

Hyphenated isotope dilution ICP-MS as an accurate tool for speciation analysis

Klaus G. Heumann, Natascha Demuth, Jens Heilmann, Nataliya Poperechna and Lothar Rottmann

Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz
Duesbergweg 10-14, D-55099 Mainz, Germany

In the past, isotope dilution mass spectrometry (IDMS) was often used for sensitive and accurate determinations of trace elements in different matrices. IDMS is internationally accepted as an accurate analytical method for trace element determinations. Since the first species analyses in 1994 by isotope dilution ICP-MS (1,2) many other investigations in elemental speciation have been carried out with the isotope dilution technique as recently an extended review on elemental speciation has documented (3). Species-specific and species-unspecific ICP-IDMS methods have been established (4), where for the first mentioned technique an isotope-labeled spike of the analyte must be used whereas for the second one any isotope-labeled compound of the element of interest can be applied after separation of the corresponding species (post column isotope dilution technique). Species-specific ICP-IDMS can also be used to validate sample preparation techniques for possible species transformations, a problem which often occurs in species analysis but cannot easily be identified by other analytical methods. This will be demonstrated by a monomethyl mercury transformation during sample pretreatment (5). However, also multiple-spiking is possible which allows to follow interconversion pathways of elemental species (6). Although the accuracy of analytical results of elemental speciation is an important task today, application of hyphenated ICP-IDMS has not become a routine method, up until now, even this technique has the best potential to get it (7).

Coupling of ICP-IDMS with separation techniques like high performance liquid chromatography (HPLC), gas chromatography (GC), capillary electrophoresis (CE) and gel electrophoresis (GE), the last-mentioned technique was recently developed in our laboratory by Bettmer and Brüchert (8), allows the determination of elemental species for many different applications covering especially environmental, biological and clinical aspects. Hyphenated species-specific and species-unspecific ICP-IDMS methods allow accurate and relatively fast "real-time" quantification of well known structurally exactly defined but also of unknown elemental species in a chromatogram or electropherogram. Examples for HPLC/ICP-IDMS and GE/ICP-IDMS, including humic substance metal complexes and metalloproteins, and GC/ICP-IDMS analyses for sulfur speciation in petroleum products will be presented. Also multi-species determinations of toxic compounds like monomethyl mercury and butyltins in seafood samples is an actual analytical problem which can properly be solved by species-specific GC/ICP-IDMS (9).

- (1) K.G. Heumann, L. Rottmann, J. Vogl, *J. Anal. At. Spectrom.* **9**, 1351 (1994)
- (2) A.A. Brown, L. Ebdon, S.J. Hill, *Anal. Chim. Acta* **286**, 391 (1994)
- (3) P. Rodriguez-Gonzales, J.M. Marchante-Gayon, J.I. Garcia Alonso, A. Sanz-Medel, *Spectrochim. Acta B* **60**, 151 (2005)
- (4) L. Rottmann, K.G. Heumann, *Fresenius J. Anal. Chem.* **350**, 221 (1994)
- (5) N. Demuth, K.G. Heumann, *Anal. Chem.* **73**, 4020 (2001)
- (6) P. Rodriguez-Gonzales, J. Ruiz Encinar, J.I. Garcia Alonso, A. Sanz-Medel, *J. Anal. At. Spectrom.* **19** (2004) 2161
- (7) K.G. Heumann, *Anal. Bioanal. Chem.* **378**, 318 (2004)
- (8) W. Brüchert, J. Bettmer, *Anal. Chem.* **77**, 5072 (2005)
- (9) N. Poperechna, K.G. Heumann, *Anal. Bioanal. Chem.* **383**, 153 (2005)