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Ion clouds in the inductively coupled plasma torch: a closer look through computations

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ABSTRACT: We have computationally investigated the introduction of copper elemental droplets in an inductively coupled plasma torch connected to a sampling cone, including for the first time the ionization of the sample. The sample is inserted as liquid particles, which are followed inside the entire torch, i.e., from the injector inlet up to ionization and reaching the sampler. The spatial position of the ion clouds inside the torch, as well as detailed information on the copper species fluxes at the position of the sampler orifice and the exhausts of the torch are provided. The effect of on- and off-axis injection is studied. We clearly show that the ion clouds of on-axis injected material are located closer to the sampler with less radial diffusion. This guarantees a higher transport efficiency through the sampler cone. Moreover, our model reveals the optimum ranges of applied power and flow rates, which ensure the proper position of ion clouds inside the torch, i.e. close enough to the sampler to increase the fraction that can enter the mass spectrometer, and with minimum loss of material towards the exhausts, as well as a sufficiently high plasma temperature for efficient ionization.

INTRODUCTION

The inductively coupled plasma (ICP) is the most popular ion source in analytical chemistry for elemental mass spectrometry (MS)¹. The sample to be analyzed is introduced with a carrier gas and will undergo several processes such as desolvation, vaporization, diffusion, ionization and excitation in the plasma. Although, these individual processes are difficult to experimentally measure, several studies have been performed to investigate the material transport through the ICP to improve the analytical capabilities of ICP-MS, both experimentally²⁻²⁵ and computationally²⁶⁻⁴⁵.

Hieftje and coworkers introduced isolated, monodisperse droplets of a sample to measure droplet desolvation rates in flames². Later on, Olesik investigated the fate of individual sample droplets in an ICP. He applied a monodisperse dried microparticulate injector (MDMI) and studied the diffusion process of a single element (Sr) after injection of droplets, or particles from dried droplets by means of laser induced fluorescence³ and side-on optical emission spectroscopy⁴. Kinzer and Olesik^{5,6} as well as Lazar and Farnsworth^{7,8} observed that the addition of high concentrations of concomitant species leads to a decrease in the number of analyte ions produced from each droplet of the sample solution. Olesik and coworkers also studied the correlations between the number of scattering events from an individual incompletely desolvated droplet and the increase in atom emission intensity and decrease in ion emission intensities⁹. Monnig and Koirtzohann¹⁰ showed that the completion of the aerosol droplet vaporization can explain the transition from the initial radiation zone to the analytical zone of the ICP.

Houk and coworkers¹¹⁻¹⁴ studied the trajectory and diffusion of analytes during their transport through the ICP. They made a comparison between wet droplets and solid particles by measuring the emission from vapor clouds surrounding the

aerosol droplets or particles^{12,13}. Several groups also compared the dried solution aerosols from a microconcentric nebulizer with solid particles from laser ablation¹⁴⁻¹⁶. Moreover, the droplet velocities in the ICP were determined from particle image velocimetry and particle tracking velocimetry¹⁵.

Niemax and coworkers showed that the spatial positions of analyte atomization and ionization depend on the injector gas flow rate, the droplet diameter, and the amount of analyte¹⁶⁻¹⁹. This study was performed by means of end-on and side-on optical emission spectroscopy (OES) and applying monodisperse microdroplets (MDMDs). The position of atomization determines the size of the analyte cloud at a particular position. In fact, this is crucial for ICP-MS since the size of the analyte ion clouds determines the detection efficiency.

Günther and colleagues investigated the vaporization process of laser-produced aerosols and the subsequent diffusion losses inside the ICP using 2D OES and ICP-quadrupole (Q)MS of individual particles^{20,21}. They reported that larger particles may vaporize incompletely or at different axial positions inside the ICP because of composition-dependent melting and vaporization enthalpies²². This variable size of atom/ion clouds in front of the MS interface yields non-representative ion extraction.

It is clear that, in order to optimize the ion transport efficiency through the ICP and to the sampler orifice, several parameters have to be taken into account, such as the size and mass of the analyte droplets, the diffusion rates of the elements studied, the gas flow rates, the applied power, the diameter of the injector inlet, the position of the sampler, as well as the diameter and the pressure drop at the sampler orifice²³⁻²⁶. However, the challenge is that these parameters all depend on each other. The effect of the individual parameters can, however, be unraveled by computational investigations, taking into account all important physical processes involved, to support the experimental optimization.

The first model for the “spectrochemical ICP”, as a modification of Miller’s model²⁷ was developed by Barnes et al.²⁸. Miller²⁷ solved a 2D energy equation with 1D electromagnetic field equations to calculate the 2D temperature field in the torch. Subsequently, Barnes et al.²⁸ predicted the temperature and velocity fields, and the plasma and analyte emission profiles. However, these models did not account for the local cooling of the plasma due to the presence of particles or aerosols. The first model for studying the plasma-particle interaction was developed by Boulos²⁹. Based on this model, Mostaghimi et al. investigated the flow and temperature fields in the ICP^{30,31}, and these simulations were combined with experiments in collaboration with Barnes^{32,33}. However, the operating conditions were not always applicable to analytical chemistry purposes and the ICP torch was not connected to a MS interface, so the relevance for ICP-MS was limited.

Benson et al. computationally investigated the droplet heating, desolvation and evaporation in an ICP^{34,35}. The total desolvation rate of sample droplets in an argon ICP as well as the trajectories of the particles through the plasma considering droplet-droplet interaction were studied. Horner and Hieftje³⁶ also studied particle melting, boiling, and vaporization inside the ICP torch, in which particles were assumed to travel along the ICP symmetry axis without significant scatter. However, in all these particle transport modeling studies³⁴⁻³⁶, the initial set of plasma conditions was needed as input by means of a separate code. Therefore, the energy loss by the plasma due to droplet evaporation could not be taken into account because of the separate modeling. Shan and Mostaghimi³⁷ developed a model to study the plasma behavior within the ICP torch as well as the droplet desolvation and trajectories. In order to determine the droplet trajectories and collisions, a stochastic technique combined with the Monte Carlo method was applied. However, ionization and the presence of the MS interface were not included in this model. Spencer et al.^{38,39} presented the first model to describe the effect of the sampler cone in ICP-MS, yet the upstream density and temperature gradients and plasma formation were not included in these models.

The first “self-consistent” model for an atmospheric pressure ICP, operating at typical analytical chemistry conditions, including ionization, was presented by Lindner and Bogaerts⁴⁰. In this model, the transport parameters were for the first time calculated self-consistently for the gas mixture under study, because the above described models typically apply transport parameters (e.g. viscosity) from literature. Therefore, the applicability of this model is not limited to specific mixtures for which the data (i.e., species and relative concentrations) are known. Especially the ionization degree is dependent on the actual composition of the plasma, which strongly affects the transport parameters. In Ref. 40, only data for pure species (e.g. argon) were taken from literature and by means of a kinetic model the transport parameters for the mixtures were calculated. This makes it possible to apply the model to a wider variety of gas mixtures, including carrier gas and sample material.

