**Abstract**

To fully understand the metal transportation and translocation system via phytosiderophores (PS) in plants, analytical tools for accurate identification and simultaneous and sensitive detection of low-molecular-weight (LMW) metal-species and their free ligands in plants are highly required.

In this PhD thesis, new methods based on capillary electrophoresis (CE) and zwitterionic hydrophilic interaction chromatography coupled to electrospray ionization mass spectrometry (ZIC-HILIC/ESI-MS) were developed to fill up the lack of analytical approaches.

A CE method (UV- and conductivity detector) was developed to separate and detect free ligands and their respective metal-complexes. For the first time, a baseline separation of PS was achieved. In addition, separation of ferric-PS-species without stability problems was realized. The CE method was applied to wheat and Arabidopsis plants and allows the characterization of changes of metal-species in a semi-quantitative way down to the µmol-level. To enhance detection sensitivity a new on-column photo reactor with an adjustable irradiation window was constructed. In particular, a sensitivity increase of a factor up to 6 (UV detector) and 4 (conductivity detector) was obtained for the iron-species in capillary flow injection (cFIA).

In addition, a more sensitive detection and unequivocal identification of LMW free ligands and metal-species was achieved by ZIC-HILIC/ESI-MS. The different metal-complexes and the same free ligands are baseline separated. Even when the signals are overlapping a confident identification was realized by ZIC-HILIC/ESI-MS. This was demonstrated for wheat and Arabidopsis plants.

Finally, metabolic profiling in plants was realized by coupling the separation unit to a Fourier transform ion cyclotron resonance-mass spectrometer (ESI-FTICR-MS). Here, metabolites down to the low micro molar concentration range were determined with peak intensity reproducibility better 5 %. The applicability to real plant samples was demonstrated by the analysis of a complete set of Tobacco plants.