Development and Evaluation of an On-Chip Droplet-on-Demand Aerosol Generator for Sample Introduction into ICP-MS

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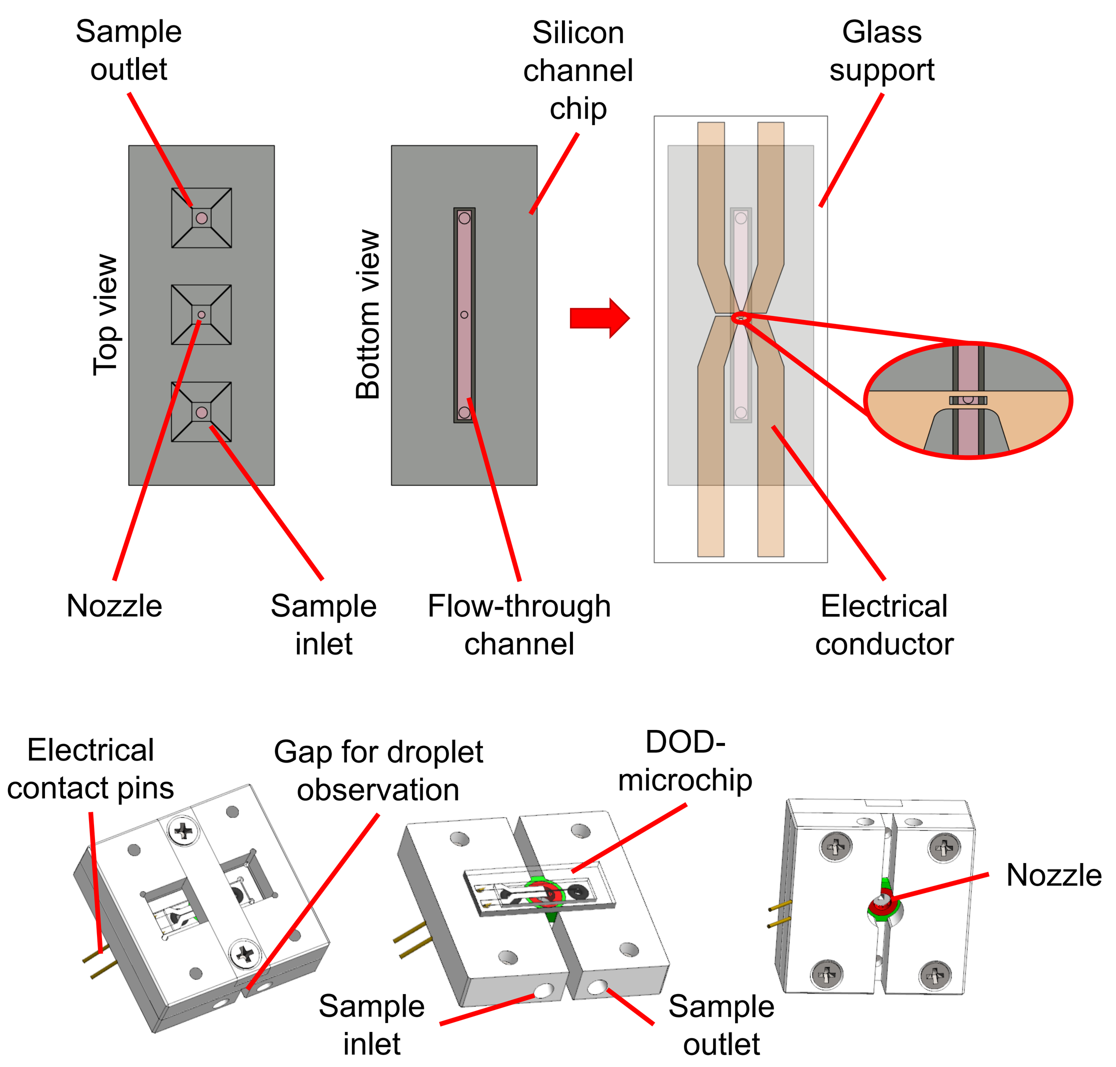
Abstract: The predominant method of introducing liquid samples into inductively coupled plasmas (ICP) involves the utilization of pneumatic nebulizers. As the primary aerosol does not meet the ideal properties for use with ICPs, the employment of spray chambers is necessary to adjust the characteristics of the aerosol. However, this approach results in substantial loss of sample aerosol, leading to reduced sensitivity and decreased detection capability, as spray chambers are acting as aerodynamic filters [1]. In 2011, a sample introduction system designed to address the aforementioned disadvantage was introduced by the research group directed by Bings in Mainz. This so-called drop-on-demand aerosol generator (DOD), based on modified printer cartridges employing the thermal inkjet principle, allows the ejection of discrete droplets through a dosing nozzle into a sample transfer line to the ICP [2]. In addition to its capability for direct aerosol generation, the DOD offers the possibility of frequency-based calibration [3].The present study focuses on the development and testing of a microchip-based system for aerosol generation. This system is also based on the thermal inkjet principle. However, in contrast to the DOD, it is designed as a flow-through system, and therefore, in principle, allows for hyphenation with separation systems. Recent results and remaining challenges will be presented and critically discussed.