Subsequently, we modeled the ICP torch connected to a MS interface cone, considering the large pressure drop from upstream to downstream (i.e. 1 atm to 1 torr)⁴¹. This model showed for the first time the effect of the presence of a cooled, grounded sampler, and of the sudden pressure drop behind it, on the plasma characteristics. We performed calculations for a

wide range of gas flow rates and applied power, and also for various sizes of the injector inlet and sampler orifice^{42,43}. In order to optimize the flow behavior inside the ICP torch, recirculation of the gas flow was specifically investigated⁴⁴. Furthermore, a model for elemental droplets, where chemical reactions do not play a role, was recently built⁴⁵. This case is relevant for LA-ICP-MS, where the sample is injected as ablated elemental particles. The inserted droplets were tracked through the ICP torch, up to the evaporation step⁴⁵.

In the present work, for the first time, the ionization of elemental droplets is included in the model. Copper droplets are taken as a case study and injected from the central inlet. By means of this model, we are now able to track the particles to determine their position, their phase (liquid, vapor or ionized), velocity and temperature, both in the ICP torch and at the sampler orifice. More specifically, the shape and position of the ion clouds, originating from the Ar flow as well as from the inserted sample material, are determined inside the torch, which is of interest for emission spectrometry studies as well as for mass spectrometry. By ion cloud we mean the sum of ion clouds from individual particles which includes both diffusion and the different radial paths that particles take through the plasma. Note that the model describes the injected material transport up to the sampling cone and the rest of the ion transport inside the mass spectrometer is not included in the current model. Moreover, as only the elemental particles are considered, the model is again relevant more to LA-ICP-MS than general ICP-MS studying. With this model, any deviation from the central axis, as well as any early/late evaporation along the torch are indicated, which are caused by non-optimal operating conditions. The effects of injection position, applied power and carrier gas flow rate are studied and the computational results are compared with experimental data from literature as much as possible, to validate the model and to explain the experimental observations.

COMPUTATIONAL MODEL

The model is a 2D axisymmetric model, based on solving partial differential equations for the gas flow dynamics (i.e., the Navier-Stokes equations), coupled with the energy conservation and Maxwell equations. It is built within the commercial computational fluid dynamics (CFD) program FLUENT 16.0.0 (ANSYS). A validation of this model by experiments was provided in Ref. 44,46. Typical calculation results obtained with the model include the gas flow behavior, as well as the plasma temperature and electron density profiles⁴¹⁻⁴⁴. The accuracy of model is tested in Ref. 46 by comparing our result with experiment which shows a deviation of 3% in temperature. Also, the calculated thermal conductivities are compared with the values given by experiment¹⁻³. The data are in good agreement (typically less than 5% deviation) for both the pure elements as well as for the example mixture of 50% He and 50% Ar (mole fraction). The maximum deviations reach values of about 10%, which is similar to deviations of the data given in e.g. Ref. 4 with respect to Ref. 3. The deviations appear in the range where significant ionization is present.

In order to study the material transport through the ICP, the sample introduction is modelled with a so-called “discrete phase model” (DPM)⁴⁵. The trajectory of each droplet is calculated by integrating the force balance acting on the droplets.

Besides their transport throughout the torch, the particles in liquid phase will undergo heating, vaporization, boiling and finally ionization. For the elemental droplets, a heat and mass balance equation is applied, which relates the particle temperature to the convective and diffusive heat transfer, and calculates the mass transfer to the vapor phase by means of a vaporization rate based on thermodynamic relations⁴⁵. The heat lost or gained by the particle as it traverses each computational cell also appears as a source or sink of heat in the subsequent calculation of the energy equation in the so-called “continuous phase model” (CPM).

Once the injected material is in the gas phase, it will be treated as individual atoms in the same way as for the carrier gas, i.e., by solving the Navier-Stokes equations and the Saha-Eggert equation to calculate the ionization degree of the sample material at the local plasma temperature, assuming LTE. From the ionization degree and the (mass and charge) conservation equations, the number densities of electrons and of the atoms and ions of the sample material can be calculated. It is justified to apply the local thermodynamic equilibrium (LTE) condition to the plasma. A direct comparison between simulation and experiment was performed as it is discussed in detail in ref. 46. By means of end-on ICP optical emission spectroscopy, we collected the light from different areas in plasma and compared with the simulation results. The plasma temperature inside the central channel was experimentally determined from the end-on collected line-to-background ratio. The calculated and measured values for the plasma temperature were found to be in good agreement (i.e., within 3% deviation). In fact, the plasma is burning at atmospheric pressure. Thus, collision times are in the order of 10 ps while one period of the rf-field takes a few ten ns. Thus, in the order of 1000 collisions with atoms take place per electron during one oscillation. In contrast to DC discharges, electrons do not gain energy on average if they do not undergo collisions since the oscillating electric field accelerates and decelerates them in the same way during one period. This means that close-to LTE conditions can be achieved. Although the assumption of LTE is not fully correct, the use of two-temperature models does not necessarily yield significantly different temperatures for electrons and heavy species⁴⁷. Therefore, we believe that the assumption of LTE can get close to the accuracy of non-LTE models for the present plasma. LTE, in particular, has the advantage that the model can be more easily formulated consistently and it requires less other assumptions (e.g. on power coupling and energy transfer from electrons to atoms and ions) and/or (sometimes imprecise) parameters. Using the capabilities of LTE simulation for thermochemical processes in ICP, Pupyshev et al.⁴⁸ calculated the formation efficiencies of singly and doubly charged ions of 84 elements within the temperature range of 4000-10,000 K by steps of 500 K which showed a good agreement with experimental data. However, one should take this into account that LTE calculations likely overestimate the heavy species temperature and therefore the ionization degree of the elements.

The ionization model is added to FLUENT as a self-written code. For any injected material, several material parameters are needed, both in liquid and gas phase. Some parameters, i.e., the viscosity, thermal conductivity and diffusion coefficients, are a function of the local gas composition and plasma temperature, and are again inserted in the model as self-written codes. The plasma species considered in the model are atoms, singly and doubly charged ions for Ar and Cu, as well as elec-

trons. The diffusion coefficient of copper droplets in Ar gas is adopted from Ref. 47 as a function of temperature. More details about transport properties calculation is provided in Ref. 40 for Ar flow. Figure 1 shows the thermal and electrical conductivity, specific heat, viscosity and Ar and Cu gas fractions as a function of temperate actual gas composition inside the entire torch at 1400 W power and 1.2, 1.2, 16 L/min flow rate of carrier, auxiliary and cooling gas, respectively.

To implement the DPM into the CPM of the ICP, a FLUENT model is built including the injection properties, material parameters and the physical models applicable for elemental particles. After obtaining convergence for the Ar plasma properties, we introduce the particles. In each iteration, the exchange of mass, momentum and energy between plasma and droplets is calculated and both the DPM and CPM are updated. Finally, the ion clouds are tracked along the torch, providing also information on the number density of each species at the sampler orifice, which yields the transport efficiency of elemental droplets.

