Towards hyphenation of a novel low-flow *drop-on-demand* aerosol generator with ion chromatography for plasma spectrochemical and speciation analysis

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Low-flow liquid sample introduction in plasma spectrometry

One recent trend in current analytical chemistry is downscaling of analytical methods and miniaturization of analytical instrumentation. There are many tasks to address in this context, but one of the most important issue is sample introduction into miniaturized instruments. Especially when modern low flow separation techniques are hyphenated to any kind of mass spectrometer an efficient aerosol generation is indispensable. Commonly, an additional sheath flow of solvent is added to the eluent flow to meet the specifications of conventional modern nebulization systems. Liquid flows in the range of a few microliters or even nanoliters, as they typically occur in capillary chromatography (capLC) or capillary electrophoresis (CE), remain a challenging task for nebulization. Therefore, when capLC or CE are coupled to a mass spectrometer, sheathless nebulization is still difficult to establish.

New approach for aerosol generation

Modified inkjet cartridges have been used as dosing devices and are capable of accurate and precise handling of pL volumes of liquids.[1] Thermal inkjet printers have already been successfully used for analytical purposes. In both fields, total reflexion x-ray fluorescence analysis (TXRF) and laser ablation ICP-MS (LA-ICP-MS), they have been used for the transfer of pL-droplets of liquid samples onto solid surfaces, leading to the proposal of new calibration strategies and their application for the analysis of micro amounts of sample material such as individual particles.[2] The conventional operating mode of commercially available inkjet printers is a discontinuous process, regularly interrupted by line-feed and cartridge cleaning intervals. Furthermore, the important parameters of the droplet generation process are locked inside the printer controller software or were predetermined by fixed hardware settings. Therefore, unmodified inkjet printers were found to be not immediately applicable as aerosol generators in analytical atomic spectrometry. The novel system employs a lab-built micro-controller, which allows to access all parameters important for driving the drop-on-demand (DOD) dosing cartridge for the generation of droplets from minimum sample volumes. The droplet generation frequency, thus the resulting liquid flow rate, is variable over a wide range from the generation of isolated droplets up to a theoretical flow rate of approximately 2 mL per minute.

DOD Interface

For coupling the novel aerosol generation system to separation devices or autosamplers a reliable interface is desired. Thus, the dosing cartridge has to be equipped with a sample inlet line to deliver the liquid to the dosing nozzles. Former versions of the interface also featured a sample outlet line, as liquid flow rates where 1 mL/min and hence much larger than the actual dosing volume of the new aerosol generator.[3] The current interface design is shown as a schematic in Fig. 1. The volume of the liquid reservoir of the inkjet cartridge is decreased by mounting a stopper plate just above the silicon wafer, which holds the dosing nozzles. A sample inlet line delivers liquid to the so formed channel and immediately to the silicon wafer. The investigated aerosol generation rate is in the range of the applied dosing flow rate of 1-5 µL/min, thus an sample outlet line is no longer needed. However, the end of the flow channel is kept open to avoid pressure build-up. Also, the dead-volume of the interface was kept as small as possible, to avoid degradation of the chromatographic resolution in further applications.

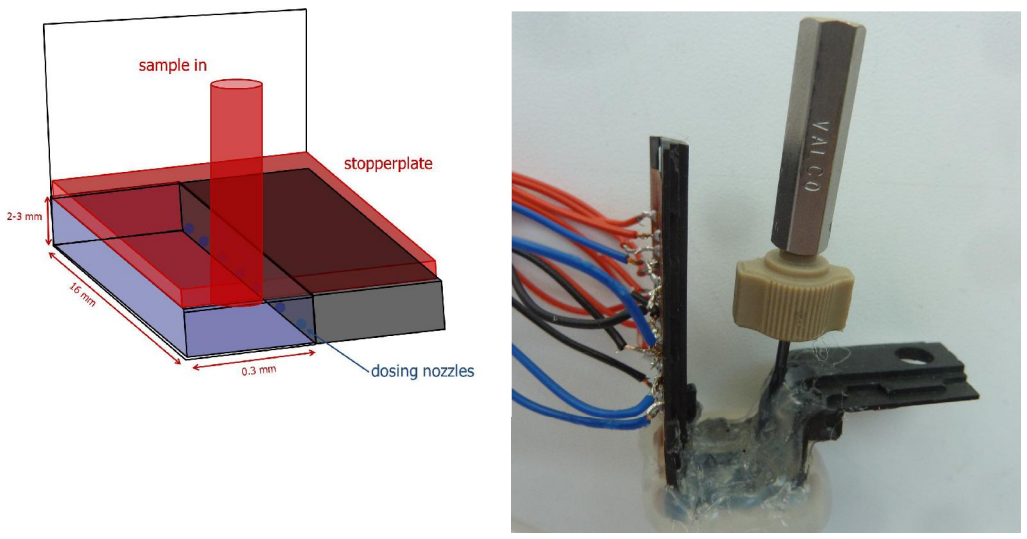

Figure 1: Schematics of the modifications of a HP45 inkjet cartridge.

Results

Before the lab-build interface can be coupled to an capillary HPLC, flow-injection experiments were carried out to determine the quality of the interface and to evaluate formed dead-volumes. The interface was coupled to a PerkinElmer Series 200 Autosampler, modified with a Rheodyne 8125 micro 6-port injection valve and an Agilent G1379 capillary pump. The sample lines have an inner diameter of 75 µm to minimize the internal volume. The DOD and its interface were compared to a state-of-the-art nebulizing system, the EnyaMist, equipped with a lab-build total consumption spray chamber with a secondary gas inlet. Fig. 2 and Fig. 3 display the results for the EnyaMist nebulizer and the DOD aerosol generator, respectively. Both transient signals are comparable regarding the signal width and peak area.