On-chip droplet-on-demand aerosol generator



- On-chip design for miniaturized sample introduction system
- Utilization of a flow-through design for hyphenation with separation techniques
- Silicon chip bonded on glass support
- Arduino-based microcontroller allowing adjustment of the heating pulse duration and the droplet-generation frequency
- Laboratory power supply allowing variation of the heating pulse amplitude

Figure 1. Setup of the on-chip droplet-on-demand aerosol generator and a mount enabling the acquisition of droplet images.

Optical aerosol characterization

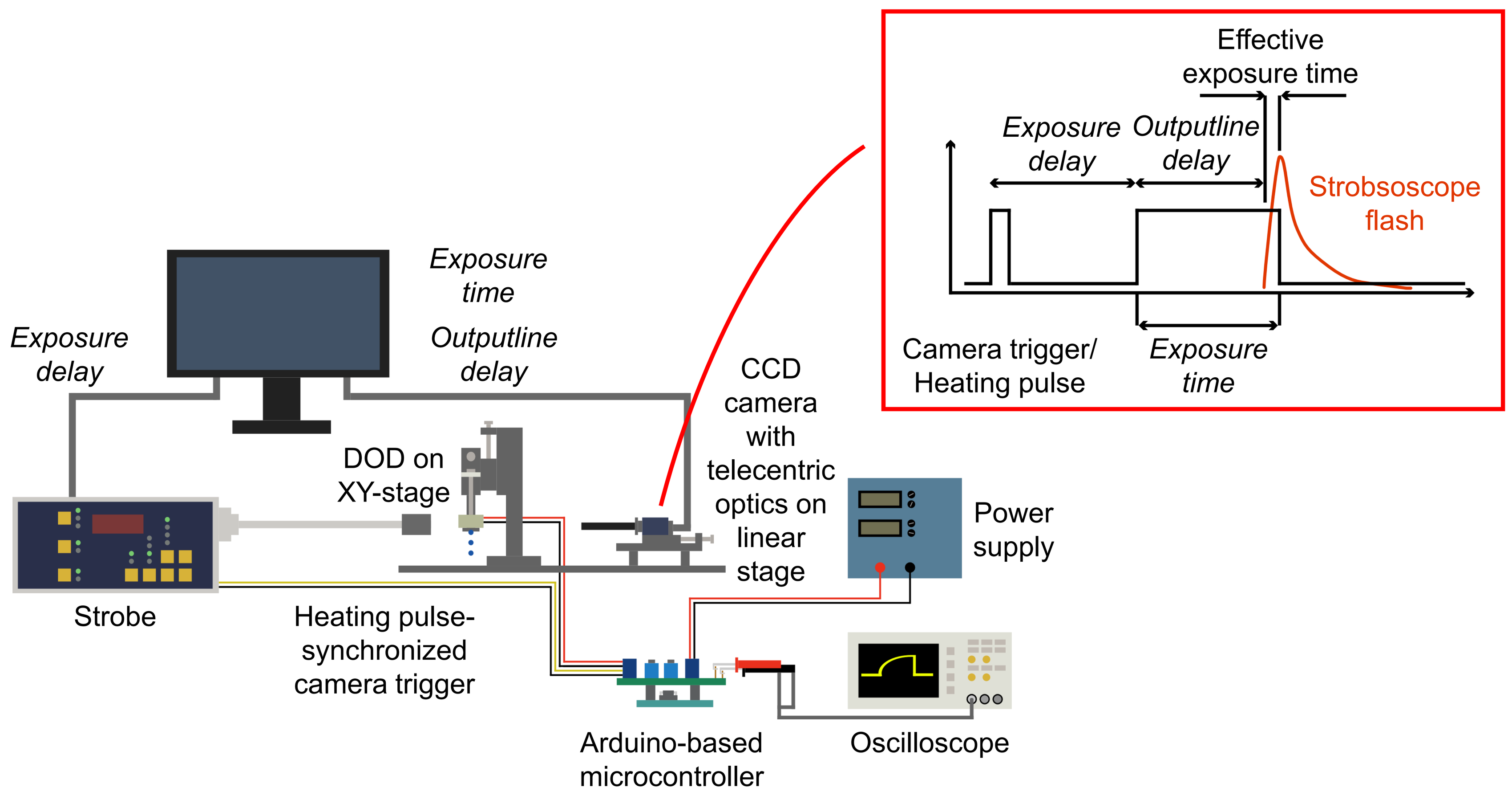