Note that in order to apply the DPM to our calculations, the introduced sample needs to be in a fluid phase, either liquid or gas. Therefore, in this work, we introduce pure copper material using liquid injection but the particles are introduced at room temperature and the transport properties are calculated based on temperature of Ar flow. Therefore, the particles are carried with the transport properties of first solid (300-1357 K) and then liquid phase (> 1357 K). In fact, “quasi-particles” are introduced, and carried with the gas flow, up to reaching the vaporization point. However, the energy exchange at melting point is not included. This assumption is justified, because the latent heat of melting for copper (203.5 kJ/kg) is much smaller than the latent heat of vaporization (5310 kJ/kg) and melting can thus be ignored in our calculations, while the quasi-droplets (which be called “particles” for simplification in the rest of this manuscript) still undergo heating from room temperature, i.e., solid phase. Note that fractional shape of particles as well as radiative heat transfer from plasma to particles is ignored in this calculation.

RESULTS AND DISCUSSIONS

General calculation results

All calculation results will be illustrated for copper droplets with a diameter of 1 μm , inserted at the central inlet with 2 mm width, at a flow rate of 100 ng/s. They are tracked through the torch up to the sampler position (i.e. 41.5 mm distance from the central inlet). The total applied power is varied between 600 and 1600 W and the carrier gas flow rate ranges between 0.4 and 1.6 L/min. The auxiliary and cooling gas flow rates are kept at 1.2 and 16 L/min, respectively.

Figure 1 shows the 2D profiles of coupled power density and temperature inside the plasma (a,e), as well as of the argon and copper species number densities, i.e. Ar, Ar⁺ and Ar²⁺ (left column; b,c,d), and Cu, Cu⁺ and Cu²⁺ (right column; f,g,h) for an applied power of 1400 W and a carrier gas flow rate of 1.2 L/min, which are typical conditions of interest for ICP-MS⁴⁸. We showed before⁴⁵ that a mass loading flow rate up to 100 $\mu\text{g/s}$ has only a minor effect on the plasma temperature profile. Therefore, the plasma temperature shown in Figure 1d is almost the same as for pure Ar (see e.g., ref. 44), as we use a mass loading flow rate of 100 ng/s for pure copper droplets in this study. This value is based on laser ablation studies and

taken from experimental values of fs-laser ablation of copper cells for a long washout time⁴⁹. For aqueous analyte solutions, feed rates up to 0.1 g/min (or 1.7 mg/s) are used, and even for these flow rates, it was reported that the plasma temperature is not affected by the sample introduction¹⁶⁻¹⁸.

The species number density profiles shown in Figure 1 are plotted on a logarithmic scale, and not in the same scale, in order to clearly show the maximum values of each species inside the torch. It is clear that most of the argon ionization takes place in the coil region, where the external power is mostly coupled to the gas flow and the maximum temperature is reached, see Figure 1(a,c-e). In the case of copper ionization, the maximum is closer to the central axis, as the copper ionization potential is much lower than that of argon (i.e., 7.73 eV vs 15.76 eV) and the ionization can thus take place at lower temperature.

Looking at the absolute values, it is clear that the Ar gas atoms are by far the most abundant (Figure 1b). Their number density when entering the torch is $2.4 \times 10^{25} \text{ m}^{-3}$, corresponding to atmospheric pressure and room temperature. However, inside the plasma, their number density drops to around $6 \times 10^{23} \text{ m}^{-3}$ due to the high temperature, and its volume integrated value over the entire torch is $7.9 \times 10^{24} \text{ m}^{-3}$. The Ar⁺ ion number density (Figure 1c) reaches a maximum of $1.7 \times 10^{22} \text{ m}^{-3}$, with a volume integrated value over the entire torch of $2.6 \times 10^{21} \text{ m}^{-3}$. This indicates that the ionization degree of Ar, at the position of maximum ionization (i.e., the position of maximum power coupling and maximum temperature, i.e., 10,200 K) is about 2.8%. This is almost in agreement with the calculated results in Ref. 48, which the ionization degree at 10000 K for argon is stated as 2.08% and at 9500 K as 1.20%. However, integrated over the entire torch region, the ionization degree of the Ar gas is about 0.033%. The maximum Ar²⁺ ion number density (Figure 1d) is only about $1.9 \times 10^{14} \text{ m}^{-3}$, hence 8 orders of magnitude lower than the maximum Ar⁺ ion number density. Thus, a negligible fraction of the Ar⁺ ions is further ionized into Ar²⁺ ions. This is logical, because of the high second ionization potential of Ar (i.e., 27.7 eV). Although the doubly charged ions are negligible in terms of total composition of the plasma, they still might be significant enough to be detected. Moreover, when low concentrations of analyte are being measured, these signals reduce the analytical signals from elements at the same mass per charge ratio and cause spectral interferences in ICPMS. The number density profile of the Cu atoms (Figure 1f) can be explained from the evaporation process and the Ar gas flow path lines, as illustrated in Figure 2. In this figure the trajectory of the three Ar gas flows originating from the central, intermediate and outer inlets are plotted in black, violet and orange, respectively. The mass transfer rate of the Cu droplets to the gas phase is also shown, and indicates that the copper droplets do not all evaporate at the same radial and axial position (see separate regions of maximum mass transfer rate). The Cu droplets injected from the outer region of the inlet (also called “off-axis”) follow different path lines of the Ar gas flow than the ones which are injected from the central region of the inlet. Indeed, the droplets injected “off-axis” move away from the central axis, and they experience the hotter regions in the plasma earlier and therefore start to evaporate earlier, while the ones that stay on axis, go more straight and will evaporate more downstream the torch. A detailed discussion about the Ar path lines, their radial expansion and backward motion can be found in Ref. 41,44,45.

As a result of the different positions of Cu evaporation, two maxima can be observed in the Cu atom density profile of Figure 1f. The initial source of atomic Cu is close to the central axis, where the evaporation takes place (see Figure 2), and therefore some “local maxima” (light green contours) are observed near the end of the cool central channel. However, due to the diffusion of Cu atoms into the Ar flow, and following the path lines of the auxiliary gas flow (see Figure 2), the Cu atoms also expand in the torch with the backward motion of the Ar gas flow. As a consequence, the maximum Cu atom density (around $6.3 \times 10^{18} \text{ m}^{-3}$) occurs close to the inlets, due to the backward motion of the gas flow, at the same place as for the Ar atom density. The plasma temperature is here near room temperature, so ionization does not take place. From this region, the Cu atoms are carried by the cooling gas to the outer exits of the ICP, or by the auxiliary gas to the center and towards the sampler.

