

# ELECTROANALYTICAL METHODS AND A NEW IN SITU SAMPLER FOR THE CHARACTERISATION OF PORE WATERS OF SEDIMENTS OF THE LAGOON OF VENICE

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The understanding of the early diagenesis processes in superficial sediments of transitional environments is particularly important in order to know the effect and fate of toxic pollutants discharged in the environment. Precious information helping in the solution of such a complex problem can be drawn by continuously monitoring of pore waters. Sampling methods providing reliable samples and analytical techniques with satisfactory precision and accuracy need to be available. Moreover, since a wide range of analyses are necessary, a good advantage could derive from using analytical techniques, preferably with speciation capabilities, able to give concentration information on a variety of substances.

Among other analytical methods, electroanalysis is increasing its importance in ecosystem studies, particularly in chemical oceanography, being many substances of relevancy in the characterization of marine waters electroactive. Moreover, electroanalysis has the advantage that measurements can be carried out directly in crude marine waters with few or none chemical pre-treatments, without altering natural equilibria.

On the other hand, as far as marine pore waters is concerned, several problems arise from the availability of suitable sampling methods and apparatus able to avoid alterations of chemical equilibria and in the natural composition of the sample.

In this communication we describe a new prototype *in situ* pore water sampler which allows temporal sampling of pore-water from intertidal sediments. The system consists of a nylon device provided with regularly spaced chambers, double filtering ports and pipes for sample recovering. The field use of this apparatus for determining sulfur species and heavy metals in pore-waters is described; a satisfactory agreement between data gained by using the proposed *in situ* sampler and by core-squeezing in proper experimental conditions is obtained.

The concentration profiles for reduced sulfur species, iron and manganese are determined by cathodic stripping voltammetry, while the concentration of copper lead and cadmium are measured by anodic stripping voltammetry. Moreover the application of new electroanalytical methods such as ion exchange voltammetry at polymer coated glassy carbon electrodes, is exploited for determining dissolved mercury.

The peculiarities and the flexibility of coupling of the here described sampling apparatus with electroanalytical methods allow to study seasonal variations and cycling as well as changes in the composition sampled in mud flats and marsh lands.

Finally, we discuss the relevance of the obtained data to understand the influence of equilibria between heavy metals and reduced sulfur species to the mobilization of the pollutants.

# THE INFLUENCE OF ORGANIC SUBSTANCES ON THE ZETA POTENTIAL OF CALCITE

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Suspended matter in river waters is the important transport mean for some contaminants, because of the mutual interaction of adsorbing mineral particles and dissolved organic or inorganic species. The attraction forces which govern adsorption processes depend on the properties of adsorbates and adsorbents, and on some physico-chemical parameters (pH, salinity, temperature). For that reason the fate of contaminants is decided in estuarine regions where those parameters change rapidly and cause:

1- adsorption which leads to flocculation and sedimentation and removal of contaminants from the water column (SONDI *et al.*, 1994);  
2- remobilization of already adsorbed material which can be carried further into the sea or become biologically available (ELBAZ-POULICHET *et al.*, 1982).

The aim of our work was to study the behavior of suspended particles in relation to changes of pH, salinity and organic matter concentration encountered in estuarine regions. For that purpose we used calcite (pure chemical precipitate) as one of representatives of mineral compounds in natural estuarine and sea waters of Adriatic region and studied its behavior in the transition from riverine to seawater. As an indicator of changes we used zeta potential ( $\zeta$ , mV), a parameter calculated from the results for electrophoretic mobility (epm). Epm measurements were made with an automated apparatus for microelectrophoresis, PenKem 3000.

The results have shown that in initial solution ( $10^{-3}$  mol dm<sup>-3</sup> NaCl representing river water) model minerals show different values of zeta potential - not only in range, but also in sign. Namely, opposite to all other minerals, calcite shows positive value for zeta potential in pure NaCl solution. Titration of the initial suspension with artificial seawater (ASW) slightly reduced zeta potential of all samples, but charge reversal of calcite was observed only after titration with natural seawater (Table 1).

Table 1: Zeta potential of model minerals in different solutions

Model mineral	10 <sup>-3</sup> mol dm <sup>-3</sup> NaCl	ASW	NSW
calcite	+ 20 mV	+ 5 mV	- 10 mV
quartz	- 50 mV	- 7 mV	- 12 mV
montmorillonite	- 30 mV	- 12 mV	- 15 mV

Where is the origin of the negative zeta potential in NSW? BISCAN and DRAGCEVIC (1993) found that the reasons could be either amorphous Fe and Mn oxides in calcite sample, or adsorbed organic material. Since the seawater contains a wide variety of organic substances our aim was to find which type of organic matter can reverse the positive charge of calcite into a negative. For that purpose we exposed calcite to the influence of some organic substances (fulvic, citric, oxalic and some saturated fatty acids - propionic, capric and myristic) in  $10^{-3}$  mol dm<sup>-3</sup> NaCl and artificial seawater (ASW). Fulvic acid caused the charge reversal at a concentration of about 0.4 mg dm<sup>-3</sup>, and citric acid caused the reversal of charge at about  $5 \times 10^{-5}$  mol dm<sup>-3</sup>. No effect on the zeta potential was observed either for oxalic acid or for the saturated fatty acids in the concentration range between  $5 \times 10^{-7}$  and  $10^{-4}$  mol dm<sup>-3</sup>. The results obtained revealed some organics which can reverse the positive charge of calcite, but they also showed that this is not just the question of the type of organic matter but also the question of concentration. Studies of the assessment of the adsorption of these organics at the calcite surface are in progress.

## REFERENCES

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