

[OP 1.5]**Determination of Arsenic (III) and Arsenic (V) in Natural Waters by Cathodic Stripping Voltammetry at a Hanging Mercury Drop Electrode**Aquilas A. Barros¹ and M. Adelaide Ferreira²¹ Centro de Investigação em Química U. P., Departamento de Química da Faculdade de Ciências do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal; e-mail: ajbarros@fc.up.pt² Laboratório do Instituto Geológico Mineiro, Rua da Amieira, 4465 S. Mamede de Infesta Codex, Portugal; e-mail: maria.adelaide@igm.pt

In this work, arsenic(III) and arsenic(V) are determined in natural waters by cathodic stripping voltammetry using a hanging mercury drop electrode (HMDE). The method requires the presence of copper(II), as it involves a pre-concentration step of a copper-arsenic intermetallic compound at the mercury electrode [1].

Generally, the methods proposed for the determination of both arsenic(III) and arsenic(V) consist of the determination of the first compound, followed by reduction of arsenic(V) to arsenic(III), and determination of total arsenic; arsenic(V) is obtained by determining the difference. The problem is that, although several methods have been proposed for the reduction [2,3,4], none of them was able to produce acceptable results. In this work, a new method is proposed involving the reduction of arsenic(V) with thiosulfate and the subsequent determination of the arsenic(III) formed; due to the presence of the reductant, the voltammetric conditions for the determination of arsenic(III) had to be modified, with a much higher amount of copper ion being required for the formation of the copper-arsenic intermetallic compound. The method is simple,

with no need for the elimination of the excess of a reductant, and has proved to be reliable.

Detection limits of 0.4 ppb for arsenic(III) and of 2 ppb for arsenic(V) were obtained in simple water solutions. No interference was observed for a great number of ions: Ca²⁺, Mg²⁺, Ba²⁺, Na⁺, K⁺, Li⁺, Si⁴⁺, Fe²⁺, Mn²⁺, Sr²⁺, NH⁴⁺, SO₄²⁻, F⁻, Cl⁻, Br⁻, PO₄³⁻, HCO₃⁻, Be²⁺, Cr³⁺, Co²⁺, Al³⁺, Ge⁴⁺, Pb²⁺, Sn⁴⁺. Severe interference was observed for the ions Se⁴⁺, Bi³⁺, Sb³⁺, S²⁻. Interference of Cd²⁺, Fe³⁺, Zn²⁺, NO₂⁻ and NO₃⁻ is important too, but only for concentrations that are not expected in spring and mineral waters. The method was used in the determination of arsenic(III) and arsenic(V) in several spring and mineral waters and the value for total arsenic correlated well with that obtained by EE-ICP with hydride generation.

[1] LI, H.; SMART, R.B. (1996): *Anal. Chim. Acta* **325**, 25[2] TRIBALAT, S. (1947): *Anal. Chim. Acta* **I**, 149[3] HENRY, F.T.; THORE, T.M. (1979): *Anal. Chem.* **51/2**, 215[4] KOTOUCEK, M.; VASICOVA, J.; RUZICKA, J. (1993): *Mikrochim. Acta* **111**, 55**[OP 1.6]****Factors that Influence the Rate and Extent of the Seawater Solubility of Aerosol Associated Trace Metals (Cu, Pb and Zn); Impact on Their Seawater Speciation**Angela Medway^{1*}, Malcolm Nimmo¹, Martha Gledhill¹, Eric Achterberg¹ and Roy Chester²¹ Dept. of Environmental Sciences, University of Plymouth, Plymouth PL4 8AA UK; * e-mail: amedway@plymouth.ac.uk² Oceanography Laboratories, Dept. of Earth Sciences, University of Liverpool L69 3BX UK

Recent recognition of the importance of micronutrient trace metal inputs in oceanic biogeochemical cycling, and of the importance of atmospheric trace metal inputs to marine waters, highlights the need to assess potentially bioavailable trace metal inputs from atmospheric sources. No study has extensively investigated the factors that influence the seawater solubility of aerosol associated trace metals (particle concentrations, temperature, seawater dissolved organic ligands, light intensity and aerosol type). Therefore, a novel experimental system has been developed to determine fast resolution kinetics of the dissolution of trace metals (Cu, Pb and Zn) from aerosol material in seawater, at environmentally realistic concentrations (50 and 300 mg l⁻¹), under controlled experimental conditions. Labile and total dissolved Cu were determined by adsorptive cathodic stripping voltammetry, with a flow cell every 30 s. The specia-

tion of Pb and Zn were simultaneously measured every 70 s during the experimental run.

The fast resolution kinetic studies provide data on the rate constants under different experimental conditions, hence the mechanisms of the dissolution of trace metals from end member aerosols in seawater. A conceptual model will be presented to aid the understanding of the effects of different factors on the extent and rate of the dissolution of trace metals from aerosol material in seawater. In future work, this model will be verified and modified using 'real' environmental samples collected from Eastern Mediterranean and UK coastal sites. Also there will be an investigation of the influence of factors on the extent and rate of the dissolution of different Fe species, associated with end member aerosols in seawater.