

PSEUDOPOLAROGRAPHY AS A TOOL FOR COMPLEXATION STUDIES OF TRACE METALS WITH DISSOLVED NATURAL ORGANIC MATTER

Y. Louis¹*, P. Cmuk², R. Nicolau¹, D. Omanović², V. Lenoble¹, I. Pižeta², S. Mounier¹

¹ Laboratoire des PROcessus de Transferts et d'Echanges dans l'Environnement (PROTEE- équipe CAPTE) Université du Sud Toulon Var, BP 20132, 83957 La Garde cedex, FRANCE - louis@univ-tln.fr

² Center for Marine and Environmental Research, Ruder Bošković Institute, POB 180, 10002 Zagreb, CROATIA

Abstract

The potentialities of pseudopolarographic approach regarding trace metal speciation were explored. Recorded pseudopolarogram of a particular metal serves as a fingerprint of the analyzed sample. It gives initial information related to qualitative and quantitative purpose: a first approximation of trace metal distribution with respect to labile and inert metal complexes and the strength of inert metal complexes present in natural sample. Several model electrolyte solutions and natural estuary/seawater samples containing different quantity of Dissolved Natural Organic Matter (DNOM) were used in this study. In addition, Differential Pulse Anodic Stripping Voltammetry (DPASV) measurements were carried out with logarithmic additions to reach information about DNOM complexing capacities and stability constants.

Keywords : Chemical Speciation, Organic Matter, Electrochemistry, Trace Elements, Metals.

Complexation of trace metals in natural waters by natural organic matter and inorganic ligands i.e. their chemical speciation, determines their mobility and bioavailability. NOM is ubiquitous in the environment and consists of a complex mixture [1]. It is known to play important roles in the fate of many contaminants due to its complexing properties. A better determination of NOM structural and functional properties can greatly improve our understanding of the underlying mechanisms responsible for heavy metals complexation.

Among the techniques allowing trace metal speciation in natural waters, voltammetry is appropriate because it offers high sensitivity, enough selectivity and ability for direct measurement with minimally disturbing of the original sample. Obtained voltammetric data are related to the physico-chemical characteristics of the electroactive metal species, and information on speciation parameters of the investigated metal could be obtained.

In this study, the ability of pseudopolarographic approach to trace metal speciation is investigated [2, 3]. Pseudopolarogram represents a series of anodic stripping voltammetric (ASV) peak current values plotted as a function of deposition potential (Fig. 1). As in classical polarography, the parameters extracted from the pseudopolarograms are half-wave potential and limiting current. The reduction half-wave potentials of inert metal complexes are separated from the reduction potential of free and labile metal complexes and are shifted towards more negative values. The amount of these shifts is the basis for the determination of the type of inert metal complexes in natural waters, because they depend on their stability constant [4]. In addition to this direct speciation mode, pseudopolarography is used to optimise a choice of accumulation/deposition potential where only free/labile metal is reduced which is a prerequisite for the procedure of metal complexing capacity (MCC) determination.

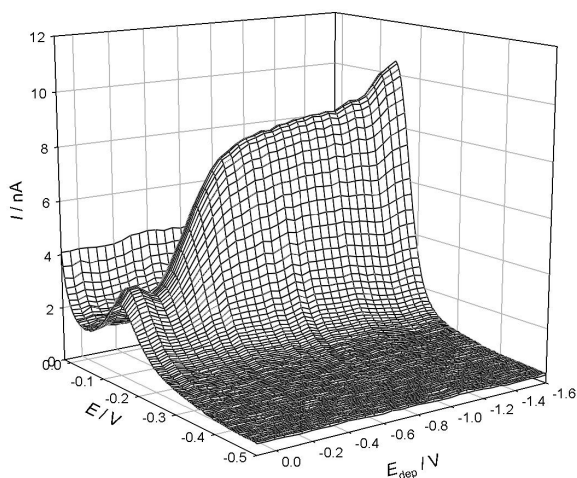


Fig. 1. Experimental 3D-pseudopolarogram of copper in seawater sample without any additions.

Several model electrolyte solutions and natural estuary/seawater samples from different locations in the Mediterranean and Adriatic Sea were used in this study. DPASV on mercury drop electrode was used in all experiments. It is experimentally verified in model electrolyte solutions containing metal complexes with known stability constants, that the shift of the half-wave potential of the inert metal complex is related to its stability constant. This relation is further used as a general rule for the estimation of the stability constants of trace metal complexes formed by DNOM in analysed natural waters. Additional effort has been made to couple standard addition method and pseudopolarography in order to obtain more information on trace metal complexation. Such measurements are very time consuming, so automated measurement system has been assembled.

The influence of accumulation potential on determination of metal complexing capacity was investigated, as well. Metal additions were performed in a logarithmic mode, allowing a wider analytical window, and therefore a better accuracy of the complexing parameters determination [5]. The voltammetric data were further modelled with PROSECE (Programmed Optimisation et de Spéciation Chimique dans l'Environnement), a very manageable software based on a discrete model [5]. Calculated metal complexing parameters (ligand concentrations and stability constants) strongly depend on accumulation potential as well as on experimental setup, which needs to be better understood and quantified.

References

- 1 - Buffle J., Tessier A., Haerdi W., 1984. Complexation of trace metals in natural waters. In: Kramer C.J.M., Duinker J.C. (ed.), The Hage, pp. 301-316.
- 2 - Bubić S. and Branica M., 1973. Voltammetric characterization of ionic state of cadmium present in seawater. *Thalassia Jugosl.*, 9: 47-53.
- 3 - Omanović D. and Branica M., 2004. Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions, *J. Electroanal. Chem.*, 565: 37-48.
- 4 - Branica G. and Lovrić M., 1997. Pseudopolarography of totally irreversible redox reactions, *Electrochim. Acta*, 42: 1247-1251.
- 5 - Garnier C., Pižeta I., Mounier S., Benaïm J.Y., Branica M., 2004. Influence of the type of titration and of data treatment methods on metal complexing parameters determination of single- and multi- ligand systems measured by stripping voltammetry, *Anal. Chim. Acta*, 505: 263-275.