



Micro/nano bubble-modified flame atomic spectrometry as a new technique for promotion of the figures of merit during determination of metal species: Improvement in the performance of pre-mixed burner



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ABSTRACT

A new micro/nano bubble-modified flame atomic spectrometry has been introduced for promotion of some figures of merit during determination of metal elements such as Pb(II) and Sn(II) via controlling the stoichiometry of an acetylene/air flame by bubbles generated through sonoelectrochemistry on the surface of nanocarbons such as carbon dots (CDs). For this purpose, the sonoelectrochemical cell is connected to a pre-mixed burner to generate both oxygen and hydrogen micro/nano bubbles during applying direct-current (DC) potential such as +8.00 V (for oxygen) or –8.00 V (for hydrogen) to a two-electrode system including a graphite rod and stainless steel inside a solution of 0.5 M NaCl as electrolyte. According to the results, introduction of each oxygen or hydrogen micro/nano bubbles to the flame atomizer not only has strong influence on controlling the stoichiometry (oxidizing and reducing behavior) and temperature of the flame, but also prevents from flashback of the flame into the pre-mixed burner. Major improvements is also observed in some figures of merit such as linearity, sensitivity, detection limit, and the selectivity during analyses of elements such as Pb(II) or Sn(II) via modification of atomic absorption/emission spectrometry (AAS, AES) with micro/nano bubbles. Generated bubbles also play significant roles like releasing and chelating agents during analysis of Pb(II). Good agreements have been evaluated between bubble-modified AAS and inductively coupled plasma during analyses of Pb(II) in some types of rice samples.

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1. Introduction

Atomic spectrometry is an analytical technique that is used for qualitative and quantitative determination of perhaps ~70 elements [1–3]. Sensitivity of atomic methods lies typically from the $\mu\text{g mL}^{-1}$ to ng mL^{-1} ranges [4]. Additional virtues of these methods are speed, convenience, selectivity, and moderate cost [1,4]. Spectroscopic determination of atomic species can only be performed on a gaseous medium in which the individual atom is well separated from each other [1,5,6]. Consequently the first step in all atomic spectroscopic procedures is atomization, a process in which the sample is volatilized and decomposed in such a way to produce an atomic gas [5]. The efficiency and reproducibility of the atomization

step determine the method's sensitivity, precision, and accuracy [1,5,7]. As a result, atomization is considered as the most critical step in any atomic spectroscopies [5,7].

Atomizer is effectively an analog of the sample holder (cuvette) in the UV–vis spectroscopy [8]. This module provides a vehicle for atomization during formation of atomic vapor (atom reservoir) [4,8]. In the atomic spectroscopy, various atomizers such as electrical arc/discharge, plasma, flame, and graphite furnace are used [1,4,5,9]. In the electrical arc/discharge atomizer in spite of its simplicity, it seriously suffers from low reproducibility [4]. In addition, atomizers such as arc/discharge and plasma are suitable only for atomic emission spectroscopy (AES) [5]. Whereas, atomizers like graphite furnace and flame are suggested in both atomic absorption and emission spectroscopies (AAS and AES) [2,5,9,10].

In any flame atomizer, only liquid samples can be introduced through the nebulizer via formation of droplets [5]. A sub-population (~10%) of these droplets is then introduced into the

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flame [5]. In this atomizer high-pressure gas is the oxidant, with the aerosol containing oxidant being mixed subsequently with the fuel [1,4,5].

Two types of general burners in atomic spectroscopy include turbulent flow (or total consumption) and laminar flow (or pre-mixed) burners. In the former burner, total amount of independently introduced fuel and oxidant are mixed with each other to form flame [11]. This burner in spite of its safety and simplicity has serious challenges such as high fluctuation and low thermal stability [2,5]. This burner is often applicable in AES [5,12]. The most common burner type is the pre-mixed burner that has a long path length [12]. As the beam of light is passed through the broad flame, long optical path provides acceptable stability in the AAS. Formation of laminar flame is considered as another advantage of this burner, due to the pre-mixing of fuel and oxidant in a container before introduction to the flame [12].

In the pre-mixed burner as the flow rate increases, the flame rises until reaching a point above the burner [5,11]. Stable flame is provided in region at which the same values are estimated for gas flow rate and the burning velocity [2]. Consequently as soon as the gas flow rate does not exceed the burning velocity, the flame propagates itself back into the pre-mixed burner that leads to have flashback [5]. Compared to the total consumption burner, this event not only prevents the use of pure oxygen as oxidant in the pre-mixed burner but also limits the introduction of nitrous oxide to special procedure during operation with AAS [5,6,13].

From another aspect, both emission and absorption spectra are affected in a complex way by variations in the flame temperature [1]. Higher temperatures tend to promote the sensitivity via enhancement in the total atom population of the flame [1]. With certain elements such as the alkali metals, however increase in atom population is more than the offset caused by the loss of atoms during ionization, but the flame temperature determines the relative number of excited and unexcited atoms in the flame. In an air/acetylene flame, for example, the ratio of excited to unexcited magnesium atoms can be computed to be $\sim 10E-8$ [5]. Whereas in the oxygen/acetylene flame which is $\sim 700^\circ\text{C}$ hotter, this ratio is evaluated to be $\sim 10E-6$ [5]. Control of the flame temperature is thus of prime importance for improving some analytical parameters such as sensitivity and selectivity during analysis of metal species with atomic spectrometric techniques [1,5].