Figure 2. Experimental setup for optical aerosol characterization and strategy to achieve ultra-short effective exposure times.

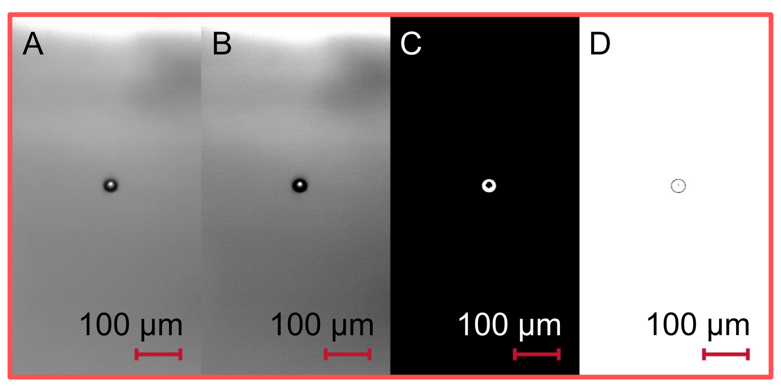


Figure 3. Procedure for droplet diameter determination.

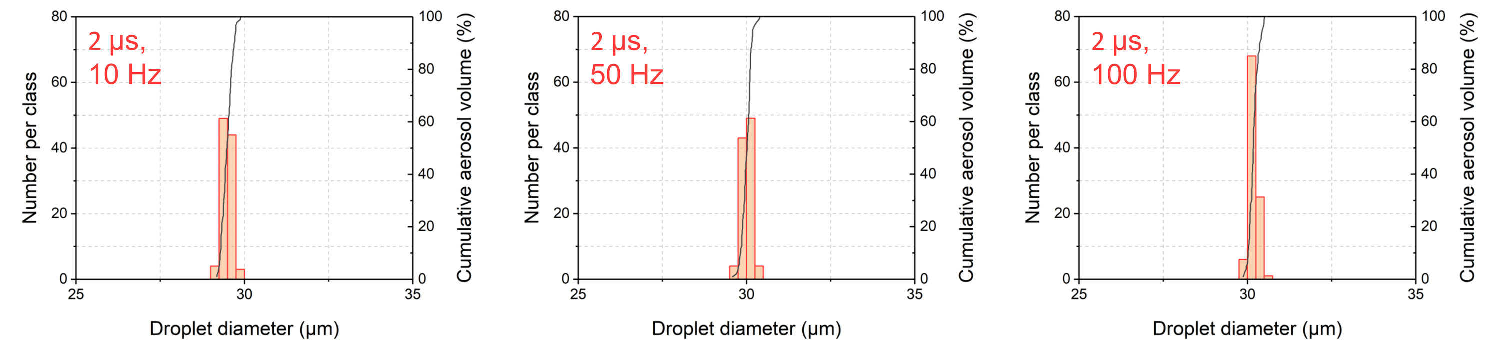
- Delay between start of exposure and stroboscope flash (*outputline delay*) to achieve ultra-short effective exposure times (< 10 µs)
- Telecentric optics to avoid perspectivic errors
- Exposure delay variation enables pseudo-cinematographic imaging → Determination of droplet velocity
- Automated image processing with respect to droplet diameter

