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Local effects of atomizing analyte droplets on the plasma parameters of the inductively coupled plasma

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ABSTRACT

Monodisperse droplets from aqueous analyte solutions with selected diameters in the range 35–67 µm are introduced into an inductively coupled plasma with frequencies between 1 to 10 droplets per second. The effect of desolvation and atomization in the ICP is studied end-on by optical emission spectroscopy employing simultaneously up to three calibrated monochromators with fast photomultipliers. The onsets of desolvation and analyte atomization and the extremely fast diffusion of hydrogen in the ICP and its effect on the plasma are studied by simultaneous measurements of hydrogen, analyte and Ar lines. The local cooling by analyte atomization is measured quantitatively in dependence on time applying the Boltzmann plot method to simultaneously recorded line intensities of atomized analyte atoms which act as plasma probes. Furthermore, it is shown that relatively small differences in analyte mass cause significant temperature changes during atomization and, as consequence, strong variations of the emission intensity of analyte lines during atomization if measured by end-on observation.

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SPECTROCHIMICA

1. Introduction

The inductively coupled plasma (ICP) is certainly the most popular plasma in analytical atomic spectrometry [1–4]. It is used as powerful atomizer for wet and dry aerosols generated by nebulization of liquid samples or processes such as laser ablation or desolvation of wet aerosols, respectively. At the same time, the high temperatures in the ICP are also important for efficient excitation and ionization of the analyte atoms which are measured by optical emission spectrometry (OES) or mass spectrometry (MS).

In the last decades, the processes essential in sample introduction and atomization have been studied independently by different research groups [5–16]. In particular the investigations with monodisperse droplets generated from aqueous analyte samples of known concentrations [5–11] gave a deeper insight into the interaction processes of analyte and plasma. For example, the trajectory of the atomizing droplet and the diffusion of analytes during their transport through the ICP have been studied applying spectral imaging with fast cameras [12–15] or by side-on observation of spectral line emission from analyte atoms and ions [6–9]. An excellent review on single droplet introduction to the ICP has been published by Olesik in 1997 [7]. We know from his and other

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preceding experiments that the droplets of analyte solution desolvate first before the analytes start to atomize and ionize. It was also demonstrated that the diffusion of atoms and ions analytes forms almost perfect spherical symmetric clouds which continuously grow by diffusion during their transport through the ICP (see, e.g., [7]). Furthermore, the influence of accompanying elements on analyte detection was studied on single droplet basis. The review paper by Olesik presents a couple of examples for elemental cross correlation and proposes possible mechanisms for these matrix effects. Unfortunately, the given proposals have not been checked since.

It has to be noted that all studies with monodisperse droplet injection into the ICP go back to earlier research of the Hieftje group who used a droplet generator first to study desolvation and atomization processes in analytical flames (see, e.g., [17] and references therein).

There is a current research project at ISAS on quantitative chemical characterization of airborne nanoparticles with diameters below 100 nm applying ICP-MS. The elaborateness of the method requires careful investigation and understanding of (i) particle atomization and its impact on the local plasma parameters, (ii) the atomic diffusion and interaction processes in the ICP, and (iii), for mass spectroscopic detection, the local ionization of the element atoms. These processes are expected to be dependent on particle size, composition and morphology on the one hand, and the trajectories and transient times of the particles through the ICP on the other.

A second important requirement is the availability of reference material for calibration. Unfortunately, it is difficult to get well characterized nanoparticles. There are a few companies selling, e.g., monodisperse SiO₂, TiO₂, Al₂O₃, Au, and Pt nanoparticles of different

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Fig. 1. The experimental arrangement.

sizes. However, the choice of nanoparticles is too limited for practical application and, in some cases, the size distribution is far from being monodisperse. Therefore, we resume the idea of producing monodisperse droplets of standard solution which have to be desolvated before introduction into the ICP. Knowing the droplet diameter precisely, the element masses can be calculated.