The Cu atom number density, volume integrated over the entire torch, is $1.13 \times 10^{18} \text{ m}^{-3}$. This indicates that the Cu atoms are more than six orders of magnitude less abundant than the Ar gas atoms in the plasma. At higher mass loading flow rates, this ratio will of course increase accordingly. In spite of this much lower Cu density, the Cu⁺ and Cu²⁺ ions are not so much less abundant than the Ar⁺ and Ar²⁺ ion densities, as is illustrated in Figures 1(g,h). At the central axis, the Cu⁺ and Cu²⁺ ions reach their maximum density near the sampler, but they also show a second maximum in the region of maximum coil power and maximum temperature, like in the case of Ar. The maximum Cu⁺ ion density is about $2.4 \times 10^{18} \text{ m}^{-3}$ (see Figure 1g), and their volume integrated density is $1.4 \times 10^{18} \text{ m}^{-3}$. Hence, the overall ionization degree of Cu, integrated over the entire torch region, is about 55 %. This is much higher than in the case of Ar, which is logical, due to the lower ionization potential (see above). Furthermore, in the regions of maximum Cu⁺ ion density (i.e., 10200 K), the local ionization degree is calculated to be more than 90%. This is again in agreement with the calculated results in Ref. 48 which the ionization degree at 10000 K for copper is stated as 91.8% and at 9500 K as 91.7%. The exact comparison is not possible as in Ref 48, the injected analytes are diluted in water. The maximum Cu²⁺ ion density is about $7.5 \times 10^{13} \text{ m}^{-3}$, and the volume integrated density is around $3 \times 10^{13} \text{ m}^{-3}$ (see Figure 1h). This indicates that only a small fraction (i.e., about 0.002%) of the Cu⁺ ions is further ionized into Cu²⁺ ions. Although this fraction is still very low, it is about 2000 times higher than for Ar, which can again be explained from the lower second ionization potential of Cu (i.e., 20.9 eV).

Figure 1 indicates that both the atom and ion clouds of both Ar and Cu can reach the sampler, but also that some parts of these clouds will also exit through the exhausts of the torch (i.e., the exhausts). By comparing Figure 1g and Figure 1h, we can deduce that the Cu²⁺ ions are all evacuated through the sampler orifice, while some of the Cu⁺ ions exit through the exhausts of the torch. However, due to the drop in temperature at the exhausts, they will recombine again to the atomic phase; for more details, see Figure 4 below.

Thus, we can summarize the steps from Cu droplets to Cu vapor and to the Cu⁺ and Cu²⁺ ions as follows, using copper just as an example of any elemental sample. The Cu droplets are inserted from the central inlet and carried by the Ar flow till they start to evaporate (blue contours in Figure 2), atomize (Figure 1f), and ionize (Figure 1g and 1h, for single and dou-

ble ionization, respectively). These figures illustrate to what extent the clouds of each species expand in the torch. This might be useful for both emission and mass spectrometry. Any displacement in the radial or axial position of the ion clouds can change the number of ions reaching the sampler orifice, which will affect on the ion signals in the MS. Likewise, for optical emission spectrometry, the ion signals are very sensitive to the exact position at which the data are obtained.

In Figure 3 we show the calculated fluxes of the Ar and Cu atoms and ions at the position of the sampler orifice, as a function of radial distance from the central axis, at the same conditions as in Figure 1, as well as the temperature profile. At the bottom of the figure, the width of the sampler orifice is indicated for clarity. In general, the ion fluxes reach a maximum at the center of the sampler orifice, corresponding to the axial velocity of the flow which reaches its maximum (~ 900 m/s) at the center of the sampler and drops towards the edge of the sampler cone, i.e., 0.5 mm from the central axis. Moreover, in the region near the sampler, the ionization reaches its maximum at the central axis, where the temperature is slightly higher. The latter can be explained by the cooling effect of the sampler, which has an orifice of 1 mm diameter. For the same reason, the atom fluxes reach their maximum at the radial position corresponding to the orifice diameter (see Figure 3). This is most apparent for the Cu flux, as it reflects the position where most of the Cu particles (i.e., on-axis, near the sampler) are vaporized. However, the atomic fluxes do not reach a minimum at the center of the sampler, because of the maximum flow speed in this region. Details of the velocity profiles of the Ar flow can be found in Ref. 41. The absolute values of the copper species fluxes in the central 1mm (i.e., within the sampler orifice width) show how many of these species can enter the MS interface per second. At the conditions of Figure 3, the total (i.e., radially-integrated) fluxes of the Cu atoms, Cu^+ ions and Cu^{2+} ions are about $7 \times 10^{19} \text{ m}^{-2}\text{s}^{-1}$, $7 \times 10^{20} \text{ m}^{-2}\text{s}^{-1}$, and $7 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$, respectively.

Effect of injection position, power and carrier gas flow rate on the sample transport efficiency from inlet to sampler

In this section, we compare the fluxes of ions passing through the sampler (by integrating the values over the entire orifice width) with the sample flux entering the torch at the inlet. This allows us to calculate the transport efficiency of the sample material from the inlet till entering the MS interface at different operating conditions. Specifically, we study the effect of injection position at the central inlet, applied power and carrier gas flow rate, and we show that these parameters determine the position of the ion clouds inside the torch, which affects the fluxes at the sampler orifice, and thus the sample transport efficiency.

Effect of injection position

In previous section, we introduced the copper particles from the entire width of the central inlet. To study here the effect of the injection position, we introduce the same amount of copper particles (100 ng/s with a diameter of 1 μm) from two different initial positions at the entrance, i.e. on-axis and off-axis. The other operating conditions are kept the same as in Figure 1. Figure 4a shows the 2D Cu^+ ion number density profile for on-axis injection (more specifically within 0.25 mm width from the center of the inlet; upper frame) and off-axis injection

(i.e., within 0.25 mm from the side wall of the inlet; bottom frame). The particle tracking of the Cu droplets is also plotted in black path lines. For the sake of comparison, only one half part of the torch is shown for each case in Figure 4a. It can be seen that the particles which are injected on-axis move more forward in a straight line throughout the torch, while the ones which are off-axis injected deviate from the central axis at an earlier axial position. Therefore, the ion cloud in the upper frame of Figure 4a is found more on the central axis and expands less, while the ion cloud in the bottom frame shows a broader expansion along the torch.

In Figure 4b, the calculated fractions of Cu^0 atoms and Cu^+ ions entering the sampler orifice, as well as the fraction of Cu^0 atoms exiting through the exhausts of the ICP torch, with respect to the total amount of Cu entering the torch at the inlet (i.e. 100 ng/s), are plotted both for on-axis and off-axis injection. Cu^+ is of course the most important species, as Cu^0 cannot be detected in the MS. The fractions of Cu^{2+} ions are not indicated, as they are 4.5×10^{-5} and 2×10^{-5} for on-axis and off-axis injection, respectively, and thus negligible compared to the other species. The effect of injection position on the transport efficiency through the sampler is quite evident. When all the droplets are injected on-axis, the dominant fraction (around 90.6%) will pass through the sampling cone in the form of Cu^+ ions, while about 6.8% of the material passes as Cu^0 atoms through the sampler, and 2.6% exits through the exhausts. However, in the case of off-axis injection, only 48% of the injected material will enter the MS interface as Cu^+ ions, while almost the same fraction (47%) leaves the ICP through the exhausts, and 5% passes as Cu^0 atoms through the sampler. This clearly demonstrates that any deviation of the injected material from the central axis will lead to a loss of intensity in the MS, which should be avoided. Indeed, the radial movement of the sample particles to the outer region of the torch lowers the chance that the sample can pass through the sampler cone. Hence, the detection efficiency becomes lower, as some part of the sample is lost in the torch (i.e. it will leave the ICP through the exhausts) and is not effectively sampled through the plasma-vacuum interface. This suggests that using smaller injector inlets will be beneficial, especially for laser ablated particles, as indeed observed experimentally in Ref. 18. To our knowledge, this is the first time that a model for ICP-MS can calculate the amount of ions at the sampler orifice and predict optimum operating conditions for this purpose (see below).

