Electrochimica Acta 188 (2016) 393–397

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Bismuth film electrode for anodic stripping voltammetric measurement of silver nanoparticle dissolution

Tea Romih[a], Samo B. Hočevar[b,*], Anita Jemec[a], Damjana Drobne[a]

[a] Department of Biology, Biotechnical Faculty, University of Ljubljana, Večna pot 111, SI-1000 Ljubljana, Slovenia
[b] Analytical Chemistry Laboratory, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 4 September 2015
Received in revised form 19 November 2015
Accepted 20 November 2015
Available online 7 December 2015

Keywords:
bismuth film electrode
anodic stripping voltammetry
silver nanoparticles

ABSTRACT

A straightforward protocol for measuring low concentration levels of Ag(I) using bismuth film electrode (BiFE) in combination with anodic stripping voltammetry was developed and studied as a suitable alternative to current methods for detecting the dissolution of silver nanoparticles (Ag NPs). The BiFE was prepared in-situ on the surface of a supporting glassy carbon electrode. Several key operational parameters were examined and optimized, e.g. accumulation potential, accumulation time and concentration of Bi(III). The BiFE revealed good linear operation in the examined concentration range of 10–90 $\mu g\,L^{-1}$ Ag(I) with r^2 of 0.998, calculated limit of detection (3σ) of 2.1 $\mu g\,L^{-1}$ obtained after 60 s accumulation, and favorable repeatability with RSD of 3.6% (50 $\mu g\,L^{-1}$, n = 10). The method was successfully tested through measuring Ag(I) in the supernatant of a commercial Ag NP suspension and the performance was superior to the potentiometric measurement using silver ion-selective electrode.

1. Introduction

Despite being a noble metal, silver is prone to corrosion under ambient conditions and continuously releases small amounts of Ag (I), which act antibacterially. The mankind has exploited this beneficial phenomenon for around 7000 years by using silver cutlery and disinfecting drinking water with silver coins [1]. Through the development of nanotechnology in the recent decade, silver nanoparticles (Ag NPs) have been commonly applied in various commercial products due to their antifungal, antiviral and antibacterial activities. They are added to consumer products including textiles, personal care products, food storage containers, laundry additives, home appliances, paints and food supplements [2]. According to the Consumer products inventory database [3], there are currently 438 products out of 1824 total listed containing Ag NPs (searched on June 19th, 2015). The increasing presence of Ag NPs in consumer products leads to the inevitable exposure to silver in everyday life and its widespread release into the environment. There is a general consensus in the nanotoxicological field that the main reason behind the Ag NP toxicity is the release of Ag(I) [1,2], thus underlining the importance of quantification of Ag NP dissolution in suspensions, in biological fluids and in environmental media.

The separation of metal ions from their source NPs is methodologically difficult and there is still a lack of dissolution testing techniques that would be simple, fast and robust. Currently, the most common approaches encompass relatively complex and time-consuming preprocessing to achieve separation of the species and rather expensive instrumentation for metal quantification. The examples are filtration, centrifugation, vacuum or centrifugal ultrafiltration, dialysis, high-performance liquid chromatography, ion exchange, capillary zone electrophoresis or field-flow fractionation coupled to some spectrometric techniques, e.g. inductively coupled plasma-mass spectrometry [4]. Other methods for quantification of Ag(I) in the presence of Ag NPs have also been developed, mainly based on fluorogenic and chromogenic probes [5] or based on the separation of particles and ions by magnetic NPs coated with either dopamine or glutathione [6]; however, when tested comparatively in complex environmental matrices, the most commonly used techniques may not always provide repeatable results [7].

Advanced electroanalytical methods offer several advantages over the listed techniques, mainly in terms of sensitivity, selectivity (particularly when silver ions are not separated from Ag NPs), reduced need for sample preparation and relatively simple, portable and non-expensive instrumentation [8]. To our best knowledge, the bismuth film electrode in combination with anodic stripping voltammetric (ASV) approach has not been implemented yet for measuring Ag(I) and in the dissolution testing of Ag NPs, although electrochemical measurements yielded good results in

---

[*] Corresponding author. Tel.: +386 1 4760 230; fax: +386 1 4760 300.
E-mail address: samo.hocevar@ki.si (S.B. Hočevar).

http://dx.doi.org/10.1016/j.electacta.2015.11.110
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

quantification of dissolved Ag(I) using either ion-selective electrode [9], rotating disc electrode with glassy carbon tip or Ultra Trace Graphite tip [10], Ag disc electrode [11], Pt ultramicroelectrode [12], or scanning electrochemical microscopy [11–14]. Since its first introduction in 2000 [15], the bismuth film electrode (BiFE) has attracted an immense interest among electrochemists as a favorable alternative to its mercury counterpart. There is still ongoing research with the aim of obtaining more insights into the attractive electroanalytical capabilities of bismuth-based electrodes, and spreading their applicability toward detection of numerous metal and non-metal analytes [16]. Hitherto, several configurations of bismuth electrodes have been reported in combination with anodic stripping voltammetry [17], adsorptive stripping voltammetry [18–21], direct voltammetry [22,23] and stripping chronopotentiometry [24–26] for detecting particularly trace (heavy) metal ions and selected organic compounds [16].

