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Optical emission spectrometric determination of arsenic and antimony by continuous flow chemical hydride generation and a miniaturized microwave microstrip argon plasma operated inside a capillary channel in a sapphire wafer

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Abstract

Continuous flow chemical hydride generation coupled directly to a 40 W, atmospheric pressure, 2.45 GHz microwave microstrip Ar plasma operated inside a capillary channel in a sapphire wafer has been optimized for the emission spectrometric determination of As and Sb. The effect of the $NaBH_4$ concentration, the concentration of HCl, HNO_3 and H_2SO_4 used for sample acidification, the Ar flow rate, the reagent flow rates, the liquid volume in the separator as well as the presence of interfering metals such as Fe, Cu, Ni, Co, Zn, Cd, Mn, Pb and Cr, was investigated in detail. A considerable influence of Fe(III) (enhancement of up to 50 %) for As(V) and of Fe(III), Cu(II) and Cr(III) (suppression of up to 75%) as well as of Cd(II) and Mn(II) (suppression by up to 25%) for Sb(III) was found to occur, which did not change by more than a factor of 2 in the concentration range of 2–20 μg ml^{-1}. The microstrip plasma tolerated the introduction of 4.2 ml min^{-1} of H_2 in the Ar working gas, which corresponded to an H_2/Ar ratio of 28%. Under these conditions, the excitation temperature as measured with Ar atom lines and the electron number density as determined from the Stark broadening of the H_β line was of the order of 5500 K and $1.50 \cdot 10^{14}$ cm^{-3}, respectively. Detection limits (3σ) of 18 ng ml^{-1} for As and 31 ng ml^{-1} for Sb were found and the calibration curves were linear over 2 orders of magnitude. With the procedure developed As and Sb could be determined at the 45 and 6.4 μg ml^{-1} level in a galvanic bath solution containing 2.5% of $NiSO_4$. Additionally, As was determined in a coal fly ash reference material (NIST SRM 1633a) with a certified concentration of As of 145±15 μg g^{-1} and a value of 144±4 μg g^{-1} was found.

Keywords: Microstrip microwave plasma; Hydride generation; Optical emission spectrometry; Arsenic; Antimony

1. Introduction

The microwave induced plasma (MIP) has received a considerable attention in analytical atomic spectrometry as a powerful radiation source. In a number of cases it could be an alternative to the inductively coupled plasma (ICP) because of the costs of the instrumentation and operation or the ease of operation [1]. Due to distinctive spectroscopic features such as high electron number density and electron temperature, the MIP has been proved to be a very beneficial radiation source for the determination of As, Sb, Se, Sn and Te, which can form gaseous covalent hydrides, when their acidified solutions react with sodium tetrahydroborate ($NaBH_4$). However, a direct introduction of the hydride generation (HG) reaction by-products, including CO_2, and an excess of co-generated H_2 as well as water moisture with the analyte hydrides into the MIP may lead to plasma instabilities and even its extinguishing. Therefore, in many previous approaches for HG coupled to the MIP, discontinuous reaction manifolds were used, in which the H_2 was separated from the analyte hydrides by trapping the hydrides in a graphite furnace [2–4] or in liquid N_2 [3,5,6]. Moreover, the HG reaction was carried out under carefully optimized conditions in this respect [6].

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Accordingly, a direct coupling of continuous flow hydride generation (CF-HG) to the MIP has not so frequently been realized. In the few papers published, special membrane-based separation of H_2 and water vapor [7,8], concentrated H_2SO_4 tanks [8,9] or water cooled condensers [10,11] for a desiccation of the gas phase before its introduction to the radiation sources were commonly used. All works cited above have demonstrated that the introduction of H_2 and water vapor into the MIP is critical for the MIP discharge and the analytical figures of merit of HG-MIP-OES. Despite the different types of microwave structures (surfatrons, cavities, microwave plasma torches) and the systems used for CF-HG, high amounts of H_2 originating from the reaction (sometimes up to 30% in the working gas [10]) normally require the operation of the discharges at a power above 100 to 200 W.

