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Spectrochimica Acta Part B 61 (2006) 686 – 695

SPECTROCHIMICA
ACTA
PART B

www.elsevier.com/locate/sab

Characterization of the supersonic expansion in the vacuum interface of an inductively coupled plasma mass spectrometer by high-resolution diode laser spectroscopy ☆

W. Neil Radicic [1], Jordan B. Olsen, Rebecca V. Nielson [2], Jeffrey H. Macedone, Paul B. Farnsworth *

Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States

Received 22 June 2005; accepted 23 September 2005
Available online 3 November 2005

Abstract

The supersonic expansion in the first vacuum stage of an inductively coupled plasma mass spectrometer has been characterized by laser-induced fluorescence of metastable argon atoms in the expansion. Atom velocities and temperatures were determined from Doppler shifts and linewidths, respectively, in the excitation spectra of the argon atoms. Shock structures characteristic of a supersonic expansion, the barrel shock and the Mach disk, were manifest as bimodal velocity distributions. The terminal velocities reached by the atoms were characteristic of conditions in the plasma source upstream from the entrance to the vacuum interface.

Keywords: ICP-MS; Laser-induced fluorescence; Supersonic expansion; Doppler shift

1. Introduction

The vacuum interface in an inductively coupled plasma mass spectrometer (ICP-MS) serves as a crucial bridge between the atmospheric-pressure ion source and the mass analyzer, which operates in a high vacuum. If an ICP-MS is to provide optimum analytical performance, ions must be transported through the vacuum interface efficiently and consistently, and without reactions that could change the composition of the sampled plasma. Considerable attention has been given to possible causes of inconsistent ion transport in the second stage of the vacuum interface, with studies focused on the possible effects of space charge on the structure of the ion beam as it enters the mass analyzer [1–15]. Comparatively little attention has been given to the first vacuum stage as a possible source of inconsistent ion transport. The difference in emphasis is understandable. The first vacuum stage is a strictly mechanical arrangement of sampling cone and skimmer cone that reduces the gas load into the mass analyzer and forms a supersonic gas jet that can be manipulated by ion optics in subsequent vacuum stages. The placement and geometries of the sampling and skimmer cones is based on principles that were established in the 1960s. All of the active beam-focusing electronics are located in the second and third vacuum stages of a typical instrument. However, there have been indications that changes in sample composition and ICP operating conditions were affecting the efficiency with which ions were transported through the first vacuum stage. Chambers, et al. [16] measured positive plasma potentials at the location of the skimmer cone and concluded that the plasma was not neutral in the first vacuum stage of their instrument. This conclusion raised the possibility of charge-induced transport of ions in the supersonic expansion upstream from the skimmer cone. We have observed apparent changes in ion transport efficiency through the first vacuum stage of an ICP-MS induced by changes in operating conditions and sample matrix [17]. The indications of variable

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☆ This article is published in a special honor issue of Spectrochimica Acta Part B dedicated to the memory of Prof. Howard V. Malmstadt, in recognition of his many outstanding contributions to spectrochemical analysis, in areas of research, leadership, and teaching.

* Corresponding author. Tel.: +1 801 422 6502; fax: +1 801 422 0153.
E-mail address: paul_farnsworth@byu.edu (P.B. Farnsworth).

[1] Current address: Department of Chemistry and Life Sciences, United States Military Academy, Bartlett Hall B21F, West Point, NY 10996.

[2] Current address: 2975 W. Marcus Road, West Valley City, UT 84119.

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doi:10.1016/j.sab.2005.09.004

ion transport efficiency in the first vacuum stage of an ICP-MS have led us to a detailed study of the first-stage expansion in a mockup instrument. In this paper we report spatially resolved velocities, temperatures, and trajectories of neutral argon atoms in the 20 mm downstream from the sampling cone. The picture of the supersonic expansion that has emerged, while consistent with well established theory, points to features of the first vacuum stage that are often overlooked in the ICP literature. This characterization of neutral gas flow provides an essential frame of reference for the study of ion behavior, and, in addition, provides valuable information about conditions upstream from the sampling cone that is difficult to obtain by other methods.

