

Direct monitoring of metabolic Fe-species equilibria in plants by CV and MS

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Uptake of iron into plants and subsequent metabolic reactions involve changes of the complexing ligand as well as changes of the redox state of iron. In grasses, a particular uptake system for iron is present, based on the excretion of phytosiderophores (PS) and uptake of respective Fe(III)-PS-species by the YS1 transporter, located in the plasmalemma membrane. Up to this point, the respective mechanism is quite well understood. The mechanism of iron release from the very stable Fe(III)-PS-species inside the plant, however, remains to be elucidated. One proposed mechanism involves the reduction of ferric phytosiderophores in the presence of a strong iron(II)-chelator, probably via ternary complex formation. In other words: the ligand exchange reaction is closely linked to a preceding, or even simultaneous, redox reaction of the iron center. In order to investigate such reaction(s), methods are needed, which can directly monitor – in real time, and without disturbing respective equilibria – all relevant species in the system. This is very difficult, if not impossible, by using separation-based analytical speciation methodology (e.g., HPLC, CE).

We present here, for the first time, a direct experimental verification of the redox-mediated conversion of ferric PS species by ascorbate in the presence of the plant ligand nicotianamine (NA), leading to the formation of the ferrous NA-chelate. The reaction is monitored by cyclic voltammetry (CV), and by high resolution mass spectrometry (Fourier transform ion cyclotron resonance mass spectrometry). CV is very sensitive to changes of the chemical composition of redox-active species, which are detected by the corresponding shift in redox potential, and MS enables an unequivocal identification of all educts and products, incl. intermediates. The results are discussed with respect to the most probable reaction mechanism and concentration dependence of the reaction rate, but also consequences for our understanding of the role of metal-PS-species in plant metabolism are highlighted. For example, the reaction rates of three different, but very similar PS were found to be inversely related to the thermodynamic stability of their ferric chelates.