Transient Sample Introduction into ICP-MS with a Novel Low Flow *drop-on-demand* Aerosol Generator

J. N. Schaper, J.H. Petersen, J. O. Orlandini v. Niessen, N.H. Bings

Johannes Gutenberg-University Mainz, Institute for Inorganic and Analytical Chemistry, Laboratory for Inorganic Trace Analysis and Plasma Spectrochemistry, Duesbergweg 10-14, 55128 Mainz, Germany, schapern@uni-mainz.de

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 combined with 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. Recently, a new method of sample introduction using modified inkjet cartridges as dosing device has been reported.[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] Therefore, a precise and reproducible droplet generation with these devices can be achieved. However, the combination of such a dosing device with separation systems and therefore the handling of transient signals is still a challenge.

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 a 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 applications.

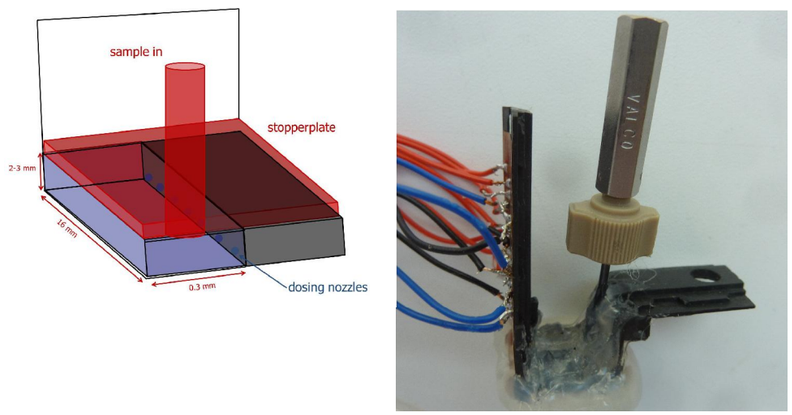

Figure 1: Schematics of the modifications of a HP45 inkjet cartridge.

Results

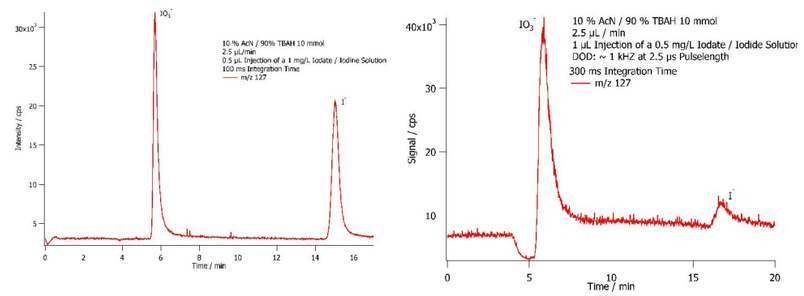

Figure 2: IPC separation of iodine and iodate using the reference system Enya-Mist (left) and the modified DOD system (right).

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. As a model system, the separation of iodine and iodate was investigated. Techically, ion chromatography would be the method of choice for this application, but here the use of an ion-pair chromatography (IPC) technique has several advantages. First, a standard C18 reversed-phase micro liquid chromatography column can be used, as micro ion chromatography columns are not available up to date. Furthermore, the IPC technique allows the use of solvent gradients, something impossible in ion chormatography. And last, the parameters used for the separation are more representative for standard microLC applications. 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. All sample lines have an inner diameter of 50 µm to minimize the internal volume. Fig. 2 displays the results for the EnyaMist nebulizer and the DOD aerosol generator, respectively. For both nebulizing systems, the two species are well resolved. However, there are differences in the chromatograms: the signal corresponding to iodine is less pronounced for the DOD system and the baseline between the two species is higher than before. This indicates that the current interface is not yet optimal regarding the dead volume. However, the current system is intended to demonstrate the ability of the new aerosol generation system and furthter development is planned to decrease the dead volume.

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, as well as low flows in the µL-range.[4] In this presentation, it could be demonstrated that the DOD combined with the new and miniaturized interface is also suitable for combination with a capillary HPLC and thus can be applied in speciation analysis. Also, the DOD system is stabel with the use of organic solvents and mixtures of solvents, a fact that is important for use in microHPLC. Results still show the existence of a small dead volume compromising the achievable chromatographic resolution. Further work will include the development and characterisation of a less complex and easy to handle design of a drop-on-demand aerosol generator. Different design layouts are discussed currently, especially with respect to a minimized dead volume.

References

[1] Orlandini v. Niessen, J.O., 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, *J. Anal. Atom. Spectrom.* **2011**, *26*, 1781-1789.

[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., Potential of a novel low-flow drop-on-demand aerosol generator for plasma spectrochemical and speciation analysis 11th Rio Symposium on Atomic Spectrometry, Mar del Plata (Argentina) **2010** (poster).

[4] Schaper, J.N., Massmann, J., Petersen, J.H., Bings, N.H., Einsatz eines neuartigen niedrigfluss drop-on-demand Aerosolgenerators in der Elementspuren- und Speziesanalytik Anakon 2011, Zurich (Switzerland) **2011** (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.