The early evaporation of samples due to deviation from the central axis affects the ion density not only upstream, but also downstream the sampler. The groups of Farnsworth and Spencer studied the velocity profiles of the argon flow entering the MS vacuum stages, by means of experiments and computations, respectively, and also concluded that any deviation of analyte from the central axis affects the transmission between the first and second vacuum stages. In fact, the gas flows passing through the sampling cone off-axis, will expand off-axis in the first vacuum stage and therefore they get lost in the skimming process^{25,38,39,50}. Again, our simulations suggest that using a smaller inlet will be beneficial to avoid these losses.

Figure 4c shows the copper species fractions at the sampler orifice for on-axis and off-axis injection, by integrating the fluxes of the Cu^0 atoms, Cu^+ and Cu^{2+} ions on the sampler orifice surface. The dominant species in both cases are Cu^+ , with a fraction above 90%, being slightly lower in the case of

off-axis injection. The Cu^0 atoms have a fraction of about 7% for both on-axis and off-axis injection, while the fraction of Cu^{2+} is only in the order of 10^{-5} %.

Effect of applied power

Figure 5a illustrates the effect of applied power, ranging from 600 to 1600 W, on the calculated fractions of Cu^0 atoms and Cu^+ ions entering the MS sampling cone, as well as the fraction of Cu^0 atoms exiting through the exhausts of the ICP torch, with respect to the total amount of Cu entering the torch at the inlet (i.e. 100 ng/s), for a fixed carrier gas flow rate of 1.2 L/min and assuming that the Cu sample is injected from the entire central inlet (i.e., no distinction between on-axis and off-axis). The fraction of Cu^{2+} ions is again not shown, because it is in the order of 10^{-7} - 10^{-5} , although increasing with power. Similar to Figure 4b, the sum of the three curves in Figure 5a is always equal to 100%, as the total amount of Cu in the torch, either as Cu^0 atoms or Cu^+ ions (and Cu^{2+} ions) must either leave the torch through the sampler orifice or through the exhausts.

The fraction of Cu^0 which enters the MS interface through the sampler orifice decreases from 25% to 10% upon increasing the applied power, while the fraction of Cu^+ ions entering the MS interface (around 50%) first slightly decreases up to 1000 W and then slightly increases. The fraction of Cu^0 atoms leaving the torch through the exhausts (about 30-40%) first slightly increases and then stays more or less constant. The most important result from this figure is that about 50% of the injected copper will pass through MS interface as Cu^+ ions. This transport efficiency of 50% is comparable to the result of Figure 5b for off-axis injection, which is quite logical because in reality, overall only a minor fraction of the sample is really injected on-axis. However, this also suggests that one should be able to improve the detection efficiency by using a narrower central gas inlet, where all the sample is injected close to on-axis.

In Figure 5b the copper species fractions at the sampler orifice are depicted for different applied powers. At all applied powers investigated, the majority of the Cu entering the MS interface will be Cu^+ ions. This fraction is 66% at a low applied power of 600 W, and 82% at a high power of 1600 W. However, note that this corresponds only to about 50% of the injected Cu from the inlet, according to Figure 5a. The Cu^{2+} ions form only a very minor fraction of the amount of Cu passing through sampling cone. By increasing the applied power, the ion fractions at the sampler increase, while the fraction of Cu^0 atoms decreases. We showed in Ref. 42 for pure Ar flow that at a fixed carrier gas flow rate, increasing the applied power inside the torch leads to a rise in the plasma temperature, and therefore also in a rise in the ionization rate, and thus in the ion number densities and fluxes.

In order to study the changes caused by the power in more detail, we plot in Figure 6 the 2D profiles of the Cu^+ ion number density (in color), as well as the contour lines of the plasma temperature (plotted in black, in the same scale as Figure 2e for the different cases, ranging from 300 K to 10,000K), for 6 different values of applied power, i.e., from 600 W to 1600 W. The carrier gas flow rate is again kept at 1.2 L/min. The temperature profiles are just added for illustration and to assist in the explanation, but they were discussed in more detail in our previous work⁴² for pure Ar. Since the copper droplet flow rate is ten orders of magnitude lower than the Ar flow rate

(i.e., 100 ng/s corresponds to only 8.36×10^{-10} L/min), the temperature profiles are unaffected upon addition of the Cu droplets, as discussed above and in Refs.16-18, 41 and 45.

The general trend of increasing the applied power is a drop in the length of the cool central channel (see the black contours). Indeed, at 600 W, the temperature at the central channel is below 1300 K up to a distance of 34.8 mm from the injector inlet, while at 1600 W, it starts rising already at a distance of 25.7 mm. This is quite logical, and was also illustrated in Ref. 42. It means that the sample vaporization can take place earlier in the torch at higher power. The same behavior was also found experimentally. Indeed, Blades et al.²³ and Chan and Hieftje²⁴ performed OES on ICPs loaded with dispersed liquids, and reported that an increase of the RF power raises the ICP gas temperature and made particles to vaporize earlier. Horner et al.^{26,36} as well as Shan and Mostaghimi³⁷ reported from their modeling studies that the height of complete desolvation decreases fairly linearly with increase of the applied RF power³⁷. Finally, also Mills et al.²⁵ reported that a higher power causes a shift in atomization and ionization toward the load coil, based on planar laser-induced fluorescence to map the density distributions in the region between the load coil and the sampler.

Besides the axial shift in sample vaporization to earlier positions in the torch, causing also the ionization to take place earlier in space, a narrowing of the Cu^+ number density profile in the radial direction upon increasing power can also be observed from Figure 6. A similar trend was also evident in the fluorescence images reported in Ref. 25 at a position of 5 mm downstream from the load coil and 5mm upstream from the sampler. This behavior can be explained as follows: As the copper is introduced here from the whole width of the central inlet and not only on-axis, we see that the ion clouds are formed in a relatively wide area (i.e., not only on-axis). Therefore, the maximum ionization occurs at different places along the torch, depending on the exact injection position. Indeed, the droplets introduced near the outer sides of the inlet (i.e. off-axis) are ionized earlier in the torch for all the cases in Figure 6, because they expand somewhat more in the radial direction, following the Ar gas path lines, and therefore they reach the hotter areas in the coil region earlier, where they will evaporate and ionize. Thus, the off-axis ion clouds are shifted upstream the load coil upon increasing power, due to the correspondingly higher temperatures, and therefore, the off-axis maxima occur earlier in the torch and the density near the sampler drops. This is the reason why the ion clouds become narrower and are located earlier in space upon increasing the applied power. Furthermore, for the droplets introduced near the center of the inlet (on-axis), an increase in power from 600 to 1000 W (left column) also leads to an upstream shift of the central ionization maximum, following the temperature profile (black contours). The vertical black dashed line indicates the maximum in Cu^+ ion density at 600 W, and thus shows how this maximum is shifted away from the sampler. This explains the slight drop in Cu^+ fraction at the sampler from 600 W to 1000W, presented in Figure 5a. This drop is more evident in figure 5c as only the very central region of the sampler orifice is measured. However, in the right column of Figure 6, (based on the two lowest temperature contours), by further increasing the power, the length of the central channel does not shorten to the same extent, but the high temperature area again shifts more to the sampler (see black contour lines), so that the maximum of the ion number density also takes place closer to the

sampler (see Figure 6d). In Figure 6e and Figure 6f, the maximum ion density is off-axis and in the coil region, originating from the droplets injected off-axis, but a secondary maximum, albeit smaller, is indeed moving closer to the sampler. Hence, these profiles, and especially the region near the sampler, explain why the flux of the Cu^+ ions is relatively high at 600 W, followed by a small drop till 1000 W, and again a slight increase towards the two highest powers investigated, as observed in Figure 5a above. Therefore, in the following we will keep the power fixed at 1400 W for studying the effect of the carrier gas flow rate.