The present paper reports on plasma spectroscopic measurements of the atomization process when monodisperse aqueous droplets of standard solutions are directly introduced into the ICP without a separate desolvation step. Free, electronically excited hydrogen atoms from the solvent water and atoms and ions from analyte atomization are used as probes for the local plasma conditions. It will be shown that desolvation and analyte atomization processes in sub-volumes of the ICP have very strong impact on the local plasma temperature. As a consequence, this dramatic, time and mass dependent effect on the local temperature has direct influence on the analyte emission line intensities and, therefore, on element analyses by ICP-OES of droplets with end-on observation. It will also be demonstrated how sensitively the line emission of a trace element depends on the concentration of a major element in the sample.

2. Experiment

The experimental arrangement is shown in Fig. 1. Monodisperse droplets of standard solution were generated by a commercial piezoelectric droplet generator with protective gas option around the droplet nozzle (Type MD-E-201 H, microdrop Technologies, Norderstedt, Germany). The number of droplets introduced into the ICP could be varied from a single droplet to 2000 droplets per second. However, typical droplet frequencies were 1 and 10 Hz during the experimental investigations. The droplet diameter produced by the generator is primarily dependent on the orifice diameter of the droplet dispenser. At constant operation condition the variation of the droplet diameter from droplet to droplet is specified by the manufacturer to be <1%. Unfortunately, this low value could not be checked using the microscope camera with stroboscopic illumination delivered with the droplet generator as standard system for droplet adjustment and observation. The absolute measurements of the approximate droplet diameters were made with the standard camera after calibration with a µm-ruler. The absolute accuracy of diameter measurements was \pm 3 µm mainly limited by the pixel size of the CCD camera used.

Two dispenser types with 30 and 50 μ m orifices were applied. The use of the 30 μ m diameter orifice resulted in droplets with diameters between 30 and 70 μ m depending on length and magnitude of the voltage pulse applied to the piezo-ceramic of the dispenser. The 50 μ m orifices produced monodisperse droplets between 50 and 100 μ m. The size of the droplets was measured using the microscope camera before introduction into the ICP. For these measurements the droplet dispenser was moved downwards from the injector tube of the ICP applying an adjustment unit. Then, the operating dispenser unit was attached to the injector tube again.

The droplets were transported by a relatively low Ar gas flow $(0.1-0.25 \text{ L} \text{min}^{-1})$ vertically through the injector tube of the ICP torch into the plasma which was operated with auxiliary and outer gas flows of 1 and 16 L min⁻¹, respectively. The transport gas was provided through the protective gas nozzles around the droplet orifice. Lower (<0.1 L min⁻¹)



Fig. 2. The end-on imaging conditions of the ICP onto the aperture of the optical fiber bundle as found experimentally by optimization of the peak intensity of analyte lines. A volume within the central channel of the ICP and its image are accentuated for better visibility. Θ_A is the maximum acceptance angle of the fiber bundle used. All lengths are in scale.

The measured Si (I), Ca (I) and Ca (II) lines, their excitation energies and transition probabilities.

Element	Wavelength [nm]	Excitation energies $[cm^{-1}]^{a}$	$A_{21} (10^8 \text{ s}^{-1})$
Si (I)	288.16	40,991.9	$2.17\pm10\%^{\rm a}$
			$1.894 \pm 15\%^{b}$
Si (I)	263.13	53,387.3	$1.06 \pm 10\%^{a}$
			$0.969 \pm 20\%^{b}$
Si (I)	251.61	39,955.1	$1.68 \pm 10\%^{a}$
			$1.212 \pm 10\%^{b}$
Si (I)	243.52	47,351.6	$0.434 \pm 10\%^{a}$
			0.4697 ^c
Si (I)	212.41	53,362.2	$2.97 \pm 10\%^{a}$
			7.201°
Ca (I)	422.67	23,652.3	$2.18 \pm 10\%^{d}$
Ca (II)	393.37	25,414.4	$1.47 \pm 15\%^{d}$

No error bars are given in Ref. [20].

Ref. [19]

^c Ref. [20].

