## Which is the best approach for on site trace metal speciation determination?

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Knowledge of the speciation of metals, especially of the free metal ion concentration, is essential to understand the fate of these elements in rivers and their effects on living organisms. The analytical challenge is to develop a reliable technique for on site determination of trace metal speciation in natural waters. In this context, electrochemical devices have the advantage of being easily available in small sizes and being battery operated. Consequently, two approaches based on electrochemical sensors have been carried out. The first one is a direct on site electrochemical stripping speciation method called AGNES (Absence Gradient Nernstian equilibrium stripping), developed and optimised for trace metal speciation analysis in natural freshwater [1]. The second method, called ISIDORE, consists in an *in situ* probe (Figure 1), based on the hyphenation of a passive sensor, the Donnan Membrane Technique device (DMT) with an electrochemical sensor, a screen-printed electrode [2].

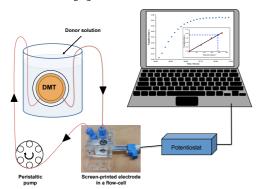


Figure 1: ISIDORE Probe

For each method, the effects of environmental conditions (ionic strength,  $O_2$ ) and the required parameters have been studied in synthetic solutions before being tested in natural freshwaters. Results appeared in good agreement with theoretical estimations computed from Visual Minteq. The ionic strength has emerged as the most important parameter to take into account for on site analyses by means of AGNES method. ISIDORE probe appeared more robust but requires a much longer conditioning and analysis time.

## References

[1] C. Parat, L. Authier, A. Castetbon, D. Aguilar, E. Companys, J. Puy, J. Galceran, M. Potin-Gautier, Free  $Zn^{2+}$  determination in natural freshwater of the Pyrenees: towards on-site measurements with AGNES, Environmental Chemistry, 12 (2015) 329-337.

[2] C. Parat, J.P. Pinheiro, ISIDORE, a probe for in situ trace metal speciation based on Donnan membrane technique with related electrochemical detection part 1: Equilibrium measurements, Analytica Chimica Acta, 896 (2015) 1-10.

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