Title: Evaluation of particle size distributions produced during ultra-violet nanosecond laser ablation and their relative contributions to ion densities in the inductively coupled plasma

Authors: Lance M. Moses^a and Paul B. Farnsworth^{a*}

^a Department of Chemistry and Biochemistry, Brigham Young University, Provo, Ut 84602, United States

Abstract: Relative contributions to ion densities in the inductively coupled plasma (ICP) of particles of various sizes produced by laser ablation (LA) were investigated. Particles generated by 266 nm, ns LA of BaF₂, CaF₂, and a scandium aluminum alloy, characterized using SEM, consisted of hard and soft agglomerates, spherical particles, and irregularly-shaped particles. Although soft agglomerates and spherical particles were common to aerosols generated by LA in all cases, hard agglomerates appeared to be unique to the scandium aluminum alloy, while irregularly-shaped exfoliated particles were unique to the calcium and barium fluoride windows. The spatial distributions of Ca, Ba, and Sc ions in the ICP were determined from laser-induced fluorescence images taken with filters of pore sizes from 1-8 μ m added in-line to the transport tube upstream from the ICP. In all cases, a significant fraction of the ions formed in the ICP originated from micron-sized particles. Differences in the penetration depths of nanometer-sized agglomerates and micron-sized particles were about 2 mm for Ca and 1 mm for Ba. Differences in the penetration depths of nanometer and micron-sized agglomerates observed in the case of aluminum scandium were much less significant. This suggests that micron-sized hard-agglomerates and nanometer-sized soft-agglomerates experience very similar vaporization patterns. Additionally, there was evidence that flow patterns in the transport tube affect the trajectories of particles entering the plasma.

Keywords: LA-ICPMS, particle size, vaporization. ion density

1 Introduction

The use of laser ablation as a sample introduction tool for ICPMS is at a critical juncture. Efficient, stoichiometric ion production in the ICP and transmission through the MS interface is essential to achieving high levels of sensitivity, precision, and accuracy. In solution nebulization-ICPMS (SN-ICPMS), significant progress has been made in characterizing the vaporization, atomization, and ionization patterns of monodisperse droplets. The spatial distribution of ions, resulting from vaporization, atomization, ionization, and diffusion, relative to the sampling cone has a significant impact on detection. Consequently, instrument parameters that influence these key ICP processes, including injector gas flow rates, injector inner diameter, type of injector gas, etc, have also been studied [1]. However, there are significant differences between the aerosol generated during LA and aerosol formed through SN. The particle size distribution of aerosol generated during UV-ns-LA is much broader than that produced by traditional SN systems [2-4]. Intuitively, differences in relative penetration depths experienced by nanometer- and micrometer-sized particles would fundamentally limit sampling efficiencies. Attempts to reduce the number of incompletely vaporizing particles would inevitably increase loss due to off-axis diffusion [5]. Given that, for UV-ns-LA, micron-sized particles constitute a large fraction of the total aerosol volume, it is plausible that loss due to off-axis diffusion of ions formed from nanometer-sized particles is trivial [6, 7]. However, because penetration depths depend heavily on ICP conditions and particle composition, reports on threshold sizes for completely vaporizing particles have varied widely [5, 8-11]. The research described here focuses on characterizing the relative contributions of different-sized particles to overall ion densities in the ICP.

In a recent paper, high resolution images obtained using LIF were used to investigate the influence of laser fluence, carrier gas, and the presence of water on various ion distributions in the ICP in LA-ICPMS [12]. Significant contributions to the observed changes in images reported in that paper were suspected to be related to particle size effects. In this work, to examine the relative contributions of the various sizes of particle produced during ablation to the resulting distribution of ions formed in the ICP, polycarbonate filters of various pore sizes were placed in line to selectively remove particles above a given diameter. Contributions of those particle sizes to the overall ion distribution were assigned by comparing images obtained using LIF with different pore size filters in line. SEM was used to qualitatively characterize the sizes and shapes of particles filtered for each image. Although time consuming, SEM allows very accurate analysis over a large range of particle sizes without limitations characteristic of alternative techniques such as differential mobility analyzers (DMA) and optical particle counters (OPC) [13].