In this work, we presented the first successful application of the in-situ prepared bismuth film electrode (BiFE) associated with anodic stripping voltammetry for measuring low concentrations of Ag(I) in the presence of dissolved oxygen. The operating parameters were optimized to enable rapid and reliable measurement of Ag(I) for the purpose of potential routine use. The new method was tested via measuring Ag(I) in the supernatant of a commercial Ag NP suspension and compared with potentiometric measurement using a silver ion-selective electrode; the comparison revealed advantageous performance of anodic stripping voltammetric approach combined with BiFE, particularly considering improved sensitivity, linear operation, and repeatability.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical grade purity. The standard solutions of Bi(III) and Ag(I) were provided by Merck (Darmstadt, Germany) and further diluted as required. For the anodic stripping voltammetric experiments, a 0.1 M acetate buffer solution with pH 4.5 was used as the supporting electrolyte. For the potentiometric experiments with silver ion-selective electrode, an ionic strength adjustment solution (perfectION^{TM} Ion Electrolyte B, Mettler Toledo, Greifensee, Switzerland) was added to the samples following the supplier's protocol. Water used throughout the work was first deionized and then further purified using Elix 10/Milli-Q Gradient unit (Millipore, Bedford, Massachusetts, USA).

2.2. Silver nanoparticle sample preparation and characterization

The Ag NPs (designated as NNV 003; batch number Parnasos_IG010305_Ag NAMA39_1202_Ag) were provided by Colorobbia S.p.A. (Florence, Italy) as an aqueous suspension with nominal particle concentration of 40 g L^{-1} stabilized with polyvinylpyrrolidone (PVP) as the surfactant. The data on particle size, shape, and ζ-potential was provided by the partners of the EU FP7 NanoValid project.

The stock suspension was diluted with deionized water to the concentration of 25 mg L^{-1}. The nominal value of suspension was checked via flame atomic absorption spectrometry (AAS, Perkin Elmer AAnalyst 100, Waltham, Massachusetts, USA) after overnight digestion in a 1.0 M HNO_3 (suspension/acid ratio 1:1 vol/vol). Then 8 mL of the diluted suspension (25 mg L^{-1}) was ultracentrifuged in triplicate at 100000 g for 30 min at 20 °C (Beckman Coulter L8-70M class H preparative ultracentrifuge with Type 70.1 Ti rotor and 10 mL thickwall polyallomer tubes). The supernatants were then divided into two aliquots for measuring silver. The first aliquot was acidified with 65% HNO_3 (Fischer Scientific, Leicester, UK) and the total silver content was measured by AAS. The second aliquot was left unacidified and was used for measuring Ag(I) potentiometrically with ion-selective electrode, and via the newly developed anodic stripping voltammetric protocol with BiFE.

2.3. Apparatus

Anodic stripping voltammetric (ASV) measurements were carried out using a PalmSens potentiostat/galvanostat (PalmSens BV, Utrecht, Netherlands) in combination with PSTrace 4.4 software (PalmSens BV). The usual three-electrode configuration was employed with the working bismuth film electrode (BiFE) prepared in-situ on a supporting glassy carbon electrode (GCE, d = 2 mm), the double-junction Ag/AgCl/KCl(satd.) reference electrode containing 0.1 M HNO_3 as the outer electrolyte to prevent chloride leakage into the sample solution, and a platinum wire as the counter electrode. A computer-controlled magnetic stirrer rotating at approximately 300 rpm was employed during the accumulation and cleaning steps. Potentiometric measurements were performed using a perfectION^{TM} Ag/S_2 combined ion-selective electrode (Mettler Toledo, Greifensee, Switzerland). All experiments were carried out at room temperature of $23 \pm 1\,^{\circ}C$ in a 20 mL one-compartment voltammetric cell. SEM/EDX images were recorded with a high resolution scanning electron microscope (SEM, Carl Zeiss, Model SUPRA 35 VP) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford Instruments, Model Inca 400).

2.4. Measurement procedures

ASV measurements: following an electrochemical accumulation step of usually 60 s at −0.6 or −0.8 V, and subsequent equilibration period of 15 s, the anodic stripping voltammogram was recorded in the quiescent solution by applying a positive-going square-wave potential scan from −0.6 V to +0.6 V with a frequency of 25 Hz, a potential step of 4 mV, and an amplitude of 50 mV. Before each measurement, a cleaning step was carried out by applying a potential of +0.4 V for 30 s.

Potentiometric measurements: the silver ion-selective electrode was submerged in a sample after the addition of ionic strength adjustment solution. The electrode potential was recorded after the equilibration for at least two minutes.

3. Results and discussion

Since the preliminary experiments with the in-situ prepared BiFE revealed its suitability for detecting low concentration levels of Ag(I), we further studied and optimized its electroanalytical performance aimed at developing an expedient, rapid and robust procedure being convenient for even more challenging applications, e.g. for measuring Ag(I) in suspensions of Ag NPs. For comparison, the experiments were also carried out using an unmodified glassy carbon electrode, as depicted in Fig. 1, which shows anodic stripping voltammograms (ASVs) for increasing concentration levels of Ag(I) in the range of 10–40 μg L^{-1} after 60 s accumulation at −0.6 V. It can be seen that after the first addition of Ag(I), the background current changed substantially due to the shift of hydrogen evolution reaction; however, for all examined concentrations of Ag(I) asymmetrical and split signals were observed at ca. +0.20 V shifting toward more positive potentials with increasing Ag(I) concentration implying on attractive forces within the metal deposit [27]. Additionally, the repeatability and linearity of the measurements were relatively poor and inadequate for practical application.