Effect of methanol and sodium dodecylsulfate on radial profiles of ion abundance in inductively coupled plasma mass spectrometry

Shulan Liu, Diane Beauchemin *

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Abstract

The radial profiles of some background ions and analytes spanning the mass range and with a wide range of first ionization potentials were investigated using inductively coupled plasma time-of-flight mass spectrometry. In particular, three different matrices were considered to assess the effect of organic modifiers: 1) 1% HNO_3, 2) 1% HNO_3 with 2%v/v methanol, 3) 1% HNO_3 with 0.2% m/v sodium dodecylsulfate (SDS). Although these concentrations of methanol and SDS induced the same sample transport increase (37%), as measured with a silica gel trap at the exit of the spray chamber, neither of them resulted in a 37% increase in signal across the mass range. In fact, the change in analyte signal as a function of m/z followed opposite trends in these two matrices. With 0.2% m/v SDS, suppression was observed at high m/z with an increasing enhancement as m/z decreased, which was ascribed to electrostatic effects in solution. In contrast, little change or enhancement was seen at high m/z while suppression was evident at lower m/z (with the notable exception of As) with 2% v/v methanol, as a result of a widening of the radial profile, which was inversely dependent on m/z. Although, the total carbon concentration was quite different in these two matrices, i.e. 0.8 M with 2% methanol and 0.08 M with 0.2% SDS, it cannot account for the completely different radial profiles that they produced. Indeed, the same bell-shaped distributions of analyte ions were observed with 0.2% SDS as in 1% HNO_3 alone. However, a bimodal distribution, with maxima on either side of the central axis, resulted in presence of 2% MeOH. This distribution was found to be similar to that of several background ions (C^+, CO^+ and ArC^+), which further substantiates the suggestion that ionization then predominantly occurs through charge transfer with carbon-containing ions. This bimodal distribution also suggests that a volatile organic solvent such as methanol quickly spreads into the surrounding area of the central channel upon sample introduction in the plasma.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Radial profiling; Matrix effect; Organic solvent; Surfactant; ICP-MS

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been developed as an accurate and sensitive technique for multi-elemental analysis of a wide range of sample matrices. However, it is still plagued by non-spectroscopic interferences (also called matrix effects) [1]. For example, the addition of organic solvents or compounds as modifiers to sample solutions can have a significant effect on the behaviors of analytes in ICP-MS. They can indeed affect ionization conditions in the plasma, the aerosol mass transport rate, the vapor mass load, or nebu-

lization processes [2]. In fact, small proportions of organic additives most often induce signal enhancement of elements, such as As [3–5], Se [3,6–10], Hg [11] and Zn [12], with ionization potentials in the range 9–11 eV [13], which cannot be ascribed to space charge effects since the latter only induce signal suppression.

Different enhancement mechanisms have been proposed. For instance, a higher transport rate contributed to enhancement effects with the addition of organic solvents, which was attributed to a smaller mean droplet size distribution of the resulting aerosol [14]. However, the enhancement observed in presence of 5% Triton X-100 [5] and 3% v/v methanol [3] was greater than what could be ascribed solely to an increase in nebulization efficiency. Furthermore, the fact that a similar enhancement was also observed with an equivalent amount of

ammonium carbonate [3], which does not affect the nebulization efficiency, clearly indicated the existence of at least another mechanism.

Under standard operation conditions, the degree of ionization of these elements is significantly less than 90% (As 52%, Se 32%, Hg 38%, Zn 75%) [15]; an increase in their degree of ionization may thus result from different ionization processes in the plasma when organic compounds are present. Indeed, carbon-containing compounds may lead to an increased ion population of carbon and carbon species, which may in turn undergo charge transfer with analyte elements [3]. The formation of analyte oxides may also be reduced as a result of a competitive reaction producing CO [13]. Similarly, organic solvents suppressed the ionization and increased the breakdown of polyatomic ions through competitive formation of ArC^+ as well as from the altered plasma conditions [16]. The end result of all these processes is an increase in the available number of analyte ions.