2 Experimental

2.1 Sample

CaF₂ windows (Exuberance Opto-electronics Technology Co.,Ltd, Beijing, China), BaF₂ windows (Laser Optex, Beijing, China), and 2% scandium in aluminum alloy disks (AMG Aluminum, Robards, KY) were used for the LA studies. The scandium-aluminum alloy disks were polished with 1000 grit sandpaper, leaving the surface highly reflective. This was done to reduce the number of particles generated, especially micron-sized spherical particles, to prevent clogging of the filters. No pre-ablation was performed on the CaF₂ or BaF₂ windows.

One of the challenges with using LIF to characterize analytes in the ICP is that the requirement for a workable fluorescence scheme that produces strong signals, minimizes scattered light at the detection wavelength, and uses readily accessible excitation lines, places significant restrictions on the choice of analytes. The elements used in these studies, Ca, Ba, and Sc, are all nearly ideal from the spectroscopic perspective, but they do not represent a wide range of analyte properties. All three have relatively low second ionization potentials, and doubly-charged ions are invisible to the fluorescence experiment. It was to address possible concerns about doubly-charged analytes that we chose to compare results from crystalline CaF_2 and BaF_2 . Calculated doubly-charged ion percentages for Ca and Ba at an ionization temperature of 7500 K are 1 percent and 9 percent, respectively [14]. Given the chemical and physical similarities between the Ca and Ba samples used in this study, one would expect any effects of doubly-charged ion formation to manifest themselves in differences between the results for the two elements. In contrast, differences between the Ca and Sc results in this study should reflect differences between the chemical composition and physical form of the samples, since the degrees of doubly-charged ion formation for the two elements differ by less than 1 percent.

The combination of laser ablation with long exposure times for the fluorescence measurements also dictated that the samples be homogeneous solids with high concentrations of the target elements. It was critical that the ablation from the samples be stable and highly reproducible. The alkaline earth fluorides were available as optical quality crystalline windows, which were ideal. Pure metallic scandium was prohibitively expensive, so the 2 percent scandium in aluminum alloy served as an acceptable substitute. Clearly, the three samples are not a comprehensive representation of all sample types, but they do represent two important sample classes: optically transparent dielectrics and metals.

2.2 Instrumentation

Important instrument settings are listed in Table 1. A detailed review of the instrumentation used for these experiments was presented in ref. [12]. A brief overview, including modifications, will be provided here. A modified Varian Redtop ICPMS (Varian, Australia) instrument was used. A XeCl excimer laser (LPX 110, Lambda-Physik, Acton, MA) was used to pump a Scanmate 2 Dye laser (Lambda-Physik, Acton, MA) tuned to a transition line of the ion being studied. The fluorescence schemes can be found in ref. [12]. The fluorescence was captured on a gated, iCCD (7361-0001, Princeton Instruments, Trenton, NJ). For Ca and Sc, LIF images were time averaged; hundreds of laser shots were integrated to achieve acceptable levels of signal to noise within a reasonable exposure time. For Ba, both time-averaged and single shot images were recorded. For the single shot images, 170 images taken of fluorescence from a single excitation laser pulse were recorded consecutively to produce a short video.

