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

COBELO-GARCÍA, Antonio, FILELLA, Montserrat

Abstract

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.

Reference


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Review article

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

Antonio Cobelo-García¹ and Montserrat Filella²,*

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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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-trichloroacetyl)carbamoyloxy-p-tert-butylicalix[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 spectrometer; LBACA-GCE, Langmuir–Blodgett film ACA glassy carbon electrode; LBDA1A-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; RFE, rare-earth elements; SbFE, antimony film electrode; SbSPCNFE, antimony film screen-printed carbon nanofibre-modified electrode; SnFe, tin film electrode; SPCE/AgBiF, screen-printed carbon electrode coated with a bismuth film; SW, square wave; TCE, technology-critical elements.

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 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/photonics and 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...
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-
procedures for detecting them at the ng L\(^{-1}\) or ng g\(^{-1}\) levels, their typical natural background concentrations are generally much lower (Table 1). Accordingly, their concentrations could only be determined in environmental matrices subject to significant contamination (Table 2).

An extremely sensitive technique using an electrochemical sensor based on a reduced graphene oxide film impregnated with Sb nanoparticles for determining Pd, Pt and Rh with detection limits of 0.00045, 0.00049, and 0.00049 ng L\(^{-1}\), respectively, in model solutions has recently been reported [32**]. Such detection limits are a few orders of magnitude lower than the background levels in environmental matrices and therefore could have important applications for the determination of these three elements. However, the authors only checked the applicability of this technique in urban dust samples; therefore, the suitability of this electrochemical sensor for the determination of these elements down to natural levels needs to be checked.

**Thallium**

The determination of Tl(I) can be carried out directly by ASV. Recent studies have mostly focused on the development of Hg-free, environmentally friendly electrodes: Ag–Au alloy electrode [33], BiF [34–36], ShF [37,38], SnF [39], disposable screen-printed electrodes with Bi precursor compounds [40], modified carbon electrodes [41–43], etc. However, all these electrodes have detection limits at the ppb concentration level and, even if authors often claim otherwise, they are not adequate for the analysis of environmental samples. Table 3 (section “ppb detection limit level”) lists some of these studies and shows that applications are for CRM which contains Tl concentrations which are not environmentally realistic, i.e. spiked or extremely polluted samples, etc. Only very few published methods have detection limits at the ppt level (Table 3, section “low ppt detection limit level”). Good detection limits are achieved with a flow injection mode that allows the medium to be exchanged between the deposition and the stripping steps, using a medium which is free from interfering species (EDTA-containing electrolyte) in the stripping stage. Łukaszewski et al. [52] achieved a detection limit of 2 ng L\(^{-1}\) for 90 min preconcentration by applying this approach, and it was subsequently improved to 0.05 ng L\(^{-1}\) with a 60-min deposition time by the same group [49**]. Using a Bi bulk annular band electrode, Wegiel et al. [47] reported a detection limit of 1 ng L\(^{-1}\), which should be enough for Tl(I) measurement in natural waters (Table 1). However, they

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology-critical elements concentrations in natural media.</td>
</tr>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>PGE</td>
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<tr>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
</tbody>
</table>

*a* Ir, Os, Pd, Pt, Ru: [7]; Rh: [8]; Ge, Ge, In, Nb, Ta, Te, Ti: [9].

*b* Values for ‘less-studied’ elements in freshwaters and soils come from FOREGS (Forum of European Geological Surveys) [10]. These values have been preferred over citation of values obtained in studies with a low number of samples and covering more limited geological catchments. Measurements were made by ICP-MS, after filtration (0.45 μm) in the case of freshwaters and total digestion in (<2.0 mm) soils. For PGE in waters, references are from Ir [11], Os [12], Pd [13], Pt [14]; for Rh and Ru, due to the lack of data in stream water, information values from oceanic waters are provided [15,16]. For PGE in soils, a value from a reference site in Austria is given [4].

