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Review article
Electroanalytical techniques for the quantification of technology-critical elements in environmental samples

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There is an increasing demand for analytical techniques which are able to measure "technology-critical elements", a set of elements increasingly used in technological applications (e.g. Pt-group elements, Nb, Ta, Te, In, Ga, Ge, Tl). For most of these their environmental and toxicological effects are unknown. Recent advances in voltammetric methods for determining these elements in environmental media are reviewed, mainly covering results published in the last decade. Methods ready to be applied, along with others which are promising, though in need of further development, have been critically evaluated and clearly identified. This review is a contribution from the COST Action TD1407: Network on technology-critical elements—from environmental processes to human health threats.

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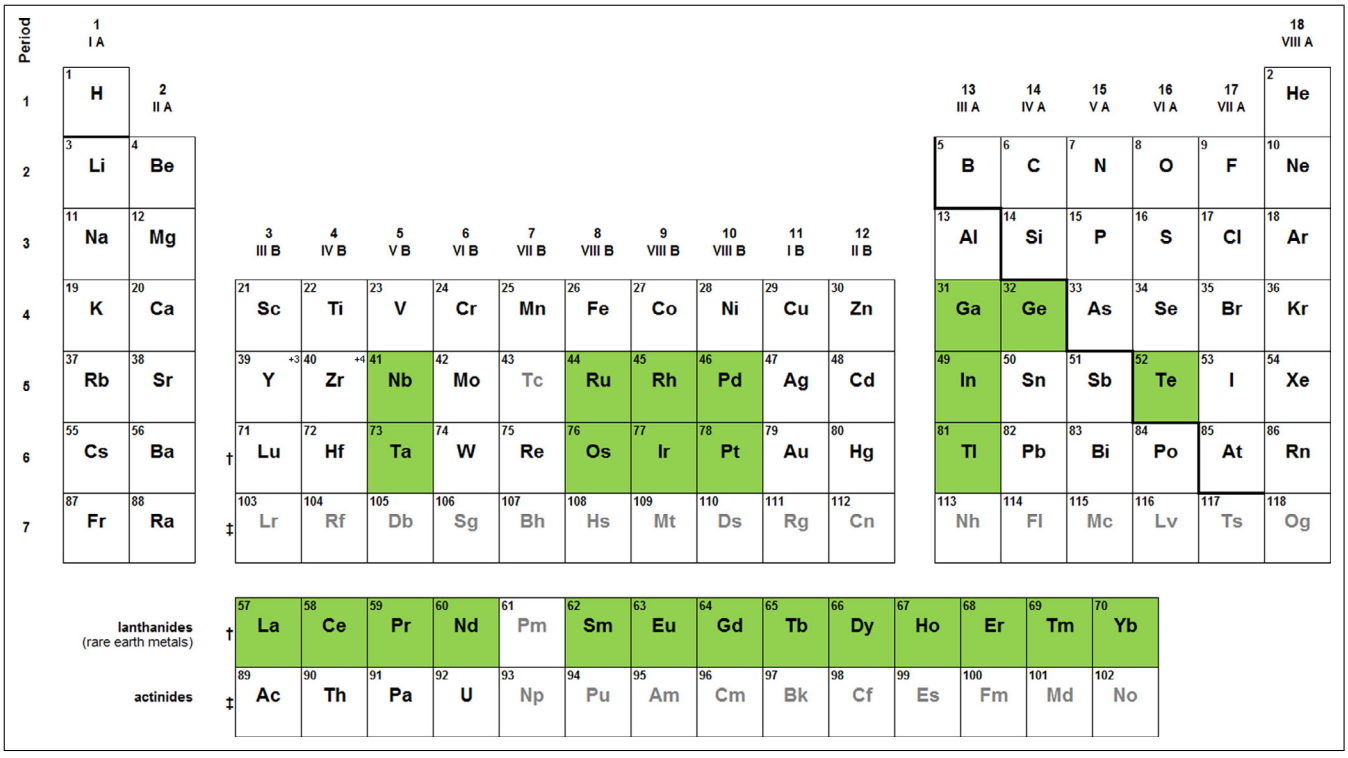
Introduction

The environmental implications and adverse effects on living organisms due to metal contamination are well documented [1] and have led to the development of a range of environmental guidelines, policies and laws (e.g. EU Water Framework Directive; WHO Drinking Water Guidelines) for several of these elements (e.g. As, Cd, Cr, Cu, Hg, Pb). However, there is a range of trace elements (e.g. Pt-group elements, Nb, Ta, Te, In, Ga, Ge, Tl) for which there is still a gap in our knowledge and understanding of their environmental levels and cycling as well as of their potential (eco)toxicological impact [2]. This is mainly explained by two factors: (i) their typical ultra-trace concentrations, making it extremely difficult and/or time-consuming to determine them analytically, and (ii) no significant previous industrial role, thus no apparent environmental implications. This situation is changing rapidly and substantially, since most of these trace elements are now key components in the development of new technologies, including information and telecommunications technology, semiconductors, electronic displays, optic/photonic or energy-related technologies [3]. These elements, labelled as 'technology-critical elements' (TCE), are shown in Figure 1.