During the last decade, micro/nano bubbles due to their significant advantages such as long lifetime, high stability and involving high pressure have possessed much attention [1,5]. It seems that introduction of bubbles into the atomizers in AAS and AES may significantly promote some figures of merit during analysis of various metal ions. To reach this purpose hereby in this study a new micro/nano bubble-modified flame AAS technique is introduced in detail.

2. Experimental

2.1. Materials

All the reagents were from their analytical grades. Materials such as KCl, KNO_3 and NaCl were from Merck; Darmstadt, Germany. Ethylenediamine tetra acetic acid (EDTA) was related to Fluka. Stock solution of 0.5 M NaCl (Merck; Germany) in water was prepared via dissolving 1.462 g of NaCl in 50.0 mL triply-distilled water. Nanocarbons such as carbon dots (CDs), graphene quantum dots (GQDs) and their hybrids (mixture) were synthesized by exfoliation method using a sonoelectrochemical cell [14]. A pressure sensor (model: 5612-015) was also utilized to record the pressure gradient during formation of micro/nano bubbles. In addition, the quantity of oxygen introduced to the burner during formation of micro/nano

bubbles was quantified using an oxygen meter (model: Lutron DO-5510). A Ni–Cr thermocouple was also adopted to study the effect of bubbles on the flame temperature.

Stock solutions ($1000\ \mu\text{g mL}^{-1}$) of Pb(II) and Sn(II) were generated via dissolving lead nitrate (Merck; Germany) and tin chloride (Merck; Germany) in two 50.0 mL volumetric flasks. Standard solutions of at ng mL^{-1} levels were daily generated via dilution of the stock solutions with triply-distilled water. Also, stock solutions of ($1000\ \mu\text{g mL}^{-1}$) of F^- and PO_4^{3-} were generated using NaF (Merck; Germany) and Na_3PO_4 (Merck; Germany) in two 50.0 mL volumetric flasks to study the interfering effect during Pb analysis.

2.2. Electrochemical generation of micro/nano bubbles

In this study, micro/nano bubbles of O_2 and H_2 have been synthesized using the sonoelectrochemical method [14]. The schematic of the sonoelectrochemical cell is shown in Fig. 1. As clearly shown, the electrochemical cell consists of a Teflon cubic cell with $10\ \text{cm} \times 10\ \text{cm} \times 10\ \text{cm}$ dimensions. A two-electrode system includes a graphite rod with 0.8 cm diameter and a stainless steel (Tip: 316) horn-shaped electrode with 2.0 and 3.5 cm bases. This two-electrode system is then positioned next to each other at the top and bottom faces of the reaction cell. Two sonicators (model: 300E13TR-1) with $\sim 900\ \text{kHz}$ are also positioned next to each other in the other two sides (left and right) of the cell. The pH of the electrolyte in the cell is simultaneously detected using a pH meter (model: Lutron pH-20). Also the temperature of the electrolyte is controlled using two peltier coolers (model: 12706 peltier module TEC.) through a thermostat. The amount of current passed through the electrolyte is also fixed via adjusting the level of the electrolyte inside the cell using a level meter (model: Acvm 514 Techron). A fixed direct current (DC) potential (+8.00 V or $-8.00\ \text{V}$) is applied to the two-electrode system using a potentiostat. Various parameters such as pH, sonication radiation, and applied bias are automatically operated through a program written in Visual Basic.

The synthesized micro/nano bubbles are characterized via following the responses of gas pressure sensor and the oxygen meter (model: Lutron DO-5510). For this purpose, briefly the pressure gradient as well as concentration of oxygen in parts per million (ppm) levels is recorded using T-way glass tubing, in which direct flow of gas is carried through two side arms and the sensors are individually positioned at the third side of this glass tubing. The enhancement in the concentration of each O_2 or H_2 during micro/nano bubble formation is evidenced via photographic imaging the burner using a charged coupled device (CCD, model: TSCO TW-1600K). Also the stability of synthesized micro/nano bubbles is evaluated via following the surface tension of the aqueous solution using photographic imaging according to the procedure reported in Ref. [15].

It should be noted that in this study, due to the formation of micro/nano bubbles on the surface of nanomaterial-based fluids such as suspension of CDs, it is impossible to characterize the morphology and size distribution of the micro/nano bubbles using electron microscopy. In addition, as a result of adoption of electrochemical method for synthesis of micro/nano bubbles [16] as well as owing to the importance of fine bubbles for supersaturation of the aqueous electrolyte, consequently it is preferred to adopt “micro/nano bubble” term for the generated bubbles using the proposed procedure.

2.3. Micro/nano bubbles-modified pre-mixed burner

In order to study the effect of bubbles on the performance of burner, the micro/nano bubble-generating system is situated as the bottom of the pre-mixed burner of an AAS instrumentation system (Shimadzu) to generate micro/nano bubbles of H_2 and O_2 on the

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