Pulses from a Nd:YAG laser (Brilliant B, Quantel, France) were used to ablate samples sealed in an ablation cell with a volume of roughly 50 cm³. All ablation experiments were performed in rastering mode with argon gas flow rates of 1.32, 1.4, and 1.3 L min⁻¹ for Sc, Ca, and Ba, respectively. Ablated aerosol was transported through a 2 meter, 7-mm I.D. PVC tube to the sheath torch connector of the ICP. At about 1 meter downstream from the ablation cell, a custom-built filter assembly, with a plastic mesh support ring, was added in line. No signal loss due to the presence of the mesh support ring was observed. Thin, track-etched, polycarbonate filter disks, 47 mm in diameter, of various pore sizes installed in the filter assembly were used to collect aerosol particles. Because filters with pore sizes below 1 µm were prone to clogging, they could not be used in these experiments. For CaF₂, glass wool was utilized upstream from the filter assembly in lieu of a 1 µm filter. With the glass wool in place, an image was taken with and

without a 0.4 μm filter in the filter assembly. Particles collected on the filter disks were characterized using SEM (Helios NanoLab 600i, Hillsboro, Or). A 10 nm coating of gold platinum was applied to the surface. SEM settings are displayed within each SEM image. Fig. 1 shows the general setup of the instrumentation.

2.3 *Image processing*

For all but the single shot images, background emission was subtracted from the corresponding fluorescence images using the Winview software, (Princeton Instruments, Trenton, NJ). Background-subtracted images were converted to ASCII format and processed with Matlab. The color scales were normalized to each image independently to allow better qualitative inspection of each ion distribution. Matlab was also used to plot the various cross sections and FWHMs. Axial cross sections were plotted along the center axis. Five rows above and below the radial center of the image were summed to improve the signal-to-noise in the axial profiles, corresponding to a physical dimension of .23 mm. FWHM values were calculated by counting the total number of pixels with intensity at least half of the peak maximum. This approach was chosen to avoid calculation difficulties associated with non-Gaussian peak shapes or significant noise. Matlab was also used to create avi files for the movies from the single shot experiments. Additionally, relative standard deviations (RSDs) for each pixel over the 170 images were calculated and used to generate a contour plot.

3 **Results and discussion**

3.1 *Barium*

3.1.1 *SEM images*

SEM images revealed that aerosol generated during ablation of BaF_2 consisted of irregularly-shaped particles, soft-agglomerates of primary particles, and spherical particles. Examples of

each particle type are presented in Fig. 2a. The sizes of soft-agglomerates, which likely form in the ablation cell [3],[15], were difficult to characterize. However, soft-agglomerations well into the micrometer range, such as the ones pictured in Figs. 2b and c, were common. The sizes of spherical particles were much more readily defined. As seen in Fig. 2c, the diameter spherical particle ranged from as low as 100 nm to greater than 1 μm . Particles larger than 1 μm were mostly irregularly-shaped particles, which often appeared to have been mechanically ejected, or exfoliated, from the surface, as seen in Fig. 2d. However, large, irregularly-shaped particles that have undergone some melt process, as those in Figs. 2e and f, were also fairly common. Mechanisms likely responsible for producing these large, irregularly-shaped particles have been described [16],[17],[18]. The somewhat poor selectivity of the filters can be seen in, for example, the 8 μm filter shown in Fig. 2g. Although particles below 8 μm were occasionally non-selectively filtered, it is apparent when comparing Fig. 2g with the 1 μm filter, shown in Fig. 2h, that the filters achieved a fairly high level of discrimination.

3.1.2 LIF images

3.1.2.1 Signal intensity

Fluorescence images obtained using various filters are presented in Fig. 3a. Cross-sectional plots of the axial distribution of Ba ions along the center axis for each image are presented in Fig. 3b. Comparing the images and cross sections taken with different filters in-line yields valuable insights into the relative contribution of various particle sizes to the ion distribution. A 39, 59, 80, 94, and 99% decrease in the peak signal intensity resulted when 8, 5, 3, 2, and 1 μm filters were added in-line, respectively. Although some particles below 1 μm were filtered by the 1 μm filter, micron-sized particles clearly contributed to the vast majority of ions generated in the ICP.

3.1.2.2 *Axial ion distribution*

In Fig. 3c, each axial cross section is normalized to its maximum value to more accurately compare changes in the shapes of the axial profiles. Information about the sizes of particles captured on each filter, gained from the SEM images presented in Fig. 2 can be used to understand the changes observed in each image.

