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Review Article

A review on electrochemical methods for trace metal speciation in environmental media

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Trace metal speciation is key to understand/predict bioavailability and potential toxicity of metals to biota and will, undoubtedly, be incorporated in future regulations. Electroanalytical methods have a role to play in such development: they offer a wide range of advantages such as speed, portability, economy, solid interpretation backgrounds and low limits of quantification. This review focusses on three selected stripping techniques: Competitive-Ligand Exchange-Cathodic Stripping Voltammetry (CLE-CSV), Scanned Stripping Chrono-Potentiometry (SSCP) and AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) reporting their working principles, characteristics (strong and weak points) and recent applications to systems of environmental relevance (such as seawaters, freshwaters or soil extracts).

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List of nomenclature and abbreviations: AdCSV, Adsorptive Cathodic Stripping Voltammetry; AFS, Atomic Fluorescence Spectroscopy; AGNES, Absence of Gradients and Nernstian Equilibrium Stripping; APDC, Ammonium 1-pyrrolidinedithiocarbamate; ASV, Anodic Stripping Voltammetry; BiFE, Bismuth Film Electrode; BLM, Biotic Ligand Model; CLE, Competitive Ligand Exchange; CSV, Cathodic Stripping Voltammetry; DHN, 2,3-dihydroxynaphthalene; DMEM, Dulbecco's modified Eagle's medium; DMG, Dimethylglyoxime; DMT, Donnan Membrane Technique; DOC, Dissolved Organic Carbon; DOM, Dissolved Organic Matter; DPP, Differential Pulse Polarogram; EDTA, Ethylenediaminetetraacetic acid; EPPS, 4-(2-Hydroxyethyl)-1-piperazinepropanesulfonic acid; EPS, Extracellular polymeric substances; EQS, Environmental Quality Standard; FIAM, Free Ion Activity Model; GSH, Glutathione; HEPES, N-2-Hydroxyethylpiperazine-N'-2'-ethanesulfonic acid; HMDE, Hanging Mercury Drop Electrode; HS, Humic Substances; I, Ionic strength; ISE, Ion Selective Electrode; LOD, Limit of Detection; MES, 2-(N-morpholino)-ethanesulfonic acid; MOPS, 3-(N-morpholino)-propanesulfonic acid; NICA, Non-Ideal Competitive Adsorption; NN, 1-Nitroso-2-naphthol; NOM, Natural Organic Matter; NP, Nanoparticles; NTA, Nitrilotriacetic Acid; OECD, Organisation for Economic Cooperation and Development; PDCA, Pyridinedicarboxylic acid; PNIPAM, Poly(N-isopropylacrylamide); POPSO, Piperazine-1,4-bis(2-hydroxypropanesulfonic acid); QD, Quantum Dot; RT, Resin Titration technique; S, Salinity; SA, Salicylaldehyde; SCP, Stripping Chrono-Potentiometry; SIA, Sequential Injection Analysis; SPE, Screen-Printed

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Introduction

Speciation (i.e. the distribution of an element among its different chemical forms [1]) has been recognized as a key factor for trace metal (bio)availability to biota, as postulated by hegemonic ecotoxicological paradigms such as the Free Ion Activity Model (FIAM) [2] or the Biotic Ligand Model (BLM) [3], both assuming that the free ion is the only bioavailable species. The limits of these models have recently been reviewed [4], highlighting numerous cases where specific fractions of metal complexes can be internalized, either directly or through the dissociation of labile complexes. Thus, there is a need to design, develop, apply and interpret analytical techniques able to provide reliable speciation information [5–7] that can be used by regulatory bodies.

Although there are numerous non-electrochemical techniques [5–13], those that are provide attractive possibilities such as speed of analysis, low-cost and miniaturization in view to on-site (and *in situ*) measurements [14], and can also provide thermodynamic (i.e. equilibrium) information (such as the amount of the free metal, the amount of complexing sites, the stoichiometry of complexes and their stability constants [15]) as well as dynamic information (such as kinetic rate constants and diffusion coefficients [16]). However, the correct signal interpretation can be difficult in natural media [16,17]. Stripping techniques, due to their low detection limits, are well suited for

Electrode; SSCP, Scanned Stripping ChronoPotentiometry; SSV, Scanned Stripping Voltammetry; TAC, 2-(2-Thiazolylazo)-p-cresol; TMFE, Thin Mercury Film Electrode; UV, Ultra Violet; VGME, Vibrating Gold Micro Electrode; VM, Visual MInteq.

environmental analysis. They are two-stage techniques, where the first stage is a deposition step that accumulates the analyte (at the electrode surface or in its volume), followed by a second stage that quantifies this analyte. Anodic Stripping Voltammetry (ASV), in its multiple variants, is the most popular and has the advantage to possibly be measuring a potentially bioavailable fraction of the metal, as shown again recently [18,19].