^d Ref. [21].

and higher gas flows (>0.25 L min⁻¹) for droplet transport resulted in droplet losses and instable transport properties. The inner diameter of the injector tube was 4 mm but tapered to 1 mm diameter at the end. It means that, depending on the gas flow applied, the velocity of the transport gas at injector exit was between 2.1 and 5.3 m s⁻¹. For quantitative line intensity measurements, the emission signals of typically between 100 and 200 sequent droplets were averaged for better statistics.

The ICP torch was taken from a prototype ICP-instrument (ELEMENT 1, Finnigan MAT, Bremen, Germany). The RF-generator (27 MHz) and the matching unit (AM/ICP-20P) were provided by RF Power Products Inc. (Marlton, NJ). The ICP power was 1000 W.

The spectral emission from the diffusing atoms of the atomizing droplets was imaged by a quartz lens (f = 11.5 cm, aperture: 40 mm) onto a 4.9 mm diameter bundle of quartz fibres. The fibre bundles split the light into three equal parts for three different monochromators. The imaging conditions chosen allowed collecting light from the central channel of the ICP.

Fig. 2 shows the optical arrangement in scale. Depending on the spatial position the magnification is slightly larger than one. The position of one to one imaging is marked by 2f. The alignment was performed by adjusting the positions of imaging lens and fibre to the maximum peak signal of the analyte in the sample solution. Variations of the imaging parameters did not only have influence on the measured intensities but also on the shape of the transient signals produced by droplet injection. A part of the inner ICP channel as well as the position of its image is accentuated by grey areas. It has to be noted that the image chosen does not allow collecting the emission from all ICP sub-volumes equally as it is demonstrated by side-on observation [7]. In particular, the spatial expansion of analyte clouds on their way through the ICP, the diffusion of emitting analytes out of the imaged ICP volume, and the difference of the aperture dependent optical collection efficiency along the plasma are affecting the measured absolute intensities. However, the relative line intensities are not affected and can be used for plasma spectroscopic measurements on analyte atoms and ions, unless elements with different diffusion velocities are studied.

The light transmitted through the fibres was imaged by three further quartz lenses onto the entrance slits of three different monochromators (1 m Spex, 1 m and 0.3 m monochromators by McPherson) equipped with photomultipliers (two 9789 QA and one 9784 QA by EMI) for detection. The photomultiplier signals were amplified (Stanford Research SR570 and Keithley 428), digitized (National Instruments DAQPad-6015) and stored by a personal computer for further evaluations. A time resolution of 30 µs was found to be adequate for unbiased recording of the transient emission signals. Therefore, the time constants of the amplifiers were set to 30 µs. The acquisition rate of the data was 60 kHz.

Aqueous Si samples (1–100 $\mu g~mL^{-1})$ made from a silicon standard stock solution by Merck (1000 $\mu g m L^{-1}$ of (NH₄)₂ Si F₆) were used as test samples and the atomic Si lines at 288.16, 263.13, 243.52, 251.61 and 212.41 nm were measured and used for evaluation of the excitation temperature. The corresponding excitation energies and transition probabilities of the lines are given in Table 1. The table also contains the data of the resonance lines of neutral Ca (422.67 nm) and its atomic ion (393.37 nm) which were measured when detecting the Ca contamination (~90 ng mL⁻¹) in a 100 µg mL⁻¹ Si solution. It is well known in ICP-OES that the detection power of elements is particularly good if strong ion lines in the spectral range >200 nm can be measured. Unfortunately, all strong Si ion lines are in the VUV. Therefore, the present measurements on Si are restricted only to Si I lines and to elevated analyte concentrations in comparison with Ca. The reason why Si was chosen as element for the present experiment is that preliminary end-on emission measurements and atomization studies have been performed in our laboratory injecting monodisperse 1 and 2 μ m SiO₂ particles into the ICP [22]. These earlier measurements revealed that SiO₂ particles of that size are too large for complete atomization.

Measurements of the integrated line intensities are required if the excitation temperature has to be evaluated by means of the Boltzmann-plot method. Therefore, the widths of the monochromator exit slits were adapted so that the total intensities of the spectral lines were recorded. The signals of the ICP recombination continuum at the wavelengths of the Si lines were subtracted from the measured intensities.

