Institute for Inorganic and Analytical Chemistry

Drop-on-demand aerosol generator for ICP-MS analysis

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Liquid sample introduction in plasma spectrometry

The introduction of liquid samples into plasma excitation and ionization sources in the field of inorganic trace analysis is commonly established through the continuous generation of aerosols via pneumatic nebulization. It is well known that this aerosol not only shows a relatively broad particle size distribution but mostly also results in a too high load for the plasma source and is thus not suitable for direct introduction into the ICP. 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 unfavourable 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. Therefore, the generation of small and preferably monodisperse droplets from liquid samples for elemental trace and species analysis is of common interest.

Aim

The developement of a new *drop-on-demand* (DOD) aerosol generator presented here is based on thermal-inkjet technology, which has already been used successfully for transferring very small amounts of liquid sample on solid targets.[1] The developement of a stand-alone microcontroller finally gives access to the important parameters for droplet generation to e.g. adjust droplet size, transfer rate and overall transferred sample mass.[2]

The coupling of the dosing device to an ICP principially allows very low flow rates of liquid samples for ICP-MS analysis and therefore opens the possibility to hyphenate low flow separation techniques without unfavourable dilution.

Direct coupling of a DOD device with ICP-MS

The *drop-on-demand* device delivers the droplets into a transfer line, where they are mixed with argon as a carrier gas. The formed aerosol is transported directly to the torch of the ICP (Agilent 4500). The *drop-on-demand* device is driven by a microcontroller, so droplet size and droplet generation frequency are adjustable over a wide range.[3] Fig.1 and Tab.1 give a schematic overview of the instrumental setup and the experimental conditions respectively. The chosen setup allows to study the influence of many parameters upon aerosol generation.

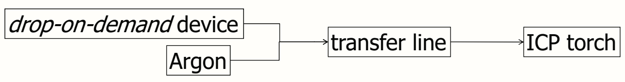

Figure 1: Schematic of the experimental setup

Table 1: Operation Conditions

ICP-MS		DOD	
R_F Power	1,200 W	Pulse width	4.2-7.3 μs
Plasma gas	16 L·min^{-1}	Frequency f_s	0.54-1.2 kHz
Auxiliary gas	1 L·min^{-1}	Voltage	12 V
Carrier gas	0.5-1.5 L·min^{-1}	droplet volume	45-119 pL
Sample depth	4.0 mm	transfer rate	<1.5-8.7 μL·min^{-1}
Integration time	0.1 s		

First results

A test solution of 100 μg/L ^{103}Rh was dosed by the described system. The plasma and background stability were monitored by $^{38}Ar^{16}O^+$. Fig.2 presents results from the very first coupling of a thermal-inkjet-based aerosol generator (the presented DOD system).

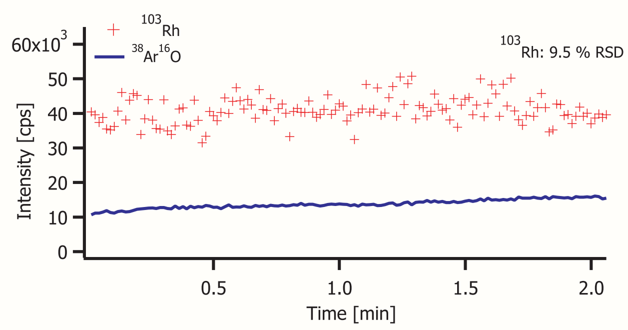

Figure 2: Very first DOD-ICP-MS coupling, signal stability of ^{103}Rh, 100 $\mu g \cdot L^{-1}$

The presented investigations consider the influence of the droplet generation frequency and droplet generation pulse width. Fig. 3 and 4 show that best results can be obtained for a frequency f_s of 0.68 kHz and pulse width of 6.5 μs.

