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Inorganic arsenic speciation in natural mineral drinking waters by flow-through anodic stripping chronopotentiometry



Dominika Jedryczko*, Pawel Pohl, Maja Welna

Wroclaw University of Technology, Faculty of Chemistry, Department of Analytical Chemistry and Chemical Metallurgy, Wybrzeze Stanislawo Wyspianskiego 27, 50-370 Wroclaw, Poland

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ABSTRACT

A simple and inexpensive method for chemical speciation of inorganic As in natural mineral drinking waters by using anodic stripping chronopotentiometry (ASCP) in an electrochemical flow-through cell with an Au wire as the working electrode was described in the present work. The presented method is an attractive alternative to laborious and time-consuming procedures requiring pre-separation of various forms of As before their detection by other flow-through and non flow-through stripping methods. The limits of detection were found to be $0.42 \mu\text{g L}^{-1}$ for As(III) and $0.55 \mu\text{g L}^{-1}$ for As(V), obtained at the deposition potentials of -350 mV and -1600 mV , respectively. The accuracy of the method was assessed by the spiking-and-recovery experiments for particular water samples and the recoveries found, being in range from 99% to 105% for As(III) and from 104% to 106% for As(V), respectively, were quantitative. The proposed method was successfully applied to speciation analysis of inorganic As in water samples with a high content of Cu.

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1. Introduction

Arsenic belongs to toxic substances that negatively affects human health [1]. One of the biggest sources of exposure to this element is groundwater. Arsenic in water is predominantly present in the form of inorganic species, i.e. arsenite, As(III), and arsenate, As(V). Minor amounts of methyl and dimethyl arsenic compounds are also being detected. The occurrence of the As(III) and As(V) forms is conditional on the redox potential of the environment and pH. pH of groundwater is often between 6 and 8. In this pH range, in more aerobic conditions, i.e. for the redox potentials of 272–352 mV (pH 6.7–7.5), the predominant form is As(V), whereas for the redox potentials from 87 to 172 mV (pH 7.5–8.2), As(III) is the most dominant form [2].

Monitoring of the As content in the environmental samples, especially in ground and drinkable waters, is a very important and popular issue and hence, numerous researches in this field with the use of the stripping electrochemical methods are reported in the literature. It seems, however, that the potential of these techniques to speciate As is still inexhaustible. To improve analytical performance of the stripping electrochemical methods in reference to selectivity and sensitivity of As(III) measurements, considerable efforts have been made to develop new

electrochemical sensors based on carbon nanotubes (CNTs) [3–6], a solid carbon paste [7], graphene [8], graphite [9] and glassy carbon [10–15], as well as microelectrodes modified with metallic or bimetallic nanoparticles (NPs) [4–8,10,12–15] for the last ten years. Despite the ng L^{-1} range detection limits (DLs) of As being obtained with these materials, their application in routine analysis seems to be very far off [16]. Apparently from the review by Luong et al. [1], there are two barriers that can explain this situation, i.e. poor reproducibility of the surface preparation of new sensors and electrodes and problematic development of commercial instruments [1]. With regard to the first of these barriers, better manufacturability of the surface preparation of the electrodes is recommended for highly precise measurements, e.g. Refs. [4,11]. However, short stability times of the electrodes (up to several days) is the major disadvantage of electrochemical measurements due to extended analysis time caused by an additional step of preparing the electrode surfaces. Practical utility of the macroelectrodes, having few millimeters in diameter, is better in this context because they are easy to handle and fabricate and offer excellent reproducibility. In our opinion, a significant limitation of new electrochemical sensors and electrodes is their ability to detect only the As(III) form, while total As in real samples is determined after pre-reducing As(V) into As(III). There is no question that a preliminary step of chemical reduction carries the risk of secondary pollution of analyzed water samples or loss of analytes. It is also an adverse event due to prolonged time of analysis. Hence, we fully agree with the observation of Cinti et al. [10] that

* Corresponding author.

E-mail address: dominika.jedryczko@pwr.edu.pl (D. Jedryczko).

further investigations are necessary to develop sensors and electrochemical microelectrodes adequate to simultaneously speciate both inorganic As species by electrochemical reduction of As(V) and As(III) at a more negative potential or by chemical reduction of As(V) to As(III) followed by anodic stripping voltammetry of As(III).

Based on previous advances in the field of electrochemical stripping techniques, we developed a new, flow-through anodic stripping chronopotentiometry (ASCP) method to simply, fast and simultaneously measure the individual inorganic As species, i.e., As(III) and As(V), concomitant in drinking mineral water samples but without any additional and commonly applied off-line chemical pretreatment of sample solutions aimed at reducing As(V) to As(III). A starting point for developing this method was a possibility to directly detect As(V) after its deposition on an Au wire electrode at a very negative deposition potential in acidic conditions. The same approach has been reported so far only in a few works [9,17,18] but we used for the first time a flow-through system in connection with the Au wire electrode and established suitable conditions for the calibrationless analysis.