The monochromators together with the fibres, lenses and photomultipliers used had been calibrated before in the wavelength range 200-400 nm using a deuterium lamp from Ocean Optics (type: DH 2000) with NIST calibration certificates.

3. Results and discussion

3.1. The effect of droplet desolvation and analyte atomization on plasma emission

The effect of desolvation and analyte atomization of a 52 µm droplet of 100 μ g mL⁻¹ Si solution in the ICP is exemplarily shown in Fig. 3. The figure displays simultaneously recorded intensities of the H_{β} hydrogen line at 486.13 nm, the neutral Ar line at 415.86 nm, and the Si (I) resonance line at 288.16 nm. The start of desolvation can be taken from



Fig. 3. The intensities of the Si 288 nm, H 486 and Ar 416 lines measured simultaneously after the injection of 52 μ m droplets of a 100 μ g mL⁻¹ Si solution. The intensities of 93 droplets were averaged. The flow of the transport gas was 0.18 L min⁻¹.

Ref. [18]. b

the onset of the H_{β} line intensity. We assume that the water of the droplet already begin to evaporate on the way from the exit of the injector tube to the border region of the plasma which is about 10 mm in our experiment. It should be noted here that Mie scattering measurements on droplets from a spray chamber by Monnig and Koirtyohann [23] revealed that there was measurable desolvation before the droplet reached the hot region of the ICP. More recent theoretical and experimental investigations by Mie scattering on droplet desolvation can be found in [24] and [25], respectively.

As the droplet is penetrating into the ICP, the plasma is locally cooled by the processes of desolvation, dissociation of the water molecules, and by excitation and ionization of their products, the hydrogen and oxygen atoms. At the experimental conditions applied (injector gas flow: 0.18 Lmin^{-1}), the time of desolvation was about 2 ms which can be read from the rise time of the $H_{\!\beta}$ line intensity. As long as the H_{β} intensity grows desolvation is not accomplished. The local cooling of the ICP can be read from a ~4% decrease of the Ar line intensity during desolvation. Note that the decrease of Ar line emission is due to plasma cooling in the sub-volume of the ICP where desolvation, dissociation, excitation and ionization take place. It has to be noted that not only the Ar line intensities are reduced but also the recombination continuum. This can hardly be seen in the Si signal shown in Fig. 3 where the unperturbed plasma background intensity was subtracted because the Si intensity was much stronger than the lowering of the continuum before the onset of analyte atomization. However, it can clearly be detected before analyte emission if the signal amplification is larger. Onset and the shape of background reduction are following the characteristics of the Ar line intensity reduction as expected. Note that the reduction of the ICP radiation is due to processes in a sub-volume in the plasma. The plasma radiation from the unaffected simultaneously measured plasma volume is unchanged.

The atomization of the analyte mass, observable by the appearance of the Si line emission from evaporated atoms, starts just after the H_{β} line intensity has its maximum value, i.e., after the end of desolvation. This is in agreement with the observation and statement given by Olesik (see e.g., [7]). At what position in the ICP the analyte atomization begins in the present experiment cannot be extracted from end-on measurements. Additional side-on observations are required.

The processes of atomization, excitation and ionization of the analyte mass also dissipate energy from the immediate vicinity inside the ICP. This effect can be qualitatively seen as a dip in the H_{β} line intensity at the time of analyte atomization. The size of the dip depends on the analyte mass. The dip disappears for blank droplets.

The transport velocity of the Si atoms through the ICP can be estimated from the length of the Si signals and the size of the plasma (total ICP-length: ~4.5 cm, see Fig. 2). Depending on the transport gas flow the length of the Si signal was between 1.5 and 3 ms. The corresponding transport velocity of the Si atoms through the ICP is between 30 and 15 m s⁻¹. This is in approximate agreement with the average Ar gas velocity known from other experimental studies [1].