determinations of Tl(I) can be carried out directly by ASV. Recent studies have mostly focused on the development of Hg-free, environmentally friendly electrodes: Ag–Au alloy electrode [33], BiF [34–36], ShF [37,38], SnF [39], disposable screen-printed electrodes with Bi precursor compounds [40], modified carbon electrodes [41–43], etc. However, all these electrodes have detection limits at the ppb concentration level and, even if authors often claim otherwise, they are not adequate for the analysis of environmental samples. Table 3 (section “ppb detection limit level”) lists some of these studies and shows that applications are for CRM which contains Tl concentrations which are not environmentally realistic, i.e. spiked or extremely polluted samples, etc. Only very few published methods have detection limits at the ppt level (Table 3, section “low ppt detection limit level”). Good detection limits are achieved with a flow injection mode that allows the medium to be exchanged between the deposition and the stripping steps, using a medium which is free from interfering species (EDTA-containing electrolyte) in the stripping stage. Łukaszewski et al. [52] achieved a detection limit of 2 ng L\(^{-1}\) for 90 min preconcentration by applying this approach, and it was subsequently improved to 0.05 ng L\(^{-1}\) with a 60-min deposition time by the same group [49**]. Using a Bi bulk annular band electrode, Wegiel et al. [47] reported a detection limit of 1 ng L\(^{-1}\), which should be enough for Tl(I) measurement in natural waters (Table 1). However, they
Table 2

Published voltammetric methods for the determination of PGE in environmental samples.

<table>
<thead>
<tr>
<th>Method</th>
<th>Complexing ligand (adsorptive methods)</th>
<th>Working electrode</th>
<th>Accuracy test</th>
<th>Detection limit (deposition time)</th>
<th>Sample type</th>
<th>Values obtained</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iridium AdsCSV</td>
<td>CTAB</td>
<td>GCE</td>
<td>PGE ore (MINTEK-SARM 7)</td>
<td>0.6 ng g⁻¹ (420 s)ᵇ</td>
<td>Contaminated (urban) atmospheric particulate matter</td>
<td>&lt;DL-15.3 ng g⁻¹</td>
<td>[20]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>CTAB</td>
<td>GCE</td>
<td>Spiked fresh (NIST-SRM 1643d) and sea water (BCR-CRM 403)</td>
<td>3 ng L⁻¹ (240 s)ᵃ</td>
<td>Contaminated water (urban waters)</td>
<td>&lt;DL-27.5 ng L⁻¹</td>
<td>[21]</td>
</tr>
<tr>
<td>Osmium CSV</td>
<td>HMDE</td>
<td>Spiked olive leaves (BCR-CRM 062) and tomato leaves (NIST-SRM 1573a)</td>
<td>2.5 ng g⁻¹ (210 s)ᵇ</td>
<td>Contaminated (urban) laurel leaves</td>
<td>&lt;DL-23.7 ng g⁻¹</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>CSV</td>
<td>HMDE</td>
<td>PGE ore (MINTEK-SARM 7)</td>
<td>0.6 ng g⁻¹ (300 s)ᵇ</td>
<td>Contaminated (urban) atmospheric particulate matter</td>
<td>&lt;DL-13.6 ng g⁻¹</td>
<td>[23]</td>
<td></td>
</tr>
<tr>
<td>Palladium AdsCSV</td>
<td>DMG</td>
<td>SPCE/BiF</td>
<td>Not tested</td>
<td>8 ng L⁻¹ (180 s)ᶜ</td>
<td>Freshwater close to PGE mining areas</td>
<td>2500–5000 ng L⁻¹</td>
