A novel low-flow *drop-on-demad* aerosol generator: Analytical characterization and its potential for transient sample introduction into ICP-MS

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Liquid sample introduction in plasma spectrometry

In the field of inorganic trace and species analysis liquid samples are introduced into plasma excitation and ionization sources mainly as an aerosol, which is produced by pneumatic nebulization. It is well known that this aerosol shows a relatively broad droplet size distribution which prevents the complete evaporation of the sample and thus causes serious disturbance of the plasma. Therefore, only small aerosol droplets with a diameter far below 10 μm are suitable for the introduction into the excitation/ionization source. Various spray chamber designs - e.g. optimized for maximum sensitivity or minimum dead volume and wash-out times - serve to overcome this problem, allowing only the small-sized droplets to pass to the plasma source. However, this might also result in an unfavorable loss of sensitivity.
In particular when hyphenating liquid chromatography (e.g. HPLC or IC) and capillary electrophoresis (CE) to plasma source mass spectrometry the efficient nebulization of very small liquid volumes is indispensable, because of low eluent volume flow rates, which necessitates special low-flow and micro-flow nebulizer/spray chamber systems.

Research goals

The generation of images by commercial inkjet printers is based on the precise transfer of pico liter amounts of ink onto paper. The main ideas behind this presented research project are

- to use the capabilities of this thermal inkjet technology for the accurate and reproducible transfer of sample and standard solutions onto solid targets[1].
- to use this new DOD system as an aerosol generator for the nebulization of liquid samples. A microcontroller has been developed to give access to the important parameters of droplet size, which allow for the development of a novel aerosol generator. The coupling of this new device to an ICP allows very low flow rates of liquid samples [2] and opens the possibility to hyphenate low-flow separation techniques without further dilution.

The relative large volume of the liquid reservoir surrounding the silica chip carrying the nozzles of the cartridge (HP™45 approx. 200 μL) hampers the direct coupling of such devices to low-flow separation techniques like capillary electrophoresis (CE), since it would deteriorate chromatographic resolution. Therefore, the reduction of the dead volume and the design of a dead volume-free coupling of separation capillaries to the device is the actual focus of the presented study. In a first step, the novel DOD device was coupled to a flow injection system (FIA) for the generation of transient signals. The resulting signal widths and ICP-MS signal intensities are evaluated and compared to such data achieved with a FIA-ICP-MS system employing a commercial low-flow nebulizer.

Results

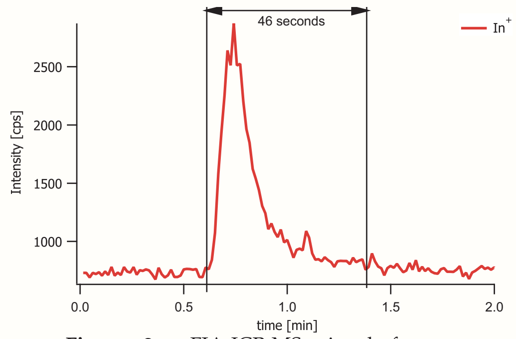

Figure 2: FIA-ICP-MS signal from a 100 μg/L In solution. A modified HP45™ printer cartridge is used as a novel DOD aerosol generator.

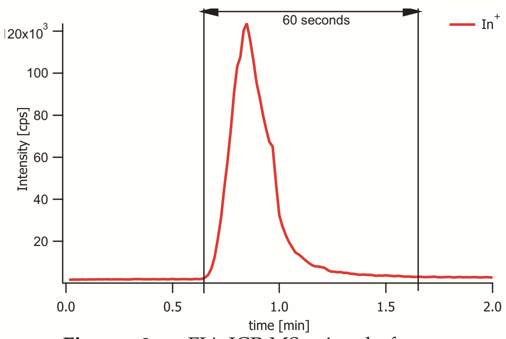

Figure 3: FIA-ICP-MS signal from a 100 μg/L In solution. A commercial "MicroMist"™ nebulizer (flow rate 33 μL·min^{-1}) is used as a reference.

Both aerosol generation systems show a good response to the injected sample, as the count rate rises steep. But both systems also show significant signal tailing. The theoretical transient signal width of 0.2 seconds could not be reached with either system due to dead volumes in the six port valve and its transfer lines. Signal widths are 46 seconds for the new designed DOD aerosol generator and 60 seconds for the "MicroMist"™ system, respectively. The observed signal widths are comparable, with slightly shorter wash-out times for the state of the art DOD generator. This underlines the possibility for coupling the new developed system with even smaller capillaries.