2. Experimental

2.1. Apparatus

All measurements were performed with an automatic electrochemical analyzer EcaFlow 150 (Istran, Bratislava, Slovakia) interfaced with a PC and controlled by the EcaCoul program (Istran). The apparatus was equipped with a compact electrochemical flow-through cell, two solenoid inert valves, a peristaltic pump and a microprocessor-controlled potentiostat/galvanostat. An electrochemical cell, type 353c, working in a three-electrode system was used. A spiral Pt wire, an Ag/AgCl (in a saturated KCl solution) electrode and an E-T/Au wire were used as auxiliary, reference and working electrodes, respectively (see Fig. 1). The working Au wire electrode (0.55 mm of outer diameter and 4 mm in length) had a total active surface of 6.91 mm². This electrode was positioned perpendicularly to the flow of the solutions. The whole flow-through system was fully automated: analyzed sample solutions and standard solutions were passed through the electrochemical cell with the aid of the peristaltic pump ensuring reproducible and stable flow rates; two valves controlled the transport of the solutions at a time.

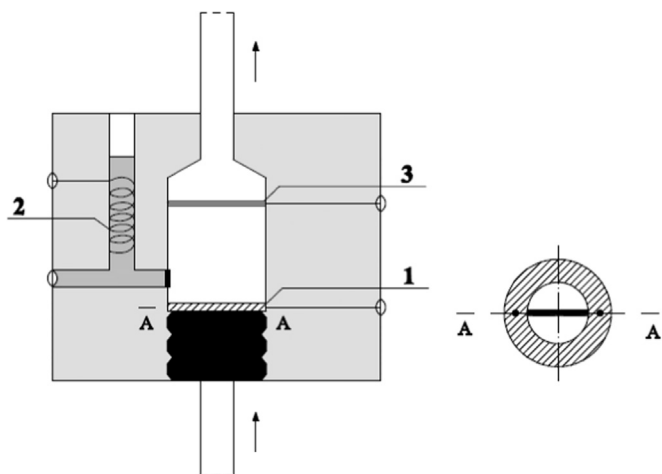


Fig. 1. A scheme of the electrochemical flow-through cell with three electrodes: 1 – an Au wire as the working electrode, 2 – an Ag/AgCl (in a saturated KCl solution) as the reference electrode and 3 – a spiral Pt wire as the auxiliary electrode.

2.2. Calibrationless method analysis and measurement procedure

In SCP, the measured analytical signal is the transition time (τ) required for re-oxidation of a deposit. Its practical evaluation is based on the combined Faraday's laws (Eq. (1)),

$$C = Q_{\text{strip}} / (R \cdot z \cdot F \cdot V_{\text{sample}}) = I_{\text{strip}} \tau / (R \cdot z \cdot F \cdot V_{\text{sample}}) \quad (1)$$

where C denotes the analyte concentration (in mol L⁻¹), Q_{strip} – the electrical charge (in C), R – the electrochemical recovery, z – the charge number corresponding to the stripping process, F – the Faraday constant (in C mol⁻¹), V_{sample} – the sample volume (in L), I_{strip} – the stripping current (in A), and τ – the transition time (in s). Apparently from the equation, for the experiments performed under the conditions approaching complete electrochemical deposition and dissolution of the analyte species ($R=1$), the amount of the accumulated material can be calculated directly from the acquired analytical signal. The application of such a calibrationless mode for determining the As concentration is a sensible facilitation in routine analysis of water samples.

The measurements were carried out according to the following sequence: the working electrode was conditioned at first for 5 s under the supporting electrolyte solution flow rate of 3 mL min⁻¹ and a supplied potential of 500 mV. The same potential was switched to the electrochemical cell during pauses before each electrolysis stripping cycle and in a standby mode. Then, untreated sample solutions were mixed on-line with the supporting electrolyte (0.1 mol L⁻¹ HCl with 0.002% (m/v) Triton X-100) and these solutions entered the electrochemical cell where the As species were deposited as the elemental As on the Au wire working electrode at a suitable deposition potential. In the next step, the solutions in the electrochemical cell were exchanged for the electrolyte, into which the deposits were galvanostatically stripped and the times corresponding to dissolution of As were acquired from the recorded chronopotentiometric signals. The background signal was registered from a respective blank sample (the supporting electrolyte) at first and the following chronopotentiometric signals for the samples were automatically corrected to obtain the net signals. In the applied flow-through system, the value of the deposition time were closely connected with the flow rate and the volume of the analyzed sample solution. In the developed method, it was 120 s and included the total time required for passing a given sample solution volume (along with the online mixing with the same volume of the supporting electrolyte) through the electrochemical cell and the time allowed for stabilization under static conditions (at the quiescence potential) with the stopped flow.

2.3. Reagents and samples

Analytical grade purity reagents were used for all experiments. A 37% (m/m) concentrated HCl solution and BioXtra purity grade Triton X-100, both from Sigma-Aldrich (Germany), were used to prepare the supporting electrolyte solutions. The As(III) and As(V) stock solutions (1000 mg L⁻¹) were made by dissolving appropriate amounts of As₂O₃ (POCH, Poland) and Na₂HAsO₄ · 7H₂O (Merck), respectively, and finally acidified with HCl to pH ~ 2. The solutions of Cd(II), Cu(II), Pb(II) and Zn(II), used for interference study experiments, were prepared by diluting TraceCERT certified single element standards (1000 mg L⁻¹) for AAS (Fluka). All working standard solutions were prepared daily. Deionized water (18.3 MΩ cm) used in all experiments was prepared using a Barnstead™ (USA) EASYpure water purification system, model D7033. Four natural mineral drinking waters with healing properties, popular in the Polish market, were chosen for speciation analysis. All waters come from deep-sea sources located on the spa

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