References

[1] N. H. Bings, J. O. Orlandini von Niessen, J. N. Schaper, *Spectrochim. Acta, Part B*, **2014**, *100*, 14–37.
[2] J. O. Orlandini v. Niessen, J. N. Schaper, J. H. Petersen, N. H. Bings, *J. Anal. At. Spectrom.*, **2011**, *26*, 1781-1789.
[3] J. O. Orlandini v. Niessen, J. H. Petersen, J. N. Schaper, N. H. Bings, *J. Anal. At. Spectrom.*, **2012**, *27*, 1234-1244.

First results

- All experiments carried out with a 35 µm diameter dosing nozzle and an applied energy per droplet generation event of approximately 42 µJ



	10 Hz	50 Hz	100 Hz
Mean droplet diameter / µm	29.5 ± 0.2	30.0 ± 0.2	30.2 ± 0.2
Mean droplet volume / pL	13.4 ± 0.3	14.2 ± 0.2	14.4 ± 0.2

Figure 4. Comparison of droplet size distributions and respective cumulated aerosol volume at three different dosing frequencies.

- Reproducable generation of droplets with volume < 15 pL at dosing frequencies between 10 Hz and 100 Hz corresponding to sample flow rates between 8 nL min^{-1} and 90 nL min^{-1}

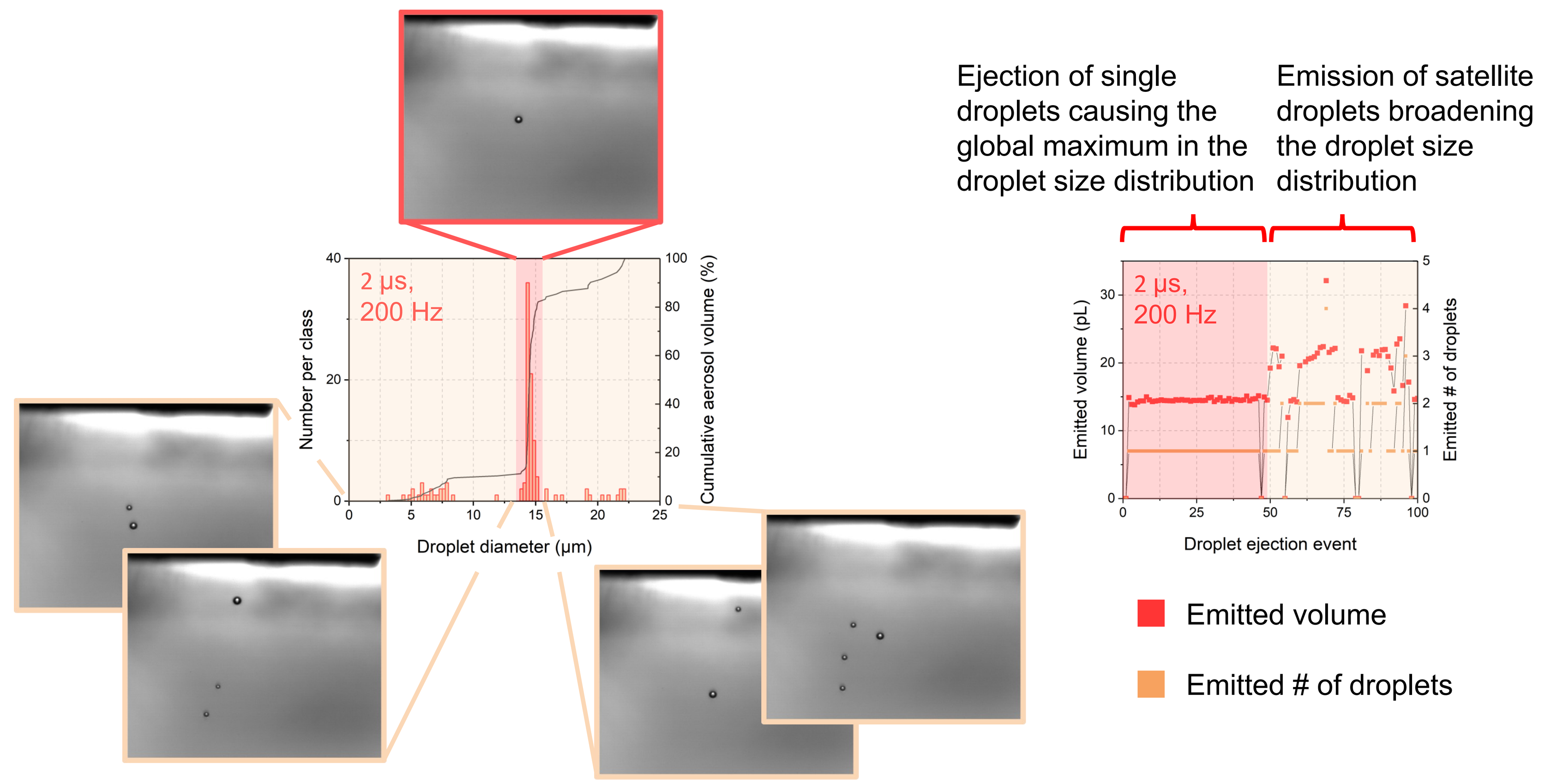


Figure 5. Droplet size distribution opposed to the volume flow and emitted number of droplets per droplet ejection event.

- Experimental data indicating drift/instabilities
