



Mini review

Electroanalysis in environmental monitoring: Tracking trace metals—A mini review

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ABSTRACT

Recent advancements in electroanalytical methodologies for the analysis of trace metals in natural waters are summarized. The research and technological progress was centered on the development of new “green” sensors, as well as well-established electroanalytical methods, comprising improvements in sensitivity, robustness, versatility, disposability and reliability.

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1. Introduction

When considering trace elements in the environment, research interest is mostly oriented on those which are environmentally relevant as pollutants or micronutrients (e.g. As, Cd, Cu, Fe, Hg, Pb, Zn, etc.) [1,2]. However, with the development of novel technologies, a new set of elements termed “Technologically critical elements” (TCE) [3] have been recognized as occurring in the environment, most of them with unknown environmental and toxicological effects. Hence, there is an increasing demand to find analytical tools for their analysis, with

electroanalytical techniques having some potential [4–7]. Despite continuous development over previous decades [2,8], the improvement of analytical performances and robustness for in-situ/on-site applications is still a great challenge. Efforts are mainly directed towards development of “environmentally friendly” solid electrodes, functionalized micro/nano-structured interfaces (modified electrodes), miniaturization and new protocols [2,9–13]. Beyond total concentrations, to understand and interpret the bioavailability, reactivity, mobility and the fate of trace metals, understanding their speciation is of crucial significance [14] and electroanalytical techniques can be used to this end [2,15,16].

Although the progress in electroanalysis of trace metals has been made, only few of new techniques are suitable for analysis at

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(ultra)trace levels. Thus, in this mini-review we report those techniques which demonstrated, or show potential to be used for 'real' environmental monitoring purposes.

2. Overview of analytical performances

Due to the benefit of the accumulation (pre-concentration) step, extremely low detection limits (~at fM-pM level) can be achieved by

using electroanalytical techniques in stripping mode [17–19]. To exemplify the electroanalytical progress, an exhaustive literature review was undertaken of electroanalytical methods for copper and iron determination. Analytical performances were categorized according to the mode of the voltammetric technique, base material and the nominal size of an electrode and historical progress (Fig. 1A–D). To account for differences in accumulation time, analytical performances were ranked by “n-sensitivity”, which was computed by multiplying limit of

