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Research note

The effects of analyte mass and collision gases on ion beam formation in an inductively coupled plasma mass spectrometer

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ABSTRACT

Planar laser induced fluorescence (PLIF) was used to evaluate the effect of matrix components on the formation and focusing of a Ba ion beam in a commercial inductively coupled plasma mass spectrometer. Cross sections of the ion beams were taken in the second vacuum stage, in front of the entrance to the mass analyzer. Under normal operating conditions, the addition of Pb shifted the position of the Ba ion beam to the right. PLIF was also used to evaluate the effect of a collision reaction interface (CRI) on Ca and Ba ion beams. A wider velocity distribution of ions and a decrease in overall intensity were observed for the CRI images. The fluorescence and mass spectrometer signals decreased with increased CRI flow rates. These effects were most obvious for Ca ions with He gas.

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is an attractive analytical technique for elemental analysis because of its low detection limits and high sensitivity. Despite the technique's maturity, its performance in some applications is still limited by poor overall ion transmission efficiency and by non-spectroscopic inter-element interferences. Gaining a fundamental understanding of the root causes of these limitations has proven to be challenging because the intense ion beam generated by the ICP is not readily modeled with commercially-available software, and experimental characterization of the ion beam within the cramped confines of the vacuum interface between the ICP ion source and the mass analyzer is extremely difficult. Over the past three decades, a number of studies have been published that have made incremental contributions to the understanding of how ions are transmitted through the ICP-MS vacuum interface [1], where the principal ion losses occur, how space charge affects ion transmission [2], and how ion transmission is affected by changes in sample composition [3–5].

In a recent publication, we demonstrated the ability to measure cross sections of the Ca ion beam in an ICP-mass spectrometer just a few mm upstream from the entrance to the mass analyzer in a working commercial instrument using planar laser-induced fluorescence (PLIF) [6]. The advantage of PLIF over previously-used beam profiling approaches is that it is element-specific and non-invasive. Our measurements exploited the unique ion reflector in the Varian 820 ICP-MS that introduces a 90-degree bend in the ion beam. The study demonstrated that the shapes and sizes of the ion beams were reasonably approximated by Simion simulations, and that the effects of mM concentrations of concomitant sample species on beam profiles were relatively small. In the Ca study three of the ion beam centers were separated by less than 0.2 mm. The notable exception was the effect of added Pb in the sample on the behavior of the Ca ion beam. The addition of 1.5 mM Pb to the sample solution shifted the Ca ion beam 1.2 mm to the right resulting, in an order-of-magnitude drop in the Ca ion signal at the mass spectrometer.

In this report we extend our study of ion beam profiles in a Varian ICP-mass spectrometer in two directions. First, to better understand the influence of analyte ion mass on the types of behavior observed in our first study, we have added Ba^+ as a probe analyte ion. Second, we have added He and H_2 as collision reaction interface (CRI) gases at the skimmer cone of the instrument to study the effects of those gases on ion beam formation.

In the 1980's collisional cell technology was introduced as a way to minimize matrix effects and spectral interferences [7]. Collision cells are placed between the ion optics and the mass analyzer. They promote collisions, reactions, or charge transfer processes in the ion beam by introducing a secondary gas like ammonia, hydrogen, or helium. While these types of cells are still used in most instruments [7–10], the technology has also been adapted into a collision reaction interface. In the CRI secondary gas flows through a channel in a modified sampler or skimmer cone and interacts with the ion beam inside the tip of the cone.

Two recent studies show that the CRI is more effective when used at the skimmer cone rather than at the sampler cone, and that hydrogen secondary gas reduces polyatomic spectral interferences more readily than helium [11,12]. However, Pereira et al. [11] found that increased CRI flow rates decrease the number of ions reaching the mass analyzer,

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and they report a sensitivity loss of 90% for CRI flow rates of only 60 ml min^{-1}. Salazar et al. [12] used internal standardization to compensate for the sensitivity loss. The beam profiles reported herein provide a direct measure of the effect of the CRI on ion beam formation.

2. Materials and methods

2.1. Planar laser-induced fluorescence

This method has been described in detail previously [6]. Briefly, a plane of laser radiation intersected the ion beam in front of the orifice to the mass analyzer of an ICP-mass spectrometer. The laser radiation excited the selected analyte ions in the beam. A CCD camera captured the fluorescence and recorded it as a function of excitation wavelength. A series of 60-s exposures were taken at 0.001 nm intervals over the Doppler width of the fluorescence excitation profile. Composite images were generated from the sums of the individual frames, normalized to incident laser power.

2.2. Solutions and CRI gases

Ca and barium analyte solutions were made from Ca nitrate and Ba nitrate (J.T. Baker Chemical Co., Phillipsburg, NJ) dissolved in trace metal grade nitric acid (Thermo Fisher Scientific Inc., Waltham, MA) and diluted to 2% HNO_3 with 18 MΩ deionized water (Millipore, Billerica, MA). The final concentrations of the solutions were 1.25 mM Ca and Ba respectively.

