

Speciation data from voltammetric methods: Ni in xylem sap – a case study

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It is well known that metal speciation in natural systems is determined by the mixture of metals and complexing agents present, as well as, by the pH, ionic strength and major ion composition. Changes in one or more of these parameters may affect the physiochemical distribution of a metal among all of its possible forms as well as the rates of formation or dissociation of the different species. This may cause perturbations that may have significant ecological consequences if the rate of reestablishment of chemical equilibrium is slow compared to rates of competing processes. So in complex natural systems in order to understand the process that govern metal distribution and uptake fluxes both thermodynamic and kinetic effects must be taken into account (1).

Voltammetric techniques are powerful not only to measure ultratrace analyte concentrations but also to determine the distribution of the various species of a given element and physical parameters of the medium such as stability and kinetic complexation constants (2). In this work we report a study of Ni complexation in xylem sap of *Q. ilex* as well as the kinetics and mechanism of Ni chelation using square wave and cyclic voltammetry at a hanging mercury drop electrode. Holm oak (*Quercus ilex*) is the dominant tree growing on the serpentine soils of northeast Portugal, characterized by elevated soil concentrations of Ni and Mg, combined with low Ca concentrations. Apparently *Q. ilex* does not suffer from excessive concentrations of Ni in the soil.

The results obtained showed that the complexes with the carboxylic acids dominate nickel speciation. Mixed complexes, Ni + oxalic acid + citric acid, are also formed in the range of concentrations found in the xylem. As to the kinetics of the association/dissociation reactions, in the operational time scale used, simple as well as mixed Ni complexes with the carboxylic acids behave as dynamic, while those with the amino acids are inert (3). From the voltammetric data apparent pseudo first order rate constants of complex formation and dissociation were determined. To test the validity of the methodology, formation rate constants of the ML complexes with citric and oxalic acids in the absence of the alkaline earth cations were evaluated that compare with the anticipated values from Eigen mechanism. The measurements show the pronounced influence of Mg(II) on the kinetics of Ni(II) complexation in a media where this alkaline earth ion is present in excess to the main organic ligands of the xylem sap. The net result is a retardation of complexation reactions that can be more important for intrinsically slow-reacting metals as is the case of nickel (4).

References

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