A 39% decrease in the peak ion signal was observed with the 8- μm filter in-line. Although the selectivity of the filters was poor, practically all of the particles collected on the 8 μm filter were large micron-sized exfoliated particles, many around 5-10 μm in diameter. Removing these particles led to a decrease in the relative ion signal in the downstream tail of the axial cross section displayed in Fig. 3c. This suggests that at least the smaller particles filtered by the 8 μm filter were completely vaporized in the ICP. Although the 5- μm filter led to a 59% decrease in the overall ion signal, the axial ion distribution did not change significantly from the 8 μm filter. This is likely due to the large number of 5-8 μm particles non-selectively filtered by the 8 μm filter.

Again, a decrease in the relative ion signal in the downstream tail of the axial cross section accompanied the 80% ion signal decrease associated with the 3 μm filter in-line. This trend was similar for the 2- and 1- μm filters. These trends are consistent with the significant number of irregularly-shaped particles in the range of 1-5 μm . Additionally, there were a large number of spherical particles around 1-2 μm . As large micron-sized are particles are more effectively filtered, the relative contributions to the ion signal of particles 1-2 μm and below increases. This is seen in increasing relative ion intensities on the rise of the peaks in Fig. 3c with decreasing pore size.

3.1.2.3 *Radial distributions*

To investigate variability in the radial distribution of each image in Fig. 3a, FWHM values calculated for each image are plotted in Fig. 3d. The decreases in FWHM from upstream positions near the onset of vaporization to the axial position of peak signal intensity likely occurs as vaporization rates exceed rates of diffusion. The increases in FWHM values downstream from the minima towards the sampling cone indicate that diffusion rates overcame vaporization rates. The second decrease just upstream from the sampling cone occurs as ions are focused by gas flow being “pinched” by the sampling orifice.

Interestingly, smaller pore size filters led to significantly smaller FWHM values near the axial position of peak ion intensity. This difference appears to be caused by the larger particles following paths that deviate to some degree from flow streamlines. We noted that the shapes of ion distribution images for samples including the large particles depended on the alignment of the sheath gas adaptor with the torch injector. If the axes of these two tubes were not precisely aligned to coincide, the resulting fluorescence image was asymmetric. In other words, the large particles preserved some memory of the angle with which they entered the injector tube. To further investigate this phenomenon, LIF images corresponding to a single excitation pulse were taken consecutively to produce a movie. Although the time resolution of the images did not allow a single vaporizing particle to be tracked, the movies provide a general sense of how ion formation evolves in time. Additionally, RSDs for each pixel were calculated from the complete set of images. Contour plots of the RSDs for images taken with no filter and a 1 μm filter are presented in Fig. 4a and b, respectively. The largest RSDs with no filter were off-axis and at distances 2-3 mm downstream from the load coil. Also, the RSDs are greater on the lower half of the image. Conversely, RSDs from images taken with a 1 μm filter in-line mirrored ion densities

in the time-averaged image. These results suggest that large particles are more prone to vaporize off-axis than sub-micron particles.

3.1.3 Possible effects of changes in mass loading on the experimental results

The forgoing discussion is based on the assumption that the conditions in the plasma were unaffected by changes in the mass of ablated material entering the plasma as filters were changed in the transfer line. There is unambiguous evidence that the plasma temperature drops significantly close to a vaporizing particle [19], and also evidence that ionization temperatures decrease with increasing sample loads [20, 21]. Because mass loads were not directly measured in the experiments presented here, we can only infer how the mass loads changed and what effects those changes may have had on the fluorescence results.

The changes in peak fluorescence intensity should track changes in mass loading with two caveats. First, changes in mass loading may be under-represented if the largest particles removed by the filters are incompletely vaporized in the plasma. Second, changes in mass loading may be under-represented by changes in fluorescence intensities if the plasma temperature increases significantly as mass loading decreases. It is safe to say, then, that the changes in fluorescence intensity set lower limits for the changes in mass loading induced by the filters.