Magnesium nitrate (Mallinckrodt Inc., St. Louis, MO), lead nitrate, and cesium chloride (Spectrum Chemical Manufacturing Corp., New Brunswick, NJ) were separately combined with Ba nitrate in trace metal grade HNO_3 and diluted with deionized water to give three solutions. The final concentrations were 1.25 mM Ba with 1.5 mM Mg, Cs, or Pb respectively. The matrix concentrations are the same as were used in our published Ca study [6]. Gases used in the CRI study were 99.999% helium and 99.995% hydrogen (Airgas, Radnor, PA)

2.3. Instrumentation and optics

All experiments were performed using a Varian 820 ICP-MS. The experiments all used a tunable CW titanium-sapphire laser (SolsTiS, M Squared Lasers, Glasgow, Scotland) as the fluorescence excitation source. The wavelength of the laser was monitored with a precision wavemeter (Angstrom WS/6, High Finesse, Tübingen, Germany). The laser light was frequency doubled in a bowtie optical cavity with a lithium triborate crystal (CASTECH INC., Fuzhou, China). An electro-optical modulator (Model 505, ConOptics, Danbury, CT) and photodiode were used to lock the cavity using the Pound-Drever-Hall method [13].

A plane of laser radiation was created using two cylindrical lenses. A CCD camera (iDus DU440A BV, Andor, Belfast, Northern Ireland) captured the fluorescence. A long-pass filter (LG-790, Corion, Holliston, MA) and a narrow band interference filter (CVI, Albuquerque, NM) with a center wavelength of 854.3 nm or 614.2 and a bandwidth of 1.1 or 1 nm, for Ca and Ba, respectively were used to prevent scattered light from reaching the CCD.

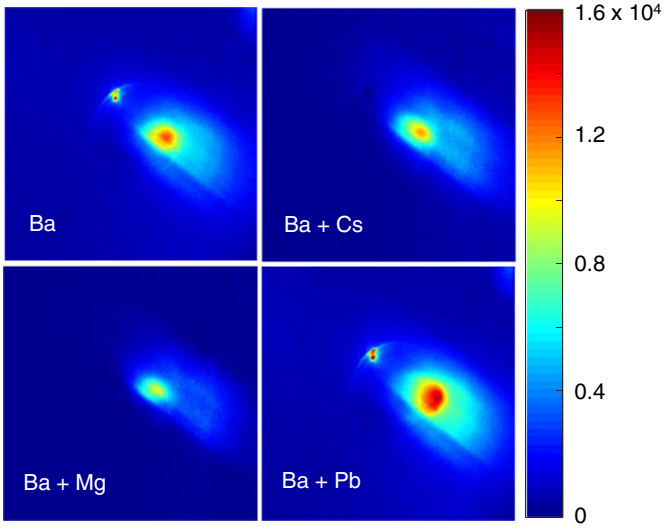

Fig. 1. Composite ion beam images for Ba ions in four matrix conditions. Images are on the same intensity scale.

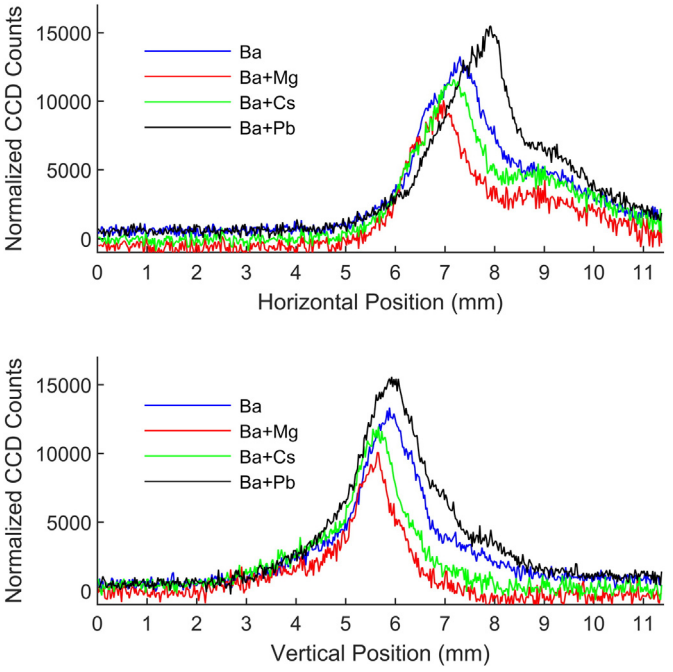

Fig. 2. Cross sections of Ba ion beam in four different matrix conditions. The top image is a cross section of the beam in the x direction, and the bottom image is in the y direction. Cross sections are chosen to be in the center of the ion beam where the fluorescence is most intense.

3. Results

3.1. Sample matrix and Ba ion beam formation

Composite images for the Ba ion beams with four matrix conditions are presented in Fig. 1. The cross sections of these images are presented in Fig. 2. The corresponding operating conditions are given in Table 1.

The ion beam containing only Ba is approximately 2.3 mm wide at 50% peak height (FWHM). The beam width does not change significantly with the addition of another matrix element. However, as

Table 1
ICP-MS operating conditions for Ba + matrix.

Flow parameters (l min^{-1})		Ion optics continued (V)	
Plasma flow	16	Extraction lens 2	−169
Auxiliary flow	1.2	Extraction lens 3	−190
Sheath gas	0.2	Corner lens	−273
Nebulizer flow	0.99	Mirror lens left	30
Other parameters		Mirror lens right	26
RF Power (kW)	1.4	Mirror lens bottom	42
Ion optics (V)		Entrance lens	0
Extraction lens 1	−2	Entrance plate	−68