Fundamental characterisation of a new *drop-on-demand* aerosol generator: introduction of single droplets into plasma excitation and ionization sources

JOHANNES GUTENBERG UNIVERSITY MAINZ
Institute for Inorganic and Analytical Chemistry

J.H. Petersen, J. Massmann, J.N. Schaper, N.H. Bings

Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany, petersen@uni-mainz.de

Introduction of liquids in plasma spectrometry - Limitation of conventional sample introduction systems

Inductively coupled plasma mass spectrometry (ICP-MS) combined with different chromatographic or electrophoretic separation techniques is a powerful and common tool for elemental speciation analysis. However, the design of the interface used for hyphenating the separation device with the ICP influences, and thus limits, the analytical figures of merit of the developed method. Due to low eluent volume flow rates, the capability of efficient nebulization of very small liquid volumes is one indispensable prerequisite for the selection of an appropriate tool and in many cases conventional pneumatic low-flow nebulizers are used to serve this goal. Still, the addition of make-up solvent flows is in most cases needed to meet the specifications of such nebulizers. Other drawbacks of such systems, which also limit the achievable power of detection, might be the noise and signal fluctuations generated by such nebulizers, as well as relatively broad droplet size distributions. The latter often necessitates the use of spray champers, which additionally compromise the overall aerosol generation efficiency.

Novel approach

Based on thermal-inkjet printing, which has been successfully used for dosing small sample volumes[1] we have developed a micro controlled drop-on-demand stand alone cartridge aerosol generator for liquid sample introduction.
Here we present first investigations on the droplet size distribution achieved with our aerosol generator. This knowledge is essential for minimizing the noise of any kind of sample introduction system. For this purpose the generator has been modified to create single droplets, which were characterized regarding their volume by ICP-MS.

Experimental setup

For this purpose the generator has been modified to create single droplets at manual control. For the first time we modified a color cartridge, with which it is possible to print up to three different solutions, each out of a set of 16 nozzles, in one print head (Fig. 1 and Fig. 2).

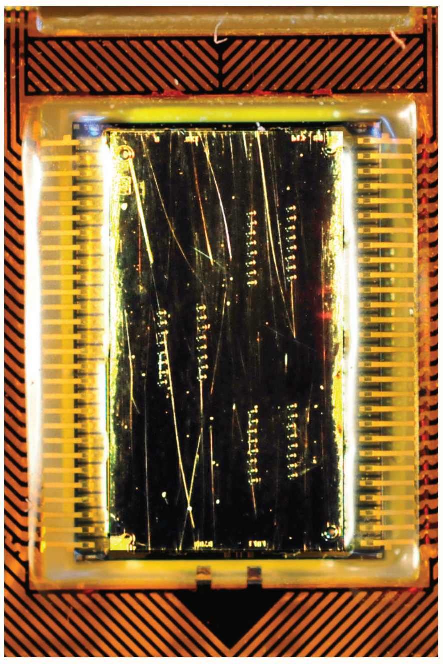

Figure 1: Nozzles of a color cartridge printer head

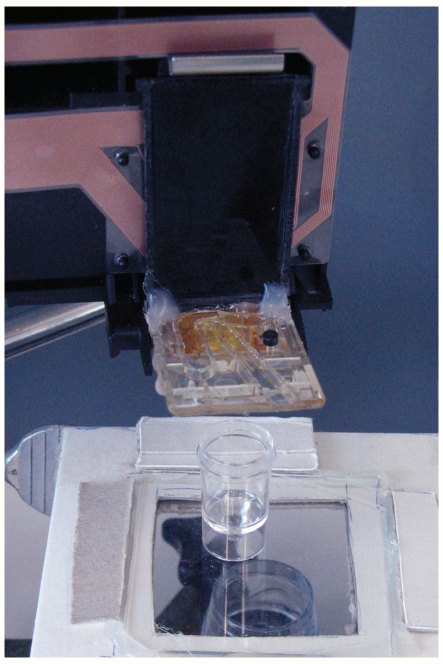

Figure 2: Modified cartridge and target table

The cartridge was cleaned and rinsed with the printing solution. As a target solution (1.0 mL, 4 % HNO_3) was pipetted in an AAS Vial which was then placed under the printer head. A single pulse (length 4.5 μs, 12 V) was applied to the selected nozzle.

Experiment 1: one nozzle was fed with a 10.0 g/L Sr in 4 % HNO_3 and the other nozzle with a 10.0 g/L Y in 4 % HNO_3 solution. The target solution was spiked with 100 μg/L Rh. The solution was quantified by external calibration and internal standardization.

Experiment 2: one nozzle was feed with Merck multi-element standard IV (1000 mg/L).