<td>[24]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>DMG</td>
<td>HMDE</td>
<td>Spiked fresh (NIST-SRM 1643d) and sea water (BCR-CRM 403)</td>
<td>11–15 ng L⁻¹ (360 s)ᵃ</td>
<td>Contaminated water (urban waters)</td>
<td>&lt;DL-24 ng L⁻¹</td>
<td>[25]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>DMG</td>
<td>HMDE</td>
<td>Spiked olive leaves (BCR-CRM 062) and tomato leaves (NIST-SRM 1573a)</td>
<td>80–89 ng g⁻¹ (240 s)ᵇ</td>
<td>Contaminated (urban) laurel leaves</td>
<td>&lt;DL-96 ng g⁻¹</td>
<td>[26]</td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>Method</th>
<th>Complexing ligand (adsorptive methods)</th>
<th>Working electrode</th>
<th>Accuracy test</th>
<th>Detection limit (deposition time)</th>
<th>Sample type</th>
<th>Values obtained</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Platinum</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Formazone</td>
<td>HMDE</td>
<td>River sediment (GSJ-JSd2)</td>
<td>0.09 ng g⁻¹ (90 s)</td>
<td>Oysters</td>
<td>0.1–0.7 ng g⁻¹</td>
<td>[27]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Formazone</td>
<td>HMDE</td>
<td>Road dust (BCR-CRM 723)</td>
<td>0.013 ng g⁻¹ (60 s)</td>
<td>Sediments</td>
<td>0.07–40 ng g⁻¹</td>
<td>[28]</td>
</tr>
<tr>
<td>Catalytic</td>
<td>Formazone</td>
<td>HMDE</td>
<td>River (NRC-SLR54), coastal (NRC-CASS4) and oceanic (NRC-NASS5) waters</td>
<td>0.004 ng L⁻¹ (300 s)</td>
<td>Sediments</td>
<td>0.02–2.9 ng L⁻¹</td>
<td>[29**]</td>
</tr>
<tr>
<td><strong>Rhodium</strong></td>
<td></td>
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</tr>
<tr>
<td>Catalytic</td>
<td>Formaldehyde</td>
<td>HMDE</td>
<td>River sediment (GSJ-JSd2) and road dust (BCR-CRM 723)</td>
<td>0.014 ng g⁻¹ (120 s)</td>
<td>Sediments</td>
<td>0.06–0.47 ng g⁻¹</td>
<td>[30]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>DMG</td>
<td>SPCE/BiF</td>
<td>Not tested</td>
<td>5 ng L⁻¹ (180 s)</td>
<td>Freshwater close to PGE mining areas</td>
<td>140–380 ng L⁻¹</td>
<td>[24]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Formaldehyde</td>
<td>HMDE</td>
<td>PGE ore (MINTEK-SARM 7)</td>
<td>0.033 ng g⁻¹ (120 s)</td>
<td>Grass (unpolluted and polluted)</td>
<td>&lt;0.03–2.1 ng g⁻¹</td>
<td>[31]</td>
</tr>
<tr>
<td><strong>Ruthenium</strong></td>
<td></td>
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</tr>
<tr>
<td>CSV</td>
<td>Formaldehyde</td>
<td>HMDE</td>
<td>Spiked olive leaves (BCR-CRM 062) and tomato leaves (NIST-SRM 1573a)</td>
<td>3.7 ng g⁻¹ (210 s)</td>
<td>Contaminated (urban) laurel leaves</td>
<td>&lt;DL-11.3 ng g⁻¹</td>
<td>[22]</td>
</tr>
<tr>
<td>CSV</td>
<td></td>
<td>HMDE</td>
<td>PGE ore (MINTEK-SARM 7)</td>
<td>0.5 ng g⁻¹ (300 s)</td>
<td>Contaminated (urban) atmospheric particulate matter</td>
<td>&lt;DL-7.7 ng g⁻¹</td>
<td>[23]</td>
</tr>
<tr>
<td>CSV</td>
<td></td>
<td>HMDE</td>
<td>Spiked fresh (NIST-SRM 1643d) and sea water (BCR-CRM 403)</td>
<td>11 ng L⁻¹ (300 s)</td>
<td>Contaminated water (urban waters)</td>
<td>&lt;DL-49.6 ng L⁻¹</td>
<td>[21]</td>
</tr>
</tbody>
</table>