A miniaturization of the MIP for spectrochemical analysis could be realized by using a microstructure-based resonant cavity with microstrip lines for power transmission [12,13]. A such microstrip plasma (MSP) in a fused-silica wafer was applied already for the determination of Hg under the use of the cold vapor technique [14,15]. In preliminary measurements it was found that the MSP could tolerate the H_2 co-produced with the volatile hydrides in chemical hydride generation at well selected conditions. This could be a result of the high field densities inside the capillary in the sapphire wafer resulting from its small diameter as well as from the small size of the microstrip antenna, which is very close to the plasma. Accordingly, in this work a direct coupling of CF-HG performed in a small volume HG system to a miniaturized, 40 W, atmospheric pressure microstrip MIP (MSP) first could be realized. For downscaling the system, a miniature fiber optic spectrometer plugged into the USB port of a PC is used for recording the spectra of the MSP, which eliminates the need for external A/D converter. The experimental conditions for the HG and the MSP features were investigated in detail. The analytical performance of the CF-HG-MSP-OES procedure was optimized for As and Sb. The linear dynamic range, the precision, the detection limits and the susceptibility to chemical interferences from transition metal ions were assessed and discussed. The procedure will be shown to be of use for determinations of As and Sb in a galvanic bath sample and of As in a coal fly ash standard reference material (NIST SRM 1633a).

2. Experimental

2.1. Instrumentation

The experimental set-up for CF-HG coupled to the miniaturized microstrip MIP (MSP) is shown in Fig. 1. The low-power atmospheric pressure 2.45 GHz MSP was operated inside a sapphire wafer (30 × 30 × 1.5 mm, LWH) covered on one side with a 0.1 μm Ti adhesion layer and a 2 μm Cu layer serving as a ground electrode. The latter was connected to a Cu base and was cooled with a fan (25 × 25 mm, LW). As described previously by Bilgic et al. [12], the microstrip structure of 0.8 mm in width was above a straight grown-in cylindrical channel of 0.9 mm in diameter provided through the center of the wafer. The power oscillator (Dirk Fischer Elektronik, Germany) was supplied with a type 2231.1 voltage regulator (Statron Geratechnik, Germany) to generate microwaves of a frequency of 2.45 GHz at an output power of up to 40 W. The microwave energy was transferred to the gas flowing in the channel through a coaxial cable. The MSP discharge used Ar as working gas, was fully sustained inside the gas channel, and was located near

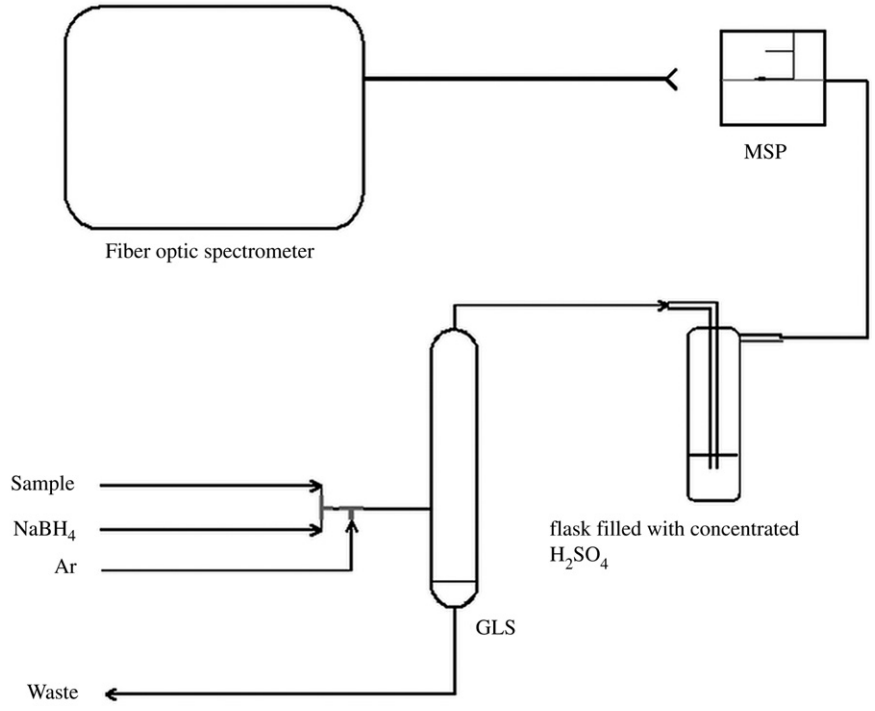

Fig. 1. Experimental set-up for the CF-HG-MSP-OES.