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Investigation of charge transfer with non-argon gaseous species in mixed-gas inductively coupled plasma–atomic emission spectrometry☆

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Abstract

Potential charge-transfer reactions with non-argon gaseous species in a mixed-gas inductively coupled plasma were probed by means of two different experimental methodologies, namely the plasma-related matrix-effect approach and the relative-intensity technique. The foreign gases, introduced one by one into the central channel, were oxygen, hydrogen, nitrogen, krypton, methane and carbon dioxide at volumetric concentrations of 15%, 10%, 5%, 100%, 3% and 3%, respectively. Both matrix effects and relative intensities showed no change in behavior for emission lines with excitation energies in the vicinity of the ionization potentials of the foreign gases. This pattern suggests that the contribution of charge transfer from the foreign-gas ion is not important to the overall ionization and excitation of the analyte, in the normal analytical zone of the plasma and at the concentration of foreign gases used here.

Keywords: Inductively coupled plasma–atomic emission spectrometry; Mixed-gas plasma; Matrix effects; Charge transfer; Hydrogen; Nitrogen; Oxygen; Krypton; Carbon dioxide; Methane

1. Introduction

Charge transfer (CT) between an analyte in its neutral-atomic state and an argon ion is recognized as an important mechanism for populating specific energy levels of particular analyte ions in ICP-AES (inductively coupled plasma atomic emission spectrometry). Charge transfer from argon ions, which are abundant in the ICP, directly connects a neutral atom to its high-energy ionic excited states via the following reaction:

$$Ar^+ + M \rightarrow Ar + M^{+*} + \Delta E$$

where M is a metal atom and M^{+*} is an excited metal ion. Various experimental techniques have been developed to study charge transfer in the ICP, namely abnormal behavior in the Boltzmann plot [1–4], interruption of radiofrequency power [5], laser-based pump-probe experiments [6,7], correlation spectroscopy [7,8] and plasma-related matrix effects [9,10]. However, most of these experimental techniques are rather complex. As a result, many studies in the literature have focused on examining the CT character of only one to three elements in a single study, and in many cases with Mg as the prototype element [1,6,11]. Thus, the CT character of many elements has remained unknown in the past.

The pioneering work of Farnsworth and co-workers [7,8], utilizing the simpler experimental approach of correlation spectroscopy, allowed them to include more candidate elements in a single study and consequently extended the knowledge of CT character to the first-row transition elements; with the exception of Mn and Cr, positive CT character was identified for elements from Ca to Cu [7]. Recently, Chan and Hieftje [9,10] described a novel method of using plasma-related matrix effects to probe CT reactions in the ICP. This new method requires only a commercial ICP spectrometer equipped with a two-dimensional imaging detector having full wavelength-coverage capability; no specialized experimental techniques or setup are needed. The method simplifies the study of charge transfer in the ICP, so a large number (twenty-two) of candidate

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elements (mainly the third and the fourth row metals) were studied [9]. These two studies significantly expanded the list of elements that showed CT character in the ICP. The periodic table shown in Fig. 1 summarizes the CT character of all reported elements in the literature [1–3,5–10]. It is interesting to note that a large fraction of studied elements showed positive CT character, in contrast to earlier reports that regarded charge transfer as a special case.

In the CT studies utilizing correlation spectroscopy by Farnsworth et al. [7,8] and plasma-related matrix effects by Chan and Hieftje [9], it was found that many elements show CT behavior for ionic energy levels that approach ~14 eV above the ground state of the neutral atom (i.e., ~2 eV lower than the ionization potential of Ar at 15.75 eV). Collisional mixing between energy levels was offered as an explanation for the CT behavior of these lower-energy ionic levels and the apparent lack of state-selective charge transfer for many elements [7–9]; this situation is unlike that encountered in many other analytical plasmas, particularly those operated at reduced pressure (e.g., glow discharges) [12–15]. By means of a laser pump-probe technique, Omenetto and Matveev [16] and Farnsworth et al. [7] showed that when a particular energy level is selectively excited by a laser, many nearby levels within ~2 eV of the excited level fluoresce, again arguing for collisional mixing.

