



Preliminary survey of matrix effects in the Microwave-sustained, Inductively Coupled Atmospheric-pressure Plasma (MICAP)

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ABSTRACT

Matrix effects caused by Na and Al in the nitrogen Microwave-sustained, Inductively Coupled, Atmospheric-pressure Plasma (MICAP) were investigated. Easily ionizable elements, such as Na, can suppress or enhance the analyte signal; Al is shown here to produce a similar effect. The influence of these matrices was examined for 18 emission lines of 8 analyte atoms and ions having a wide range of excitation and ionization energies. The plasma operating conditions were fixed during all experiments at a total nitrogen flow of 19.4 L min⁻¹ and a microwave power of 1.5 kW. An Fe solution was used to determine the excitation temperature of the plasma by the Boltzmann plot method at selected matrix concentrations. In addition, vertical emission profiles of the plasma were measured. The matrix effect becomes worse at higher concentrations of an easily ionizable element. The effect is caused not only by a shift in ionization equilibrium but also by a possible change in plasma ionization temperature. Correction methods to reduce the matrix effects were tested and are discussed.

1. Introduction

Plasma sources for trace element analysis were introduced more than 50 years ago and have found widespread use for atomic emission spectrometry (AES) and as ionization sources for atomic mass spectrometry (MS) [1]. The inductively coupled plasma (ICP) is the most popular such plasma source and can achieve detection limits below ng/L, when combined with MS [2]. Detection limits for ICP-AES are usually higher; however, the possibility of using alternative emission lines of an analyte atom makes it possible to detect some elements (e.g. fluorine) that cannot readily be measured by ICP-MS [3]. Moreover, in ICP-MS, some isotopes suffer spectral interference; examples include ⁴²Ca which overlaps with ⁴²Ar, or ⁵⁶Fe, compromised by ⁴⁰Ar¹⁶O⁺ [4,5]. Quantification of these elements by ICP-MS requires the use of additional equipment such as collision cells or high mass resolution sector-field mass spectrometers [6,7].

Both ICP-AES and ICP-MS require substantial flows of the plasma-support gas (Ar), which leads to high operating costs. Accordingly, plasma sources employing alternative gases have been developed throughout the last decades and have received considerable attention [8–15]. Microwave-induced plasmas (MIPs) have been explored by many workers; however, most early MIP setups were operated at

200–300 W (up to 500 W), which provides insufficient plasma energy for efficient desolvation, vaporization and dissociation of aerosol droplets [9,16–18]. Later, high-power MIPs were developed that could determine some elements not easily measured by Ar-ICP-MS or Ar-ICP-AES [19,20]. For example, Pb detection limits in MIPs are usually better than for ICP-AES [21,22]. Also, for some special applications such as the sizing and elemental analysis of microparticles, MIP-AES was found to be more useful than ICP-AES [23,24].

Matrix effects are a continuing problem in atomic emission spectrometry. Generally, such effects are much more severe in MIPs than in the Ar-ICP [25]. For both ICP and MIP, several studies investigated the influence of easily ionized elements (EIEs) on analyte signals [26–28]. Elements such as Na, Ca, K or Li can cause suppression or enhancement of analyte signals and therefore hamper quantification of samples. The influence of EIEs on emission response is a matter of significant practical relevance and has to be examined before any new method for plasma generation can be used routinely for analytical applications. The influence of EIEs on the Microwave-sustained, Inductively Coupled Atmospheric-pressure Plasma (MICAP) has not been reported so far. In the present work, we describe the effect of Na on 18 emission lines of 8 analyte elements in the nitrogen MICAP. The effect of Al on the emission lines is compared to that of Na. Vertical profiles of emission

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intensity have been measured to study the effect of Na on the spatial intensity distribution. Additionally, excitation temperatures were determined by the Boltzmann plot method by using iron emission lines [29]. A comparison with matrix effects in other microwave-sustained nitrogen discharges is provided and methods to overcome matrix effects are considered.

2. Experimental

The MICAP setup employed throughout this study is similar to that described earlier [30]. A 1.5 kW magnetron was used to generate a microwave field that was directed into the resonator chamber by means of an aluminum waveguide. Within the chamber, two alternative Meinhard (Golden, CO) Leeman-type quartz ICP torches (ML155020 and ML155023) with a 1.5 mm or 2.5 mm inner diameter (i.d.) injector, respectively, and 18 mm i. d. outer tube were installed vertically. Most results shown here were measured with the torch having a 1.5 mm i.d. injector. For experiments to overcome the matrix effect, the 2.5 mm i.d. injector was used. Three gas streams of nitrogen were provided to the torch, with flows of 18, 0.4 and 1 L min⁻¹ for the outer, intermediate and central channels, respectively, except where noted otherwise. The gas streams were regulated by mass flow controllers. The outer-channel flow controller was a model GR116-10 from Fathom Technologies (Georgetown, TX), while the intermediate and inner-channel controllers were model AW9411059 from Tylan General (San Diego, CA). To ignite the MICAP, nitrogen was provided only to the outer channel, while microwave power (1.5 kW) was applied to the waveguide and resonator. At the same time, an argon flow (2 L min⁻¹) was briefly (~2 s) introduced into the intermediate channel, while a Tesla coil generated a spark within the gas line. After plasma ignition, the argon flow was turned off and the intermediate-channel and central-channel nitrogen flows initiated. Support gases consisted of industrial grade nitrogen ($\geq 99.998\%$ purity) and ultra-high purity argon ($\geq 99.999\%$), all supplied by Airgas (Radnor Township, PA). Sample solutions were introduced into the plasma by a Glass Expansion concentric nebulizer (model AR30-1-UC2TLL, Pocasset, MA) in conjunction with a single-pass cyclonic spray chamber (Meinhard, model C18303). Sample solutions were fed at a rate of 1 mL min⁻¹ by a Gilson (Middletown, WI) Miniplus 3 peristaltic pump. After introduction of each sample solution, the tubing was flushed with blank solution to prevent contamination and carryover.