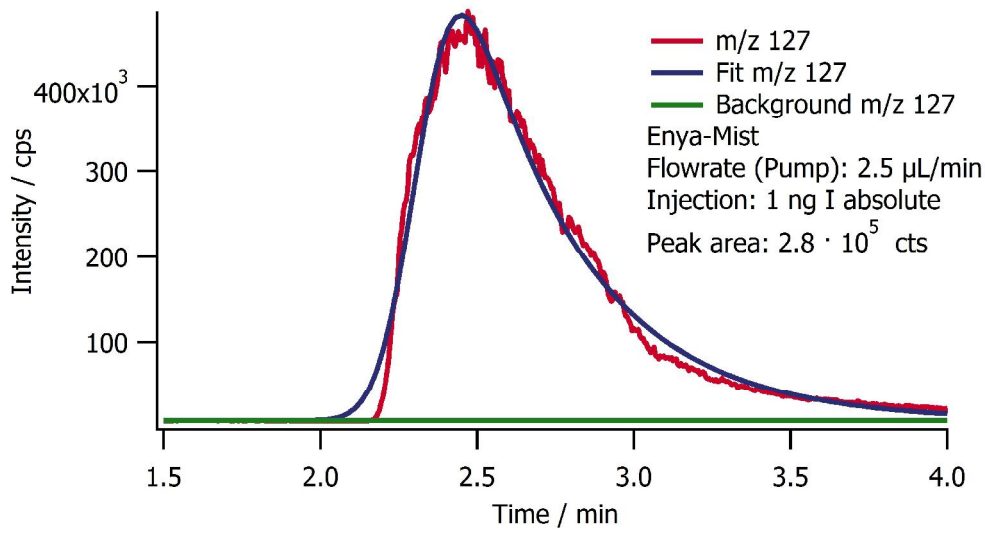

Figure 2: ICP-MS flow injection analysis using the EnyaMist nebulizer.

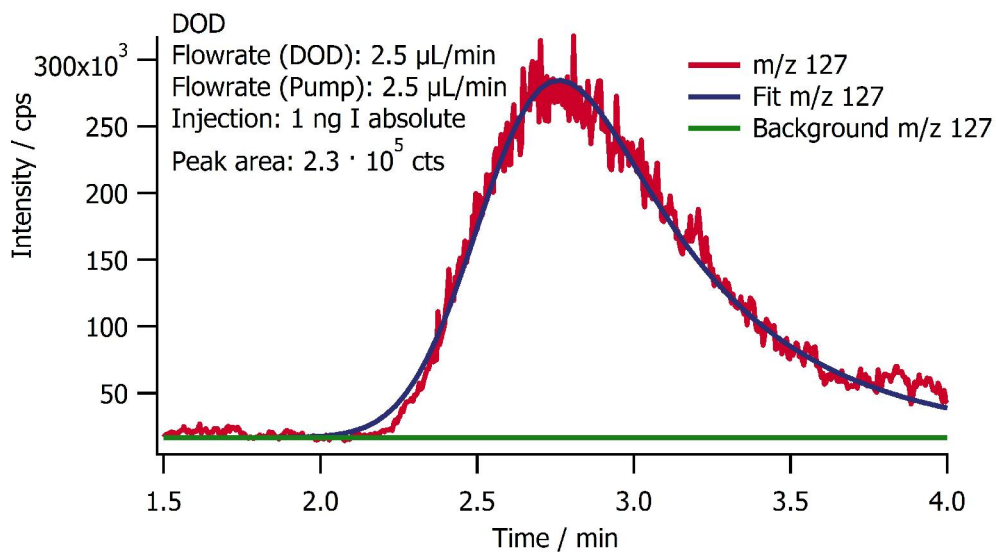

Figure 3: ICP-MS flow injection analysis using the DOD aerosol generator.

Discussion and Outlook

Earlier studies outlined, that the DOD aerosol generator in combination with a suitable interface can be used for FIA-ICP-MS couplings and is capable of handling liquid flow rates in the mL-range.[4] In this presentation, it could be shown that the DOD combined with a new and miniaturized interface is also suitable for liquid flow rates in the range of a few micro liters per minute. In principle, this interface allows the easy coupling of conventional miniaturized separation techniques to the new aerosol generation system. Further work will include the integration of the new developed aerosol generator into analytical workflows. Thus the use of autosamplers in combination with modern low-flow separation techniques has to be addressed. Also the robustness of the developed DOD system against organic solvents will be investigated in the future to determine the systems' limitations in modern HPLC-ICP-MS applications.

References

[1] Orlandini v. Niessen, J., Schaper, J.N., Petersen, J.H., Bings, N.H. Development and characterization of a drop-on-demand aerosol generator for micro-volume sample introduction in analytical atomic spectrometry, *JAAS* **2011**, *submitted*.

[2] Fittschen, U.E.A.,Bings, N.H. *et al*., Characteristics of Picoliter Dropled Dried Residues as Standards for Direct Analysis Techniques, *Anal. Chem*. **2008**, *80*, 1967-77.

[3] Schaper, J.N., Massmann, J., Petersen, J.H., Bings, N.H., 11th Rio Symposium on Atomic Spectrometry, Mar del Plata (Argentina) **2010** (poster).

[4] Schaper, J.N., Massmann, J., Petersen, J.H., Bings, N.H., 2010 Winterconference on Plasma Spectrometry, Fort Myers (USA) **2010** (poster).

Acknowledgment

The authors would like to thank the German Research Foundation (DFG) and the interdisciplinary research training program "Trace analysis of elemental species: development of methods and applications" for financial support as well as Peter Schöffel and Waldemar Maidanjuk from the machine shop of the institute for inorganic and analytical chemistry of the University of Mainz for their practical help.