OP 4.4

Speciation investigation of trace metal ions using complexing resins as sensors for the free metal ion concentration in real samples

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The free metal ion concentration in a solution in contact with a ion exchange resin, in which only the free metal ion is adsorbed, is proportional to the concentration of adsorbed metal.
It can be demonstrated that $[\mathrm{M}] = c\,V / K^{*}\,w$ (1,2).
c is the concentration of metal ion adsorbed in mmol/ml of the solution phase, V is the solution volume (ml), w is the amount of resin (g), and K^* is the partition coefficient of the metal ion between the two phases, i.e. the ratio of the metal ion concentration in the resin phase and the metal ion concentration in the solution phase.
The aim of the present communication is to show that very low free metal ion concentration can be accurately measured in this way, if the fraction of sorbed metal ion is between 0.1 and 0.9, i.e. if the conditions leading to the proper detection window are employed. Concentrations of free copper(II) and lead(II) as low as 10^{-18}-10^{-20} M can be evaluated.
Notice that the concentration of sorbed metal ion can be accurately determined after elution from the resin, by methods with low detection limits.
This is demonstrated for copper(II), aluminium(III) and lead(II), by comparing the free metal ion concentration determined by the method here proposed and that calculated from the literature complexation constants of known ligands. For all these metal ions K^* was evaluated considering the sorption equilibria which were previously characterized by the Donnan model for the ion exchange resins.
The proposed method for determining the free metal ion concentration has been proved to be helpful for the titration of unknown ligands in natural samples, for example for the simultaneous evaluation of the side reaction coefficients of aluminium(III), uranyl, copper(II) and lead(II) in a seawater sample at different acidities, and different *V/w* values. The data were treated according to the well known Ruzic-van den Berg linearization method: $\frac{[M]}{[ML]} = \frac{1}{K' c_L} + \frac{[M]}{c_L}$, modified for the acidity variation. Very high side reaction coefficients were determined for the low metal ions concentration present in natural waters.
A further example is given by the titration of the unknown ligands of copper in an Italian wine. The presence of strong copper(II) species was demonstrated.
Potentiometry by ion selective electrodes, and other electrochemical methods, as for example ASV, have not so low detection limits in complex matrices as those here considered.

(1) M. Pesavento, G. Alberti, A. Profumo, *Anal. Chim. Acta*, 405 (2000) 309-319.
(2) M. Pesavento, R. Biesuz, F. Dalla Riva, G. Alberti, *Polyhedron*, 21 (2002) 1345-1350.