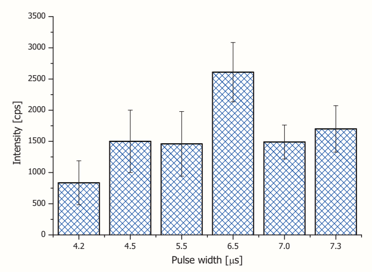

Figure 3: Signal intensities for ^{103}Rh depending on DOD pulse width (f_s=0.54 kHz)

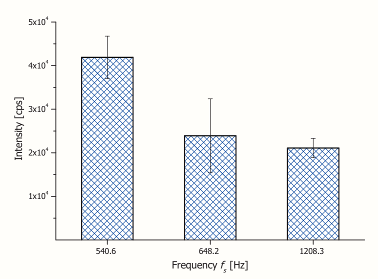

Figure 4: Signal intensities for ^{103}Rh depending on DOD frequence (pulse width 4.5 μs)

Comparison DOD generator vs "MicroMist" Nebulizer

Comparing the new aerosol generator with a conventional nebulizer system a "MicroMist" Nebulizer (AR40-1-FM007E) combined with a cyclonic spray chamber was selected. For both systems the total amount of ^{103}Rh were calculated from the sample flow rates.

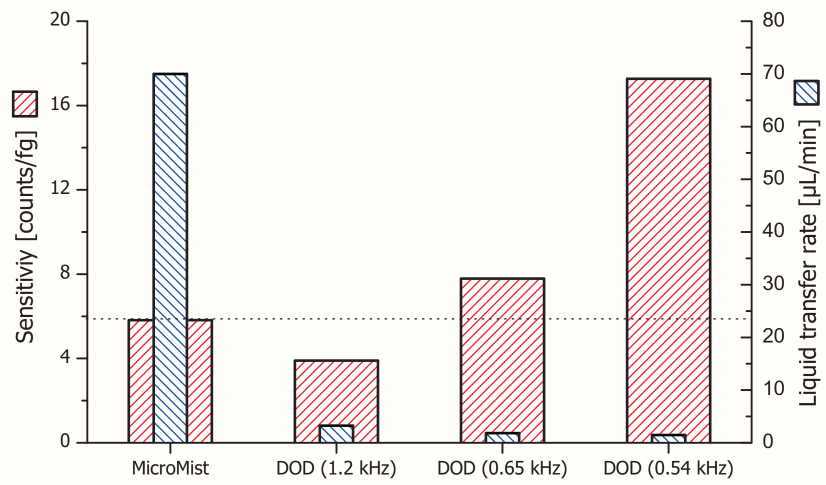

Figure 5: "MicroMist" vs. DOD

Table 2: "Micromist" vs DOD

	MicroMist	DOD		
Frequency f_s[kHz]		1.2	0.65	0.54
Total sample transfer [$\frac{\mu L}{min}$]	70.0	3.25	1.84	1.46
Mean relative sensitivity [$\frac{counts}{fg}$]	5.82	3.90	7.79	17.3

Advantages • Future work

- Efficient aerosol generation at low sample flow rates ($\frac{nL}{min} - \frac{\mu L}{min}$)
- Improved sensitivity compared to conventional "MicroMist" nebulizer
- Adjustable dosing parameters, thus variable flow rates at constant dosing efficiency
- Direct coupling to ICP no spray chamber necessary: minimised dead-volume and sample loss

Future work:

- Reproducibility and noise power spectra
- Achievable figures of merit (LODs, etc.)
- Hyphenation with (minimized) separation techniques (eg. HPLC, CE)
- Applicability for real samples
- Calibration strategy based on variable liquid transfer rate

Conclusion and outlook

The succesfull coupling of a *drop-on-demand* device is presented for the first time. Hyphenated to an ICP-MS and compared to a standard low-flow "MicroMist" nebulizer, the first prototype of the new developed aerosol generator allwos improved sensitivity at drastically reduced sample flow rates.

However, the design and robustness of the DOD-system has to be optimized to improve e.g. the achievable stability.

References

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[2] Massmann, J., Petersen, J.H., Broekaert, J.A.C, Bings, N.H., Development and characterisation of a *drop-on-demand*-aerosol generator for the introduction of small sample volumes in plasma spectrometry, *Colloquium Spectroscopicum Internationale XXXVI*, Budapest **2009**, (poster).

[3] Massmann, J., Entwicklung und Charakterisierung eines neuarigen *drop-on-demand*-Zerstäubers für die Zuführung kleinster Probenvolumina in der analytischen Atomspektrometrie, *Diplomarbeit*, Universität Hamburg, **2009**.

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