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Short communication

Stripping voltammetry microprobe (SPV): A new approach in electroanalysis

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ABSTRACT

This paper describes how electrochemical trace analysis can be performed in micro samples based on the precipitation of a sparingly soluble compound and its immobilization on an electrode surface. Precipitation is performed in a solution droplet put on the electrode in an upside-down position in air. The solvent of the droplet is then evaporated and the immobilized residue is subjected to a voltammetric measurement after introducing the electrode to an electrolyte solution. This methodology can be used for the quantification of dissolved ions (after precipitation) as well as for that of dispersed solids. As example, here the quantification of silver ions following precipitation as AgCl is described.

1. Introduction

Combining *trace analysis* with *micro analysis* is a great challenge. Voltammetric analysis of sub-micromolar concentration is generally based on stripping protocols which involve an in-situ preconcentration step preceding the voltammetric signal generation [1–4]. All stripping voltammetric techniques are directed on achieving low detection limits in terms of concentration. The analysis of sub-micromolar concentrations and micro samples, be it volumes (μL) or masses (μg), has not been in the focus of recent developments in electrochemical trace analysis. Of course, the determination of sub-micromolar concentrations *in* micro samples is a very serious task which needs to be addressed to meet the demands of modern technologies as well as of life sciences. Thus the analysis of low concentrations in micro-droplets or bubble inclusions is a great challenge for modern analysis. Non-electrochemical techniques of analysis, e.g., mass spectrometry, have already successfully addressed such tasks, e.g., by combining the spectrometry with single droplet microfluidic handling systems [5,6]. Until now, the preconcentration step in stripping voltammetric techniques was either (a) a cathodic accumulation of metals (or metal compounds) in *anodic stripping voltammetry* [1–4], (b) an anodic accumulation of sparingly soluble salts with the metal ion generated by oxidation of the electrode (e.g., mercury or silver) in *cathodic stripping voltammetry* [1–4], (c) an adsorption of compounds on the electrode surface in *adsorptive stripping voltammetry* [1,2,4], or (d) a chemical reaction in *anodic* and *cathodic stripping voltammetry* [7–9]. All these previously developed stripping voltammetric techniques require rather large volumes of solutions (in the mL range). Many cathodic stripping techniques suffer further from the fact that the anodically formed precipitates (e.g., AgCl and AgBr) still have an appreciable solubility: If the concentration of the halide anions is too small to form a precipitate on the electrode surface, the technique is principally not applicable.

Further, the above listed analysis methods have the great disadvantage of not allowing the study of phenomena that occur at the microscopic level and which are particularly impairing material performance in industrial applications, such as electronics, aviation and spaceflight, ground transportation, fluid transport. Thus the scientific community is trying to understand localized corrosion processes, which lead to the development of pits and/or crevices on a metal surface. In fact microdevices have been created on purpose in order to inject locally aggressive solutions [10], whose variation in composition, closely related to the corrosion process, have been monitored by scanning electrochemical microscopy (SECM). Moreover, trace elements, play a considerable role in physiology and pathology of biological systems. Metallogenomics, metalloproteomics, and metallomics are among the emerging disciplines which are critically dependent on spatially resolved concentration maps of trace elements in a cell, sweat or tissue, on information on chemical speciation and metal-binding coordination sites [11]. An example of this is determination of chloride in biological fluids such as sweat, in the diagnosis of electrolyte disorders associated with cystic fibrosis [12,13] and diabetes [14]. Currently used nickel electrodes for chloride ion monitoring of sweat samples of individuals suffering from erectile sudomotoras [15]. The methodology involves an elaborate measuring

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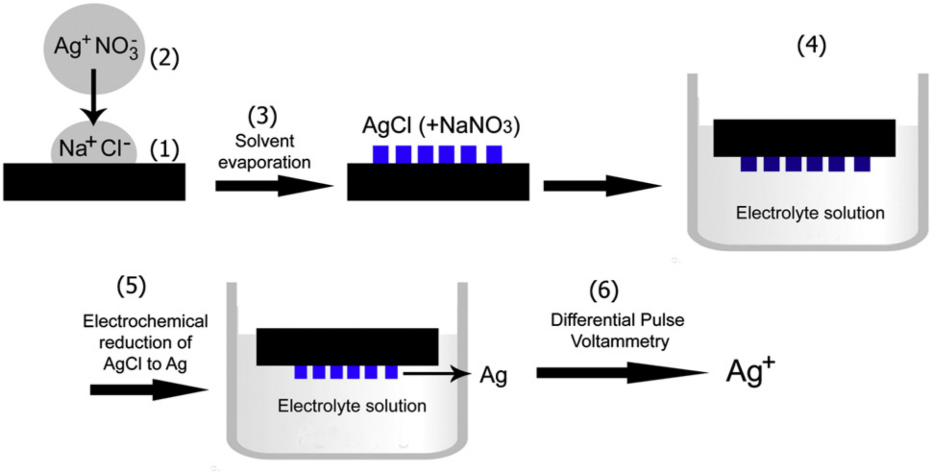

Fig. 1. Scheme of the precipitation–immobilization protocol for stripping voltammetry applied to μL-size samples.

protocol. Clearly, if it were possible to determine chloride ion through the use of microvolumes, the described procedure could be much facilitated. Therefore, the development of a technique to determine the composition of analyte in microsamples is essential for the understanding of phenomena that take place at the micro level in size and volume. Here we report a new protocol for stripping voltammetry which overcomes two of the discussed drawbacks of the previously reported techniques: (i) it allows the analysis of μL-samples, and (ii) it overcomes the constraints of solubility of compounds precipitated for preconcentration.