This critical evaluation focusses on three techniques that are known powerful tools for metal speciation: AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) and SSCP (Scanned Stripping Chronopotentiometry), that are relatively recent techniques, together with the more established CLE-CSV, Competitive Ligand Exchange (or Equilibration)-Cathodic Stripping Voltammetry. Principles, recent applications, weak and strong points are reviewed.

CLE-CSV (Competitive-Ligand Exchange-Cathodic Stripping Voltammetry)

CLE-CSV is an equilibrium-based method that determines complexation parameters, namely ligand concentrations and conditional stability constants, allowing indirect determination of the free metal ion concentration. The method consists in the addition of a ligand (L_{add}) that forms an electroactive complex ML_{add} with the metal M of interest. Once equilibrium between the natural ligands (L_x) and L_{add} is achieved (typically few hours), quantification of ML_{add} adsorbed on the sensor (Figure 1) by CSV in a minimum of 12 aliquots at increasing concentrations of M leads to a titration curve ($I_{\text{p}}(ML_{\text{add}})$ vs. $c_{\text{T},M}$) that can be fitted with the presence of up to typically two classes of ligands of specific concentrations [L_x] and conditional stability constant K'_x . Recent CLE-CSV studies published in the last 2 years were applied almost exclusively to marine systems, looking at the speciation of biologically important metals, mostly Cu [20*–29] and Fe [30–36], but also Zn [37,38] or Co [39]. The analytical method is powerful and can give insights into potential biological limitation (e.g. free Cu^{2+} limitation for Cu-dependent ammonia oxidizing archaea [40]), toxicity (e.g. high free Cu^{2+} in coastal waters [41]) or for studying the effect of ocean acidification on future Cu and Fe speciation [27]. It is also used to indirectly look at the biogeochemical cycling of the ligands, from their origins (e.g. sediments [22], peat [21], biological productivity in water column [29], stormwater [42]), and identity (e.g. humics [24], polysaccharides [43]) to their seasonal [31] and spatial [35*,36] variations, as well as stability [21].

Recent analytical developments to note include the catalytic detection of Fe by oxygen in the presence of SA [44] and the use of reverse titrations [45,46], where the concentration of the ligand, not that of the metal, is varied. New methods for the determination of humic substances, HS (based on the adsorption and quantification

of Cu–HS complex at the Hg drop electrode [28**], similarly to the Fe–HS method [47]), have demonstrated that the same HS are involved in the complexation of both Cu and Fe in coastal waters of Liverpool Bay, accounting for 97 and 65% of the total ligands for Fe and Cu, respectively [28]. This competition for ligands implies that the complexation of Fe–HS might be dependent on Cu levels, or other metals, and vice versa. Various fitting methods can be used to determine speciation parameters from the titration curves (current vs. total metal concentrations). However, both the experimental [48] and fitting [49*,50] procedures are far from trivial and latest recommendations [49*] are, if time allows, to run multiple titrations at different detection windows (i.e. with different concentrations of the added ligand e.g. [51,52]) to decrease errors. Freely available software such as ProMCC [53*] or others (see [49*] and references therein) are available to help fitting the data correctly. However, no matter how well data are fitted, CLE-CSV does not give any indication related to potential kinetics and bioavailability of the various complexes. When internalization is fast enough to develop a free metal concentration profile close to the consuming interface, fast dissociating organic complexes (e.g. Cu–HS substances [54]) may also participate to the metal flux to organisms and methods based on anodic stripping voltammetry can estimate this bioavailable fraction [19,55*].

CSV in the presence of relatively high concentration of added ligand(s) is also widely used as a detection technique and is very helpful in gaining insights into the cycling of various metals, such as that of Zr, Mo, V and Ti at increasing salinities [56]. Although the Hg drop electrode is still used for developments of new CSV methods (e.g. for Ga [57], Te [58] or Fe [59]), a large amount of research is now devoted to greener and more user-friendly solid and/or film electrodes. Latest development for analysis of water samples include methods for Ni [60], Ag [61], Co [62], Mn [63], V [64,65], U [66], Ga [67] and Cr [68]. These methods are developed using common carbon paste electrodes [60,61] or screen-printed ones [69,70], but also use more recent substrates such as e.g. lithographically produced Bi microelectrode array [71], tin–bismuth alloy [62,66] or indium-oxide [63]. Although progress is coming fast, up to now, only the Hg drop electrode is used for CLE-CSV speciation studies (due to yet unrivalled stability over the time required to perform a titration).

SCP/SSCP (Scanned Stripping Chronopotentiometry)

Stripping Chronopotentiometry (SCP) was developed in the early 2000s by Town and van Leeuwen [72] mainly to address the problems caused by electroodic adsorption of organic matter in trace metal analysis in environmental waters. The main difference in this technique is that, in the stripping step, a sufficiently small reoxidation current is used such that a small diffusion gradient inside the electrode is created. Therefore full depletion of the

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