It is interesting that the length of the $H_{\!\beta}$ signal is much larger than what is expected from the Ar gas flow. Hydrogen atoms are even still in the ICP 6 ms after the Si atoms have left the plasma. This documents that the diffusion velocity of hydrogen atoms (and their ions) is much larger than the transport velocity of the plasma gas, i.e., a significant fraction of the hydrogen atoms is leaving the ICP even in backward direction. Furthermore, it is interesting that the Ar line intensity is overshooting the value before droplet injection by about 1%. Note that the Ar line intensity is decreasing as the H_{β} intensity drops. The overshooting should indicate an increase of the population density of the excited Ar atoms by a slightly higher plasma temperature. This effect could be due to the better heat conductivity from higher to lower temperature regions in the ICP caused by hydrogen. It is known effect in ICP spectroscopy that the addition of a few percent hydrogen enhances analyte signals considerably due to the better heat conduction by H from the hotter plasma regions into the central volume with the analytes [26–28]. However, it can be also not totally excluded that the coupling of energy into the ICP is distorted by the desolvation and atomization process of the droplet and give rise to the overshooting of the Ar line intensity. For 52 µm droplets the Ar line came back to the intensity level before droplet injection after about 10 ms.

The effect of water on the Ar line intensities becomes significant if the droplets are larger. For example, 62 μ m droplets of the same Si solution (100 μ g mL⁻¹) which contain about 70% more water and analyte than 52 μ m droplets caused a ~10% decrease of the Ar line intensity during desolvation and a ~4% increase after. In has also to be noted that the time for desolvation of 62 μ m droplets was slightly longer.

The reproducibility of the analyte signal at periodic injection of monodisperse droplets from analyte solution is shown in Fig. 4. 49 μ m droplets of 100 μ g mL⁻¹ Si solution were injected with a droplet frequency of 1 Hz. The standard deviation of the Si line (288 nm) peak intensity for the signals displayed was found to be 9.6% while the RSD of the peak areas was 3.3%.

The local cooling of the ICP by analyte atomization has not only an effect on the emission of hydrogen lines but can also affect the line



Fig. 4. (a) 49 μ m droplet with 100 μ g mL⁻¹ Si, and (b) OES signal of the 288 nm Si line at 1 Hz droplet injection frequency.



Fig. 5. The intensities of the Si (I) 251.6 nm and the Ca (II) 393.4 nm lines measured simultaneously with 67 μ m droplets of 100 μ g mL⁻¹ Si solution including ~90 ng mL⁻¹ Ca as a trace element. The intensities of seven droplets were averaged. The transport gas flow was 0.18 L min⁻¹.

intensities of accompanying elements. Fig. 5 displays simultaneously measured emission intensities of a trace element (Ca II 393.4 nm) as well as of the Si I 251.6 nm line. The droplet size was 67 µm, the concentration of Si 100 μ g mL⁻¹, and the transport gas flow 0.18 L min⁻¹. Ca was present as a very small contamination (90 ng mL⁻¹, as determined by graphite furnace AAS). It can be seen that the atomization of the relatively larger silicon mass is also affecting the intensity of the Ca II line similarly as the $H_{\!\beta}$ emission in Fig. 3 where the Si atomization created a dip in the $H_{\!\scriptscriptstyle\rm B}$ intensity. The Ca II line intensity increases first but decreases a little later before it grew again. The intensity dip is correlated with the Si peak intensity. We believe that dips in line emission should in general be observable if the spatial vapor distribution of the radiating trace element is larger than of the major element during atomization what is assumed to be the case for Ca in comparison with Si. It is important to note that the Ca II/Si I line intensity ratio is constant for t > 0.7 ms. This can be taken as indication that the plasma sub-volume with Ca and Si atoms is, within experimental uncertainty, characterized by steady state conditions in the respective sub-volume of the ICP including the analyte cloud during its transport through the plasma. Quantitative measurements of the excitation temperature which indicate complete atomization of the analyte Si for t > 0.7 ms and the formation of equilibrium conditions in the plasma will be presented in the following paragraph.

