated as 2SD.

Following significant advantages can be noted when applying this method for the hyphenation of chromatographic techniques with MC-ICP-MS: (i) possibility to measure delta-values in the case when the standard and the sample have significantly different concentration; (ii) possibility to measure delta values in different species versus single species presented in the bracketing standard, for example species Hg^0 , MeHg^+ , Me_2Hg and Hg^{2+} were bracketed with Hg^{2+} species of NIST-3133 standard; (iii) possibility to measure delta-values for low abundant isotopes, such as $\delta^{196}\text{Hg}$.

This new method can be successfully applied for other chromatographic measurements of isotopic ratios in species by MC-ICP-MS. For some applications this methodology is advantageous over continuous sample introduction.

The new method has been applied for several applications, including fractionation of Hg isotopes during transformation from specie to another, and Hg isotopic composition in different species of environmental and biological samples.

1. Fietzke, J.; Liebetrau, V.; Gunter, D.; Gurs, K.; Hametner, K.; Zumholz, K.; Hansteen, T.H.; Eisenhauer, A. *Journal of Analytical Atomic Spectrometry* 2008, 23 (7), 955-961