Although the method of evaporating the solvent from a micro-sample has been previously used in the determination of some heavy metals, this requires a local change in the hydrophilic/ hydrophobic properties of the working electrode surface [16]. In the technique presented here, the electrode surface is a single receiver of a micro-volume of sample, requiring no further treatment than the evaporation.

2. Experimental

All reagents were of analytical grade. Silver standard solutions (9.27×10^{-6}, 1.854×10^{-5}, 4.635×10^{-5}, 9.27×10^{-5} mol L^{-1}) were prepared by diluting a Certipur Merck standard solution (9.27×10^{-3} mol L^{-1}) with bidistilled water. The electrochemical measurements were performed at 25 °C in a three-compartment cell provided with a Luggin capillary and N_2 gas inlet. The nitrogen used was ultra pure. A saturated calomel electrode was used as reference, and a platinum wire spiral (10 cm length, 0.05 cm diameter) served as auxiliary electrode. Electrochemical measurements were performed using a potentiostat–galvanostat CH Instruments model 1100 (Austin, USA). Prior to experiments, the edge plane ordinary pyrolytic graphite electrodes were mechanically polished with 1200, 2400 and 4000 grit SiC grinding papers, followed by sonication for 5 s in bidistilled water. The electrolyte, 0.1 M oxalic acid (pH 1.3) was deaerated by purging with N_2 for 10 min. Then the electrode was cycled 10 times between −1.0 and 0.2 V at a scan rate of 0.1 V s^{-1}. The baseline of the differential pulse voltammetric (DPV) response was recorded in the same potential window. Oxalic acid was selected as electrolyte, in order to compare the results with those reported before [17].

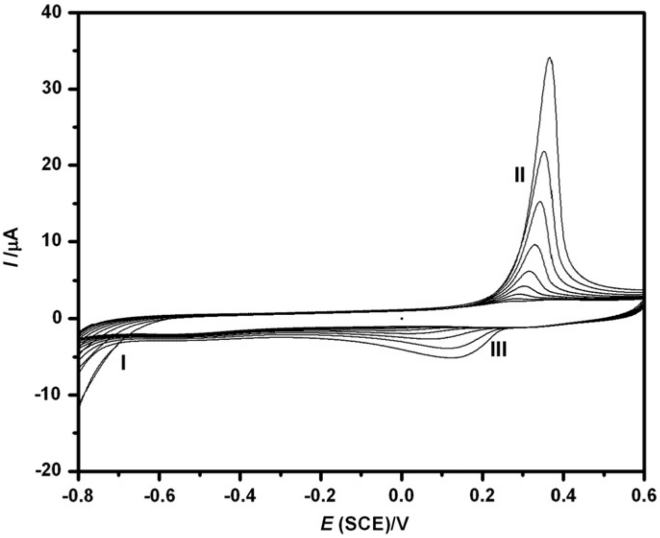

Fig. 2. Cyclic voltammetry of AgCl(s) obtained from the deposition of 5 μL of 10 ppm $AgNO_3$ solution, and 5 μL of 0.005 M NaCl, on the surface of graphite. Measurements recorded in 0.1 M oxalic acid, starting at −0.7 V vs. SCE in the cathodic direction, showing the first ten cycles.

The new protocol is based on the following steps (cf. Fig. 1): (1) A μL-sized sample (e.g., chloride solution) is attached as droplet to an electrode surface, with the electrode positioned upside-down (in air). (2) A reagent droplet is added to produce a precipitate (e.g., containing Ag^+ to produce AgCl). (3) The solvent is evaporated in a drying cabinet. If the precipitate that has not yet formed in step 2, it will form in any case now during solvent evaporation. (4) Then the electrode is inserted in an appropriate electrolyte solution and the electrochemical measuring step is commenced without delay by (5) a reduction of AgCl to Ag at −0.7 V, followed by (6) electrochemical dissolution of Ag using DPV, so that the AgCl precipitate has hardly a chance to dissolve before its electrochemical conversion providing the signal generation. The proposed *Stripping Voltammetry Microprobe* combines the high sensitivity of stripping voltammetry with microsampling, thus providing a platform for the determination of low absolute amounts of analytes. The new protocol is demonstrated here for the case of determination of silver ions (or chloride ions) in 5 μL droplets.

3. Results and discussion

Silver chloride precipitated and immobilized on a graphite electrode according to Fig. 1 is electrochemically active. Fig. 2 shows cyclic voltammograms exhibiting three signals: I is due to the reduction of solid AgCl to Ag metal accompanied by the release of Cl^- to the solution. Due to the micrometer size of the AgCl crystals, the reduction leads to the formation of a closed silver shell (8–10 nm thickness), which of course terminates the reduction (the AgCl crystal is silverized). This scenario has been elucidated in a previous in situ AFM electrochemistry study of immobilized silver halide crystals [18]. The formed silver layer is oxidized in the anodic scan (peak II) releasing a “cloud” of silver ions