

Determination of Inorganic Arsenic as Arsenite in Water Samples by a Paper-Based Microfluidic Sensor System

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Abstract

Sensing using disposable microfluidic paper-based analytical devices (μ PADs) meets the increasing needs of rapid, accurate and low-cost monitoring and analysis for environmental protection and healthcare. μ PADs utilize the capabilities of cellulose fibres in paper to transport liquids by capillary force. This paper describes the development of a μ PAD for the determination of inorganic arsenic in aqueous samples as arsenite (As(III)). This is the first μ PAD implementing a hydride generation approach on a paper-based platform for inorganic As determination. Arsine generated by the reaction of As(III) with sodium borohydride diffuses across a hydrophobic porous PTFE (Teflon) tape into the detection zone of the paper-based sensing system where it is oxidized by Au(III). The Au nanoparticles produced as a result of this reaction change the colour of the detection zone which can be related to the concentration of As(III) being reduced to arsine. Under optimal conditions the μ PAD is characterized by a limit of detection of 0.99 mg As(III) L⁻¹.

Key words: microfluidic paper-based analytical devices (μ PADs), inorganic arsenic determination, hydride generation, water analysis.

Introduction

Arsenic pollution is of considerable environmental and health concern due to its ubiquitous nature. The toxicity of arsenic compounds depends significantly on their chemical form. Inorganic arsenic species are believed to be considerably more toxic than organoarsenicals [1]. The dominant inorganic arsenic species are arsenite (As(III)) and arsenate (As(V)), with the former being considerably more toxic than the latter [2]. The determination of inorganic arsenic has been successfully conducted in flow analysis systems utilizing a hydride generation approach where inorganic As has been reduced to arsine (e.g., [3-5]). Arsenite can be reduced more efficiently to arsine than arsenate and therefore in a number of studies the combined concentration of As(III) and As(V) has been determined after off-line reduction of As(V) to As(III) (e.g., [5]).

This paper described the first μ PAD for the determination of As(III) using a hydride generation approach combined with gas-diffusion separation of arsine from the sample matrix prior to its optical detection involving its oxidation by Au(III).

Fabrication of the μ PAD

The proposed μ PAD was credit card size (78 mm \times 58 mm) and contained fifteen sensors, each consisting of 3 circular hydrophilic zones (Figure 1): (1) a sample zone (Zone 1), impregnated with 12 μ L of 0.8 M hydrochloric acid solution; (2) a reagent zone (Zone 2) impregnated with 12 μ L alkaline sodium borohydride solution (1% (w/v) NaBH₄ and 0.1% (w/v) NaOH); and (3) a detection zone (Zone 3) impregnated with 1.5 μ L of 5 mM HAuCl₄ solution. Zone 2 and Zone 3 were separated by a PTFE hydrophobic microporous membrane. The μ PAD was oven-dried for 5 min at 40 °C and laminated for maintaining the alignment of the circular zones of each of its sensors and prevent the evaporation of the sample and HAuCl₄ solution during the detection process. A Japanese screw punch was used to punch a sample insertion hole of 2 mm in diameter in the plastic cover over the centre of each sample zone (Zone 1) and Milli-Q water insertion hole at the end of the transport channel of each detection zone (Zone 3) (Figure 1).

Analytical procedure

Prior to sample introduction, 1.5 μL of Milli-Q water were deposited into the detection zone of each one of the 15 sensors of the μPAD through the corresponding insertion hole. The analytical procedure was conducted at room temperature and involved the deposition of 12 μL of sample or standard solutions into the individual sample insertion holes of the laminated μPAD , which were subsequently covered with a masking tape to prevent sample evaporation or loss of arsine gas. Arsine, produced in the sample and reagent zones, diffused across the PTFE (Teflon) tape and reduced Au(III) to Au nanoparticles thus changing the colour of the detection zones. These zones were scanned after a predetermined period of detection time using a conventional flatbed scanner.

Scanned images of the μPAD were stored in JPEG format (1200 dpi). The mean intensity of the green colour of the center of detection zones was measured using ImageJ software (National Institute of Health USA, <http://imagej.nih.gov/ij>) and was subsequently converted to absorbance (eq. (1)) by the method of Birch and Stickley [6].

$$A = -\log(I/I_0) \quad (1)$$

where I is the mean green colour intensity corresponding to the sample or standard and I_0 is the mean green colour intensity of the blank.

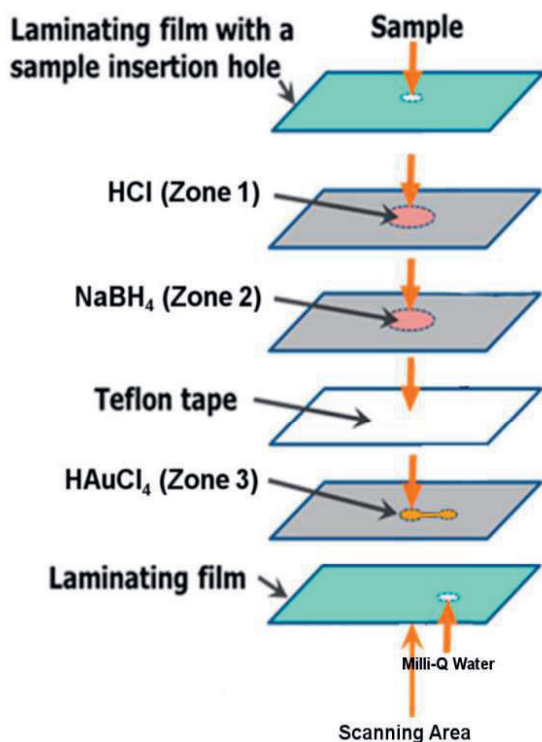


Fig. 1. Schematic representation of the hydride generation μPAD for inorganic As determination.

Optimization of the μPAD

Table 1 lists the parameters which were optimized together with the optimization ranges and the corresponding optimal values.

Tab. 1: Optimization results.

Parameter	Range	Optimal value
HCl (Zone 1) [M]	0.05 - 2.0	0.80
NaBH_4 (Zone 2) [% (w/v)]	0 - 1.6	1.0
HAuCl_4 (Zone 3) [mM]	1 - 15	5
Sample volume [μL]	6 - 18	12
Detection time [min]	1 - 30	5

Analytical figures of merit of the μPAD

Table 2 lists the analytical figures of merit.

Tab. 2: Analytical figures of merit.

Parameter	Value
Limit of detection for As(III) [mg L^{-1}]	0.99
Interdevice repeatability (3 μPADs) [%]	4.32
Intradvice repeatability (3 μPADs) [%]	5.07

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