

DIRECT DETERMINATION OF DISSOLVED URANYL(VI) IN SEAWATER BY CATHODIC STRIPPING VOLTAMMETRY

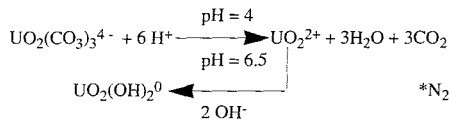
Renata DJOGIC and Marko BRANICA

Center for Marine Research Zagreb, Ruder Boskovic Institute,
P.O.Box 1016, 41001 Zagreb, Croatia

The dissolved uranyl(VI) is present in seawater at an almost constant concentration of 3.3 $\mu\text{g/l}$ (KU *et al.*, 1977). It has been accepted that the anionic uranyl(VI)-tricarbonato complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ is the predominant chemical form of dissolved uranyl(VI) in seawater (DJOGIC *et al.*, 1986). As a consequence of ion pairing reactions, the complex could be more precisely described as $\text{Na}_2(\text{UO}_2(\text{CO}_3)_3)^{2-}$. At an elevated hydrogen peroxide concentration (in euphotic zone) uranyl(VI) appears partially as a mixed uranyl-dicarbonato-hydrogenperoxo complex $\text{UO}_2(\text{CO}_3)_2(\text{HO}_2)^{-}$ (DJOGIC and BRANICA, 1991). This study has been performed to develop the simple electrochemical procedure for quantitative determination of uranyl(VI) in natural seawater samples.

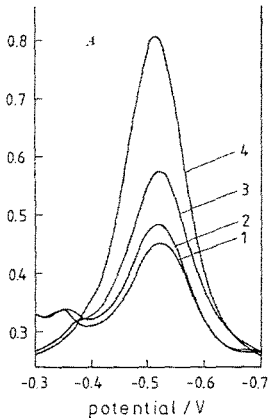
Solubilities and mobilities of various uranyl(VI) species which exist under the nuclear waste disposal conditions, as well as their adsorption on soil particles and their leaching into waters are very important environmental problems. Because of this, the need of a direct method to determine the concentration of uranyl(VI) in natural waters is of great prominence. To accomplish this, it is necessary to clarify the mechanisms of uranyl(VI) physico-chemical processes in natural water.

Negative highly charged ion of uranyl(VI)-tricarbonato complex is not adsorbed on the solid particles and sediments in marine environment. In accordance with its solubility, adsorption at the electrode surface is not possible. To transform this species into an adsorbable one, the destruction of carbonato complexes and formation of uncharged uranyl species is needed. This process is achieved according to the following equations.



* by bubbling N_2 carbon dioxide was eliminated from sample in the electrochemical cell.

This uncharged hydrolyzed uranyl(VI) species is favored to be adsorbed at the electrode surface (DJOGIC and BRANICA, 1994). Consequently by this procedure uranyl(VI) is transformed in such a way that its concentration can be determined by square wave cathodic stripping voltammetry. The standard addition method (Fig. 1), can be successfully applied at very low concentration such as 10^{-8} mol l^{-1} in which uranyl(VI)-ion is present in seawater. The results from different stations of seawater samples will be discussed.

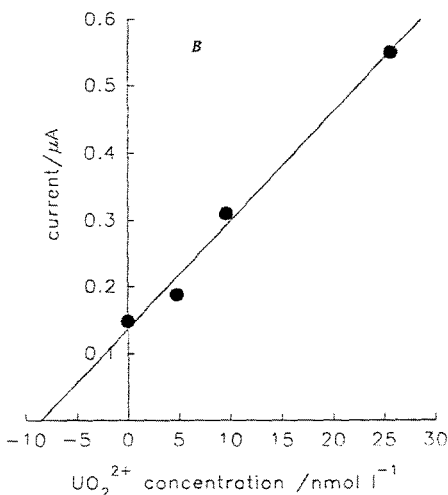


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Fig. 1A : A SWCS Voltammograms in seawater (acidified to pH = 4 and adjusted to pH = 6.5 at different uranyl(VI) concentrations (1) seawater samples, (2) $4,8 \times 10^{-9}$, (3) $9,6 \times 10^{-9}$, (4) $2,56 \times 10^{-8}$ mol l^{-1}

Fig. 1B : Dependence of SWCS peak current on uranyl(VI) concentrations in natural seawater