Highly sensitive and selective analytical techniques are needed if we are to assess the extent to which these new and expanding technologies may influence the environmental impact of these TCE, which are present at ambient ultra-trace concentrations. The currently available analytical techniques (e.g. ICP-MS) are generally sensitive enough to analyse these elements in solid samples (e.g. sediments/soils and biota), although prior separation/preconcentration procedures sometimes need

Abbreviations: AdsCSV, adsorptive cathodic stripping voltammetry; ACA, *p*-allylcalix[4]arene; AgAuE, Ag–Au alloy electrode; ASV, anodic stripping voltammetry; BiABE, bismuth bulk annular band working electrode; Crown-6-SPCNFE, 4-carboxybenzo-18-crown-6 screen-printed carbon nanofibre-modified electrode; CSV, cathodic stripping voltammetry; CTAB, cetyltrimethylammonium bromide; DCA, 25 27-dimethoxy-26-(*N*-trichloroacetl)carbamoyloxy-*p-tert*-butylcalix[4]arene; DCH-MCPE, dicyclohexyl-18-crown-6 modified carbon paste electrode; DL, detection limit; DMG, dimethylglyoxime; DP, differential pulse; FI, flow injection; GCE, glassy carbon electrode; HMDE, hanging mercury drop electrode; ICP-MS, inductively coupled plasma mass spectrometry; LB_{ACA}-GCE, Langmuir–Blodgett film ACA glassy carbon electrode; LB_{DCA}-GCE, Langmuir–Blodgett film DCA glassy carbon electrode; MFE, mercury film electrode; ND, not detected; NMFE, Nafion mercury film electrode; NMGCE, Nafion-modified glassy carbon electrode; PGE, platinum-group elements; RDBiFE, rotating-disc bismuth film electrode; REE, rare-earth elements; SbFE, antimony film electrode; SbSPCNFE, antimony film screen-printed carbon nanofibre-modified electrode; SnFE, tin film electrode; SPCE/BiF, screen-printed carbon electrode coated with a bismuth film; SW, square wave; TCE, technology-critical elements.

Figure 1



Technology-critical elements considered in this review.

to be applied to eliminate potential interference that may lead to erroneous results (e.g. [4]). The situation is less favourable in waters, where the ultra-low environmental concentrations usually found can be under the detection limits or at concentrations suffering from severe interferences, thus often requiring previous preconcentration steps (e.g. [5]). Here, stripping voltammetry may offer some advantages for several of these elements in certain matrices due to (i) its inherent sensitivity derived from the electrochemical preconcentration of the analyte at the electrode surface, as well as (ii) the ability to discriminate between different redox species and/or labile from non-labile metal complexes, with applications for metal speciation studies [6••].

Here, we critically review the electroanalytical techniques available for analysing TCE in environmental matrices (soils and sediments, biota and waters). Rather than presenting a full list of published methods, we have focused largely on those with a successful track record in analysing real environmental samples. We also discuss methods that offer high capabilities but still require further development. In order to help the reader to evaluate the needs and capabilities of existing methods, a general overview of TCE concentrations in natural media is given in Table 1. Rare-earth elements (REE) have not been included despite being an important group of TCE (Figure 1). Although electroanalytical methods are available for several REE (e.g. La, Ce, Pr, Eu [17–19]), their current capabilities cannot compete with the commonly used ICP-MS technique, mainly because their detection limits are too high, but also because their single-element analysis capabilities are not well adapted to these elements for which most environmental studies require the full range of REE to be analysed.

Platinum-group elements (PGE)

Platinum has been successfully measured in natural waters, biological matrices, soils and sediments, even at ambient background levels (Table 2) using the highly sensitive catalytic method at the HMDE (e.g. [29••]). A similar approach has been employed to determine Rh in sediments, taking advantage of the improved detection obtained with the aid of the second derivative signal transformation of the stripping scans [30]. The low detection limit reported, 0.02 ng L^{-1}, using a relatively short deposition time (120 s), suggests that this method could also be useful in determining this element in natural waters.

The situation is certainly less favourable for Pd, Ir, Os and Ru; despite the availability of electroanalytical pro-