Conclusion

- successful FIA-DOD coupling
- good response to injected sample
- "MicroMist"™ and new DOD generator show very similar signals
- setup allows easy and fast sample change with standard devices
- further improved sensitivity can be achieved by using our state-of the art DOD spray chamber (see our poster TP06 "Development and characterization of a *drop-on-demand* generator for sample introduction of very small volumes for plasma spectrometry" for comparison of DOD generator and "MicroMist™)
- still significant FIA signal tailing due to remaining dead volume of capillary and DOD coupling

Experimental setup

For the generation of transient signals, a 3 μL sample loop was used in the in-house-made FIA system. The coupling with the DOD aerosol generator was established through capillaries with an inner diameter of 0.7 mm. They were mounted directly over the orifice plate to reduce the overall dead volume. The commercial "MicroMist"™, model AR40-1-FM007E, was coupled to the FIA system via a T-junction to allow self-aspiration. Both aerosol generators where mounted via specific spray chambers to the torch of an ICP-MS (Agilent 4500). Tab. 1 summarizes the operation conditions of the different parts of the setup.

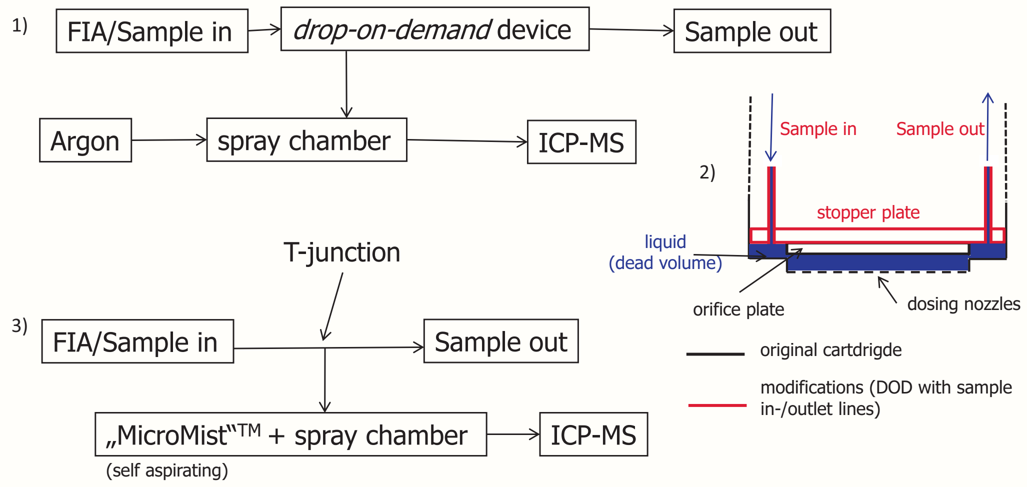

Figure 1: Schematics of the setups: 1) FIA-DOD coupling 2) DOD-capillary coupling 3) FIA-"MicroMist"™ coupling.

As an additional advantage, this setup will allow an easy and fast way to change the sample solutions by transferring the liquids to the DOD device followed by stopping the peristaltic pump. After data acquisition and rinsing the device, the next sample can be transported to the aerosol generator. This would open the possibility to use standard instrumental equipment for liquid handling in combination with the new minimized aerosol generating system regardless of the dead volume stemming from coupling the transfer line to the DOD system.

Table 1: Operation Conditions

ICP-MS		DOD	
		Pulse width	2.5-7.3 μs
R_F Power	1,250 W	Frequency f_s	0.54-2.68 kHz
Plasma gas	17 L·min^{-1}	Sample transfer rate	2.8-8.7 μL·min^{-1}
Auxiliary gas	1 L·min^{-1}		
i.d. Torch	2.5 mm	**FIA**	
Carrier gas	0.5-1.1 L·min^{-1}	Sample loop volume	3 μL
Sample depth	4.0 mm	Liquid flow rate	0.85 mL·min^{-1}
Integration time	0.1 s		
		"MicroMist"™	
		Sample uptake rate	33 μL·min^{-1}

Outlook

The next step towards a new interface for CE-ICP-MS coupling via the DOD aerosol generator is further reducing the dead volume of the DOD device to match the dimensions of a CE capillary.
Furthermore the dosing device has to be optimized to allow for easy sampling through the use of standard sample delivery components.

Acknowledgement

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DFG

References

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[2] Schaper, J.N., Bings, N.H. *et al.*, *Drop-on-demand* aerosol generator for ICP-MS analysis, *Colloquium Spectroscopicum Internationale XXXVI*, Budapest **2009**, (poster).