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Test for arsenic speciation in waters based on a paper-based analytical device with scanometric detection

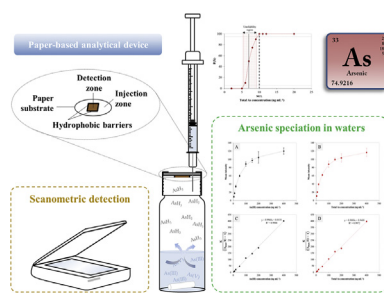
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HIGHLIGHTS

- A low-cost non-instrumental method for As speciation analysis is proposed.
- The method involves three phase microseparation with colorimetric reaction at the PAD's detection area.
- The physical separation of detection and injection zones avoids chemical incompatibility.
- The method enables determination of As(III), As(V) and total As in waters.
- The assay can be applied as a vanguard analytical system for total As screening.

GRAPHICAL ABSTRACT



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ABSTRACT

A rapid, simple and affordable method for arsenic speciation analysis is described in this work. The proposed methodology involves *in situ* arsine generation, transfer of the volatile to the headspace and its reaction with silver nitrate at the detection zone of a paper-based analytical device (PAD). Thus, silver nitrate acts as a recognition element for arsine in the paper-based sensor. The chemical reaction between the recognition element and the analyte derivative results in the formation of a colored product which can be detected by scanning the detection zone and data treatment with an image processing and analysis program. Detection and injection zones were defined in the paper substrate by formation of hydrophobic barriers, thus enabling the formation of the volatile derivative without affecting the chemical stability of the recognition element present in the PAD. Experimental parameters influencing the analytical performance of the methodology, namely color mode detection, composition of the paper-based sensor and hydride generation and mass transfer conditions, were evaluated. Under optimal conditions, the proposed method showed limits of detection and quantification of 1.1 and 3.6 ng mL⁻¹, respectively. Remarkably, the limit of detection of the method reported herein was much lower than the maximum contaminant levels set by both the World Health Organization and the US Environmental Protection Agency for arsenic in drinking water, unlike several commercially available arsenic test kits. The repeatability, expressed as relative standard deviation, was found to be 7.1% (n = 8). The method was validated against the European Reference Material ERM[®]-CA615 groundwater and successfully applied to the determination of As(III), As(V) and total inorganic As in different water samples. Furthermore, the method can be used for the screening analysis of total arsenic in waters when a cut-off level of 7 ng mL⁻¹ is used.

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1. Introduction

Groundwater contamination with arsenic has become a major global issue. Millions of people worldwide are exposed to this pollutant at concentrations above current drinking water standards. The situation is especially worrisome in Bangladesh, where 35–77 million people have been estimated to be chronically exposed to arsenic contaminated drinking water [1]. Although the maximum contaminant level (MCL) for this pollutant in drinking water has been set at 10 ng mL^{-1} by both the US Environmental Protection Agency (USEPA) and the World Health Organization (WHO), many developing countries still retain a 50 ng mL^{-1} standard. Remarkably, more stringent and challenging drinking water standards are expected to be set for arsenic in the future [2–4]. Thus, the development of rapid, cost-effective and sensitive analytical methodologies for arsenic monitoring in drinking water samples that meet with current and future standards for arsenic is of paramount importance.

Arsenic is predominantly present in the form of inorganic species in water samples, namely As(III) and As(V), whereas organic arsenic species such as methylarsonic acid, dimethylarsinic acid or trimethylarsine oxide are not considered of quantitative importance in waters [3,5]. The determination of arsenic species rather than the total content is highly desirable bearing in mind that they significantly differ in toxicity. Chromatographic techniques coupled with elemental detection systems are typically employed for arsenic speciation [6–8]. Alternatively, non-chromatographic methodologies, including electrochemical methods [9,10] or the combination of spectrometric detection techniques such as atomic absorption spectrometry [11–13], atomic fluorescence spectrometry [14], inductively coupled plasma mass spectrometry [15] or UV-vis spectrophotometry [16,17] with selective extraction of arsenic species [11,12,15] or hydride generation [14,16,17] have also been reported in the literature [3,18].