3.2. Quantitative measurements of plasma cooling by localized analyte mass atomization

The intensities of three different Si I lines with different excitation energies measured with 50 um droplets of 100 ug mL $^{-1}$ Si solution at a transport gas flow of 0.15 L min⁻¹ are plotted in dependence on time in Fig. 6a. Differences in the shapes of the intensity curves can be seen if the line intensities are normalized. This was done in Fig. 6b where the intensities were normalized to 1 at 1 ms. Despite large difference of their excitation energies (up to ~12,400 cm^{-1}) the normalized line intensities are the same for t>0.5 ms within their mutual error bars. It means that the atomization of the analyte mass is completed after at ~0.5 ms and the excitation temperature in the ICP sub-volume with the analyte cloud reaches the local equilibrium conditions. Differences in the intensity response are visible at the beginning of atomization pointing out a strong reduction of the excitation temperature by the atomization process of the analyte mass including about 6.6 pg Si and additional mass from the accompanying elements in the solution. The excitation temperature T_{ex} was derived from the Boltzmann plot formula $k \ln \frac{l_{m\lambda}}{gA} = -\frac{E_{ex}}{T_{ex}}$, where *k* is the Boltzmann constant, l_{int} the integrated line intensity, λ the wavelength, A the transition probability, and g the statistical weight of the excited state energy level at $E_{\rm ex}$. As mentioned before, the wavelengths, excitation energies, and transition probabilities of the lines used for excitation temperature determination are given in Table 1. Explicit Boltzmann plots for two different times (0.017 and 0.75 ms after the start of analyte atomization) taking into account the integrated intensities of three different Si lines and the transition probabilities of a recent compilation by NIST [18] are shown in Fig. 7. The error bars of the data points measured at 17 µs are very large due to the low Si line intensities measured at early time. The absolute excitation temperature of 8100 ± 860 K at 0.75 ms is comparable with the highest excitation temperatures measured by the Boltzmann plot method [1]. It has to be noted that the temperature at 0.75 ms is lower if the 212.4 nm line is not taken into account or if the transition probability of Ref. [20] is used. A lower excitation temperature is also derived if the Si 263.1 nm line and the transition probabilities of [18] or [19] are applied. This is in agreement with the results of recent preliminary excitation temperature measurements at SiO₂ particle injection [22] where only two Si lines (288.2 and 263.1 nm) and the transition probabilities of [19] were used. The 263.1 nm line was not measured in the present experiment because the intensity is weaker than of the 212.4 nm line and, therefore, can be only measured for a shorter time. It is interesting that the $k \ln \frac{l_{im}\lambda}{gA}$ data for 0.75 ms are on a perfect straight line if the transition probability of the 212.4 nm line given by [20] is included instead of the corresponding value in the NIST compilation which is originally from a paper by O'Brian and Lawler [29] who reported lifetime measurements in an atomic beam after pulsed laser excitation. The excitation temperature derived with the transition



Fig. 6. (a) The intensities of the Si 288.2, 212.4, and 243.5 nm lines plotted in dependence on time. The intensities shown are derived from 207 droplets and corrected for the spectral response of the respective monochromator. The error bars include the uncertainties in intensity and spectral response determination. The error bars of the 243.5 nm data points have the size of the symbol used. (b) The line intensities normalized to one at 1 ms. For visual clarity, not all error bars are plotted. (c) The excitation temperature in dependence on time. The error bars include the experimental error and the uncertainties of the monochromator calibrations and of the atomic transition probability. Only a few error bars are plotted for the sake of visual clarity. The droplet diameter was 50 μ m, the Si concentration 100 μ g mL⁻¹ and the Ar gas flow 0.15 L min⁻¹.



Fig. 7. The Boltzmann plot for two times (0.017 and 0.75 ms) after the start of analyte atomization using the line intensities plotted in Fig. 6a. The experimental parameters are given in the caption of Fig. 6. The statistical errors of the data points for 0.75 ms have the size of the data points. The dashed lines are straight line fits through the experimental points weighted by error bars.

probability of [20] is about 5600 K which is comparable with the lowest excitation temperature measured by the Boltzmann plot method in the ICP. Note that the NIST compilation data are used throughout this paper. It has to be stressed that the choice of the transition probability data set is affecting the absolute but not the relative excitation temperatures which are more important for the investigation of local effects of analyte atomization on the plasma parameters in an inductively coupled plasma.