All sample solutions were prepared in dilute (0.1 M) nitric acid, obtained from concentrated reagent-grade stock, purified in-house with a sub-boiling polytetrafluoroethylene distillation unit, and deionized water of 18.2 M Ω cm⁻¹ specific resistance. Primary analyte stock solutions (1000 mg L⁻¹ concentration) were obtained from High-Purity Standards (Charleston, SC) or prepared from analytical reagent-grade (or better) nitrate salts and dissolved in 0.1 M nitric acid. Samples of lower concentration were obtained by serial dilution (in 0.1 M nitric acid) of the primary stock standards. To investigate matrix effects, sodium or aluminum solutions (as NaNO₃ or AlCl₃·6H₂O, dissolved in 0.1 M nitric acid) were added to the analyte solutions. Concentrations of 25, 75 and 200 mM (0.58, 1.73 and 4.60 g L⁻¹) of Na and 25 mM (0.68 g L⁻¹) of Al were chosen.

Radiation from the MICAP was imaged by a plano-convex quartz lens (100-mm focal length, 50-mm diameter) with a magnification of 0.3 onto the 7-mm high, 10- μ m wide entrance slit of a 0.64 m Czerny-Turner spectrograph (model ACTIVA-M, Horiba Jobin-Yvon, Longjumeau, France) outfitted with two gratings. The first grating was used over the wavelength range of 120–430 nm, had a groove density of 4343 grooves mm⁻¹ and was used for the collection of spectral data from 200 to 430 nm. The second grating (2400 grooves mm⁻¹) was used for the collection of data from 430 to 800 nm. In order to match the numerical aperture of the quartz lens ($f/2$) to that of the spectrograph ($f/8.5$), an iris was placed immediately behind the lens, reducing the beam diameter to approximately 12 mm. Throughout all

experiments, the MICAP was viewed radially, and the observation zone covered 15–36 mm above the alumina resonator.

A two-dimensional, back-illuminated CCD detector (Andor, Belfast, Ireland, model DU-440-BU2-380), Peltier cooled to -38 °C, was coupled to the spectrometer for detection. In this configuration, the CCD provides a two-dimensional image, with wavelength displayed on the horizontal axis, and vertical position in the plasma shown vertically. For all experiments, the camera was operated with a readout rate of 1 MHz; a 10-s integration (or its equivalent in summed exposures) was used. In each case, three images were collected for every measurement from the CCD by using the manufacturer software bundled with the ACTIVA-M spectrograph (ACTIVAnalyst v5.4.2). These images were subsequently processed offline with custom-programmed National Instruments (Austin, TX) LabVIEW® software or Matlab® (The MathWorks, Inc., Natick, MA).

Spatially resolved emission patterns of the investigated analyte species were measured in the presence as well as in the absence of the chosen interfering matrix. To obtain a vertical spatial profile of a particular emission line, 10–30 pixels (depending on the intensity of the emission line) around the center of the line were averaged horizontally (across the wavelength axis). The vertically resolved plots show these wavelength-averaged values, with zero on the spatial axis representing the upper edge of the MICAP ceramic resonator.

Spectra were extracted from the CCD images by vertically binning all pixels along the columns of the camera (i.e. across the vertical image of the MICAP), thereby summing emission intensity from 15 to 36 mm above the MICAP resonator, and thus representing column averages through an extended zone of plasma. Background spectra were collected from the nitric acid or blank matrix solution; all spectra shown here are background-subtracted. The reported values for analyte signal from these spectra are peak areas, integrated along the wavelength axis. The relative emission intensity was calculated as emission signal of a chosen spectral line in the presence of a matrix divided by the value in the absence of the matrix, at the concentration listed in Table 1. Values of relative emission intensity above one indicate that emission of the selected spectral line is enhanced by the matrix, whereas values below one represent signal suppression.

3. Results

3.1. Effect of sodium and aluminum on analytical signals

Addition of an EIE to a sample solution can cause either suppression or enhancement of MICAP emission lines, depending mainly on whether the lines arise from an analyte neutral atom or ion. An example is given in Fig. 1 for 1 μ g mL⁻¹ Mg in 0.1 M HNO₃. Upon addition of 75 mM Na, the Mg II 279.55 nm and Mg II 280.27 nm ion lines are suppressed, while the atomic Mg I 285.21 nm line is enhanced. This trend of suppression of ionic emission and enhancement of atomic emission suggests that the effect involves a simple shift in ionization equilibrium [31–33].

Table 1 shows the effect of 25, 75 and 200 mM Na on 18 spectral lines of the analyte elements investigated in this study. Fig. 2 summarizes the relative emission intensities separately for ionic lines and atomic lines. For all ionic lines and at all Na matrix concentrations, suppression (values below 1.0) that increases with sodium concentration is observed. The presence of sodium at concentrations of 75 mM and above results in enhancement for all neutral-atom lines of Rb I, K I, Li I, Re I, and Mg I. The threshold energy sum (excitation plus ionization energy) for transitions to be either enhanced or suppressed was found to be between 4.4 eV and 7.7 eV. At lower sodium concentrations, the threshold for enhancement of emission lines shifts to lower excitation energies. Similar trends have been observed for a high power N₂-MIP sustained with an Okamoto cavity, where the effect was explained by a shift in atom/ion equilibrium [27].

Table 1 shows also the effect of 25 mM aluminum on the relative

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