Since their inception in 2007 [19], the development and application of paper-based analytical devices (PADs) has undergone a continuous growth due to their simplicity, low-cost, portability and feasibility for the non-instrumental analysis by means of everyday communications and information technology (IT) equipment [20,21]. The applicability of PADs in the analysis of biomedical, food, and environmental samples has been extensively demonstrated [22–25]. However, the reduced sensitivity of PADs usually hinders their applicability to the monitoring of target analytes present at trace and ultratrace levels. With the aim of overcoming this drawback, a number of preconcentration approaches have been reported in the literature, most of them being applicable to the enrichment of non-volatile compounds [26–31]. It is noteworthy, however, that the number of reports devoted to monitoring volatile analytes or derivatives by using PADs is yet scarce, and the limits of detection (LODs) achieved with them are within the ppm level when preconcentration is not involved [31–33]. This fact represents a serious hindrance in monitoring environmentally relevant volatile analytes or derivatives by means of PADs. An appealing approach involving the headspace solid phase extraction of *in situ* generated H_2Se by a quantum dots-based PAD has been recently reported for determination of selenium in urine samples on the basis of fluorescence quenching, providing an advantageous PAD with improved sensitivity and selectivity [31]. However, the recognition element used in the reported PAD covered the whole area of the paper substrate, so a lack of chemical compatibility of the recognition element with the chemicals involved in the *in situ* generation of volatiles could restrict or even prevent the applicability of the PAD in alternative analytical systems.

The main aim of this work involves the development of a novel

PAD for speciation analysis of arsenic in water samples. The method relies on the microreaction of arsine generated *in situ* with silver nitrate at the detection zone of a paper substrate and subsequent scanometric analysis of the colored product. Formation of hydrophobic barriers in the paper substrate is proposed herein to physically separate detection and injection zones in the PAD, thus overcoming the reduction of silver ions produced by injection of sodium borohydride solution through the substrate. The possibility of carrying out speciation analysis with the reported PAD was assessed by carefully controlling the hydride generation conditions.

2. Experimental

2.1. Reagents and materials

All chemicals were of analytical reagent grade. High-purity deionized water was produced from a PETLAB ultrapure water system (Peter Taboada, Vigo, Spain). Stock solutions of As(III) and As(V) were prepared from As_2O_3 and As_2O_5 (Merck, Darmstadt, Germany), respectively. Working standard solutions were prepared daily by appropriate dilution of the stock solutions. AgNO_3 (Riedel-de Haën, Seelze, Germany) was used as recognition element. Hydrochloric acid (Prolabo), citric acid monohydrate (Sigma-Aldrich, St. Louis, MO, USA), and NaBH_4 (Merck) stabilized with 0.1 mol L^{-1} NaOH (Prolabo, Paris, France) were used for hydride generation. The following reagents were used for evaluation of potential interferences: K_2HPO_4 , $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaNO_2 , $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and H_2SeO_3 (Panreac, Barcelona, Spain), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Probus, Badalona, Spain), NaCl and $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ (Merck), NaHCO_3 , Na_2SO_4 and SbCl_3 (Carlo Erba, Milan, Italy), Na_2TeO_3 (Sigma-Aldrich) and humic acid (Fluka Chemie, Buchs, Switzerland).

Whatman No. 1 ($180 \mu\text{m}$, 87 g m^{-2}) and Whatman No. 3 ($390 \mu\text{m}$, 185 g m^{-2}) filter papers obtained from Whatman (Maidstone, Kent, UK) were assessed as paper substrates. A Lumocolor permanent pen 318-9 fine 0.6 mm (Staedtler, Nuremberg, Germany) was used to prepare the hydrophobic barriers on paper substrates.

Microextraction experiments were carried out by using 40 mL -amber vials sealed with screw top hole caps with PTFE faced-septa.

An HP 4500 desktop scanner was used to digitize PADs after microextraction experiments. Alternative systems such as digital cameras, cell phones or smartphones could also be used for quantitative readout as reported in the literature [22].

2.2. Characterization of PADs

A JEOL JSM 6700 FEG-SEM scanning electron microscope equipped with an Oxford Inca Energy 300 energy-dispersive X-ray spectrometer (EDS) was used for characterization of PADs. SEM images were obtained with an acceleration voltage of 10 kV using backscattered electron detection. EDS spectra were obtained at 15 kV .

2.3. Preparation of PADs

First, Whatman No. 3 filter papers were cut into circular pieces of 20 mm diameter. Then, PADs were prepared following previously reported fabrication processes [34,35]. Accordingly, hydrophobic barriers with a square side length of 8 mm were drawn on the upper side of the paper substrate with a permanent marker to define the detection area and, after the ink solvent was evaporated, the process was repeated on the lower side of the paper substrate. Once the ink solvent was evaporated, $10 \mu\text{L}$ of AgNO_3 solution was spotted in the detection zone and the prepared PAD was allowed to

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