

Foreword: voltammetry in environmental chemistry

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Voltammetry has been a key tool in the development of the field of analytical chemistry and subsequently environmental chemistry. Voltammetry's genesis was from the fundamental electrochemical works of Humphry Davy, Michael Faraday, Hermann Helmholtz and Walther Nernst among others, but its real application to chemistry was with the invention of polarography in 1922 by Jaroslav Heyrovský, for which he received the Nobel Prize in Chemistry in 1959^[1] (For a complete historical and future perspective on polarography see the recent articles by Michael Heyrovský.^[2,3]) As polarography progressed under Heyrovský's tutelage it also saw the first application of the method of standard additions by Hans Hohn,^[4] a technique that is now common place in a wide range of analytical techniques.^[5] A further critical development in polarography came with the invention of the hanging mercury drop electrode (HMDE) by Wiktor Kemula.^[6] The significance of polarography as an analytical tool was seized upon by the outstanding analytical chemist Izaak Kolthoff^[7] who along with his students, most notably James Lingane^[8] and Herbert Laitinen,^[9] developed the background theory and first methods for use in environmental trace metal analysis and biological sensors.^[10–12]

Advances in solid state electronics during the 1950s and 60s saw the development of cheaper and more robust voltammetric systems, and alongside this was the development of new pulse polarography techniques^[13] leading to more sensitive analysis for many analytes. The high ionic strength of seawater lends itself to voltammetric methods and the first applications of voltammetry to seawater chemistry began with the work of Marko Branica and colleagues at the Rudjer Bošković Insitute in the late 60s and 70s, to assess metal speciation in seawater.^[14–16] At the same time, in Australia, Mark Florence and Graham Batley began to link their speciation work in seawater with trace metal bioavailability^[17–20] helping to develop the free ion association model.^[21] From the early 80s, further new developments in electronics improved significantly the electrochemical systems and they were applied to sediment porewaters and in coastal and open ocean waters for speciation for the first time; efforts spearheaded most notably by Ken Bruland,^[22–25] Stan Van Den Berg^[26–31] and George Luther.^[32–35] Freshwater studies also benefited from the application of electrochemical approaches during the same period particularly through the works of the groups of Jacques Buffle^[36–40] and Bill Davison.^[41–44] The application of voltammetry to oceanographic and freshwater studies has led to a better understanding of the distribution, speciation and biogeochemical cycling of

trace elements in the global environment and has played a large part in the subsequent development of environmental chemistry.

However, the routine application of these methods to seawater analysis came too late to play a role in the first major geochemical and biogeochemical investigations of the oceans (e.g. GEOSECS 1973–76^[45]). Subsequently though the use of voltammetric techniques in international oceanographic programs has steadily increased since the 80s with involvement in JGOFS (www.who1.edu), SOLAS (www.solas-int.org), IMBER (www.imber.info) and GEOTRACES (www.geotraces.org, all websites last accessed 14 April 2014). Although other techniques (e.g. flow injection, mass spectrometry) are increasingly becoming more predominant for trace metal analysis in seawater, voltammetric methods are still playing a significant role, most importantly in speciation studies.

This Research Front grew out of a COST Action (www.cost.eu) ES801 workshop on 'Voltammetry and GEOTRACES' held at the Rudjer Bošković Insitute in Šibenik, Croatia, during 6–9 October 2012. The aim of the meeting was to critically discuss the role of voltammetric techniques for today's chemical oceanography and especially in the current international GEOTRACES program.^[46] Special attention was paid to new advances in voltammetry (e.g. new types of sensors, green chemistry, improvements in analytical and modelling trace metal speciation by voltammetry) valuable for the scientific community working under the GEOTRACES program, but not solely limited to seawater applications.

This Research Front features 11 contributions examining a wide range of modern topics in environmental chemistry illustrating the applicability and adaptability of electrochemical methods.

Three papers deal with the determination of complexation parameters in natural waters, a research theme that voltammetry has traditionally held all on its own among analytical techniques. Murray et al.^[47] present data for Cu, Zn, Pb and Cd complexation for a near-pristine estuarine system in Ireland and in a complementary study provide evidence that macroalgae are also sources of Cu and Zn complexing ligands.^[48] The third paper on this theme, by Gerringa et al.,^[49] provides a valuable assessment of the steps involved in the calculation of Fe binding ligands in seawater and provides a framework for improving this type of analysis. A related work on Pb speciation in seawater by Diaz-De-Alba et al.^[50] applies two newer voltammetric techniques: (i) absence of gradients and Nernstian equilibrium stripping (AGNES) and (ii) stripping

chronopotentiometry at scanned deposition potential (SSCP). A new aspect of voltammetric work is the use of non-Hg based electrode systems for speciation analysis and the work in this issue using a rotating Bismuth film electrode with scanned stripping potentiometry by Pinheiro et al.^[51] is an important link in the development and application of new 'green' chemistry approaches to electrochemistry. Chronopotentiometry is also employed in the work of Strmečki et al.,^[52] who used a constant current chronopotentiometry stripping approach to characterisation organic matter in seawater from the Adriatic. The complex story behind the deposition of metal sulfides at the Hg electrode in seawater is investigated by Milanović et al.^[53] and they provide new insights into the experimental design of such work in order to avoid artefacts in interpreting the bulk solution composition related to the surface formation of metal sulfides. A novel new application for voltammetry is reported by Penenzič et al.,^[54] who developed a wafer based device with flow through chip-based mercury (Hg) microelectrode coated with a phospholipid-triglyceride mixed layer that allowed determination of PAHs (anthracene, phenanthrene, pyrene and fluoranthene) using rapid cyclic voltammetry.

Another key theme in this issue is the application of voltammetric methods to the determination of nanoparticles in the environment. Two papers present work on the development of electrochemical techniques to determine nanoparticles in the environment. In the first of these works, Marguš et al.,^[55] present results from a combined voltammetry and in situ electrochemical scanning tunnelling microscopy (EC-STM) study of FeS in NaCl and find that a Gold electrode shows promise for this approach. In the 2nd part of their investigation of FeS in NaCl, Bura-Nakić et al.,^[56] use a chronoamperometric approach show that the observed reduction current transients appear to be related to the size of the FeS nanoparticles and is consistent with parallel dynamic light scattering (DLS) measurements, opening up the potential use of electrodes for particle sizing. The third paper under the nanoparticles umbrella by Town and van Leeuwen,^[57] is an important contribution providing a theoretical framework for interpretation of the labilities of nanoparticle metal complexes as they pertain to electrochemical techniques. This work helps fill an important conceptual gap in linking theory to observations and show the importance of kinetics in the analysis of nanoparticles.

This collection of papers highlights the role voltammetry, and electrochemical methods in general, have in driving new avenues of research in environmental chemistry in the modern era and the future. The traditional strengths of voltammetry are still there, most notably in the pursuit of speciation and kinetic information from natural and polluted waters. However new technology and methods are being continually developed, as shown here, and are opening up new avenues into non-traditional and emerging fields of research such as nanoparticles and organic pollutants. It looks as if voltammetry will remain a vital piece of the environmental chemist's toolbox for some time to come.

I would very much like to thank all the authors contributing to this special issue – their dedication to expanding the frontiers of electrochemical methods to new applications in environmental chemistry has led to this collection of high quality papers which it has been my pleasure to edit. Last, but by no means least, the timely and constructive help of the electrochemical and environmental chemistry communities for reviewing these papers is warmly acknowledged.

Peter Croot, Editor

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