Aerosol detection efficiency in inductively coupled plasma mass spectrometry ☆

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A B S T R A C T

An electrostatic size classification technique was used to segregate particles of known composition prior to being injected into an inductively coupled plasma mass spectrometer (ICP-MS). Size-segregated particles were counted with a condensation nuclei counter as well as sampled with an ICP-MS. By injecting particles of known size, composition, and aerosol concentration into the ICP-MS, efficiencies of the order of magnitude aerosol detection were calculated, and the particle size dependencies for volatile and refractory species were quantified. Similar to laser ablation ICP-MS, aerosol detection efficiency was defined as the rate at which atoms were detected in the ICP-MS normalized by the rate at which atoms were injected in the form of particles. This method adds valuable insight into the development of technologies like laser ablation ICP-MS where aerosol particles (of relatively unknown size and gas concentration) are generated during ablation and then transported into the plasma of an ICP-MS. In this study, we characterized aerosol detection efficiencies of volatile species gold and silver along with refractory species aluminum oxide, cerium oxide, and yttrium oxide. Aerosols were generated with electrical mobility diameters ranging from 100 to 1000 nm. In general, it was observed that refractory species had lower aerosol detection efficiencies than volatile species, and there were strong dependencies on particle size and plasma torch residence time. Volatile species showed a distinct transition point at which aerosol detection efficiency began decreasing with increasing particle size. This critical diameter indicated the largest particle size for which complete particle detection should be expected and agreed with theories published in other works. Aerosol detection efficiencies also displayed power law dependencies on particle size. Aerosol detection efficiencies ranged from 10^{-5} to 10^{-11}. Free molecular heat and mass transfer theory was applied, but evaporative phenomena were not sufficient to explain the dependence of aerosol detection on particle diameter. Additional work is needed to correlate experimental data with theory for metal-oxides where thermodynamic property data are sparse relative to pure elements. Lastly, when matrix effects and the diffusion of ions inside the plasma were considered, mass loading was concluded to have had an effect on the dependence of detection efficiency on particle diameter.

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1. Introduction

1.1. Inductively coupled plasma mass spectrometry

Inductively coupled plasmas have long been used in analytical chemistry to excite chemical species for atomic emission spectrometry and mass spectrometry. This study focuses on thermal processes, which occur inside the inductively coupled plasma mass spectrometer. For this reason, a few basic characteristics of the ICP, and the plasma environment, lend to better understanding of aerosol-plasma interactions and experimental results obtained in this study.

Radio frequency (RF) power is coupled into the outer annulus of the plasma. Heat is conducted from the outer annulus in to the central aerosol flow where analyte and matrix species are atomized (broken down into atomic constituents) and ionized through collisions with electrons. The heavy particle temperature, or plasma gas temperature (T_g), is associated with atomization. The electron temperature is associated with ionization [1]. Most analyte elements are easily ionized in the normal analytical zone of the plasma torch [2]. As particles move along the axis of the torch, there is an increase in temperature between the initial radiation zone, at temperatures on the order of 1000 Kelvin (K), and the normal analytical zone [3]. Plasma temperature then decreases as the axial position transitions from the normal analytical zone to the plasma tail [4]. The plasma temperature along the axis of the torch, in the central aerosol flow, is cooler than in the outer annulus where RF power is coupled into the plasma. The plasma velocity in the central channel ranges from 15 to 25 m/s [5,6]. The gas-kinetic temperature decreases with increasing central gas flow rates [7] where the location of the initial

hot region moves downstream along the axis even though the central velocity remains relatively unchanged [8,9]. Gas flowing through the torch is assumed to be a neutral plasma stream with an approximate gas kinetic temperature of 5000–6000 K in the normal analytical zone [9–11]. Argon ion densities are on the order of 10^{15} ions/cm^3 at these temperatures [12]. The Saha equation has been applied to show that less than approximately 0.1% of argon gas is ionized in the ICP, which suggests the plasma can be treated as a hot gas to good approximation [13]. The effect of central gas flow rate on plasma gas kinetic temperature has been observed where the central flow was 1000 K cooler when the aerosol flow rate was increased from 0.25 to 0.5 L/min [14].

Local thermodynamic equilibrium is often assumed in both experimental and computational studies. Local thermal equilibrium (LTE) is defined as the condition at which electron temperature equals the gas kinetic temperature [15]. Deviations from LTE can occur due to differences in conductivity for gas particles and electrons. Non-LTE conditions can occur due to the presence of interferents and other conditions leading to local gas temperatures as much as 2000 K less than the local electron temperatures. LTE conditions are often assumed for atmospheric pressure plasmas which are the focus of this work. In actuality, both non-LTE and LTE conditions occur inside an ICP torch where the central core more closely satisfies the definition of LTE conditions and the peripheral does not. ICP plasma property modeling capabilities of electron density, electron temperature, and gas temperature are within 10–20% of experimentally observed values [16].

After analytes are atomized and ionized, ions undergo supersonic expansion as they are transported through the sampler cone where the pressure drops from atmospheric pressure to vacuum. ICP-MS signals result from analyte ions close to the center of the torch (within a millimeter) where the sampler cone draws gases from the torch [17]. The pressure is again reduced to lower vacuum through the skimmer section where ions are focused with ion optics and directed to the mass analyzer and ion detector. The total gas flow through skimmer is approximately 1% of the flow through the sampler, and the overall transfer efficiency from skimmer to detector is 0.02–0.2% [18]. Typical overall detection efficiencies of ICP-MS range from 10^{-5} to 10^{-6} [8] and result from losses in the torch, sampler, skimmer, and transport from the skimmer to the ion detector.

