Assessment of accuracy and precision in speciation analysis by CLE–CSV: application to Antarctic samples

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Speciation analysis by Competitive Ligand Equilibration – Cathodic Stripping Voltammetry (CLE – CSV) has been widely used in the last three decades for determining the species of trace elements in natural waters.

This kind of selective detection of the labile metal has the advantage to combine simple sample treatment, very high sensitivity and to rely on relatively few assumptions (mainly that equilibrium is reached after allowing for a long enough equilibration time). In general, the advantages of the CLE-CSV speciation scheme over other CLE methods derive from the added ligand being both the competitor and the direct detection mean. Moreover, this procedure requires a limited time, taking less than two hours to analyse a sample, after allowing a twelve hour, operator free, equilibration time. Two data are obtained by this analysis: the concentration of the natural ligand(s) (usually referred to as complexing capacity) and the conditional constant for the formation of the complex between the natural ligand(s) and the metal under investigation.

Aim of the present research is to assess the analytical performances of the CLE-CSV procedure and to estimate the accuracy and precision that can be attained for the determination of strong ligands at the ultra trace level. A thorough validation procedure may be difficultly applied; reference materials are not available in this field, as complexes of metal at trace levels in natural waters are not sufficiently stable. The assessment of analytical figures was consequently performed by analysing synthetic solution containing trace level of ligands showing known complexing characteristics. The whole protocol was evaluated. The side reaction coefficient alpha for the formation of the complex between the added ligand and the investigated metal was initially determined as usually done in the CLE-CSV protocol. The method was subsequently applied to the analysis of solution with known complexing characteristics and ligand concentrations ranging from 5 to 50 nM. Copper was used as model metal ion and ethylenediaminetretraacetic acid (EDTA) as a model ligand.
Results evidenced that the CLE-CSV protocol is not affected by systematic errors in the determination of both ligand concentration and the side reaction coefficient alpha. Good precision is obtained for ligand concentrations, with relative standard deviations (RSD%) in the range 3 – 15% (four replicates for each ligand level). Random errors associated with alpha coefficients showed higher figures with RSD% in the range 30 – 40%. The possibility to detect different classes of ligands is clearly strongly limited by the precision in the alpha coefficient values.

The CLE-CSV protocol was subsequently applied to the detection of strong ligands in water samples collected in Antarctica. The figures of merit of the protocol were demonstrated not to degrade for the analysis of real samples and the procedure was confirmed to be able to detect strong ligands at ultratrace level.