Development and characterization of a *drop-on-demand*-generator for sample introduction of very small volumes for plasma spectrometry

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Introduction

The introduction of liquid samples in the field of plasma spectrometry is still a major bottleneck due to considerable losses in this step. Conventional pneumatic nebulization is the most common way of introducing liquid samples into excitation sources in inorganic analysis. However, well-known drawbacks from the use of these pneumatic nebulizers such as e.g. liquid flow rate dependent aerosol formation efficiency and peristaltic pump-based signal fluctuations are limiting further enhancements. This is especially the case if only minute amount of sample material is available and downscaling of the instrumentation becomes necessary.

Among other tasks which have to be addressed in this context, miniaturization of analytical devices requires the accurate handling of small sample volumes. Hyphenated techniques, based e.g. on the combination of capillary electrophoresis (CE) and plasma mass spectrometry via pneumatic nebulizers, require additional make-up solvent flows to meet the specifications of conventional systems used for sample introduction into the plasma source.[1] To minimize the risk of contamination, to avoid sample dilution and the degradation of chromatographic resolution a new strategy for direct and flexible introduction of liquid samples into the ICP is desired.

Description of developed DOD-system

In this poster we present a new approach for the nebulization of liquids via stand-alone *thermal-inkjet*-print cartridges. Such print cartridges have successfully been used for analytical purposes in total reflexion x-ray fluorescence and laser ablation ICP-MS.[2] The former inkjet cartridges were driven by self-designed microcontroller. The resulting droplet volumes of the presented drop-on-demand (DOD) systems are variable and also the frequency of droplet generation is tunable over a wide range, so that in combination of these two parameters the total flow rate is adjustable over four orders of magnitude.[3]

The developed system was characterized regarding the magnitude of the resulting linear range and stability in ICP-MS (HP-4500) analysis. Furthermore, the analytical figures of merit were compared to such data achieved with different conventional nebulization systems.

Characterization of DOD-system by ICP-MS

Signal stability was investigated by time-resolved measurement of the signal intensity. Therefore a solution of 100 μg/L of each In and Y was dosed with a droplet generation frequency of 2.69 kHz. As shown in Fig. 1 the signal intensity is stable after a rise time of 2.0 minutes. Minimal RSD-values of less than 5.7 % (In) and 7.0 % (Y) were observed between 2.0 and 9.0 minutes (n=450).

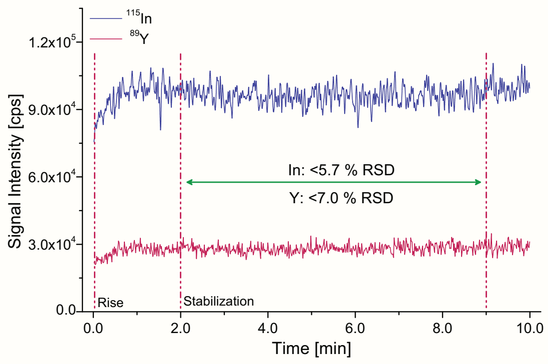

Figure 1: Stability of DOD-ICP-MS signals for In and Y (100 μg/L each).

The linearity of the developed DOD-system was proven by investigating the signal-to-analyte concentration correlation. Solutions containing In+Y in various concentrations were dosed under univariate conditions (see above). The results and corresponding linearity of the calibration curves are shown in Fig. 2.

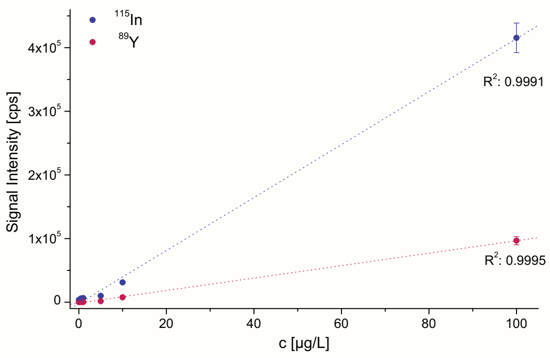

Figure 2: Calibration curves for In and Y in DOD-ICP-MS.

System characterization - used setups

For system characterization a first and second-generation version of the novel DOD-aerosol generator were compared to two conventional sample introduction systems (Tab. 1). Setup **D** represents the state-of-the-art and currently most advanced DOD-system of our group.

Table 1: Key data of compared systems.

A	• Concentric nebulizer • Scott-Type spray chamber • Peristaltic-pump	**B**	• *MicroMist*™ nebulizer • Cyclonic spray chamber • Self-aspirated
C	• DOD system, 2.69 kHz, 5.0 μs • Self-designed interface chamber • *HP*™ ink cartridge type 26 • Single droplets down to 80 pL	**D**	• DOD system, 2.69 kHz, 3.0 μs • Self-designed minimized interface chamber with dual gas-inlet • *HP*™ ink cartridge type 45 • Single droplets down to 15 pL

System characterization - results

The comparison of the four systems with respect to achievable absolute detection limits (Fig. 3), sensitivity (Fig. 4), linearity and sample transfer rates (Tab. 2) shows the outstanding performance of our newly developed DOD-system as a liquid sample introduction system in ICP-MS analysis. Our most advanced system (**D**) reaches similar or better values in all areas.