2. Experimental

2.1. Probe species

Ideally, one would like to characterize the supersonic expansion in the first vacuum stage by monitoring the most abundant species, ground state argon atoms. Unfortunately, no practical method exists in our lab for probing the population of argon atoms in the ground state. We chose instead to use metastable argon atoms in the 4s [3/2] 2 state. These metastable atoms are present in easily detectable quantities at all points in the first vacuum stage that we examined. We assume that the velocities and temperatures that we measure for the metastable atoms are representative of those quantities for all neutral atoms.

2.2. Instrumentation

2.2.1. Plasma generator and vacuum chamber

The plasma was maintained by a 27 MHz generator extracted from an Elan 500 ICP-MS (Perkin Elmer, Norwalk, CT). The three-turn load coil, used as purchased from the manufacturer, was grounded in the center. The entire impedance matching and torch assembly was mounted on an *x-y-z* stage that provided precise positioning of the torch with respect to the sampling cone. The torch (PG-450-05, Precision Glassblowing of Colorado, Centennial, CO) had a 1.5-mm injector tube. A commercial sampling cone with a 1-mm orifice (VG-1001-Ni, Spectron, Ventura, CA) was mounted to a water-cooled flange, which in turn was mounted to an open vacuum chamber maintained at a pressure close to 1 Torr, measured in an isolated section of the chamber, well-removed from the conduit to the vacuum pumps. The chamber contained no skimmer cone, ion optics, or mass analyzer.

Table 1
Instrument operating conditions

Incident power	1.25 kW
Reflected power	<5 W
Outer gas flow	12 L min^{-1}
Intermediate gas flow	0.4 L min^{-1}
Nebulizer gas flow	1.4 L min^{-1}
First stage vacuum pressure	1 Torr
Sampling depth	10 mm

A standard set of operating conditions was chosen that maximized barium ion density, measured by laser-induced fluorescence, on the expansion axis at a position 10 mm downstream from the sampling cone. Those conditions are summarized in Table 1. They were used except as noted in the text. The sample introduction system was an ultrasonic nebulizer (U-5000, Cetac, Omaha, NE), which, unless otherwise noted, delivered deionized water with no analyte to the plasma. The water was pumped on to the face of the nebulizer transducer at a flow rate of 1.0 ml min^{-1}. The nebulizer incorporated a desolvator, consisting of a heater and condenser in series, that reduced the water load to the plasma to 39 mg min^{-1}.

2.2.2. Optics

The optical layout for the experiments is shown in Fig. 1. The excitation laser was an external-cavity diode laser (2010, EOSI, Boulder, CO) operating at 801.48 nm. A portion of the laser beam was split into a confocal etalon with a nominal free spectral range of 750 MHz. The remainder of the beam was chopped, and a second portion was split into an argon-filled hollow cathode lamp. A final 50:50 beam splitter directed laser radiation through a variable attenuator onto a fiber optic coupler, and the excitation radiation was carried into the vacuum chamber via a 0.4 mm diameter fused silica fiber optic. The excitation and collection optics have been described in detail in references [17] and [18]. The geometry of the optics was critical for the measurements described in this paper. The excitation and emission axes formed adjacent sides of a square pyramid, each at an angle of 45° with the base. The line perpendicular to the base through the apex of the pyramid was parallel to the axis formed by the ICP torch and the sampling cone. Excitation and emission optics were mounted to a rigid frame, which in turn was mounted on a computer-controlled *x-y-z* stage. The *x*- and *y*-axes for the stages were parallel to the planes containing the excitation and emission axes, respectively. The *z*-axis was parallel to the axis defined by the torch and the sampling cone.

The laser-excited fluorescence at 842.465 nm was coupled into an optical fiber, carried out of the vacuum chamber, and passed through an interference filter before detection by a photomultiplier tube. Two interference filters were used in the course of the experiments. The first, with a 10-nm bandpass (S10-840-F-S752, Corion Corp., Franklin, MA), also passed emission from a strong argon line at 840.821 nm. It was replaced in later experiments with a 1-nm bandpass filter (842.5 nm, Andover Corp., Salem, NH), which significantly reduced emission noise in the regions close to the sampling cone.

2.3. Data acquisition and signal processing

A 10 mHz triangle wave applied to the piezoelectric tuning element in the diode laser cavity scanned the laser frequency over a range of approximately 10 GHz. The DC output of the etalon photodiode was processed with a low-noise preamp (SR560, Stanford Research Systems, Sunnyvale, CA) and the