The excitation temperature evaluated with the transition probabilities of the NIST compilation from the intensities in Fig. 6a is displayed in Fig. 6c. As can be seen, the atomization, excitation and ionization processes of Si and accompanying elements of the dried sample mass lowered the temperature within ~17 μ s from the first measurable value of about 5300 K to ~4000 K. The first data point at 5300 K has a similar large error bar as derived for the temperature measurement at 17 µs in Fig. 7. The temperature of the ICP sub-volume where the sample starts to atomize and first Si atoms penetrate into the plasma cannot be measured with sufficient accuracy. Behind the minimum the excitation temperature increases to T>7000 K in about 0.2 ms. The excitation temperature in the ICP sub-volume with the expanding atomic and ionic element cloud during the transport through the ICP is increasing to ~8100 K at 0.8 ms and decreases again to slightly below 7000 K at 2 ms where the intensity of the Si 243.5 nm line becomes very weak. Most likely the increase before the maximum temperature and decrease from about 8100 to a temperature below 7000 K reflects the changes of the plasma temperature in the inner. analyte transporting channel of the ICP which is imaged onto the fiber bundle (see Fig. 2). The uncertainty of the absolute excitation temperature is indicated for some data points in Fig. 6c. It includes not only the statistical error of the intensity measurements but also the uncertainties of the monochromator calibration and the transition probabilities of the lines (Table 1). Except for the first 25 µs, where the line intensities are small and the scatter of the data large, the uncertainty of the relative excitation temperature is relatively small. As can be seen in Fig. 7, it is given by the magnitude of the statistical error bars which are smaller than the data points. Therefore, it is assumed that the relative temperature differences displayed are relevant.

The flow of the transport gas in the range $0.12-0.21 \text{ L min}^{-1}$ has primarily influence on the length of the emission signal (upper part of Fig. 8). Here, the Si line intensities were measured with 60 µm droplets produced also from the 100 µg mL⁻¹ solution. The different signal lengths might reflect that the start of the atomization is

dependent on the velocity of the transport gas. Increasing the gas velocity tends to move the location more into the plasma and, therefore, shortens the length of the signal. Note, that the peak intensities are independent of the gas flow within the experimental uncertainties. The evaluation of the excitation temperature from the 288 and 212 nm Si lines in dependence on time is shown in the lower part of Fig. 8. The minimum temperature was found to be about 3400 K which is 600 K lower than the minimum temperature measured with 50 μ m droplets of the same sample (see Fig. 6c). The difference should be due to the ~73% larger analyte mass compared with the 50 μ m droplet experiment whose atomization is cooling the local sub-volume of the ICP more effectively.

Differences in local plasma cooling by analyte atomization have also to be taken into account if end-on ICP-OES measurements of monodisperse droplets with more than one analyte are performed. For example, the atomization of the major element has a direct impact on the local plasma temperature and, therefore, also on the emission intensity of a trace element line during atomization. This can nicely be seen in Fig. 5 where the local cooling in particular by atomization of Si and the accompanying element in the solution can even be seen as a dip in the intensity of the Ca II resonance line. A variation of the Si concentration causes a different local plasma temperature and affects, therefore, also the population density of trace atoms in excited atomic and ionic states. As a consequence the line emission of a trace element is dependent on the concentration or mass of the major elements during the time of atomization. Note that the peak as well as the integrated intensity of a trace element line is dependent on the concentrations of the major elements in the sample. Nevertheless, the intensity ratios of trace and matrix elements are independent of time when atomization is accomplished. In the case of Ca in a Si matrix (see Fig. 5), the Ca II to Si I line ratio is independent of time for t>0.7 ms



Fig. 8. The intensity of the 288. 2 nm line in dependence on time for three different gas flows (a) and the corresponding excitation temperatures (b). The droplet diameter was 60 μ m and the Si concentration 100 μ g mL⁻¹. The intensities of 100 sequent droplets were averaged.

indicating the end of atomization and equilibrium conditions in the ICP sub-volume including the atomized sample cloud.