* Obtained from the calibration plot in fresh and sea water using the method of standard addition.

* Obtained from the calibration plot in the solid sample digest using the method of standard addition.

* Obtained for MQ water containing the optimised electrolyte conditions.

* Calculated as three times the standard deviation of the results from digestion blanks.
Table 3
Published voltammetric methods for the determination of thallium(I) in environmental samples.

<table>
<thead>
<tr>
<th>Method</th>
<th>Working electrode</th>
<th>Accuracy test</th>
<th>Detection limit (deposition time)</th>
<th>Sample type</th>
<th>Values obtained</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low ppt detection limit level</strong></td>
<td></td>
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</tr>
<tr>
<td>DP ASV</td>
<td>BiABE</td>
<td>Surface water (SPS-SW1, SPS-SW2) CRM</td>
<td>1 ng L⁻¹ (300 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[47]</td>
</tr>
<tr>
<td>ASV (double deposition and stripping)</td>
<td>2 BiFE</td>
<td>Spiked natural waters</td>
<td>4.3 ng L⁻¹ (2 × 300 s)</td>
<td>Lake water</td>
<td>ND</td>
<td>[48]</td>
</tr>
<tr>
<td>FI DP ASV</td>
<td>MFE</td>
<td>Soil (GBW 07401) CRM</td>
<td>0.05 ng L⁻¹ (3600 s)</td>
<td>Water extract of soil</td>
<td>0.21 ng L⁻¹</td>
<td>[49**]</td>
</tr>
<tr>
<td>SW ASV</td>
<td>Graphite µ electrode</td>
<td>Spiked synthetic samples</td>
<td>10 ng L⁻¹ (300 s)</td>
<td>Ground water</td>
<td>430 ng L⁻¹</td>
<td>[50]</td>
</tr>
<tr>
<td>SW ASV</td>
<td>NMFE</td>
<td>Spiked natural waters</td>
<td>10 ng L⁻¹ (300 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[51]</td>
</tr>
<tr>
<td>FI DP ASV</td>
<td>MFE</td>
<td>Spiked synthetic and real water samples</td>
<td>2 ng L⁻¹ (5400 s)</td>
<td>Tap water</td>
<td>5–2040 ng L⁻¹</td>
<td>[52]</td>
</tr>
<tr>
<td><strong>ppb detection limit level</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DP ASV</td>
<td>Ex situ-SbSPCNFE + crown-6-SPCNFE</td>
<td>Spiked tap water</td>
<td>8.6 µg L⁻¹ (120 s)</td>
<td>-</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>SW ASV</td>
<td>SnFE</td>
<td>Lake water (TM-24.3) CRM</td>
<td>1.1 µg L⁻¹ (240 s)</td>
<td>-</td>
<td>-</td>
<td>[39]</td>
</tr>
<tr>
<td>DP ASV</td>
<td>Screen printed:</td>
<td>Lake water (TM-23.3) CRM</td>
<td></td>
<td></td>
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<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Bi aluminate</td>
<td></td>
<td>1.0 µg L⁻¹ (120 s)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Bi oxide</td>
<td></td>
<td>0.9 µg L⁻¹ (120 s)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Bi zirconate</td>
<td></td>
<td>1.1 µg L⁻¹ (120 s)</td>
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</tr>
</tbody>
</table>

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Table 3 (continued)

<table>
<thead>
<tr>
<th>Method</th>
<th>Working electrode</th>
<th>Accuracy test</th>
<th>Detection limit(^a) (deposition time)</th>
<th>Sample type</th>
<th>Values obtained</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP ASV</td>
<td>DHC-MCPE</td>
<td>Freshwater (SRM 1643d)</td>
<td>0.860 µg L(^{-1}) (300 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CRM</td>
<td></td>
<td>Well water</td>
<td>ND</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Waste water</td>
<td>4.2 µg L(^{-1})</td>
<td></td>
</tr>
<tr>
<td>SW ASV</td>
<td>LB(_{DCA})-GCE</td>
<td>Spiked samples</td>
<td>4 µg L(^{-1}) (90 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lake water</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>SW ASV</td>
<td>RDBiFE</td>
<td>Not tested</td>
<td>2.2 µg L(^{-1}) (120 s)</td>
<td>Polluted river water</td>
<td>2.2 µg L(^{-1})</td>
<td>[35]</td>
</tr>
<tr>
<td>ASV</td>
<td>MFE</td>
<td>Spiked samples</td>
<td>0.7 µg L(^{-1}) (60 s)</td>
<td>Soil sample</td>
<td>15.0 ng g(^{-1})</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>BiFE</td>
<td></td>
<td></td>
<td>Seawater</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hydrothermal fluid</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>Flow-ASV</td>
<td>BiFE</td>
<td>Rain water (TMRAIN-95)</td>
<td>0.12 µg L(^{-1}) (300 s)</td>
<td>-</td>
<td>-</td>
<td>[36]</td>
</tr>
<tr>
<td>SW ASV</td>
<td>AgAuE</td>
<td>Not tested</td>
<td>1.4 µg L(^{-1}) (400 s)</td>
<td>Polluted moss</td>
<td>2.85 µg g(^{-1})</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom sediment</td>
<td>15.1 µg g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>DP ASV</td>
<td>LB(_{DCA})-GCE</td>
<td>Spiked samples</td>
<td>1.0 µg L(^{-1}) (150 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lake water</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>DP ASV</td>
<td>HMDE</td>
<td>Water (TMDA-54.3) and cabbage (BCR 679) CRM</td>
<td>0.7 µg L(^{-1}) (400–600 s)</td>
<td>Sewage water</td>
<td>2.03, 2.45 µg L(^{-1})</td>
<td>[45,46]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Polluted sediments</td>
<td>0.41–15.3 µg g(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Limit of detection values are not always comparable because different definitions are used. All studies use the signal-to-noise approach with S/N = 3, except [39,43] (LOD = 3 \(\sigma_b / b\) where \(\sigma_b\) is the standard deviation of the intercept and \(b\) the slope of the calibration plot), [43] (as before but with \(\sigma_b\) the standard deviation of the mean value of the current of the blank) and [50] (IUPAC upper limit approach).
were not able to detect Tl in tap or river water, only in certified surface waters with concentrations of 0.5 and 2.5 μg L⁻¹ (i.e. well above natural levels).

