

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/aca

Optimization and comparison of chemical and electrochemical hydride generation for optical emission spectrometric determination of arsenic and antimony using a novel miniaturized microwave induced argon plasma exiting the microstrip wafer

Pawel Pohl^{a,b}, Israel Jiménez Zapata^a, Nicolas H. Bings^{a,*}

^a Institute for Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

^b Analytical Chemistry Division, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Stanisława Wyspiańskiego 27, 50-370 Wrocław, Poland

ARTICLE INFO

Article history:

Received 1 August 2007

Received in revised form

31 October 2007

Accepted 1 November 2007

Published on line 19 November 2007

Keywords:

Arsenic

Antimony

Microstrip microwave plasma

Chemical hydride generation

Electrochemical hydride generation

Optical emission spectrometry

ABSTRACT

Continuous flow (CF) chemical hydride generation (CHG) and electrochemical hydride generation (ECHG) directly coupled to a novel 40 W, atmospheric pressure, 2.45 GHz microwave microstrip Ar plasma exiting a microstrip wafer has been developed for the emission spectrometric determination of As and Sb using a miniaturized optical fiber spectrometer and a CCD-array detector. The experimental conditions for both procedures were optimized with respect to the relative net intensities of the As I 228.8 nm and Sb I 252.8 nm lines and their signal-to-background intensity ratios. Additionally, the susceptibility to interferences from Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn and other hydride-forming elements in the determination of As and Sb using the CHG and ECHG techniques was investigated in detail. Under the optimized conditions, it was found that ECHG is more prone to interferences compared to CHG. The detection limits (3σ) of As (6 ng mL^{-1}) and Sb (7 ng mL^{-1}) obtained for the ECHG–MSP–OES method are about three times lower than in the case of the CHG–MSP–OES method due to a two-fold lower amount of H_2 introduced into the MSP in case of the ECHG, resulting in a better plasma stability and reduced background level. The linearity ranges for both calibration curves to a concentration of up to $5 \mu\text{g mL}^{-1}$ and a precision between 2% and 7% ($2 \mu\text{g mL}^{-1}$ and $0.050 \mu\text{g mL}^{-1}$ of As and Sb, respectively) were found for both methods. The developed ECHG–MSP–OES method was validated for As through the analysis of a certified coal fly ash standard reference material (NIST SRM 1633a) after sample dissolution. The derived concentration ($140 \pm 8 \mu\text{g g}^{-1}$) was found to agree well with the certified data ($145 \pm 15 \mu\text{g g}^{-1}$). The method was also successfully applied to the analysis of both a galvanic bath sample, which contained Sb and was spiked with As, and a tap water sample spiked with both analytes. Recovery rates of 99–101% and a Sb concentration of $6.6 \mu\text{g mL}^{-1}$ in the galvanic bath sample were revealed. The latter value showed a good agreement with the data obtained from ICP–OES analysis, which was also used for validation purpose.

© 2007 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +49 40 42838 2332/6075; fax: +49 40 42838 4381.

E-mail address: nicolas.bings@chemie.uni-hamburg.de (N.H. Bings).

0003-2670/\$ – see front matter © 2007 Elsevier B.V. All rights reserved.

doi:10.1016/j.aca.2007.11.001

1. Introduction

A microwave induced plasma (MIP) is a very suitable tool for the excitation of dry aerosols and gases [1], but a direct coupling of continuous flow chemical hydride generation (CF-CHG) with the MIP is still challenging due to the plasmas relatively low gas temperature. The introduction of volatile hydrides of As, Bi, Sb, Se, Te and other hydride-forming elements generated through the reaction with NaBH_4 in acidic media is therefore problematic. Indeed, CF-CHG is very efficient [2] and the MIP offers favorable conditions for the excitation of hydride-forming elements, but water moisture and the excess of H_2 co-generated with the volatile hydrides, continuously transferred to the low power atmospheric pressure MIP discharges, often lead to an instability of the plasma and even its extinction [2–4]. Particularly, the introduction of an increasing amount of H_2 , which has a higher thermal conductivity compared to Ar and He commonly used as plasma gases, and a high-dissociation temperature [5], often results in a deterioration of the analytical performance of the CF-CHG-MIP system with respect to achievable precision and the detection limits [6].