Effect of carrier gas flow rate

We already showed that for any specific injector inlet diameter, there is a transition flow rate for the carrier gas below which the central channel does not occur⁴⁶. The transition flow rate for the inlet diameter of 2 mm which is used in this study is 0.4 L/min. Therefore, we chose 0.4 L/min as the lowest flow rate and studied the effect of carrier flow rate up to 1.6 L/min. In Figure 7, we show the fractions of Cu^0 atoms and Cu^+ ions at the sampler and of Cu^0 atoms leaving the torch through the exhausts, with respect to the total amount of Cu at the inlet (a), as well as the Cu species fraction at the sampler orifice (b), for different carrier gas flow rates ranging from 0.4 to 1.6 L/min. The fraction of Cu^{2+} ions is not shown in Figure 7a, because it is only in the order of 10^{-5} - 10^{-6} , decreasing with flow rate. Again the sum of the three curves in Figure 7a is always equal to 100%, as the total amount of Cu in the torch, either as Cu^0 atoms or Cu^+ ions (and Cu^{2+} ions) must either leave the torch through the sampler orifice or the exhausts.

Figure 7a indicates that the fraction of Cu^+ ions which pass through the sampler orifice increases upon increasing the gas flow rate from 0.4 to 0.6-0.8 L/min, followed by a drop for higher gas flow rates. The fraction of Cu^0 atoms entering the sampler orifice slightly increases in the entire range of flow rates, and the fraction of Cu^0 atoms leaving the torch through the exhausts decreases from 0.4 to 0.6-0.8 L/min, followed by a small increase. This means that a carrier gas flow rate of 0.6-0.8 L/min yields a maximum transport efficiency, because it leads to a maximum in the fraction of Cu^+ ions reaching the sampler (56%) and at the same time to a minimum of Cu^0 atoms wasted at the exhausts (33%). The maximum of Cu exiting through the exhausts (43%) occurs at the minimum flow rate of 0.4 L/min.

The maximum and minimum in the fractions of Cu^+ ions at the sampler and Cu atoms at the exhausts, respectively, indicate that rising the carrier gas flow rate above the transition flow rate and up to 0.8 L/min shifts the sample more forward along the axis, which leads to a later evaporation, resulting in more species flowing towards the sampler than to the exhausts. However, a further increase in the gas flow rate at a fixed applied power leads to a drop in the plasma temperature and thus in the ion number densities⁴². In general, around 60-65% of the Cu sample will pass through the sampler, with a dominant contribution from the Cu^+ ions (between 47% and 56%). Indeed, it is clear from Figure 7b that at all flow rates investigated, the majority of the Cu entering the sampler orifice will be Cu^+ ions. The Cu^{2+} ions form only a very minor fraction of the amount of Cu entering the sampler orifice.

In Figure 9, we show the fractions of Cu^+ ions at the sampler, with respect to the total amount of Cu at the inlet for different carrier gas flow rates ranging from 0.4 to 1.6 L/min.

Figure 9 shows increasing from 0.6 to 1.6 L/min results in about 35% lower transport through central 0.05 mm of the orifice. The discussed drop in Figure 7a is more pronounced in Figure 9 as only the very central region of the sampler orifice is measured. Note that the 35% decrease might become more evident as the ions passing through the skimmer and the rest of their journey inside the MS.

Figure 8 presents more details about the changes occurring upon increasing the carrier gas flow rate, for 3 different values of the flow rate. The black contours (again plotted in the same scale for the 3 figures, ranging from 300 K to 10,000K) show how the temperature profiles change when varying the carrier gas flow rate. It is clear that the highest temperature contour line (the area in the plasma above 10,000 K) becomes smaller and is further away from the central axis upon increasing gas flow rate. This raises the length of the cool central channel inside the torch, as is seen from Figure 8. Therefore, the analyte evaporation, atomization and ionization processes will be strongly shifted downstream when the carrier gas flow rate increases. A shift of ~12 mm along the axis is observed between a carrier gas flow rate of 0.4 and 0.8 L/min and a further shift of 10 mm occurs from 0.8 to 1.6 L/min. This is not only due to the higher transport velocity of the carrier gas in the ICP, but in particular also due to the relatively large downstream shift of the plasma boundary (as indicated by the contour lines) and the lower maximum temperature due to the larger amount of cold gas volume injected. In fact, varying the flow rate from 0.4 to 0.8 L/min (corresponding to a rise of 0.4 L/min), as seen in Figure 8a to 8b, results in a longer shift than further increasing the flow rate to 1.6 L/min, which corresponds to a rise of 0.8 L/min (cf. Figure 8b to 8c). This explains why the highest Cu^+ fraction at the sampler is predicted around 0.6-0.8 L/min. A further shift to the sampler upon further increasing the flow rate does not help, as the temperature drops by loading too much Ar to the plasma.

It is also apparent from Figure 8 that the ion cloud size changes significantly for the 3 different cases. As mentioned above, at the lower carrier gas flow rates, the ionization occurs earlier and the cloud expands more in the radial direction, while at the higher flow rates, the ion cloud is smaller and closer to the sampler. The reduction in ion cloud size upon increasing carrier gas flow rate was also reported by side-on fluorescence images of barium species²⁵. In fact, the size of the ion cloud depends also on the composition of the sample droplet²¹, which is of course not yet included in our present model. When the ion cloud size is large due to more radial diffusion, it will be beneficial to shift the ion cloud towards the sampler by increasing the carrier gas flow rate (see Figure 8a and 8b). Indeed, the detection efficiency in ICP-MS is the best when the diffusion of analyte ions at the position of the MS sampler is limited, as was also reported in Ref. 18. Furthermore, the plasma temperature in the analyte - plasma interaction region has to be as high as possible to guarantee the most effective atomization and ionization. This explains why further increasing the carrier gas flow rate above 0.8 L/min does not increase the fraction of Cu^+ ions at the sampler.