Such collisional mixing is fast; the non-resonance fluorescence from nearby energy levels lags only nanoseconds behind the resonance fluorescence. The high pressure (atmospheric), electron number density and temperature in the ICP lead to frequent and efficient collisions between atoms and electrons. As a result, any excess population in a given level is rapidly spread to adjacent levels; consequently, even energy levels that are not excited directly by CT can show CT character if they are close to a direct-CT energy level [7]. Also, any state-selective CT character will be easily masked [7]. Although the results from the laser pump-probe experiments provide solid evidence and offer a valid explanation for CT behavior of emission lines with energy levels near ~14 eV, they do not preclude the possibility that charge transfer from other ionic species contributes to the excitation of these 14 eV ionic levels. For example, oxygen and hydrogen ions from the dissociation of water are abundant, and the ionization potentials of both oxygen (at 13.62 eV) and hydrogen (at 13.60 eV) match very well with the energy of such levels. In fact, the efficient collisional mixing that occurs in the ICP might make verification of such a possibility difficult because if charge transfer does occur from oxygen or hydrogen ions, the effect will very likely be blended with and masked by the collisionally mixed indirect-CT from Ar ions. Considering that charge transfer from an Ar ion is so common among elements (cf. Fig. 1), it might be expected that charge transfer with other ionic species is also likely in the ICP, at least if the concentration of these CT-active species is high.

The objective of the present study is to investigate whether charge transfer from non-argon gaseous species also contributes measurably to the ionization and excitation of analyte species in the ICP. There are several reasons why it is important to know whether CT occurs commonly with non-argon gaseous species in an ICP. First, from a fundamental viewpoint, charge transfer with non-argon species in an argon-dominated ICP has not been evaluated in the literature, although studies on CT with foreign gases in a pure foreign-gas or foreign-gas dominated ICP have been reported [17–19]. It is also well known that the plasma characteristics change when a foreign gas is doped into the plasma. However, almost all fundamental studies have focused on the physical properties of the mixed-gas plasma; for example, on changes in plasma temperature and electron properties (i.e., electron temperature and number density), or energy transfer caused by the added gas [20–25]. To our knowledge, there has not yet been a study that focuses on the

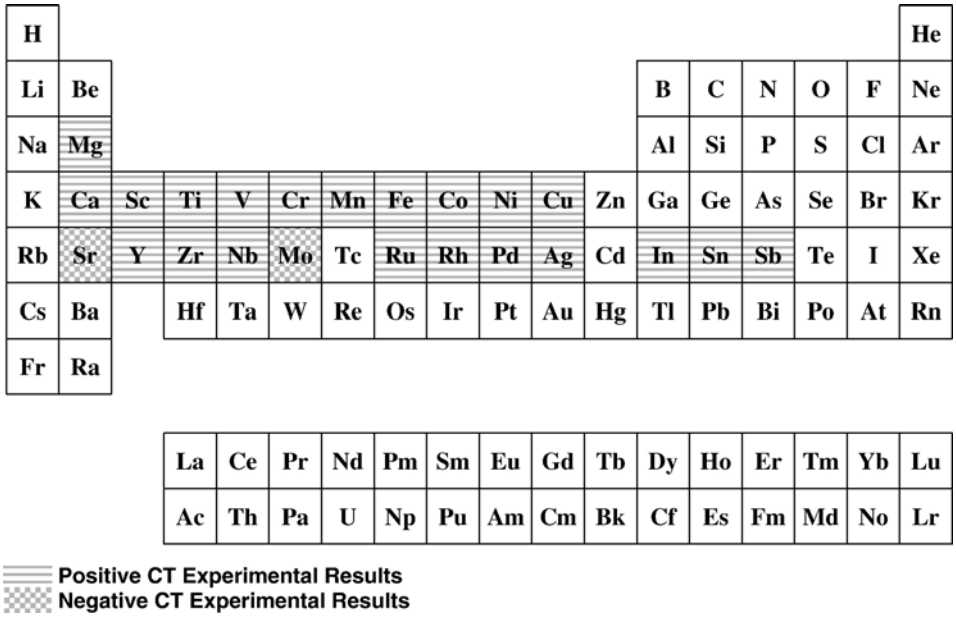

Fig. 1. Periodic table highlighting elements that exhibit charge-transfer character with Ar^+ ion as reported in the literature.