

C-I1

Application of synergistic adsorption for the pulse voltammetric determination of Uranium in natural seawater

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The synergism in the solvent extraction means the manyfold enhancement of the metal ion extraction from aqueous solutions to the organic phase by application of two organic ligands mixture (1).

Mercury drop surface can be a good replacement for the organic phase due to its hydrophobic character. By the combination of the appropriate pair of organic ligands (organic acid as an chelate and a neutral alkyl-phosphorous ester as an synergist), metal ions can form mixed complexes which are more hydrophobic than each of them separately. Mixed complex can be formed at the mercury drop electrode surface with very strong adsorption. In this way the concentration of metal ions is many times enhanced at the electrode surface, so it is possible to detect and determine very low metal-ion bulk concentration level corresponding to the concentration in natural aquatic systems, i.e., in seawater and in fresh waters.

As an example of the application of mentioned synergistic adsorption we choose uranyl-ion. In this way uranyl concentration in seawater samples from the Adriatic Sea was determined.

As a system of organic ligands which gave such a synergistic effect we used salicylic acid and tri-n-butylphosphate (TBP). Salicylic acid forms with uranyl-ion complex in the solution (2). TBP, adsorbed strongly at the electrode surface, substitutes the remaining water molecule in the coordination sphere of the uranyl-complex, forming mixed $UO_2(HSal)_2TBP$ complex which is strongly adsorbed at the electrode surface, too.

The measurements were performed by normal pulse voltammetry, which showed to be sensitive enough for the uranyl concentration level present in natural seawater sample: pH of the solution was adjusted at 3.6 and the concentration of salicylic acid was 1.4×10^{-3} and TBP 2×10^{-4} mol dm^{-3} . By measurements of the reactant adsorption maximum height on the pulse voltammograms detection limit obtained was about 10^{-9} mol dm^{-3} UO_2^{2+} .

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C-I2

Determination of ionic alkyllead compounds in environmental water

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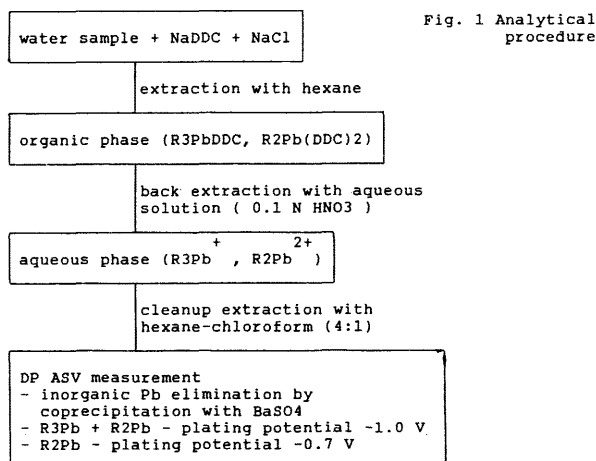
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Organolead compounds are introduced into the environment by their usage as antiknock additive in gasoline. Under natural conditions tetraalkyllead species are subject to degradation to inorganic lead (1). Intermediate compounds in this process are ionic alkyllead compounds (tri- and dialkyllead) which are relatively soluble in water and considerably more stable than the initial compounds. It is not surprising then, that organolead compounds are present in natural waters almost exclusively in the form of ionic alkyllead compounds (1).

Anodic stripping voltammetry (ASV) was found to be a convenient method for detection of ionic alkyllead compounds (2). It was successfully applied to studies of tri- and dialkyllead distribution in an estuary polluted from tetraalkyllead manufacture (3). Although it can be directly applied to very polluted waters (at $\mu g/l$ organolead levels), it is not sensitive enough to measure the concentration of these compounds in natural waters.

By use of a specific enrichment step we improved the detection limit of the ASV method. A complexometric extraction with sodium diethyldithiocarbamate (NaDDC) was applied, a technique commonly used in combination with GC AAS detection (4). In our method the extracted ionic alkyllead species are back extracted into the acid aqueous solution and tri- and dialkyllead species are simultaneously determined by ASV. Inorganic lead which interferes with organic lead determination by ASV, and which is partly extracted with the procedure applied, is eliminated from the solution in the electrochemical cell by coprecipitation with barium sulphate. It was found that during extraction a small quantity of complexing agent is back extracted into aqueous solution. Under the condition used ($pH < 2$) DDC is very unstable and undergoes rapid decomposition. However, when natural water samples with high organic matter contents are extracted, stabilization of DDC in final acid solution is noticed. It can affect ASV measurements, because DDC is electroactive, with its oxidation peak potential close to the lead reoxidation potential. It was the reason why we introduced a cleanup step including an additional extraction of the final aqueous solution with a mixture of hexane and chloroform. During this extraction DDC is transferred to the organic phase, whereas ionic alkylleads remain in the water solution. Analytical procedure is shown at fig.1.

Repeated experiments with standard solutions proved that recoveries for ionic alkyllead compounds are about 90 %, with the reproducibility of the entire procedure 10-20 %, depending on the concentration level. The detection limit of the method is estimated at 0.2 ng Pb/l for total ionic alkyllead compounds for 2.5 l of sample volume. The practical applicability of the method developed is demonstrated on a number of natural waters and atmospheric precipitate. In lake water (near urban area) 0.3-2 ng Pb/l of trialkyllead was found, whereas in seawater (near harbour) 0.8-10 ng Pb/l could be detected. The impact of a gasoline station and boat traffic on ionic alkyllead levels in surrounding seawater was studied by the proposed method.



Literature

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