A downstream shift in analyte vaporization, atomization and ionization upon rising flow rate was also observed in experiments^{3,18,25}. Indeed, in Ref. 25 a downstream shift of ~10 mm for a carrier gas flow rate rising from 0.87 till 1.52 L/min was reported, for an inlet diameter of 1.5 mm, and in Ref. 3 an increase of the carrier gas flow rate from 0.8 L/min to 1.0

L/min caused a 7 mm downstream shift in the position at which the droplets of 13 μm diameter were completely desolvated. Shan and Mostaghimi also indicated that the height of complete desolvation increases linearly with increase of the carrier gas flow rate³⁷. By means of OES with end-on and side-on observation of the plasma, Niemax et al. determined the location of atomization in the ICP and the spatial distribution of diffused analyte ions at positions where the MS interface is typically placed in ICP-MS. They report a shift of 25 mm for a rise in carrier gas flow rate from 0.25 to 0.5 L/min. They indicated that both a downstream shift of the atomization and a high temperature can be achieved by using injectors with a small inner diameter (1 mm) and higher injector gas flow rates^{18,19}. It is important to realize that, compared to aerosol droplet introduction, dry particles as for example produced by LA of solid samples will start to evaporate earlier when they penetrate into the ICP. Consequently, analyte diffusion begins further upstream in the ICP and the ion cloud will be larger at the position of the sampler than with aerosol droplets, thus decreasing the analyte ion detection efficiency. In order to increase the ion detection efficiency of LA-ICP-MS, the plasma boundary position has to be shifted downstream, e.g., by increasing the carrier gas flow rate¹⁸.

Although the lowest carrier gas flow rate of 0.4 L/min (Figure 8a) leads to a large ion cloud early in the plasma, which is not beneficial for the detection efficiency, the maximum Cu^+ ion density is here much higher than for the other gas flow rates, i.e., $5.3 \times 10^{18} \text{ m}^{-3}$ (thus significantly larger than the maximum of the color scale), while it is $3.2 \times 10^{18} \text{ m}^{-3}$, and $2.4 \times 10^{18} \text{ m}^{-3}$ for the carrier gas flow rates of 0.8, and 1.6 L/min, respectively. This is of course also attributed to the higher plasma temperature at the lower flow rate (cf. above).

From both Figure 7 and 8, we can conclude that a carrier gas flow rate between 0.6 and 0.8 L/min is the optimum range for the current setup. Indeed, according to Figure 7a, the carrier gas flow rate of 0.6-0.8 L/min yields the highest fraction of Cu^+ ions at the sampler, and Figure 8b shows that at this flow rate the ion cloud is properly shifted toward the sampler. A further increase is not recommended because the temperature and ion density drop along the axis and this condition cannot provide sufficient heat to complete the desolvation and ionization (see Figure 8c). Furthermore, the analyte atoms will diffuse and become ionized, forming ion vapor clouds with increasing diameter downstream the plasma¹⁹. It should be realized that early evaporation and more radial expansion from the central axis, which is the case for the flow rates below 0.6 L/min in this study, may cause that some part of the sample ions does not reach the sampler orifice, which thus represents a loss¹⁹. Moreover, even if they are not lost, it may cause a delay in detection time, for example when different elements in an expanded ion cloud are carried by different Ar path lines, which have different axial velocity along the torch, especially when arriving at the sampler, as was observed in Ref. 48.

CONCLUSION

We studied the transport, evaporation and ionization of copper droplets through an inductively coupled plasma, connected to the sampling cone of a mass spectrometer, by means of a computational model. Our aim is to obtain a better insight into the particle transport, evaporation and ionization inside the ICP torch and to optimize the transport efficiency of the injected sample material through sampling cone. This model

provides us, for the first time, detailed profiles of all atomic and ionic species inside the torch, as well as at the sampler orifice. Our calculations show that the droplets follow different path lines of the Ar gas flow in the torch and expand differently in the radial direction from the central axis, depending on their exact position of injection.

The 2D profiles of the various ion number densities provide us the axial and radial position at which the ionization occurs, which depends on the plasma temperature along the torch. They also show to what extent the ion cloud moves in the radial direction and deviates from the central axis. In a group of droplets injected from the central inlet, the ones introduced near the center of the inlet (on-axis) move in a more straight line along the torch and experience a later evaporation and ionization compared with the droplets introduced near the outer region of the inlet (off-axis). Thus, on-axis injection reduces the probability of losing the sample inside the torch or the occurrence of a detection delay, by preventing the droplets from early radial expansion inside the torch. Also, it ensures less expansion in the first vacuum stage and therefore a lower amount of sample lost through the skimmer.

Besides the 2D density profiles of the various ions and atoms, we also focussed especially on their fluxes at the position of the sampler orifice. More specifically, we calculated the fraction of Cu^+ and Cu^{2+} ions and Cu^0 atoms entering the sampling cone, as well as the fraction of Cu^0 atoms leaving the torch through the exhausts, for both on-axis and off-axis injection, and for a range of different applied powers and carrier gas flow rates, to determine the transport efficiency of the sample material at these different conditions. As mentioned above, on-axis sample injection yields a significantly higher fraction of Cu^+ ions entering the sampler orifice, i.e., 90% vs 48% in the case of off-axis injection.

The effect of applied power was studied in the range of 600-1600 W. We showed that the entire ion cloud moves upstream inside the torch upon increasing applied power up to 1000 W, but for higher power values, a secondary maximum is observed near the sampler, and this explains why the Cu^+ fraction entering the sampler orifice first slightly decreases (up to 1000 W) and then slightly increases upon increasing power. Our calculations predict that for the conditions under study (i.e., geometrical setup, Ar gas flow rates and copper mass loading flow rate), a power of around 1400W is preferable to move the ion cloud close to the sampler.

Furthermore, increasing the carrier gas flow rate in the range between 0.4 and 1.6 L/min leads to cooling of the central plasma temperature. As a consequence, the position of maximum ionization moves downstream to the sampler. We showed that a rise from 0.4 to 0.6-0.8 L/min leads to a higher ion density at the sampler, with the highest Cu^+ fraction entering the sampler at 0.6-0.8 L/min. Taking into account the amount of gas consumption, a further increase in flow rate is not recommended as it does not improve the Cu^+ ion density at the sampler, because of cooling of the plasma inside the torch. In fact, within central 0.05 mm of sampler orifice, a 35% drop in transport efficiency is calculated by increasing from 0.6 to 1.6 L/min. This might be more pronounced in the next stages of ion journey inside the MS and at the detection point.

Our calculated results, especially for the effect of power and carrier gas flow rates, are compared with experiments from literature as much as possible, and good qualitative agreement is reached. In general, we may conclude from our calculations

that about 50% of the injected copper will pass through the sampling cone. This value will be slightly higher with increasing power and carrier gas flow rate up to 0.8 L/min. However, when all droplets can be injected on-axis, the transport efficiency rises to about 90%. This suggests that one should be able to improve the transport efficiency by using a narrower central gas inlet, where all the sample materials is injected close to on-axis.

