Further Development of an *on-chip* Drop-on-Demand Aerosolgenerator for Plasma Spectrometry

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For analysis of liquid samples in plasma spectrometry, due to low nebulizer / spray chamber efficiency and thus limited achievable sensitivity, the limited variation range of liquid / gas flow rates without influencing nebulization efficiency and aerosol quality and the difficulties of hyphenating low-flow seperation techniques like HPLC and CE, sample introduction via pneumatic nebulization is still considered the Achilles‘ heel for ICP-MS. A promising and independent alternative approach is the second generation of the drop-on-demand aerosol generator, which is based on the concept of thermal inkjet printing. The analytical suitability of the first generation DOD has already been demonstrated by Bings et al.[1-3] to be comparable or superior to conventional nebulizers, even with high matrix loaded samples like synthetic urine. Although the current system reproducibly produces droplets in the pL-range (15 pL) with a high repetition rate (500 Hz), signals are still not detectable when hyphenating the DOD through various in-house-made aerosol transport chambers with a latest generation 7800 ICP-MS and using a wide variety of aqueous elemental standard solutions.

1. System components

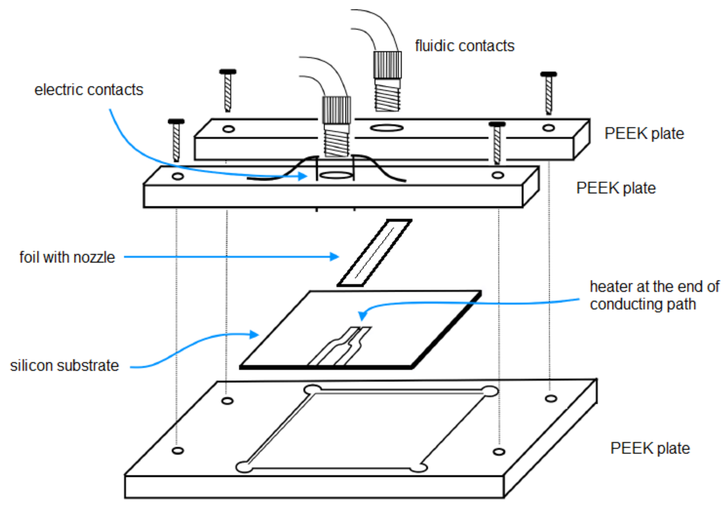

Fig. 1: Schematics of the chip-integrated DOD-device and its mount including electrical and fluidic contacts.

- PEEK-mounting connects fluidic and electric contacts to the chip
- Easy assembly/disassembly
- Transport chamber is easily connected to chip and nozzle
- Flow rate 0.2 – 3 µL/min, depending on dosing frequency
- Continuous & adjustable flow through channel in the foil
  - ➢ hyphenation with separation techniques possible

2. Chip design

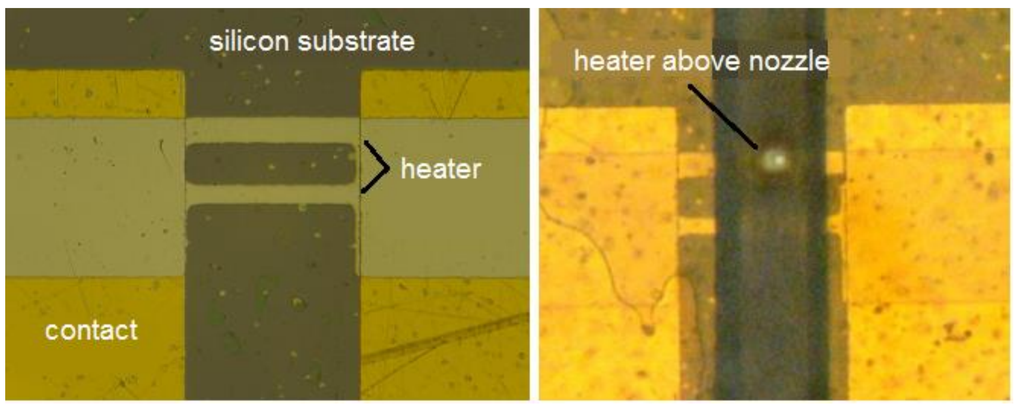

Fig. 2: Heater structure and contacts (right and left).

- Investigation of suitable materials and heater structures
  - ➢ Inert materials withstand thermal stress
  - ➢ Parallel heater: simplest design, best results compared to other heaters
- Positioning of the foil is essential for effective droplet generation
  - ➢ „stop bubble“ facilitates this process

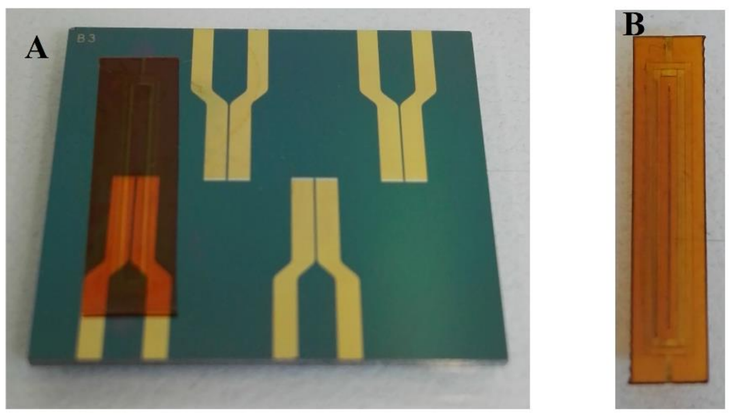

Fig. 3: (A) chip with 4 conductor/heater structures; (B) foil with channel and nozzle.