Typically, to minimize the described disadvantages the CF-CHG reaction has to be carried out under carefully optimized conditions regarding the NaBH_4 concentration and the flow rates of a sample and a reducing agent, as they determine the amount of H_2 produced in the HG reaction [7]. In few previous studies on coupling CF-CHG with a MIP sustained in different resonators, an elimination of H_2 and water vapor was carried out by using special membrane-based separators [4,8]. Concentrated H_2SO_4 [8,9] and water-cooled condensers [10,11] were also used for a desolvation of the gas phase before its introduction into the MIP source.

Instead of using CHG with NaBH_4 as a reducing agent for the formation of hydrides, electrochemical hydride generation (ECHG) performed in an electrolysis cell can also be used as an alternative. As it has been shown [12–14], that such an approach usually allows a better analytical performance in the case of the MIP, mostly because of a higher achievable plasma stability due to reduced volumes of co-generated H_2 compared with CHG.

Recently, a miniaturized Ar MIP fully sustained and operated in a microstructure-based resonant cavity with the microstrip lines for power transition (so called microstrip plasma, MSP) has been used for the optical emission spectrometric (OES) determination of As and Sb using CF-CHG [15]. In the present study further improvements have been made through using both a MSP exiting the wafer and a miniaturized ECHG electrolysis cell to gain better analytical performance and enhanced power of detection. For that purpose, an Ar MSP provided inside a substrate, in which the geometry of the microstrip relatively to the open end of the gas channel enables the plasma to exit from the wafer, was investigated and was optimized for OES using a miniaturized optical fiber spectrometer equipped with a CCD detector. Volatile hydrides of As and Sb were generated by CF-HG using NaBH_4 and complementary ECHG using a miniaturized three-dimensional electrolysis cell. The operating conditions were investigated in detail and were thoroughly optimized for both

HG manifolds and the Ar MSP. The analytical performance of both HG–MSP–OES methods, including linear dynamic ranges, achievable precision and detection limits and the susceptibility to chemical interferences from transition metal ions and other hydride-forming elements were assessed and discussed. The method was used for the analysis of galvanic bath and tap water samples and for the quantification of As in a certified coal fly ash standard reference material (NIST SRM 1633a).

2. Experimental

2.1. Microstrip plasma

The miniaturized low power atmospheric pressure microwave-induced plasma based on microstrip technology (MSP) was operated in a square sapphire wafer (30 mm in length and 1.2 mm in height), in which a straight cylindrical channel (0.64 mm in diameter) for introduction of Ar working gas was grown-in. A photograph of the MSP operated in Ar can be seen in Fig. 1a. In contrast to the structure recently used in our laboratory for the MSP, which was operated inside the gas channel of the wafer [15,16], in the actual design the microstrip line (0.8 mm in width) is extended to the edge of the wafer, causing the plasma to exit the gas channel by about 3 mm. The position of a compensated edge and a matching element in this new design is also changed to keep the reflected power to a minimum [17]. As in case of the other MSP designs, a Cu ground electrode sputtered on the backside of the wafer was connected to a Cu socket, cooled by an active air cooler. The microwave radiation at a frequency of 2.45 GHz was generated with a solid state rf generator (Dirk Fisher Elektronik, Germany) and was coupled to the MSP by a coaxial connector. The MSP was sustained in Ar at a maximum forward power of 40 W. For ignition of the plasma a high voltage spark was used. The Ar carrier gas loaded with volatile hydrides was introduced into the gas channel of the wafer using a metal capillary. For controlling the Ar flow rates a mass flow controller (F-201C-FB-33V, Bronkhorst High-Tec, Netherlands) was used.

The radiation emitted by the MSP was collected by a collimating lens and was transmitted through an optical fiber to a miniaturized spectrometer equipped with a high-performance 2048-element linear CCD-array detector (ILX511, Sony). The distance between the lens and the wafer was 45 mm. Additionally, a quartz slide was used in between the lens and the MSP to protect the lens from hot gases released by the MSP. A list of the used instrumental components is given in Table 1.

2.2. Hydride generation manifolds

For CHG, the acidified (1 mol L^{-1} HCl) analyte solution containing As and Sb and the alkaline (0.02 mol L^{-1} NaOH) solution of NaBH_4 (0.3%, m/v) were delivered at a flow rate of 0.65 mL min^{-1} by means of a two-channel peristaltic pump to a T-piece where the HG reaction was initiated. The reaction mixture was then passed to a small 6-mL gas-liquid phase separator (GLS) to separate the gaseous products of the HG reaction from the spent solution. The hydrides and

Download English Version:

<https://daneshyari.com/en/article/1170112>

Download Persian Version:

<https://daneshyari.com/article/1170112>

[Daneshyari.com](https://daneshyari.com)