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REFERENCES

- (1) Houk, R. S. *Anal. Chem.* **1986**, 58 (1), 97A–105A.
- (2) Hieftje, G.M.; Malmstadt, H.V. *Anal. Chem.* **1968**, 40, 1860–1867.
- (3) Olesik, J.W. *Appl. Spectrosc.* **1997**, 51, 158A–175A.
- (4) Olesik, J.W.; Hobbs, S.E. *Anal. Chem.* **1994**, 66, 3371–3378.
- (5) Olesik, J.W.; Kinzer, J.A. *Spectrochim. Acta, Part B* **2006**, 61, 696–704.
- (6) Kinzer, J.A. Inductively Coupled Plasma Spectrometry (CE-ICP): Elemental speciation and fundamental studies of matrix effects in the ICP, Ph.D. Thesis, The Ohio State University, 1997.
- (7) Lazar, A.C.; Farnsworth, P.B. *Appl. Spectrosc.* **1999**, 53, 465–470.
- (8) Lazar, A.C.; Farnsworth, P.B. *Appl. Spectrosc.* **1997**, 51, 617–624.
- (9) Olesik, J.W.; Smith, L.J.; Williamsen, E.J. *Anal. Chem.* **1989**, 61, 2002–2008.
- (10) Monnig, C.A.; Koirtjohann, S. R. *Anal. Chem.* **1985**, 57, 2533–2576.
- (11) Winge, R. K.; Crain, J. S.; Houk, R. S. *J. Anal. Atomic Spectrom.*, **1991**, 6, 601–604.
- (12) Houk, R. S.; Winge, R. K.; Chen, X. *J. Anal. At. Spectrom.* **1997**, 12, 1139–1148.
- (13) Aeschliman, D. b.; Bajic, S. J.; Baldwin, D.P.; Houk, R. S. *J. Anal. At. Spectrom.* **2003**, 18, 1008–1014.
- (14) Perdian, D. C.; Bajic, S. J.; Baldwin, D. P.; Houk, R. S. *J. Anal. At. Spectrom.* **2008**, 23, 325–335.
- (15) Jorabchi, K.; Brennan, R. G.; Levine, J. A.; Montaser, A. *J. Anal. At. Spectrom.* **2006**, 21, 839–846.
- (16) Groh, S.; Garcia, c. C.; Murtazin, A.; Horvatic, V.; Niemax, K. *Spectrochim. Acta, Part B* **2009**, 64, 247–254.
- (17) S. Groh, P. Diwakar, C.C. Garcia, A. Murtazin, D.W. Hahn, K. Niemax, *Anal. Chem.*, 2010, 82, 2568–2573.
- (18) Murtazin, A.; Groh, S.; Niemax, K. *Spectrochim. Acta, Part B* **2012**, 67, 3–16.
- (19) Niemax, K. *Spectrochim. Acta, Part B*, **2012**, 76, 65–69.
- (20) Gschwind, S.; Flamigni, L.; Koch, J.; Borovinskaya, O.; Groh, S.; Niemax, K.; Günther, D. *J. Anal. At. Spectrom.* **2011**, 26, 1166–1174.
- (21) Flamigni, L.; Koch, j.; Günther, D. *Spectrochimica Acta, Part B* **2012**, 76, 70–76.
- (22) Koch, J.; Günther, D. *Appl. Spectrosc.* **2011**, 65, 155A–162A.
- (23) Blades, M. W.; Horlick, G. *Spectrochim. Acta, Part B* **1981**, 36, 861–880.
- (24) Chan, G. C. Y.; Hieftje, G.M. *J. Anal. At. Spectrom.* **2009**, 24, 439–450.
- (25) Mills, A. A.; Macedone, J. H.; Farnsworth, P.B. *Spectrochim. Acta Part B* **2006**, 61, 1039–1049.
- (26) Horner, J. A.; Lehn, S. A.; Hieftje, G. M.; *Spectrochim. Acta Part B* **2002**, 57, 1025–1042.
- (27) Miller, R. C.; Ayen, R. J. *J. Appl. Phys.* **1969**, 40, 5260–5273.
- (28) Barnes, R. M.; Schleicher, R. G. *Spectrochim Acta, Part B* **1975**, 30, 109–134.
- (29) Boulos, M. I. *IEEE Trans. Plasma Sci.* **1978**, 6, 93–106.
- (30) Mostaghimi, J.; Pfender, E. *Plasma Chem. Plasma Process.* **1984**, 4, 199–217.
- (31) Mostaghimi, J.; Proulx, P.; Boulos, M. I. *Numer. Heat Transfer* **1985**, 8, 187–201.
- (32) Yang, P.; Barnes, R. M.; Mostaghimi, J.; Boulos, M. I. *Spectrochim. Acta, Part B* **1989**, 44, 657–666.
- (33) Mostaghimi, J.; Proulx, P.; Boulos, M. I.; Barnes, R. M. *Spectrochim. Acta, Part B* **1985**, 40, 153–166, 1985.
- (34) Benson, C. M.; Gimelshein, S. F.; Levin, D. A.; Montaser, A. *Spectrochim. Acta, Part B* **2001**, 56, 1097–1112.
- (35) Benson, C. M.; Zhong, J.; Gimelshein, S. F.; Levin, D. A.; Montaser, A. *Spectrochim. Acta, Part B* **2003**, 58, 1453–1471.
- (36) Horner, J. A.; Hieftje, G. M. *Spectrochim. Acta, Part B* **1998**, 53, 1235–1259.
- (37) Shan, Y.; Mostaghimi, J. *Spectrochim. Acta, Part B* **2003**, 58, 1959–1977.
- (38) Spencer, R. L.; Krogel, J. T.; Palmer, J.; Payne, A.; Sampson, A.; Somers, W.; Woods, C. N. *Spectrochim. Acta, Part B* **2009**, 64, 215–221.
- (39) Spencer, R. L.; Taylor, N.; Farnsworth, P. B. *Spectrochim. Acta, Part B* **2009**, 64, 921–924.
- (40) Lindner, H.; Bogaerts, A. *Spectrochim. Acta, Part B* **2011**, 66, 421–431.
- (41) Aghaei, M.; Lindner, H.; Bogaerts, A. *J. Anal. At. Spectrom.* **2012**, 27, 604–610.
- (42) Aghaei, M.; Lindner, H.; Bogaerts, A. *Spectrochim. Acta, Part B* **2012**, 76, 56–64.
- (43) Aghaei, M.; Lindner, H.; Bogaerts, A. *J. Anal. At. Spectrom.* **2013**, 28, 1485–1492.
- (44) Aghaei, M.; Flamigni, L.; Lindner, H.; Günther, D.; Bogaerts A. *J. Anal. At. Spectrom.* **2014**, 29, 249–261.
- (45) Aghaei, M.; Bogaerts, A. *J. Anal. At. Spectrom.* **2016**, 31, 631–641.
- (46) Lindner, H. Murtazin, A. Groh, S. Niemax, K. Bogaerts, A. *Anal. Chem.*, **2011**, 83, 9260–9266.
- (47) Yang, P.; Horner, J. A.; Sesi, N. N.; Hieftje, G. M. *Spectrochim. Acta Part B* **2000**, 55, 1833–1845.
- (47) Murphy, A. B. *J. Phys. D: Appl. Phys.* **1996**, 29, 1922–1932.
- (48) Borovinskaya, O.; Aghaei, M.; Flamigni, L.; Hattendorf, B.; Tanner, M.; Bogaerts, A.; Günther, D. *J. Anal. At. Spectrom.* **2014**, 29, 262–271.
- (49) Lindner, H., Untersuchungen zur Partikelverteilung und -zusammensetzung beim Laserabtrag, Thesis, Universität Dortmund, **2004**.
- (50) Radicic, W. N.; Olsen, J. B.; Nielson, R. V.; Macedone, J. H.; Farnsworth, P. B. *Spectrochim. Acta, Part B* **2006**, 61, 686–695.