‘Less-studied’ TCE
Published studied are gathered in Table 4 and typical environmental levels are found in Table 1.

**Gallium.** Piech twice reported a similar method for determining Ga (as its catechol complex) using a mercury film silver-based electrode with detection limits of 7 and 25 ng L⁻¹ [55,56]. In the more recent of these studies, the method allowed for simultaneous determination of Ge. The method was applied to tap and river waters as well as to soil and sediment samples. Ga in food samples (at the 120–150 ng g⁻¹ level) were determined using cathodic adsorptive voltammetry of the Ga-Alizarin Red S complex at a carbon paste electrode with a detection limit of 10 ng L⁻¹ [65]. This low detection limit looks promising for the applicability of the method to environmental samples. Grabarczyk and co-workers have recently developed adsorptive methods for Ga determination with cupferron as the complexing agent and using different electrodes: HMDE [54], *in situ* plated Pb film [66] and Bi film [53] electrodes. The detection limit of the method using PbFe was disappointing (265 ng L⁻¹) but the other electrodes gave much better limits: 9 ng L⁻¹ (HMDE) and 7 ng L⁻¹ (BiFe). In spite of this, measurements were only possible in spiked freshwater samples [54] and in “strengthened” certificate reference material seawater (NASS-S) [53].

**Germanium.** A sensitive procedure for determining Ge is attained by means of adsorptive catalytic CSV at the HMDE in the presence of V(IV) and 3,4,5-trihydroxybenzoic acid (gallic acid) or 3,4-dihydroxybenzaldehyde (DHB) with detection limits as low as 1.4 [57**] and 3.6 ng L⁻¹ [67], respectively. These methods were successfully applied for the determination of Ge in ore and vegetable samples [57**],67 as well as in one mineral water sample [67]. Both methods look suitable for environmental measurements. Piech reported a method for the simultaneous determination of Ga and Ge (as their complexes with catechol) in the same scan using a mercury film silver-based electrode [55] but the detection limit for Ge (58 ng L⁻¹) is much less satisfactory than that of the abovementioned methods. Catalytic amplification of the reduction current appears to be needed to obtain low enough Ge detection limits [57**],67. A series of potential oxidants (bromate, chlorate, hydrogen peroxide, V(V), V(IV) and nitrite) were tested by Li and co-workers [57**], with V(IV)-EDTA giving the best results.

**Indium.** A number of methods have been proposed for voltammetric determination of In [68] but their detection limits are mostly largely outside the values needed to determine this element in environmental samples. Even methods that claim to be able to measure In in natural waters (Table 4) show detection limits in the range 13–19 ng L⁻¹, which are higher than expected environmental concentrations in waters (Table 1). Accordingly, these studies could only detect In in spiked samples. Some older adsorptive methods not intended to be applied to environmental samples but with relatively low detection limits (17 ng L⁻¹ with oxine, [69]; 50 ng L⁻¹ with morin, [70]) probably deserve to be explored further together with some methods in Table 4. It should be mentioned that the lowest detection limit reported for In (0.5 ng L⁻¹) remains the one obtained more than 40 years ago with a MFE by Florence and co-workers [71]; the method included previous separation of In from Pb and Cd by coprecipitation on ferric hydroxide and separation by ion exchange chromatography from HCl solutions before measurements were taken.

**Niobium, tantalum.** A few voltammetric methods for Nb have been published [72], mostly in difficult to access old Chinese journals (referred in the Chemical Abstracts) but none seem to have been applied to real natural samples. Nevertheless, these studies might be a useful starting point for developing new adsorptive methods for the element. The numerous colorimetric methods developed in the past for Nb and Ta [73] are another source of potentially interesting ligands.