3.3. Consequences for ICP spectrometry with single monodisperse droplet injection

There are several implications for end-on ICP-OES measurements applying monodisperse single droplets injection:

- the integral intensities of analyte lines measured by end-on ICP-OES of aqueous solutions of a single element should not be exactly linearly dependent on the analyte concentration because the intensities measured during analyte atomization are affected by the reduced local plasma temperature which is a function of analyte mass.
- the integral intensities of analyte lines are not only non-linearly dependent on its own concentration but also on the concentration of accompanying elements and their respective evaporation enthalpies.

Experiment to prove these conclusions are currently under way in our laboratory.

The consequences for ICP-OES and also ICP-MS for single droplet analyses are the following:

- analyte line emission should preferably be measured side-on in the upper part of the ICP where the analyte masses are completely atomized, i.e., the intensity ratios of analyte lines are independent of the position of the analyte vapor cloud.
- the contribution of emission from the ICP volume where atomization and plasma cooling occurs to the total analyte signal should effectively be reduced by proper optical imaging if end-on observation is mandatory.
- The local cooling by analyte atomization in the lower part of the ICP should not be important for analyses of monodisperse droplets by ICP-MS since the element ions are sampled in the upper part of the ICP.

3.4. ICP-OES with sample introduction by nebulization

Desolvation, dissociation and excitation of the solvent as well as the atomization of the analytes should also affect the end-on emission measurements in ICP-OES with sample nebulization, in particular when element concentrations are in the $\mu g m L^{-1}$ range. However, the droplets generated by nebulizers are usually much smaller than those injected in the present experiment. The upper cut-off diameters are typically of the order of 30 µm unless spray chambers for production of even finer aerosols are used [4]. The atomization of 10 to 100 times smaller analyte masses than studied in Fig. 6 or 8 will be faster and is expected to cool the ICP locally less efficient. Nevertheless, it would be interesting studying the local cooling of the ICP by droplet with smaller analyte masses than in the present experiment in order to get a feeling for possible systematic errors in end-on ICP-OES with sample introduction by nebulization. Preferentially solutions of elements having ion lines in the spectral range >200 nm should be used in these experiments since ion lines are usually stronger than neutral lines in ICP-OES and allow measuring lower analyte masses than in the present Si experiment. Si is unsuitable for such investigations because the strongest ion lines are all in the VUV spectral range as mentioned above.

4. Conclusion

End-on ICP-OES measurements of injected monodisperse droplets from analyte solutions deliver insights into the desolvation and analyte atomization processes in the ICP. Contrary to side-on OES measurements the end-on arrangement allows studying the interaction of a single droplet with the plasma from the introduction, during the entire transport through the ICP, up to the moment its components are leaving the plasma. Taking into account the present first spectroscopic end-on studies with monodisperse droplets from Si solutions it can be concluded from the impact on the intensities of Ar lines that the desolvation process and the presence of the dissociation products of water molecules seem to have only little influence on the plasma conditions if the droplets are significantly smaller than 50 μ m. For such small droplets changes of Ar line intensities are smaller than the noise of the end-on measured signal. However, the impact on the local plasma temperature is very severe when the desolvated analyte is atomizing. The temporal temperature reduction has a direct influence on the integral emission intensity of spectral lines. Once the atomization is accomplished the intensity ratios of atomic and ionic spectral lines of analytes seem to be independent on time within the experimental uncertainty, at least for the analytes Si and Ca studied. Only different element specific diffusion velocities leading to spatial separations of the analytes in the ICP and energy transfer processes between free atoms and ions may alter this conclusion. Therefore, the diffusion of atoms and atomic ions which are of interest in ICP spectrometry as well as the influence of mutual inelastic collisions have to be studied in the future. The processes of finite diffusion and atomization need further experimental investigations and similar theoretical modeling as recently performed by Dalyander et al. for aerosol analysis in laser induced plasmas [30].

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