The major difference between the compared systems is the achievable sample transfer rate. The possibility to use variable droplet generation frequencies and a variable number of nozzles allows for both, flow rates in the mL/min-range and ultra-low flow rates of a few nL/min.

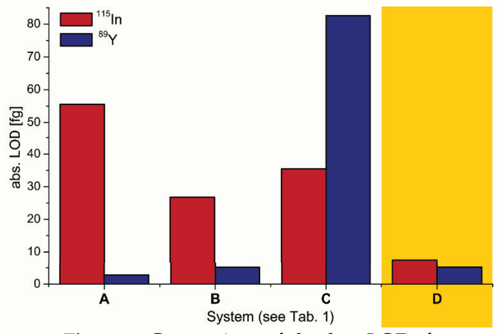

Figure 3: Comparison of absolute LODs for In and Y. Values are shown in Tab. 2.

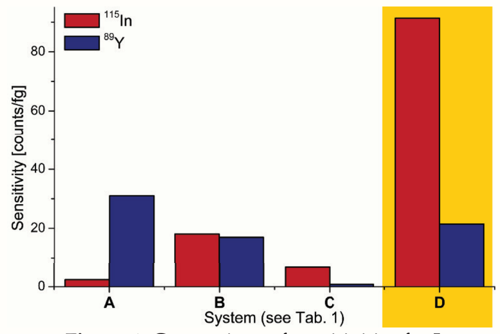

Figure 4: Comparison of sensitivities for In and Y. Values are shown in Tab. 2.

Table 2: Comparison of achievable analytical figures of merit.

System	abs. LOD [fg] ^{115}In	abs. LOD [fg] ^{89}Y	sample transfer rate [μL/min]	linearity R^2 ^{115}In	linearity R^2 ^{89}Y	sensitivity [counts/fg] ^{115}In	sensitivity [counts/fg] ^{89}Y
A	56	3	932	0.9999	0.9996	2.35	31.0
B	27	5	33	0.9991	0.9990	18.1	17.0
C	36	83	12.9^{A}	0.9720	0.9570	6.59	0.80
D	8	5	2.73^{B}	0.9991	0.9995	91.4	21.5

A: Calculated, based on $n=1.4 \cdot 10^6$ droplets, *B*: Calculated, based on $n = 1.6 \cdot 10^6$ droplets

Conclusion

- Former *thermal-inkjet* printing cartridges in combination with self-developed microcontrollers have been successfully used as *drop-on-demand*-aerosol generators for liquid sample introduction in plasma spectrometry.
- The presented DOD-system in combination with ICP-MS is most suitable for external calibration.
- The performance of the DOD-system **D** is significantly better compared with conventional concentric nebulizers and miniaturized systems such as the MicroMist™-system **B**.
- Different behaviours regarding achievable sensitivities and LODs were observed for both selected elements.
- Additional studies have to be performed to further characterize possible limitations of the novel system.

Outlook

Future work will focus on the application of the novel DOD-aerosol generator to different calibration strategies. For external calibration only one standard solution would be needed, while the amount of analyte, which will be transferred into the plasma is controlled via the droplet generation frequency (*single solution calibration*). In a first approach the signal intensity shows a second order correlation with the number of droplets per time (Fig. 5). This calibration technique would allow to keep sample and standard consumption at absolute minimum and efforts regarding sample/standard dissolution could be minimized or even avoided.

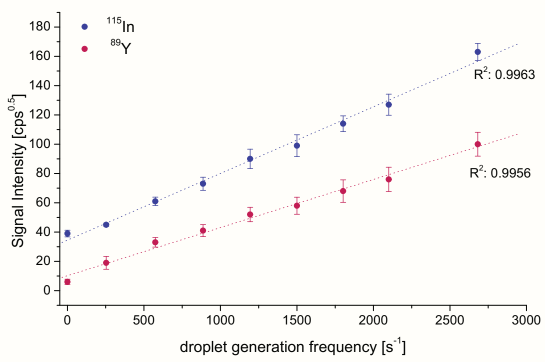

Figure 5: *Single solution calibration* technique - different droplet generation frequencies dictate the transferred volumes of sample and standard from a single solution into the ICP.

References

[1] Taylor, K., Sharp, B., *et al.*, Design and characterization of a microconcentric nebulizer interface for capillary electrophoresis-inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* **1998**, *13*, 1095-1100.

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

[3] Massmann, J., Petersen, J.H., Schaper, J.N., J.A.C. Broekaert, N.H. Bings, XXXVI. Colloquium spectroscopicum int., Budapest (**2009**), poster.