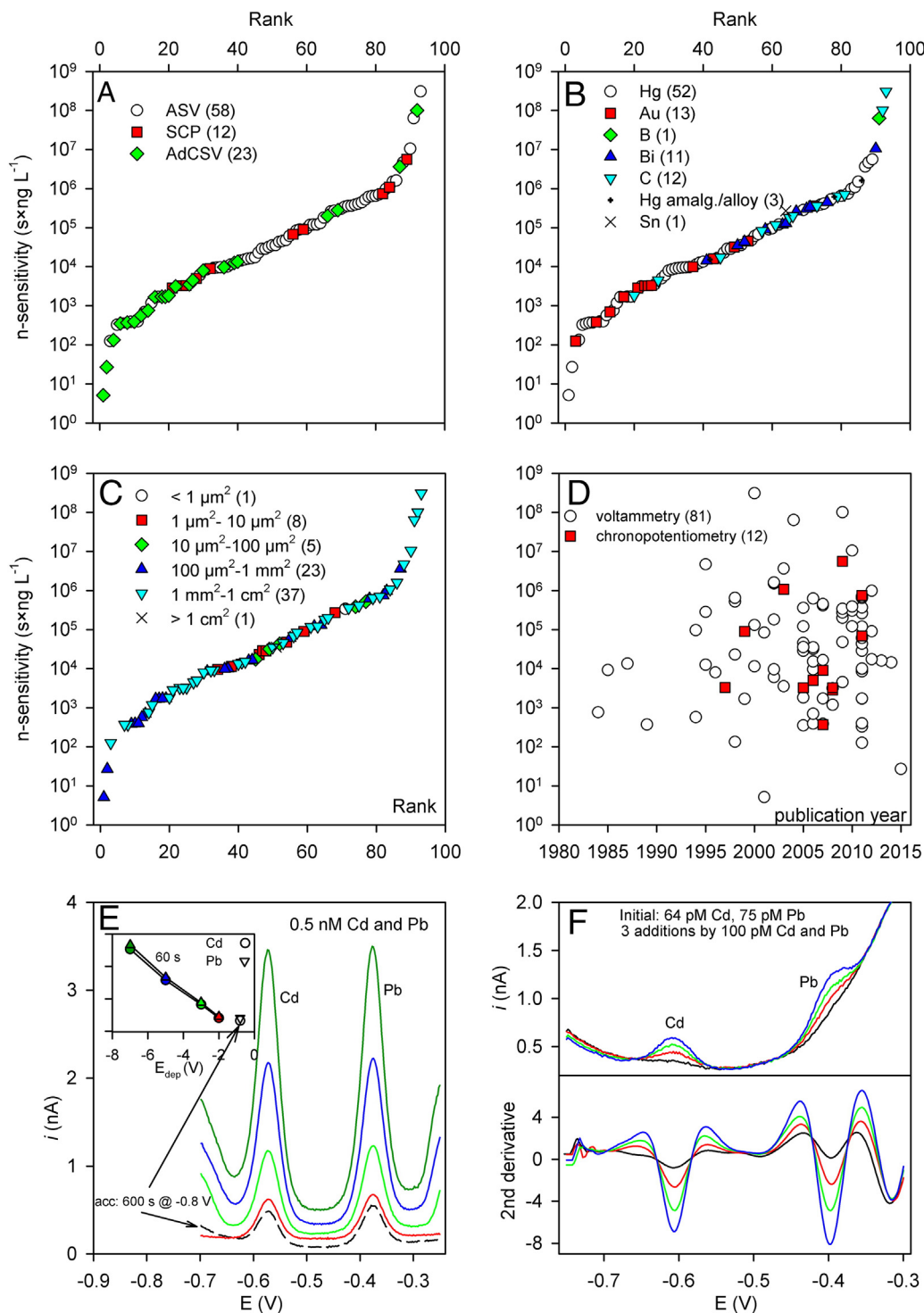


Fig. 1. N-sensitivities plotted against technique used (A), electrode material (B), nominal electrode size (C) and publication year (D). Numbers in parentheses denote number of separate data in each category. Voltammograms of 0.5 nM Cd and Pb obtained in acidified MQ water at different E_{acc} with $t_{acc} = 60$ s (E, full lines); dashed line corresponds to voltammogram obtained at $E_{acc} = -0.8$ V with $t_{acc} = 600$ (inset: i_p vs E_{acc}). Original voltammograms (F, top) and corresponding 2nd derivative transformations (F, bottom) of Cd and Pb in seawater sample.

detection (LOD) with the overall analysis time (result given in $s \times \text{ng L}^{-1}$).

Even if techniques based on anodic stripping voltammetry (ASV) are the most frequent, a good analytical performance (low n-sensitivity) could result from other two techniques considered (adsorptive cathodic stripping voltammetry – AdCSV and stripping chronopotentiometry – SCP), meaning that the mode of voltammetric procedure is not the most critical point explaining its efficiency (Fig. 1A). The techniques with the lowest n-sensitivity are mostly based on Hg or Au electrodes (Fig. 1B). Concerning the electrode surface (Fig. 1C), even if some micro-electrodes ($\sim 10 \mu\text{m}^2$) could provide the correct range of sensitivity, the most used and sensitive ones are larger ($\sim \text{mm}^2$). Obviously, the final sensitivity is also driven by the combination of many other parameters (e.g. metal itself, electrode geometry and surface modification, diffusion layer thickness, accumulation potential, scanning mode, etc.). Finally, it seems there has been little or no real progress over the examined period in terms of electroanalytical methods for ultra-trace determination of Cu and Fe (Fig. 1D). However, such conclusion does not refer necessarily to other elements, for which very low LODs were reached [18,20,21].

