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Use of a gold nanostructured electrode for the electrochemical determintion of Hg. Optimisation, characterization and evaluation of its applicability for fish products-analysis

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Mercury is a metal with interesting properties and it is widely used in various sectors as industry, medicine and science. However, it has been extensively studied for its high toxicity. Each species of this metal (elemental, organic and inorganic mercury) is responsible for significant human health problems and environmental pollution, even at low concentration. Therefore, it is important to develop sensitive analytical methods for its determination.

Good results are obtained with electrochemical methods, primarily using anodic stripping voltammetry (ASV), using various working electrodes. Gold is an excellent material for Hg determination since it exhibits a high affinity for Hg, thereby improving the effects of pre-concentration before stripping.

Metal nanoparticles can be exploited in electroanalysis for their ability to catalyze the redox processes, since they facilitate the electron transfer; moreover, the large surface area of the deposited nanoparticles could permit an improvement of the analytical performance.

This study focuses on the determination of Hg by ASV using a home-made gold nanoparticle-modified glassy carbon electrode (AuNPs-GCE). The performance of this electrode and of the technique have been show in previous works [1]. The aim of this work is to continue the evaluation of the possible fields of applicability of the optimized technique: in this case the "fish products" (fish, fish oil, dietary supplements containing fish oil,..)

Modification with gold nanoparticles was performed by dipping the electrode into a 50 mg/l or 100 mg/l $HAuCl_4$ $3H_2O$ solution and applying a potential of 0.80 V for 6 min. In this study the use of two different gold salts for the deposition was compared: the salts present different level of purity declared by the producer: ≥49,0% (used in the previous studies) and ≥99,9%.

Repeatability, linearity and detection limit were evaluated for the different AuNPs-GCE obtained by changing gold salt and the concentration of the gold solution adopted for the deposition. Better results are obtained using 50mg/l gold solution for both salts. Using $HAuCl_4$ $\cdot 3H_2O$ with purity ≥99,9 % we observed a greater sensitivity of the determination in comparison with that obtained using the other salt.

However, conflicting results obtained during mercury determination drove us to characterize the gold salts and the quality of the final gold layer. Gold salts were characterized by pH measures, ICP-MS and ICP-OES quantitative-qualitative analysis. No relevant differences between both salts were observed.

Cyclic voltammetry (CV) has been applied to monitor gold surface [2]. This study is used to value both the presence of gold nanoparticles (strictly related to an anodic peak in the graph) and the amount of deposited gold (related to a cathodic peak) on electrode surface. We observed a partial dissolution of the active layer and modifications of its physical structure.

Then, the gold surfaces were characterized by scanning electron microscopy (SEM). SEM images show many surface irregularities of the carbon electrode surface and the presence of a gold film instead of gold nanoparticles. The use of a glassy carbon working electrode with a more homogeneous surface (verified by SEM) permitted us to obtain a gold nanoparticle layer showing the influence of the carbon surface morphology on the formation of gold nanoparticles.

We valued the performance of the optimized technique previously for the determination of Hg in synthetic solutions, then in the sample ISPRA T220 "tuna fish"[3]. Finally, we valued the possibility to apply the method for the analysis of real sample.

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