If the insertion of the filters is causing increases in plasma temperatures due to reductions in mass loading, then changes in the axial profiles in fig. 3 are difficult to distinguish from changes caused by the removal of the largest particles. In both cases, one would expect a shift in the axial fluorescence profiles toward the torch, as is observed. Additional experiments will be required to unambiguously separate the two possible contributions to changes in the distributions of ions in the ICP.

3.2 Calcium

3.2.1 SEM images

Similar to BaF_2 , aerosol generated during ablation of CaF_2 consisted of irregularly-shaped particles, soft-agglomerates of primary particles, and spherical particles (Fig. 5a-d). These are consistent with other SEM images of LA generated particles of fluorite reported by Kuhn et. al. [3]. However, compared to BaF_2 described in section 3.1.1., there were more irregularly-shaped particles in the range of 5-10 μm , such as those shown in Fig. 5a and b. Particles collected downstream from the glass wool are shown in Fig. 5e. Only small soft-agglomerations passed through the glass wool.

3.2.2 LIF images

Images obtained using various filters are presented in Fig. 6a. The ion densities along the center axis are plotted for each of these images in Fig 6b. Results were very similar to BaF_2 . A 29, 55, 75, and 92% decrease in the peak signal intensity resulted when placing the 8, 5, 3, and 2 μm pore size filter in-line, respectively. Likewise, a 97% decrease was observed when placing the glass wool upstream from the filter assembly.

Trends in the normalized axial cross section presented in Fig. 6c follow much the same patterns as BaF_2 . Unlike the 8- μm filter for BaF_2 , no significant change in the peak shape was observed for CaF_2 . This suggests that the massive irregularly-shaped particles in the 8-10 μm range were not completely vaporized within the axial length imaged. It is an interesting possibility that the decrease in the ion density downstream from the axial position of the signal maximum partly results from a decrease in the rate of ion production associated with decreasing mass of the particle, as suggested by Olesik et. al. [11].

Axial cross sections of the 2 μm filter and the glass wool in-line were very similar. This could suggest that very few particles larger than the soft-agglomerates in Fig. 6e and smaller than 2 μm were present to contribute to the ion signal. When a 0.4 μm pore filter was placed downstream from the glass wool, no ions were detected by fluorescence. Because no ion signals were detected with both the glass wool and 0.4 μm pore filter in-line, the signal in the image obtained with just the glass wool present can be assigned to the particles collected on the 0.4 μm filter. This indicates that particles below 0.4 μm do not significantly contribute to the images presented here.

FWHM values calculated for the images in Fig. 6a are plotted in Fig. 6d. Trends in the FWHM values were very similar to BaF_2 . Again, smaller pore sizes led to significantly smaller FWHM.

3.3 Scandium

3.3.1 SEM images

Ablation of scandium aluminum led to aerosol consisting of soft- and hard-agglomerates, both depicted in Fig. 7a. Hard-agglomerates were typically micron-sized, whereas soft-agglomerates were composed of small strands of nanometer-sized particles of varying thickness. Higher magnifications of the soft and hard agglomerates are shown in Fig 7b and c, respectively. No micron-sized spheres or irregularly-shaped particles were observed. This is consistent with previous reports of ns-LA of metals, particularly at low fluence [18]. Only soft-agglomerates were present on the 0.4 μm filter added downstream from the glass wool. As with CaF_2 , the signal in the image obtained using the glass wool can be completely ascribed to the particles collected on the 0.4 μm filter.

3.3.2 LIF images

3.3.2.1 *Signal intensity*

LIF images obtained using various filters are presented in Fig. 8a. The ion densities along the center axis are plotted for each image in Fig 8b. A 22% and 46% decrease in the peak signal intensities resulted when the 8- and 5- μm filters, respectively, were added in-line. Likewise, a 56% decrease occurred with the glass wool added upstream from the filter assembly. These decreases are much less than occurred with either Ba or Ca. This is not surprising considering that only micron-sized hard-agglomerates were generated during LA of scandium aluminum.