The literature to date seems to indicate that the carbon source need not be an organic solvent, which often has the drawback of increasing the solvent load in the plasma. In particular, the fact that analyte signal enhancement was observed in presence of a surfactant [5] warrants further investigation. Indeed, in addition to constituting a source of carbon for the mechanisms mentioned above, it may also change the physical properties (density, viscosity, surface tension) of liquid samples, resulting in improved nebulization efficiency and, hence, improved signals for all analytes. Surfactants can be used during sample preparation to improve leaching efficiency [17], for cloud point extraction [18,19], and as emulsifiers for the determination of metals in organic matrices [20]. They are also useful for the generation of volatile analyte species, such as hydride and alkylcompounds of metals [21–23], because the self-aggregation of surfactant molecules forms a quite different microenvironment in comparison to the bulk solution.

The objective of this work was to investigate the matrix effects induced by organic additives of different volatility, i.e. organic solvents and different surfactants, using radial profiling of analytes and background ions distribution. Spatial profiling has played an important role in the development of ICP-MS, from the determination of optimum sampling position as a function of plasma parameters, to allowing a theoretical framework for proposed ionization mechanisms [24]. While axial profiling provides information about the energy and time needed to form ion species, radial profiles can provide insight on ionization mechanism in the plasma in addition to information that is not known intuitively [24].

2. Experimental

2.1. Instrumentation

A time-of-flight ICP-MS instrument (Renaissance, LECO Corp., St. Joseph, MI., USA) was used in its standard configuration (i.e. with a Meinhard concentric nebulizer (type

C, model # TR-30-C3) and Smith-Hieftje cyclonic spray chamber (Renaissance, LECO Corp., St. Joseph, MI., USA)) with the operation conditions shown in Table 1. A previous study showed that the secondary discharge was minimal on this instrument since the intensity of the LaO^+ signal increased while that of La^{2+} decreased when either the aerosol carrier gas flow rate increased or sampling depth (Z position) decreased [25]. Hence, spatial profiles should be representative of ions distribution in the plasma. To protect the detector, which unlike with other types of ICPMS instruments, is continuously exposed to ions, deflection windows were set to reduce the signal intensity at m/z 11–23, 28, 30–40, 56, 80. These deflection windows also affected the signal intensity of ions at nearby m/z (such as m/z 52).

2.2. Reagents

Several 20 µg/L multi-elemental solutions of Al, Co, Ni, Zn, Cu, As, Se, Mo, Cd, Sb, La, Pb and their corresponding blanks were prepared in different matrices from mono-elemental stock standard solutions (SPEX Industries Inc. Edision, N.J. and SCP Science, Champlain NY, USA) and dilution with purified water (18 Ω cm^{-1} Milli-Q, Millipore, Harrick Scientific corporation, Ossining N.Y., USA). All contained 1% high-purity nitric acid (trace metal grade, Fisher Scientific, Ontario, Canada). In addition, some sets of standard and blank also contained 0.2% (m/m) sodium dodecyl sulfate (SDS, GC grade Sigma-Aldrich Canada Ltd., Oakville, ON., Canada), 2% (v/v) methanol (HPLC grade, BDH Inc., Gibbstown, N.J., U.S.A), 2% (v/v) acetone (HPLC grade, Sigma-Aldrich Canada Ltd., Oakville, ON., Canada) or 2% (v/v) ethylene glycol (Sigma-Aldrich Canada Ltd., Oakville, ON., Canada). The surfactants methoxypolyethylene glycol (Sigma-Aldrich Canada Ltd., Oakville, ON., Canada) and Triton X-100 (electrophoresis grade, Fisher Scientific Corporation, Fair Lawn, N.J., U.S.A) were also used to investigate matrix effects.

2.3. Procedure

Mass calibration of the instrument was performed each day using a 5 µg/L solution containing Ba, Bi, Co, In, Pb, Li, Mg, Sc, Y, in 1% HNO_3. The $^{115}In^+$ signal was then maximized, without sacrificing the signals of the other analytes, by adjusting

Table 1
ICP-MS operating conditions

ICP source	RF power	1.35 (1.5 [a]) kW
	Frequency	40.68 Hz
	Aerosol carrier gas flow rate	0.87 L/min
	Auxiliary gas flow rate	0.85 L/min
	Plasma gas flow rate	15 L/min
	Sample uptake rate	0.65 mL/min
Mass spectrometer	Detector	−2600 V
	Integration time	1 s
	Ion lens 1	−500 V
	Ion lens 2	−450 V

[a] With methanol.