3. Electrode materials and assemblies

Due to toxicity of liquid mercury (Hg) electrodes and the lack of portability, researchers have explored variety of alternative materials including metal and carbon based materials (Au, Pt, Ir, Ag, C-based, etc.) in order to create more environmentally friendly and portable sensors.

3.1. Thin-film plated electrodes

Due to large potential window and negligible toxicity, bismuth film electrode (BiFE) acquired a high popularity mainly for analysis of Zn, Cd, Pb, Ni and Co [22]. Recently, Pinto and Lemos [23] showed that its use could be extended to determination of Cu (which interferes with Bi peak). Using partial least squares regression (PLS) treatment, they lowered limit of quantification of simultaneously analyzed Zn, Cd, Pb and Cu down to 0.85, 0.05, 0.12 and 0.57 nM, respectively. Compared to classical BiFE, by modification with Nafion, 2-mercaptoethanesulfonate (MES)-tethered polyaniline (PANI-MES), an increased sensitivity of BiFE was achieved (LOD of 0.44 and 0.19 nM for Cd and Pb, respectively) [24]. BiFE was used in numerous applications by the Hočevar group, the last one related to BiFE use in acidic media for Zn analysis [25]. Instead of voltammetry, for analysis of Cd and Pb in freshwater Rocha et al. [26] used stripping chronopotentiometry (SCP) with rotating BiFE. Rocha et al. [27] further demonstrated for the first time application of BiFE for the determination of free Pb concentration by using “absence of gradients and Nernstian equilibrium stripping” (AGNES) approach. Aside of BiFE, the Hočevar group introduced an in-situ antimony film electrode (SbFE) [28], recently used for determination of Hg in water samples [29], and a novel in-situ prepared copper film electrode (CuFE) [30] used for analysis of trace Hg and Pb in the presence of dissolved oxygen (LOD: 0.5 and 0.29 nM of Hg and Pb, respectively).

3.2. Micro and nano sized solid electrodes

Due to the enhanced mass transport of electroactive species at micro- and nano-sized electrodes and their arrays [31], as well as significantly improved signal-to-noise ratio, these types of sensors have undergone a rapid development and application in electroanalysis. Progress was achieved in Liverpool Electrochemistry group, by Stan van den Berg and Pascal Salaün. An initially excellent performance of Au-microwire with LOD of 6 and 25 pM for Hg and Cu in model solutions [32] was further improved by using it as a vibrating Au-microwire electrode (VGME) [33]. Microwire electrodes of different sizes (5, 10 or 25 μm) were used for determination of traces of Zn, Cd, Pb, Cu, Hg, As,

and Sb in various environmental samples [19,34–37]. Using VGME with optimized voltammetric procedure (LOD below 0.1 nM), Salaün et al. were able to measure As(III) and Sb(III) at nM level in seawater samples [38]. The same group showed that even As(V) was possible to be measured at natural pH [39]. Finally, voltammetry with a VGME combined with a battery powered potentiostat was tested for in-situ monitoring of labile Cu in coastal waters [36]. While a vibrator motor was usually utilized, for determination of uranyl ions (UO_2^{2+}) using vibrating electrode, Peled and Mandler [40] used a simple loudspeaker connected to the waveform generator. Recently, a gold plated Ir-based microelectrode (Au-IrM) for determination of As(III) at low nM level and at natural pH was presented by Touilloux et al. [41]. The key advantage of this approach is the ability to renew the Au layer (with a lifetime of ~ 7 days) by electrochemical procedure. Taking advantage of mild hydrogen evolution at a bimetallic Au–Pt nanoparticles modified GC electrode, Bu et al. were able to determine As(III) in real water samples at nM level [42]. Comparing different types of unmodified carbon electrodes for Sb(III) determination at nM level, Lu et al. [43] found that unmodified edge plane pyrolytic graphite (EPPG) outcompetes boron doped diamond (BDD) or screen-printed electrodes (SPE), showing $100\times$ higher response than classical bare GC. An ultra-sensitive determination of Sb (LOD = 1.64 fM) based on anodic stripping of electrodeposited Sb atomic layers onto a GCE in overpotential region was demonstrated by Fang et al. [18]. Exceptional sensitivity for the determination of Pb (LOD = 80 fM; only 1 s pre-concentration time) is achieved when the mercury monolayer-on-carbon electrode (MMCFE) is used with fast (>1 kV/s) ASV [21]. High sensitivity was ascribed to ionization of Pb atoms in the mercury layer, which catalyzes the oxidation of atomic hydrogen adsorbed at the Hg layer.

