OP 3.4

Investigation of non-covalent metal-phytosiderophore species by electrospray-high resolution-mass spectrometry

Heiko Hayen[1], Günther Weber[1] and Nicolaus von Wirén[2]

[1] ISAS-Institute for Analytical Sciences, Bunsen-Kirchhoff-Str. 11, 44139 Dortmund, Germany, hayen@isas.de
[2] Molecular Plant Nutrition, Institute of Plant Nutrition, University of Hohenheim, Fruwithstr. 20, 70593 Stuttgart, Germany

The direct analysis of metal species in complex biological samples is a prerequisite for understanding the biological role(s) of these metals in different biosystems. Especially, the analysis of small, non-covalent metal complexes is challenging because the latter can be highly reactive, and there is always a risk of changing metal species equilibria during analytical procedures. Another problem is the unequivocal identification of unknown metal species, which often must be done at very low concentrations and sometimes also in very low volumes, due to the limited amount of isolated biological samples.

Therefore, we developed a method for the direct analysis of small non-covalent complexes based on high-resolution mass spectrometry applying nano-electrospray ionization-Fourier transform ion cyclotron resonance MS (nano-ESI-FTICRMS). The use of FTICRMS not only provides high resolution but also high mass accuracy, enabling the unambiguous determination of elemental compositions. Hence, this enables the unequivocal identification of non-covalent metal chelates.

The applicability of this method is demonstrated by the investigation of the iron uptake and translocation in grasses via phytosiderophores and the non-proteinogenic amino acid nicotianamine (NA). Equilibria of DMA and NA in the presence of Fe(II) and Fe(III) are controversically discussed in the literature, and the relative stability (and thus importance) of different iron species in planta is not clear.

The method enables the direct analysis of NA and DMA complexes with Fe(II) and Fe(III) in one solution without separation. Although the two ligands differ only by one mass unit, and consequently there are pairs of iron species (i.e. Fe(II)-NA and Fe(III)-DMA), which differ only by 0.0239 m/z units, the use of FTICR-MS enables the unequivocal identification of all four iron species (NA-Fe(II), NA-Fe(III), DMA-Fe(II), DMA-Fe(III)). (1) Advantages of the method are the low sample consumption (only some µL of solution are needed), and the possibility to verify the stoichiometry of metal species with high accuracy and to assign the redox state of the chelated iron. Additional work includes the investigation cadmium-phytosiderophore complexes also with respect to ligand exchange prosseses. (2)

REFERENCES

(1) G. Weber, N. von Wirén, H. Hayen: Analysis of Iron(II) / Iron(III) Phytosiderophore-Complexes by Nano-Electrospray-Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry; Rapid Commun. Mass Spectrom. , 20 (2006) 973-980.
(2) A. R. Meda, E. B. Scheuermann, U. E. Prechsl, B. Erenoglu, G. Schaaf, H. Hayen, G. Weber, N. von Wirén: Iron Acquisition by Phytosiderophores Contributes to Cadmium Tolerance, Plant Physiol., 143 (2007) 1761-1773.