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Copper film electrode as an electrochemical sensor for the determination of trace concentrations of lead ions in environmental waters by anodic stripping voltammetry

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Summary:
Metallic film electrodes are currently experiencing a major development as environmentally friendly electrochemical sensors used in stripping voltammetry. Their development began when attention was drawn to the toxicity of mercury electrodes commonly used as working electrodes in voltammetric procedures. Some of the first non-mercury metallic film electrodes to be developed since 2000, when they were introduced by Wang's team, were bismuth electrodes [1]. The next ones of great interest were lead film electrodes introduced by Korolczuk's team [2]. We wish to propose in this work the use of a film copper electrode for the determination of trace concentrations of lead ions in natural waters. The aim of this work was to optimize the conditions for generating a copper film electrode on glassy carbon as a substrate and then to optimize the conditions for concentrating the analyte, which was lead in metallic form, and then to obtain an analytical signal by anodic stripping voltammetry.

Keywords: electrochemical sensor, copper film electrode, anodic stripping voltammetry, Pb(II) determination, environmental waters

Introduction

Lead is one of the elements that is enjoying constantly growing interest. Lead is toxic and has the property of accumulating in the human body, mainly in bones. Its sources are food, air and water, into which lead gets, among other things, through industrial effluents. Therefore a constant need for simple, rapid and sensitive procedures for the determination of lead ions in environmental water emerges. One method ideally suited for this purpose is stripping voltammetry, which is why there are numerous voltammetric procedures for the determination of Pb(II) using various non-mercury working electrodes, such as bismuth–nafion film screen-printed gold electrode [3], carbon rod electrode [4], modified screen-printed electrode [5], boron-doped nanocrystalline diamond electrode [6]. We proposed using a film-generated copper electrode on glassy carbon in combination with anodic stripping voltammetry for the determination of low Pb(II) concentrations as a working electrode.

Measurement procedure

The glassy carbon electrode on which the film copper electrode was generated was cleaned at the beginning of each measurement day by polishing with alumina, and between measurements the electrode was electrochemically cleaned by applying to it a potential of -1.25 V for 5 s initially and then +0.4 V for 15 s. The copper film electrode was generated in situ by applying a potential of -0.8 V to the glassy carbon (GC) electrode for 80 s. During this time, copper ions introduced into the test solution were simultaneously reduced to form a metallic film, and lead ions present in the water sample analysed were reduced to metallic form. After this step, the potential was changed to a more positive value, producing a voltammetric signal with a well-formed lead peak at a potential of -0.5 V.

Optimisation of measurement conditions

Optimization of the proposed procedure involved the selection of a number of parameters, such as the type and concentration of the supporting electrolyte and the concentration of Cu(II) ions introduced into the analyzed sample. The results obtained are presented in Fig. 1 and Fig. 2. Based on these results, the following optimum solution composition was selected: analyzed sample + 0.5 M HCl + 5 10^{-5} M Cu(II). ASV measurement parameters, such as copper film formation potential and time and metallic lead accumulation potential and time and signal re-registration potential range, were also selected. The

results obtained confirmed that the copper film formation step can take place simultaneously with lead accumulation I finally both processes occurred at a constant accumulation potential of -0.8 V for 80 s and then the voltammetry was recorded as the potential changed from -0.8 V to -0.4 V.

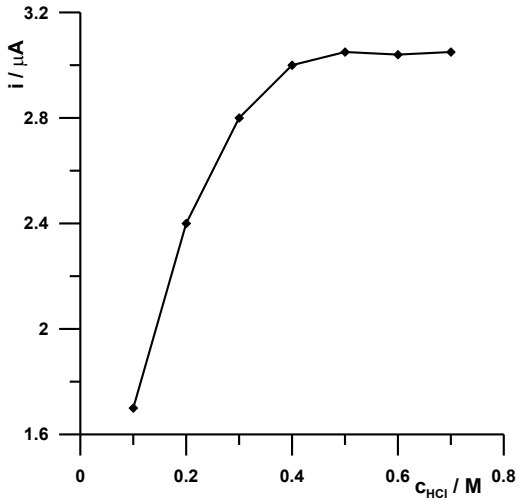

Fig. 1. Influence of supporting electrolyte HCl concentration on lead peak current. Concentration of Pb(II) 5 × 10^{-8} M.

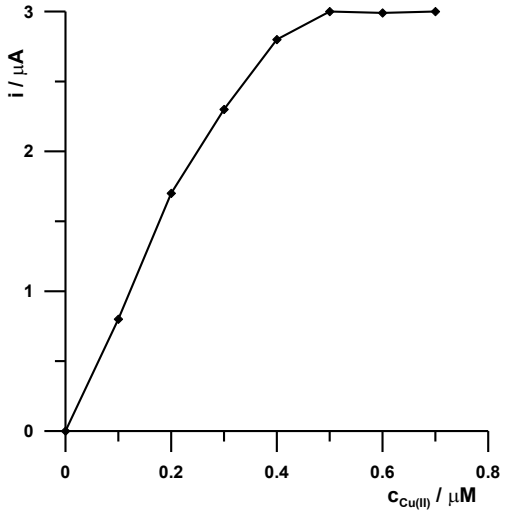

Fig. 2. Influence of Cu(II) concentration on lead peak current. Concentration of Pb(II) 5 × 10^{-8} M.

Analytical Characteristics

Using the previously optimized parameters such as supporting electrolyte concentration, copper concentration, accumulation potential and time measurements were carried out to obtain a calibration curve. The calibration plot was linear in the range from 3 × 10^{-9} mol L^{-1} to 3 × 10^{-7} mol L^{-1} with linear correlation coefficient r = 0.994. For the developed procedure, the detection limit was found to be 1 × 10^{-9} mol L^{-1} estimated from three times the standard deviation for the lowest studied Pb(III) concentration.

Conclusion

Based on the experiments discussed above, general observations and conclusions can be made:
- the copper film electrode can be a good alternative to mercury electrodes for the determination of Pb(II) by anodic stripping voltammetry;
- the formation of a copper film on the GC by the in situ method and the simultaneous accumulation of lead in metallic form allows a significant reduction in measurement time;
- the developed procedure for the determination of lead is simple and does not require expensive equipment.

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