3. Aerosol Characteristics

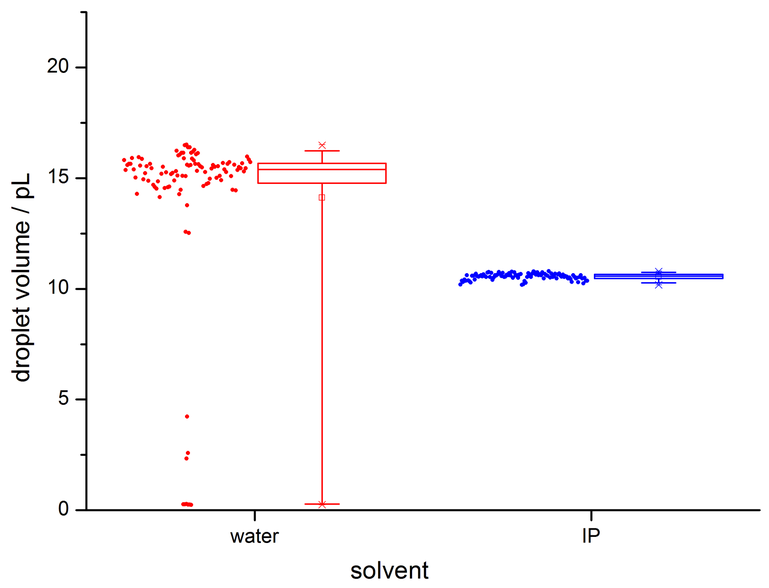

Fig. 4: comparison of the aerosol characteristics for water and isopropyl alcohol as solvent.

- Generation of almost monodisperse aerosol
- Low degree of satellite droplet formation
- Aerosol characteristics can be influenced by variation of electric parameters
- Stable & reproducible droplet generation over a large energy and frequency range
  - ➢ System suitable for dosing-frequency based calibration

Tab. 1: Characteristics of wated-based aerosol.

Volume	Velocity	Diameter	Flow rate nozzle	Frequency
15 pL	3-6 m s^{-1}	31 µm	450 nL/min	500 Hz

4. Simulation of Droplet Path for ICP-MS Hyphenation

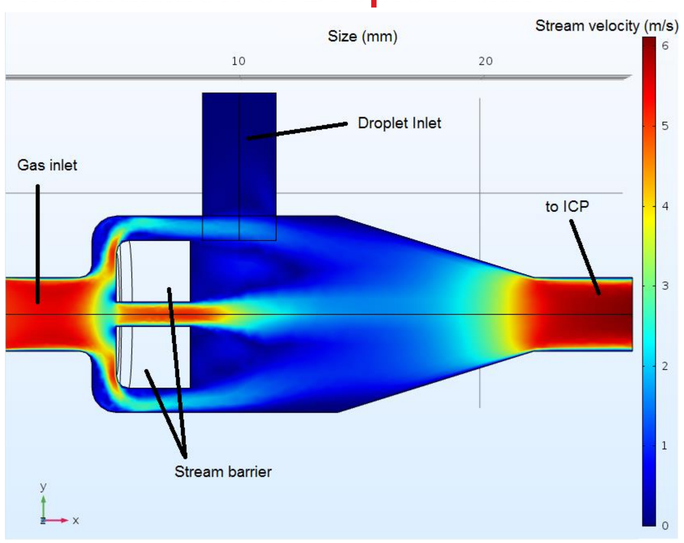

Fig. 5: Optimized aerosol chamber design based on the simulation of the flow profile for x-y µm-sized droplets.

⇨ Optimized chamber design should lead to improved aerosol transport efficiency to the ICP

- Rigid sphere model applicable to generated droplets
  - ➢ No deformation of droplets via gas stream
- Iterative simulation in order to optimize transport chamber desgin
- Analytical approach to estimate droplet evaporation and thus the influence on their flight path

Summary and Outlook

- Thermal actuation of droplets leads to nearly monodisperse aerosols with reproducible characteristics, stable aerosol generation covering a wide frequency and energy range
- Next generation chip-design in progress: Gas corona surrounding the nozzle, providing an additional gas stream to guide the droplets into the aersosol transport chamber
- Application of optimized (simulation) aerosol transport chamber to improve transport efficiency of the droplets into the ICP

[1] Niessen, Jan O. Orlandini v.; Schaper, J. N.; Petersen, J. H.; Bings, N. H. *J. Anal. At. Spectrom* 26 (2011) 1781.
[2] Niessen, Jan O. Orlandini v.; Petersen, J. H.; Schaper, J. N; Bings, N. H. *J. Anal. At. Spectrom.* 27 (2012) 1234.
[3] Niessen, Jan O. Orlandini v.; Krone, K. M.; Bings, N. H. *Spectrochim. Acta B* 92 (2014) 51-59.

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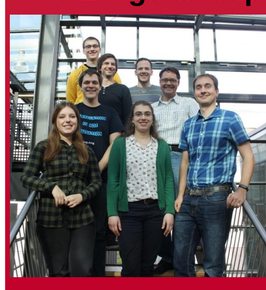

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