- Durability of the heating resistors still limited due to thermal stress

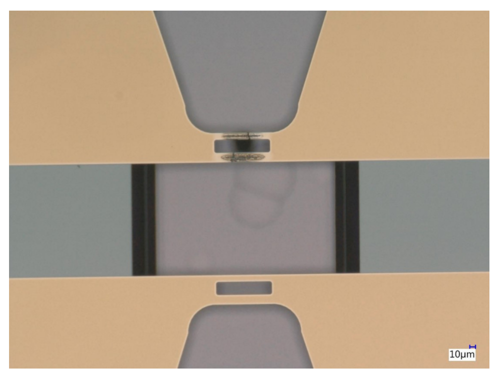


Figure 6. Thermally damaged heating resistor.

Summary

- Reliable ejection of single droplets
  → Applicable of the DOD for calibration of LA-ICP-MS by means of standard addition
- Reproducible generation of discrete droplets with mean volume below 15 pL
- Dosing frequencies (10 – 100 Hz) allow sample flow rates of 8 – 90 nL min^{-1}
- At droplet generation frequencies > 100 Hz:
  Emission of satellite droplets → Broadening of droplet size distribution

Outlook

- Heating resistors durability could potentially be increased by utilization of an alternative heating resistor material with higher melting point/higher resistance to thermal stress
- If the observed broadening of the droplet size distribution is indeed overheating-related, cooling of the microchip may be necessary (Peltier element)
- Systematic investigation of the following variables influence on the aerosol characteristics:
  - Nozzle diameter
  - Width of the flow-through channel
  - Additives (e.g. glycerine) to influence the fluids viscosity and surface tension
  - Alternative heater geometry