Spectrochimica Acta Part B 106 (2015) 75–80

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Technical Note

Characterization of rapidly-prototyped, battery-operated, argon-hydrogen microplasma on a hybrid chip for elemental analysis of microsamples by portable optical emission spectrometry

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ARTICLE INFO

Article history:
Received 29 September 2013
Accepted 22 January 2015
Available online 4 February 2015

Keywords:
Microplasma Optical Emission Spectrometry
Battery operation
Rapid prototyping
Polymeric substrate
Portable spectrometer

ABSTRACT

A rapidly-prototyped, battery-operated, atmospheric-pressure, self-igniting Ar-H_2 microplasma was interfaced to a portable fiber-optic spectrometer. The microplasma-spectrometer combination was used to document the spectral lines emitted when μL of dilute solutions of single element standards of Ag, Ba, Ca, Eu, Pd, Rb and Sr were first dried and then vaporized into the microplasma. A small-size, electrothermal vaporization system was used for microsample introduction. Identification of the prominent spectral lines for these elements is reported. It was found that the most prominent spectral line for Ba, Ca and Sr was different than that emitted from an inductively coupled plasma (ICP). In general, prominent spectral lines with low excitation energy were dominating, thus resulting in spectra simpler than those emitted from an ICP. Detection limits were between 45 and 180 pg (expressed in absolute amounts). When expressed in relative concentration units, they ranged between 15 and 60 μg/L (obtained using 3 μL diluted standards). Calibration curves were linear (on the average) for 1.5 orders-of-magnitude. Average precision was 15%. Analytical capability and utility was demonstrated using the determination of Ca and Mg in (medicinal) thermal spring water.

1. Introduction

Microplasmas have been defined arbitrarily as those with one critical dimension less than 1000 μm (e.g., in the sub-mm range) or those that have been microfabricated [1]. In addition to their small dimension as a key characteristic, microplasmas can be classified in a number of ways [1–11]. To name but a few, according to their operating pressure (e.g., atmospheric-pressure or low-pressure); according to the type of electrical power used to sustain them [8–11]; as gas-liquid microplasmas (e.g., those that use an electrolyte solution as part of an electrode [12–16]); according to their geometric shape (e.g., planar [10], microhollow [17]); and, according to their method of fabrication (e.g., micromachined or rapidly-prototyped microplasmas on planar, postage-stamp size 2D-chips or 3D-printed microplasmas on 3D-chips [18–25]). Thus far, microplasmas of the type classified above received attention in the literature, such as, in review articles [1–7], in books [26,27] and in a growing list of papers describing their use in chemical analysis [7–25] and in other related applications [28,29]. Their small-size and low-weight, and their low electrical power and reduced gas-consumption (as compared to lab-scale plasmas, such as an ICP or Inductively Coupled Plasma) decrease operating costs and enable portability and battery-operation (for potential use in bringing part of the lab type of applications).

For analytical applications, introduction of samples into microplasmas is a challenge. Initially, gaseous sample introduction was used to demonstrate analytical capability and utility of gas-phase microplasmas [1,8–11, 17]. Introduction of liquid samples, however, has been problematic (at best) [1,18,19], because microplasmas are extinguished when liquid samples are introduced into them. This is primarily due to use of low levels of electrical power (for instance a few Watts for a microplasma as opposed to ~1.5 kW typically used by an ICP). We addressed this operational difficulty by introducing dried solution residues into microplasmas using a specially designed, electrothermal vaporization microsample introduction system [18,19,28,29]. Others employed an electrolyte solution as one of the electrodes for their gas-liquid microplasmas [12–16].

In addition to sample introduction, knowledge of the spectral lines emitted by a microplasma when a diluted, single element solution is introduced into them is important for two key reasons. One reason is because it will help identify the prominent emission lines of the element under consideration. This information is critical because the most prominent lines emitted by microplasmas are often different than those emitted by an ICP. Lead is a case in point: in an ICP, the best spectral line is the ion line at 220 nm, in a microplasma it is the atom line at 405 nm [21]. In such cases, ICP-based wavelength tables of prominent emission lines [30] are of limited use. The second reason is that spectral simplicity (or complexity vis-à-vis spectra emitted by an ICP) will help address the

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http://dx.doi.org/10.1016/j.sab.2015.01.009
0584-8547/

question: would a portable spectrometer with a short focal-length have adequate resolution for atomic emission measurements?

The objectives of this work are three-fold. The first is to document optical emission spectra from 200 nm to 850 nm and to identify the prominent emission lines for Ag, Ba, Ca, Eu, Pd, Rb and Sr. These have never been reported before for a microplasma of the type described here. The second is to obtain analytical performance characteristics (e.g., detection limits) for these elements using their most prominent spectral line and a portable spectrometer. And the third is to demonstrate analytical capability and utility using the determination of Ca and Mg in (medicinal) thermal spring water as an example.

2. Instrumentation and operating conditions

A block diagram of the instrumentation used in this work is shown in Fig. 1. With the exception of an increase in inter-electrode distance from 12 mm to 15 mm [21] (that improved stability of microplasma background emission), the instrumentation was identical to that described previously [21]. The power supply with a peak-to-peak voltage of about 5 kV was a commercial one [details in 21]. The microplasma was formed between two stainless-steel needle electrodes (Fig. 1) that were inserted at the opposite ends of a chip with a microplasma channel rapidly prototyped [22–24] out of Teflon®.