The samples were analyzed by ICP-MS (Agilent 4500; Rf Power 1,250 W; Plasmagas 16 L/min; Auxillary gas 1.0 L/min; Carrier Gas 1.0 L/min (Injector ID 2,5 mm) Sample depth 4.0 mm; Integration time 0.1 s; Nebulizer PFA μFlow 100-2118)

Conclusion and outlook

Our new aerosol generator has been successfully modified to dose single droplets. The reproducibility with RSD values down to 7.6 % and the high tolerance for matrix load are very promising results for further work on single droplet generation. Possible fields of applications are all dosing processes were small and well defined droplets are essential, such as spiking and matrix matched calibration of surface analysis using laser ablation or total reflection x-ray fluorescence.[1]
Further work is necessary to improve the reproducibility after more than 10 repetitions. Also the reduction of the transferred mass is in the focus of further investigations. One important task is to proof these results with independent analysis techniques like graphite furnace AAS or via electro analytical methods.

Results and discussion

Within the first 10 repetitions a good reproducibility could be achieved (Tab. 1). After this a significant increase of transferred mass can be observed (Fig. 3).

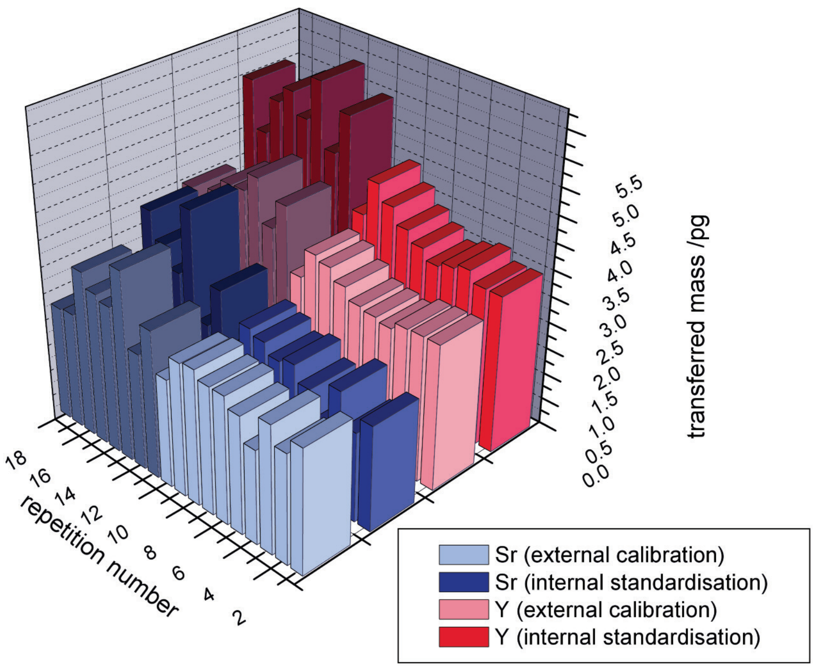

Figure 3: Experiment 1: Reproducibility of the transferred mass by single droplets

Table 1: Transferred mass and RSD values for the first 10 repetitions

Element	Mean (ext.) [pg]	RSD (ext.) [%]	Mean (int.) [pg]	RSD (int.) [%]
Sr	2.1	16	2.3	11
Y	3.3	10	2.8	8

In the target solution concentrations between 2.1 and 4.1 ppb could be found which corresponds to transferred masses between 2.1 and 4.1 pg. This indicates droplet sizes of 210 to 410 pL which does not correspond to experiments done in the continues printing mode of our aerosol generator.[2] This might be a result of different effects. The droplet sizes calculated for the continues mode are mean values of several thousand droplets. As a consequence of this one big drop transferred at the beginning of the continues droplet generation process would not influence the experimental result significantly. Also the printing solutions for the single droplets were highly concentrated (10.0 g/L), witch might lead to dried residues in- and outside the nozzle. This might also be responsible for worsening reproducibility observed after 10 repetitions. Further experiments are necessary here to investigate the different behavior observed for the single and continues mode of our *drop-on-demand* aerosol generator.
The results of the second experiment presented here, show that our generator is able to dose solutions with high ion matrices and a great number of different elements. As the printing solution consists of 23 elements (each 1.0 g/L) the ion load is even higher than in the first experiment.

Table 2: ICP-MS signals for transferred multi-element solution

Element	Intensity [cps]	RSD [%]	Element	Intensity [cps]	RSD [%]
^{7}Li	6600	11	^{111}Cd	840	14
^{53}Cr	440	27	^{115}In	7500	18
^{55}Mn	5500	21	^{137}Ba	900	26
^{66}Zn	6300	63	^{205}Tl	4500	13
^{69}Ga	3900	19	^{208}Pb	3400	12
^{88}Sr	5000	11	^{209}Bi	6000	17
^{107}Ag	1600	12			

number of repetitions 10, except for Zn = 9.

The data shown in Tab. 2 are blank corrected intensities only. The estimated transferred sample mass is around 0.16 pg, which equals to 160 ppt of the target solution.

References

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

[2] Massmann, J., *et al.*, Development and characterization of a drop-on-demand aerosol generator for the introduction of small sample volumes in plasma spectrometry, *TraceSpec 2009*, Poster.