

Further Developments on the CE-DAD-ICP-MS Coupling for the Investigation of the Lanthanides/Actinides-Humic Substances Complexation

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In earlier studies [1], it has been shown that the CE-DAD-ICP-MS (capillary electrophoresis diode array detector ICP-MS) coupling can be applied for the investigation of the complexation of metal ions with humic substances. The separation of the different species was performed in the CE and the species were identified using the two detectors. Fig. 1 presents a typical electropherogram obtained for the separation of a solution containing iodine marked Aldrich humic acid (AHA) and Ho. The humate complexation of Ho and separation took place in 0.1 M NaClO₄. 1 M AcOH was used as a buffer for the CE. The interpretation of the electro-pherogram obtained by ICP-MS (lower part of Fig.1) is rather complicated without the help of the second detector. After applying the necessary time correction for the two electropherograms, a firm assignment of the signals could be done, as depicted in Fig.1.

iodine marked AHA was used only for calibration. In the peak marked in brown, besides the iodine detected by DAD and ICP-MS a peak is detected by ICP-MS on the mass of Ho, and a third DAD peak is noticed at 235 nm, a characteristic AHA absorption wavelength. Thus, this signal has been assigned to metal-humate complex. A significant tailing can be observed in the ICP-MS electropherogram on the mass of Ho. This has been assigned to the metal ion species which are dissociated from the metal ion humate complexes during the separation. It is supposed that these are dissociated from the "weak binding sites" of the humic acid. These species carry lower negative charges than the Ho-AHA complexes, and become gradually positively charged, as confirmed by the presence of the EOF in the middle of the tailing. The EOF was identified with the help of the DAD and is marked red in Fig. 1. The last ascending part of the tailing is associated to the positively charged free metal ions.

It can be observed in Fig. 1 that it is rather difficult to make an accurate separation of the species due to the tailing of the Ho electropherogram detected by ICP-MS. The complexation constants that were determined at concentrations of metal ion varying between 0.21 – 2.01 ppm were systematically too low as compared to values in the literature [2]. Using the actual setup we were not able to work with lower concentrations of metal ion. By employing a new coupling technique, i.e. the MiraMist CE, it is expected to reduce the detection limits of the technique. At lower concentrations of metal ion, the complexation at the "weak binding sites" is less likely to take place, allowing thus a more precise determination of the complexation constants of humic substances with metal ions. The first test experiments with a MiraMist CE nebulizer (total consumption nebulizer) have already been performed [3].

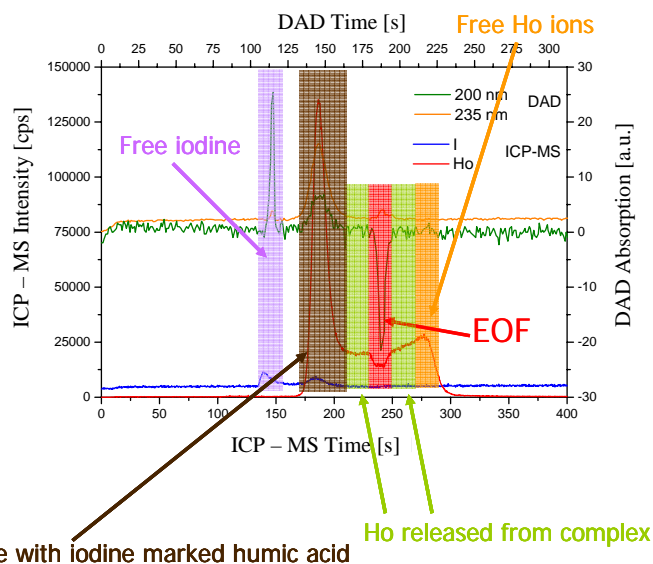


Figure 1: Separation of a solution containing Ho and iodine marked AHA, by CE-DAD-ICP-MS

Iodine was used for marking the AHA, because it can be easily detected by both detectors, facilitating the identification of the species. It can be seen that a big part of the iodine was removed from the AHA during, or before the separation. It is not clear whether the presence of iodine influences the complexation of actinides with humic substances, thus the

References:

- [1] D. Kutscher et al.: Annual Report, Institut für Kernchemie, Universität Mainz, **C 17**, (2006)
- [2] D. Kutscher: Diploma Thesis, Institut für Kernchemie, Universität Mainz, (2007)
- [3] Th. Wunderlich et al.: Annual Report, Institut für Kernchemie, Universität Mainz, **this issue**, (2007)