**Tellurium.** This element is present in natural systems in the IV and VI oxidation states. The reduction of Te(VI) in an acidic medium involves a proton catalytic reduction, which has been used for the analytical determination of this element. Accordingly, Biver et al. [6**] reported a limit of detection of about 5 ng L⁻¹ in natural waters by means of catalytic CSV at the HMDE; such a low detection limit allowed Te to be determined in mineral, river and coastal sea waters at ambient levels [6**]. Using a similar approach, Ferri et al. [64] were able to determine Te in geochemical materials down to 5 ng g⁻¹. Since only Te(VI) is electroactive, special care must be taken during the reduction step of Te(VI) to Te(VI) when total Te is to be determined, but this opens the possibility for the determination of Te speciation [6**],64.

**Summary**
Accurate measurement of TCE concentrations in environmental samples using the current mainstream technique (ICP-MS) is far from as straightforward as generally perceived because of the presence of significant isobaric and polyatomic interferences for several of these elements (e.g. Ga, Ge, In, Pd, Rh, Te) and/or insufficient detection limits (e.g. Ge, In, Rh, Nb, Ta, Te). With lower running costs, speciation capabilities and the potential for *in situ* method development for all TCEs (with the exception of REE), electroanalytical techniques are a competi-
Table 4
Published voltammetric methods for the determination of ‘less-studied’ TCE in environmental samples.

<table>
<thead>
<tr>
<th>Method</th>
<th>Complexing ligand (adsorptive methods)</th>
<th>Working electrode</th>
<th>Accuracy test</th>
<th>Detection limit(^a) (deposition time)</th>
<th>Sample type</th>
<th>Values obtained</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td></td>
<td></td>
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<tr>
<td>AdsCSV</td>
<td>Cupferron</td>
<td>In situ plated BiFE</td>
<td>‘Strengthened’ seawater (NASS-5) CRM</td>
<td>7 ng L(^{-1}) (180 s)</td>
<td>-</td>
<td>-</td>
<td>[53]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Cupferron</td>
<td>HMDE</td>
<td>Spiked natural water</td>
<td>9 ng L(^{-1}) (30 s)</td>
<td>River water</td>
<td>ND</td>
<td>[54]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Catechol</td>
<td>MFE</td>
<td>Spiked water and soil samples</td>
<td>25 ng L(^{-1}) (60 s)</td>
<td>Tap water</td>
<td>15.2 µg L(^{-1})</td>
<td>[55]</td>
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<td></td>
</tr>
<tr>
<td>Germanium</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Catechol</td>
<td>MFE</td>
<td>Spiked natural water</td>
<td>7 ng L(^{-1}) (90 s)</td>
<td>Tap water</td>
<td>71, 83 ng L(^{-1})</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>20.9 µg L(^{-1})</td>
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<tr>
<td>Indium</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Catalytic AdsCSV</td>
<td>Gallic acid</td>
<td>HMDE</td>
<td>Certified ore</td>
<td>1.4 ng L(^{-1}) (120 s)</td>
<td>Mineral water</td>
<td>82 ng L(^{-1})</td>
<td>[57**]</td>
</tr>
<tr>
<td>SW ASV (double deposition and stripping)</td>
<td></td>
<td>2 BiFE</td>
<td>Spiked natural water</td>
<td>17 ng L(^{-1}) (2 × 300 s)</td>
<td>River water</td>
<td>ND</td>
<td>[58]</td>
</tr>
<tr>
<td>Method</td>
<td>Complexing ligand (adsorptive methods)</td>
<td>Working electrode</td>
<td>Accuracy test</td>
<td>Detection limit&lt;sup&gt;a&lt;/sup&gt; (deposition time)</td>
<td>Sample type</td>
<td>Values obtained</td>
<td>References</td>
</tr>
<tr>
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</tr>
<tr>
<td>AdsCSV</td>
<td>Cupferron</td>
<td>In situ plated PbFE</td>
<td>Spiked natural water</td>
<td>19 ng L&lt;sup&gt;−1&lt;/sup&gt; (60 s)</td>
<td>Lake water</td>
<td>ND</td>
<td>[59]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Cupferron</td>
<td>MFE</td>
<td>'Strengthened' wastewater (SPS-WW1) and surface water (SPS-SW-1) CRM</td>
<td>17 ng L&lt;sup&gt;−1&lt;/sup&gt; (30 s)</td>
<td>River water</td>
<td>ND</td>
<td>[60]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Cupferron</td>
<td>In situ plated BiFE</td>
<td>Spiked natural water</td>
<td>96 ng L&lt;sup&gt;−1&lt;/sup&gt; (90 s)</td>
<td>Lake water</td>
<td>ND</td>
<td>[61]</td>
</tr>
<tr>
<td>AdsCSV</td>
<td>Xylenol orange</td>
<td>HMDE</td>
<td>Spiked natural water</td>
<td>13 ng L&lt;sup&gt;−1&lt;/sup&gt; (300 s)</td>
<td>Well water</td>
<td>ND</td>
<td>[62]</td>
</tr>
<tr>
<td>ASV</td>
<td>-</td>
<td>NMGCE</td>
<td>Spiked natural water</td>
<td>86 ng L&lt;sup&gt;−1&lt;/sup&gt; (120 s)</td>
<td>Tap water</td>
<td>ND</td>
<td>[63]</td>
</tr>
<tr>
<td>Tellurium</td>
<td>Catalytic CSV</td>
<td>HMDE</td>
<td>Comparison with published values</td>
<td>5 ng L&lt;sup&gt;−1&lt;/sup&gt; (300 s)</td>
<td>River water</td>
<td>10-44 ng L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[6**]</td>
</tr>
<tr>
<td>DP CSV&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>HMDE</td>
<td>NIST SRM 2709 (soil), 1649a (sediment); USGS GRX 1 to 6 CRM</td>
<td>Not provided</td>
<td>Tap water</td>
<td>6.1 µg L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[64]</td>
</tr>
</tbody>
</table>