CHARACTERIZATION OF ORGANIC MATTER IN THE NORTH ADRIATIC SEA USING O-NITROPHENOL AS A PROBE

B. GASPAROVIC and B. COSOVIC

Center for Marine Research Zagreb, Ruder Boskovic Institute
P.O. Box 1016, 41001 Zagreb, Croatia

Naturally occurring organic matter represents a complex system, not enough investigated so far (80% of all dissolved organic matter species is not characterized), composed of a great variety of compounds which undergo different types of reactions (physical, chemical and/or biological) leading to formation of inorganic or new organic matter. Organic matter is present in the water column in the dissolved, colloidal and particulate state, but its main part is in the dissolved state. North Adriatic sea is a shallow basin rich in organic matter. This region is affected by anthropogenic inputs of organic matter and of nutrients, mainly by the influx of the Po river, leading to algal blooms and excessive production of photosynthetic organisms. This part of the Adriatic sea exhibits pronounced seasonal variations of organic matter as well as horizontal and vertical distribution related to the biological activity (COSOVIC *et al.*, 1985). Usually, the concentrations of dissolved organic matter in the north Adriatic varied within a range of 1-2 mg dm^{-3} (83-166 $\mu\text{M C}$) (ASCOP, 1992/93).

With the aim to find out the method for characterization of organic matter in the natural waters, simple electrochemical method was developed using o-nitrophenol (ONP) as an electrochemical probe. ONP was chosen as a model system according to its appropriate alternating current voltammetry characteristics for studying processes involving organic matter (GASPAROVIC and COSOVIC, 1984). Characterization of the dominant type of organic matter is made by the comparison of the electrochemical characteristics of ONP probe in natural sample with different model systems. It is based on the fact that electrochemical characteristics of ONP (peak potential, half-peak width, peak height and shape) are strongly influenced in the presence of organic matter, which tends to accumulate on the phase boundaries. Model systems contained selected organic substances expected to be found in the natural aquatic environment as naturally occurring organic matter (humic acid, fulvic acid, some fatty acids as representatives of lipid materials, dextrans as representatives of sugars and albumine as a representative of proteins), and organic compounds of anthropogenic origin (tenzides).

Seawater samples are collected monthly at sampling stations presented in Fig. 1 along the transect between croatian and italian coasts. Concentration and composition of the dominant type of organic matter are investigated in seawater samples and in phytoplankton culture media to find out main excretion products during the phytoplankton growth.

Results for the period of 1994 will be discussed. Typical a.c. voltammograms of ONP in absence and in presence of model substances and naturally occurring organic matter in seawater samples are presented in Figs. 2a and 2b, respectively. Comparison is made also to the surfactant activity measurements performed by phase sensitive a.c. voltammetry (COSOVIC *et al.*, 1985) and to DOC values of the samples. The results of this work demonstrate the relevance of the developed model to the real natural waters.

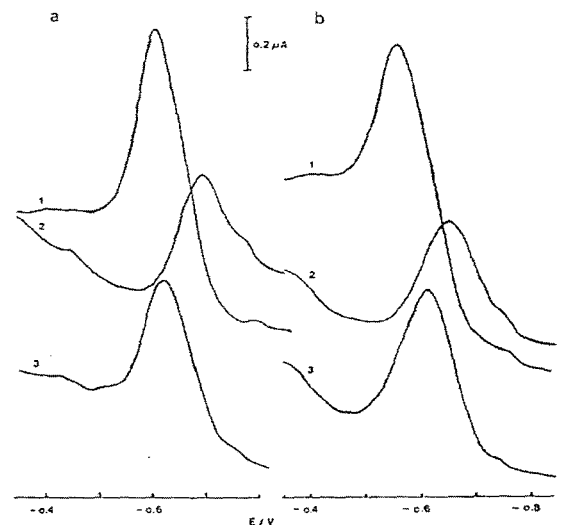


Fig. 2. (a) A.c. voltammograms of 10^{-4} M ONP in 0.5 M NaCl, pH 8.4; without SAS, acc. time 180 s (curve 1); in the presence of 1 mg/l albumine, acc. time 180 s (curve 2) and 1 mg/l humic acid, acc. time 60 s (curve 3). (b) A.c. voltammograms of 10^{-4} M ONP in seawater samples, Station 107, 0.5 m, May 17, 1994 (curves 1 and 3), Station 105, 0.5 m, May 17, 1994 (curve 2). Acc. time (1) 0, (2) and (3) 180 s.

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