Since the introduction of amalgam electrodes by Mikkelsen and Schröder [44], they were sporadically used, despite exhibiting a good performance. Recently, Bi et al. [45] revisiting a carbon, gold and silver microwire electrodes under vibrated conditions for detection of Pb and Cd traces in seawater showed that only Hg-coated silver electrode is suitable when preplated. Under optimized conditions, a silver amalgamated microwire (SAM) electrode exhibited low LOD for Pb (4 pM) and for Cd (100 pM), which was sufficient for their analysis in open Atlantic and Pacific seawater samples [46].

3.3. Screen-printed electrode types

Screen-printed type of electrodes (SPE) became very attractive for the broad range of applications including the sensing of trace metals [11,13]. Although the analytical performance of these sensors could not compete with classical electrodes, due to portability they could be used for field applications [47]. Taking advantage of vibrating motor, Gamboa et al. enhanced analytical performance of the commercially available SPE of gold nanoparticle-modified carbon nanotubes for As(III) determination, which could be attractive for portable systems and in-situ measurements [48]. Recently, a disposable lab-on-a-chip sensor with integrated bismuth microelectrode arrays for analysis of metals was developed in Economou group [49]. Its good performance was verified by measuring Cd, Pb and Ni in unstirred and deoxygenated freshwater samples. A review of stripping voltammetry at micro-interface arrays was recently published by Herzog and Beni [50] indicating a possible use of these microsystems in tracing metal ions. For example, Herzog et al. [51] developed on-chip electrochemical microsystems with a platinum microelectrode array for measurements of Cu in artificial seawater by underpotential deposition-stripping voltammetry. Recently, C.E. Banks group demonstrated for the first time a proof-of-concept for the electroanalytical sensing of Pb by using a novel screen-printed back-to-back microband electroanalytical sensor [52]. An innovative new probe (ISIDORE probe) based on the hyphenation of a Donnan Membrane Technique device (DMT) to a carbon screen-printed electrode through a flow-cell for determination

of the free Zn, Cd and Pb in natural samples was presented by Parat and Pinheiro [53].