In many ICP applications, sample materials are digested in acids and then sprayed into the ICP torch using carefully designed nebulizers to limit the size of droplets. In other applications, it is preferable to avoid acid digestion since it can be hazardous, a source of contamination, result in the loss of volatile materials, and introduces the potential for incomplete dissolution. Digestion also increases the time required for analysis, which is undesirable in some applications. Slurry atomization and laser ablation are two methods which have been used to characterize solid materials without digestion. In past works, the effect of droplets and solid particles on ICPs has been noted. Substantial fluctuations in signal intensities have been observed with time periods on the order of 10 μs. These fluctuations were attributed to incompletely desolvated droplets or incompletely vaporized particles [17]. Droplet desolvation refers to the process of evaporating aqueous components of the analyte droplet where the solute remains and is detected. Eliminating hydrogen and oxygen from the plasma also reduces polyatomic interferences where analytes form hydrides and oxides [19,20].

Hartley et al. utilized a thermoelectric cooler to desolvate slurries prior to injection into ICP-MS [19]. They attributed enhanced transport and atomization efficiencies to the removal of water jackets surrounding solid particles prior to entry into the plasma. RF power coupling into the plasma can also be affected by plasma impedance changes due to the presence of droplets [21]. Energy sinking required for desolvation can result in the reduction in ionization temperatures by approximately 500 K [4]. Others have found that incompletely desolvated droplets and vaporizing particles cool the plasma by 1000 K or more within 1–2 mm of the particle or droplet [22]. This cooling corresponds to 10-fold decrease in electron number density,

which subsequently affects the number of analyte atoms that are ionized in the plasma [22].

From early works with slurry atomization, it was suggested that solid particles must be less than approximately 3 μm in diameter to be atomized efficiently [2]. Later works with particles of varying size measured atomization efficiencies of 20–25% for 10 μm silica particles and 60–70% for 5 μm particles [23]. When slurries were desolvated, it was found that 100% atomization efficiencies were possible for 8 μm solid particles, whereas a shift down to 4 μm particles was observed when plasma energy was diverted to the boiling off of the water jacket [19]. A significant body of literature exists aimed at understanding the fundamental interactions between aerosol droplets and solid particles and inductively coupled plasmas.

1.2. Laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS)

LA-ICP-MS is simply, or not so simply, coupling a laser ablation cell onto the front end of an ICP-MS to analyze solid samples directly by creating aerosols with laser ablation. This enables direct characterization of solid surfaces without sample digestion or wet chemistry. Spatial inhomogeneity of solid samples can also be characterized and material characterization can be performed more rapidly using LA-ICP-MS. Although promising, sample fractionation (preferential sampling and detection of certain elements) can occur and is difficult to mitigate without matrix-matched certified reference materials. This is partially due to complex aerosol generation processes, which occur during laser ablation and complex aerosol-plasma interactions which occur in the ICP. It has been recognized that laser ablation and ICP-MS technologies must be optimized for use with one another [24]. In this section, we present the complexity of laser ablation generated aerosols as motivation for studying particle-plasma interactions in ICP.

Elemental fractionation represents a challenge for LA-ICP-MS [25]. There are numerous parameters affecting fractionation and the combination of those parameters is complex and difficult to model [26]. One common approach used to mitigate these complex effects is the use of external calibration methods via matrix-matched standards. Others have noted the need for internal calibration standards since ablation rates are material dependent and mass loading effects can be significant in some cases [27]. One suggestion for calibration, when matrix matched standards are not available, has been to co-inject calibration aerosols of known size and composition in parallel to the laser ablation aerosol [28]. Some studies have attempted this calibration technique using optical particle counters but OPCs are limited to particles larger than approximately 100 nm in size [29–31].

Complex thermal processes and aerosol transport that occur during the ablation step make it difficult to know, a priori, particle size distributions and compositions of aerosol particles aspirated by the ICP-MS. Subsequent thermal and transport processes in the ICP then govern detection efficiencies in ICP-MS by affecting the breakdown of aerosol particles into constituent atoms, the process of ionization, and transport through the sampler and skimmer. Again, the focus of Section 1.2 is to review aerosol processes, which occur during laser ablation to motivate additional study of how those particles are then processed inside the ICP. The effects of particle and plasma properties on ICP-MS detection efficiencies will be explored in greater detail in Sections 1.3 through 1.6.

Aerosol generation processes have been characterized for metal and glass solid samples [32,33]. Glaus et al. showed that enhancements to LA-ICP-MS were achieved by moving from infrared laser wavelengths to deep ultraviolet wavelengths and reducing laser pulse durations from nanoseconds to femtoseconds [34]. These two modifications in laser characteristics lead to narrower particle size distributions which aid in efficient atomization in ICP-MS. There is a transition between thermal heating of the solid above a wavelength of 250 nm to breaking chemical bonds at wavelengths below 200 nm [27]. Thermal diffusion in the solid material is significant for picosecond and nanosecond laser