<sup>a</sup> Limit of detection values are not always comparable because different definitions are used. All studies use the signal-to-noise approach with S/N = 3, except [62] (S/N = 2). [58] (LOD = 3 σ<sub>B</sub>/b where σ<sub>B</sub> is the standard deviation for a low In(III) concentration and b is the slope of the calibration plot) and [6**] (alternative method based on evaluating σ<sub>B</sub> from the variance of the regression residuals of a set of calibration data).

<sup>b</sup> Samples filtered with filter paper, preconcentrated by boiling, heated to dryness with H<sub>2</sub>SO<sub>4</sub> to destroy organic matter.

<sup>c</sup> The method includes preconcentration with a chelating resin (Fe(III) loaded).
tive alternative to ICP-MS. At present, methods with adequate characteristics exist for determining environmental concentrations of Ga, Ge, Pt, Rh, Te and Tl in solid matrices requiring sample mineralisation. In waters, ready to use methods capable of measuring low, natural concentrations are available for Ge, Pt, Te and Tl. For Ru, Os and Ir, available methods are only capable of measuring contaminated (solid and water) samples with high concentrations. In the case of Ga and Rh, the existing analytical procedures for successfully determining them in solid sample digests appear to have the potential to be extended to their determination in natural waters. Further development is especially demanding in the case of In, Nb and Ta, where basically no electroanalytical methodologies are available (Nb, Ta) or the existing methods are not sensitive enough and are only applicable at elevated concentrations (In).

Acknowledgement

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- Paper of special interest
- Paper of outstanding interest


Dissolved Te and its redox speciation (IV and VI) is determined in natural waters at natural concentrations by means of cathalytic CSV, providing better sensitivity than other analytical techniques. The study includes a detailed study of reduction methods and a working scheme for analysis in hard waters and in the presence of natural organic matter.


The authors demonstrate that the use of signal transformation (e.g. second derivative) can significantly improve the quantification of ill-defined peaks leading to more sensitive and accurate measurements, as exemplified by the determination of Pt in waters and solid sample digests.


An electrochemical sensor based on a reduced graphene oxide film impregnated with antimony nanoparticles was developed, achieving extremely high sensitivities for Pt, Pd and Rh at the sub-ppb L^−1 level, showing promising capabilities for the determination of PGE in environmental samples.


Thallium was determined at the pM level in water extracts of soil samples by means of anodic stripping voltammetry using a flow injection device using a long accumulation time of 1 h.


A highly sensitive catalytic adsorptive cathodic stripping voltammetry determination of Ge in the presence of gallic acid, with a detection limit of 1.4 ng L\(^−1\) was optimized and shown to be applicable for the determination of this element in natural waters.