Microvolume samples of liquids were introduced into the microplasma using a small-size electrothermal vaporization microsample introduction system (shown in some detail in Fig. S1) and described in some detail in Refs. [21,28] and [29]. This system is akin to a larger, electrothermal, near-torch vaporization (NTV) system developed for use with ICPs [31]. The outlet of the vaporization chamber was connected to the microplasma inlet (Fig. 1), thus the carrier-gas through the sample introduction system also served as the microplasma support gas.

Microliter volume samples were pipetted on a coil made from rhenium (Re) filament (Fig. S1). The coiled-filament was attached to a ceramic support. Electrical power-transfer cables running through the support connected the coiled-filament to an external dc power supply. A mixture of Ar-H_2 (3% H_2) at 250 mL/min was used as the carrier-gas and as the microplasma support-gas. Hydrogen was used because it reduces or eliminates oxidation of the Re filament [31]. The temperature of the coiled-filament was measured using an IR (infrared) thermometer (Model M90-R-2, Mikron Instrument Co., Wyckoff, NJ).

When electrical power (in the form of ~5 kV high-voltage ac) was applied between the electrodes, a self-igniting, atmospheric-pressure microplasma was formed between the electrodes inside the microplasma channel (Figs. 1 and S1). Continuous application of high voltage ac (HVac) sustained the microplasma. The HVac was generated from an 18 V dc rechargeable battery (8 V with max current = 0.65 A) using a dc-to-HVac converter [21]. The battery was re-charged using a portable solar panel [21,23].

Microplasma background optical emission spectra and analyte signals were monitored by positioning the fiber optic cable on top of the microplasma (Figs. 1 and S1). The fiber-optic cable was connected to a portable spectrometer (an EPP 2000C, StellarNet Inc., Oldsmar, FL) with an integrating, 2048 pixel, photodiode array (PDA) detector with a 12-bit analog-to-digital (ADC) converter used for digital readout. The spectrometer was powered from the USB-port of the controlling computer.

3. Experimental

The sequence for sample (and blank) runs was as follows: with the microplasma off, the ceramic support with the coiled-filament on it (Fig. S1) was retracted from the vaporization chamber. Microliter volumes of samples were pipetted onto the filament using an Eppendorf™ pipette. Solutions were prepared by serial dilution with 18.2 MΩ·cm water from 1000 μg/mL standard solutions. Subsequently, the coil with a sample on it was re-inserted into the vaporization chamber (Fig. S1) and low electrical power (~0.33 W, translating to ~100 °C) was applied to the coil for 90 s, thus drying the sample on it. Then the microplasma was ignited, it was allowed to stabilize for 10–30 s per-run and relatively higher electrical power (e.g., 40 W) was rapidly applied to the coil. Rapid heating vaporized the sample residue that remained on the coil after drying. The vaporized sample was transported to the microplasma by the Ar-H_2 carrier-gas where it interacted with the microplasma thus generating an atomic emission signal with a time-dependence (Figs. S2a and S2b).

To enable acquisition of time-domain emission signals using the integrating array detector installed on the portable spectrometer (Fig. S1), successive spectral episodes (or spectra) were acquired one-at-a-time at consecutive time-intervals of 47.6 ms each (Fig. S2). Each spectral episode covered the full wavelength range of the spectrometer (i.e., from 200 nm to 850 nm). Spectral episodes were acquired, processed and plotted in 3 dimensions (3-d) as intensity vs. wavelength vs. time plots (Fig. S2a and S2b) or as more conventional 2-d spectra (Fig. S2c) [21].

Sustaining microplasmas with reproducible background emission levels and spectral lines intensities was challenging. Microplasma stability depended on a number of inter-dependent operational parameters [21], with inter-electrode distance being key among them. The inter-electrode distance was changed from 12 mm [21] to 15 mm and this provided a microplasma with a more stable background emission (as observed visually and spectroscopically). In this case however, the most stable microplasma was obtained at 5.2 W (rather than 4 W

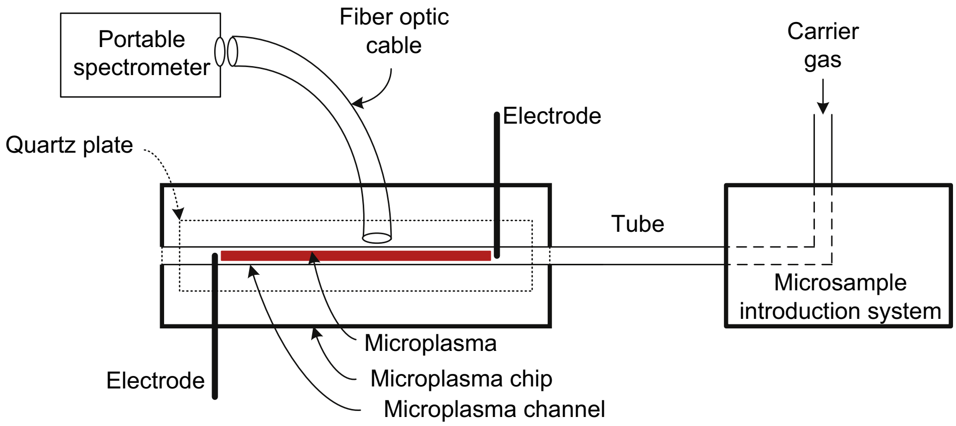

Fig. 1. Block diagram of the microplasma-microsample introduction system-fiber optic spectrometer combination used for this work. A quartz plate was used due to its transparency to UV.