3.3.2.2 *Axial ion distribution*

Axial cross sections normalized to their own peak maximum are presented in Fig. 8c. There were practically no changes in the relative axial distributions of ions with different filters in-line. Only a slight upstream shift in the relative ion distribution was observed with the glass wool in place. Particles collected on the 0.4 μm filter indicate that only nanometer-sized soft-agglomerates passed through the glass wool. The fact that only a minor decrease in the tail-end of the ion distribution occurred with the glass wool in-line suggests that the micron-sized hard-agglomerates experience very similar vaporization patterns as the smaller nanometer-sized agglomerates. It seems likely that the micron-sized hard-agglomerates largely break up into smaller nanometer-sized agglomerates and only experience slightly greater penetration depths than the soft-agglomerates.

3.3.2.3 *Radial diffusion*

FWHM calculated for the images in Fig. 8a are plotted in Fig. 8d. Similar to Ca and Ba, FWHM values calculated for images with no filter and an 8 μm filter in-line were significantly larger than for both the 5 μm filter and glass wool in-line. A steady increase in the FWHM downstream from the FWHM minima, around 6-7 mm from the load coil, support the idea that both soft- and

hard-agglomerates break into smaller nanometer-sized particles that rapidly vaporize. If hard-agglomerates experienced greater penetration depths than nanometer-sized soft-agglomerations, we would expect their FWHM minima to occur farther downstream and the subsequent rise to be less pronounced than that of the soft-agglomerates.

3.4 Penetration depths

Differences in the axial position of peak ion signals for each image can be used to estimate differences in penetration depths of the particle sizes contributing to the image. A clear upstream shift in the axial position of peak ion densities occurred for both Ba and Ca with decreasing filter pore size. Based on the differences in the axial position of peak ion signals, relative differences in the penetration depths of particles around 8 μm and particles below 1 μm were about 2 mm for Ca and 1 mm for Ba. Alternatively, only minor differences in the penetration depths of micron-sized hard-agglomerates and nanometer-sized soft-agglomerates occurred with Sc. Given that significant decreases in the ion intensity occurred with no accompanying change in the axial ion distribution, we consider it unlikely that observed shifts were caused by reduced cooling due to the removal of large particles.

4 Conclusion

The relative contributions to ion densities in the ICP of differently-sized particles were examined. Particle sizes were characterized off-line with SEM. Aerosols generated during LA of BaF_2 and CaF_2 consisted of soft-agglomerates, spherical particles, and irregularly-shaped particles, whereas only soft- and hard-agglomerates were generated from ablation of scandium aluminum. In all cases, micron-sized particles produced most of the ions formed in the ICP. For Ba and Ca, differences in axial positions of peak ion signal of 2- and 1- mm, respectively, were

observed between nanometer- and micron-sized particles. Differences in the penetration depths of nanometer-sized soft-agglomerates and micron-sized hard-agglomerates observed in the case of scandium aluminum were much less significant. We conclude that the soft- and hard-agglomerates generated during ablation of scandium aluminum experience very similar vaporization patterns in the ICP. There was evidence that flow patterns in the transport tube influence the trajectories of aerosol particles entering the ICP. The results described here address significant gaps in the current literature regarding vaporization patterns of LA aerosol of broad particle size distributions, such as is common with 266 nm-ns-LA.

Acknowledgements

The authors acknowledge the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Science, Office of Science, U.S. Department of Energy, grant no. DE-FG02-03ER15410 for support of this research. Also, a special thanks to Brett Cash from Bruker for technical support on the Varian ICPMS, AMG Aluminum for generously providing the aluminum-scandium alloy, and Dr. Jaron Hansen of BYU and GE for the filter disks.