4. Approaches in analytical performance improvements

Aside of new sensing materials, analytical performance could also be improved by simple methodological or procedural adjustments. For example, a few papers were recently published describing the benefit of using “ultracathodic” deposition potential. Up to $10\times$ increase of sensitivity was reported by Rodrigues et al. [54] when overpotential deposition was applied on HMDE in conjunction with ASV for determination of Zn, Cd, Pb and Cu. Using only 10 s of deposition, LODs as low as 0.3, 0.6, 1 and 0.5 nM for Zn, Cd, Pb and Cu, respectively were estimated. The same effect was noticed on Au-microwire electrode by Salaün et al. [19] who reported the most sensitive method for Sb(V) determination with LOD of 5 pM after 1 min of accumulation. The procedure was successfully applied for Sb(V) determination in real water samples. The increased sensitivity is ascribed likely to both mercury drop oscillations and added local convection at the mercury surface caused by the evolution of hydrogen bubbles and in case of Au-electrode by combination of migration current contribution, electron transfer rate increase, and catalytic effect during stripping by formed nascent H° . Tests performed in our laboratory with Hg-electrode in acidified MQ water showed that accumulation potential could be lowered far beyond -2 V, leading to a $\sim 70\times$ gain in n-sensitivity (Fig 1E). However, due to the hydrogen evolution, the stability of the Hg drop is compromised which may lead to drop dislodge, especially in natural samples for which strong acidic conditions are required ($pH < 1$). The same approach, depositing beyond the hydrogen wave, was used by Lu et al. [55] in R.G. Compton group for ASV analysis of Sb(V) using an unmodified edge plane pyrolytic graphite (EPPG) electrode. Recently, the same group provided a proof-of-concept technique for sensitivity improvement of ASV. This approach is based on enhanced deposition of metal (illustrated by the detection of Ag in this case) during the accumulation step on pre-created small metal nuclei at the surface of the electrode which act as nucleation sites for subsequent metal deposition [56]. A $40\times$ higher signal at low nM level of Ag was obtained compared to unmodified electrode. An application of Cloud Point Extraction (CPE) in combination with glassy carbon electrode (CPE-GC) was recently for the first time reported by Rusinek et al. [57] on the example of Cd analysis by ASV. A $20\times$ increase of sensitivity compared to ASV without CPE was achieved providing LOD of 1.7 nM, which was sufficient for Cd analysis in tap and river water samples. A novel approach for high-resolution temporal monitoring of trace metals at ppb level using environmentally friendly “green” sensors (Hg-free) was suggested by Hashemi group [58–60]. By combining carbon-fiber microelectrode (CFM; $\sim 7/150$ μm radius/length) and fast-scan deposition-stripping voltammetry (FSDSV; 0.3–1.2 kV/s), the time-resolution (scan to scan) of 100 ms for analysis of Cu and Pb was achieved. The sensing of metals is based on their rapid adsorption onto activated CFM. A further development of the technique is directed towards in-situ application for studies of environmental and biological processes.

Aside of miniaturization of the sensors, working in a small sample volume is desired by some applications. Recently, Monticelli et al. [61] described a modified voltammetric cell characterized by $20\times$ reduction in sample size (from 10 to 0.5 mL) for determination and speciation of metals at ultra-trace level by using conventional voltammetric instrumentation. Using this cell and a new methodology of Fe(III) analysis by AdCSV using oxygen as catalyst (instead of bromate), the LOD as low as 5 pM of Fe(III) for only 30 s of accumulation was achieved [62].

Eventually, sensitivity and reliability of measurements could be significantly improved by mathematical treatment of voltammetric curves [63], as demonstrated by Pt and Rh analysis at pM level [5,64]. As an example, Fig. 1F (top) shows typical voltammograms of Cd and Pb corresponding to their analysis in seawater samples. While peaks

without addition could be hardly distinguished, by using 2nd derivative transformation, well-defined signals for both Cd and Pb appeared (Fig. 1F, bottom), allowing their accurate analysis.

5. Autonomous systems and speciation of trace metals

Due to their portable nature, electrochemical sensors are suitable for measurements at remote location. Despite prominent advantages of electrochemical techniques, publications describing the development of fully equipped autonomous systems are scarce. Few systems were assembled in recent years which were successfully applied for real-time monitoring of trace metals in clean and polluted waters [36, 65–67], demonstrating the advantage of automated systems for monitoring of trace metals temporal variations [66]. The benefit of continuous and remote sensing was recently highlighted by Noyhouzer and Mandler [68] who developed a new electrochemical flow cell as a part of an autonomous flow system for heavy metals analysis in aquatic environments. Zhang et al. [67] presented a fully in-house developed automatic voltammetric system, based on gold-band microelectrode array as a sensor.

While in the majority of applications only simple measurement of total metal concentrations is needed, metal speciation analysis is crucial in studies of bioavailability of trace metals in aquatic environments. Voltammetric methods are still the most utilized for this purpose [2]. Although the use of other electrode types was reported [69], methodology is largely based on Hg electrodes. Methodological progress was mainly directed to updating measurement procedures, as is the case for Fe(III) determination with AdCSV using salicylaldoxime (SA) [70] or 2,3-dihydroxynaphthalene (DHN) [62] as competing ligands, new approaches [71], miniaturization [61] or data treatment tools [72]. Achievements of trace metal speciation are provided in the paper of Pižeta et al. [16], in which results of inter-comparison study were analyzed, methodological approaches summarized and some tips and tricks highlighted.

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