References

- [1] K. Niemax, Considerations about the detection efficiency in inductively coupled plasma mass spectrometry, *Spectrochim. Acta, Part B*, 76 (2012) 65-69.
- [2] J.J. Gonzalez, C. Liu, S.-B. Wen, X. Mao, R.E. Russo, Metal particles produced by laser ablation for ICP-MS measurements, *Talanta*, 73 (2007) 567-576.
- [3] H.-R. Kuhn, D. Gunther, The agglomeration state of nanosecond laser-generated aerosol particles entering the ICP, *Anal Bioanal Chem*, 383 (2005) 434-441.
- [4] J.J. Gonzalez, C. Liu, S.B. Wen, X. Mao, R.E. Russo, Glass particles produced by laser ablation for ICP-MS measurements, *Talanta*, 73 (2007) 577-582.
- [5] L. Flamigni, J. Koch, D. Günther, Experimental and theoretical investigations about the vaporization of laser-produced aerosols and individual particles inside inductively-coupled plasmas — Implications for the extraction efficiency of ions prior to mass spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 76 (2012) 70-76.
- [6] M. Guillon, H.-R. Kuhn, D. Gunther, Application of a particle separation device to reduce inductively coupled plasma-enhanced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry, *Spectrochim. Acta, Part B*, 58B (2003) 211-220.
- [7] M. Guillon, D. Gunther, Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry, *Journal of Analytical Atomic Spectrometry*, 17 (2002) 831-837.
- [8] H.-R. Kuhn, D. Günther, Elemental Fractionation Studies in Laser Ablation Inductively Coupled Plasma Mass Spectrometry on Laser-Induced Brass Aerosols, *Analytical Chemistry*, 75 (2003) 747-753.

- [9] J.W. Olesik, N. Casey, Investigation of vaporization of laser ablation generated aerosol and monodisperse particles in a dry Ar ICP using time-resolved mass spectrometry, *Spec. Publ. - R. Soc. Chem.*, 301 (2005) 164-174.
- [10] K.-S. Ho, K.-O. Lui, K.-H. Lee, W.-T. Chan, Considerations of particle vaporization and analyte diffusion in single-particle inductively coupled plasma-mass spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 89 (2013) 30-39.
- [11] J.W. Olesik, P.J. Gray, Considerations for measurement of individual nanoparticles or microparticles by ICP-MS: determination of the number of particles and the analyte mass in each particle, *J. Anal. At. Spectrom.*, 27 (2012) 1143-1155.
- [12] L.M. Moses, W.C. Ellis, D.D. Jones, P.B. Farnsworth, Fluorescence imaging of ion distributions in an inductively coupled plasma with laser ablation sample introduction, *Spectrochim Acta B*, 105 (2015) 47-59.
- [13] H.-R. Kuhn, J. Koch, R. Hergenroeder, K. Niemax, M. Kalberer, D. Guenther, Evaluation of different techniques for particle size distribution measurements on laser-generated aerosols, *J. Anal. At. Spectrom.*, 20 (2005) 894-900.
- [14] R.S. Houk, Mass-Spectrometry of Inductively Coupled Plasmas, *Anal Chem*, 58 (1986) A97-A105.
- [15] P. Dewalle, J. Vendel, J.-M. Weulersse, P. Herve, G. Decobert, Influence of Carrier Gas Flow Rate, Laser Repetition Rate, and Fluence on the Size Distribution and Number of Nanoparticles Generated Per Laser Shot During Paint Laser Ablation, *Aerosol Science and Technology*, 45 (2011) 1429-1440.

- [16] V. Craciun, D. Craciun, M.C. Bunescu, R. Dabu, I.W. Boyd, Scanning electron microscopy investigation of laser ablated oxide targets, *Journal of Physics D: Applied Physics*, 32 (1999) 1306.
- [17] R. Hergenroder, Laser-generated aerosols in laser ablation for inductively coupled plasma spectrometry, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 61 (2006) 284-300.
- [18] R.E. Russo, X. Mao, J.J. Gonzalez, V. Zorba, J. Yoo, Laser Ablation in Analytical Chemistry, *Analytical Chemistry*, 85 (2013) 6162-6177.
- [19] S.E. Hobbs, J.W. Olesik, Inductively coupled plasma mass spectrometry signal fluctuations due to individual aerosol droplets and vaporizing particles, *Anal Chem*, 64 (1992) 274-283.
- [20] J. Koch, M. Walle, J. Pisonero, D. Gunther, Performance characteristics of ultra-violet femtosecond laser ablation inductively coupled plasma mass spectrometry at [similar]265 and [similar]200 nm, *J Anal Atom Spectrom*, 21 (2006) 932-940.
- [21] M. Gäckle, D. Merten, Study of plasma parameters influencing fractionation in laser ablation-inductively coupled plasma-mass spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 65 (2010) 991-1001.

Figure captions

Figure 1 General overview of the instrumental setup.

Figure 2 SEM images of aerosol particles generated during ablation of BaF_2 , collected on polycarbonate filter disks with 1-, 5-, 2-, 2-, 5-, 3-, 8-, and 1- μm pore sizes presented in a-h, respectively.

Figure 3 LIF images of Ba ion distributions formed in the ICP from aerosol particles generated during LA with filters of various pore sizes, as labelled in (a). Raw (b) and (c) normalized cross-sectional plots of the axial distributions of Ba ions along the center axis for each image. (d) FWHM calculated from radial cross-sections of Ba ion intensities. Legends are as follows: (—x—) no filter, (—+—) 8- μm filter, (—◇—) 5- μm filter, (— —) 3- μm filter, (—□—) 2- μm filter, and (—) 1- μm filter.

Figure 4 Contour plots of RSDs for each pixel calculated over 170 images with (a) no filter and (b) with a 1 μm filter in-line. The color scales for the images are not the same.

Figure 5 (a-d) SEM images of aerosol particles generated during ablation of CaF_2 , collected on 2 μm polycarbonate filter disks. The scaling shown in (b) is the same for (a-d). (e) Particles collected on a 0.4 μm with glass wool added upstream to the transport tubing.

Figure 6 LIF images of Ca ion distributions formed in the ICP from aerosol particles generated during LA with filters of various pore sizes in-line, as labelled in (a). Raw (b) and normalized (c) cross-sectional plots of the axial distribution of Ca ions along the center axis for each image. (d) FWHM calculated from radial cross-sections of Ca ion intensities of each image. Legends are as

follows: (—x—) no filter, 8 μm (—+—) filter, (—◇—) 5 μm filter, (—□—) 3 μm filter, (— —) 2 μm filter, and (—) glass wool.

Figure 7 SEM images of aerosol particles generated during ablation of scandium aluminum, collected on various pore size polycarbonate filter disks. Scales are listed on each image.

Figure 8 (a) LIF images of Sc ion distribution formed in the ICP from aerosol particles generated during LA with filters of various pore sizes, as labelled. (b) Raw and (c) normalized cross-sectional plots of the axial distribution of Sc ions along the center axis for each image. (d) FWHM calculated from radial cross sections of Sc ion intensities from each image. Legends are as follows: (—x—) no filter, (—+—) 8 μm filter, (—◇—) 5 μm filter, and (—) glass wool.

Table 1. Experimental conditions	
<i>Ablation Laser</i>	<i>Brilliant B</i>
Nd:YAG	266 nm
Pulse length	5 ns
Fluence (Ca/Ba)	18 J cm ⁻²
Fluence (Sc)	50 J cm ⁻²
Spot size	90-120 µm
Rep rate	10 Hz
Raster speed	0.1 mm s ⁻¹
Beam profile	Gaussian
<i>ICPMS</i>	<i>Varian Redtop</i>
Sampling depth	12 mm
Carrier gas	See Text
RF Power	1300 W
Plasma gas	16 L min ⁻¹
Auxiliary gas	2.0 L min ⁻¹
Sheath gas	0.2 L min ⁻¹

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)