Towards a new calibration method for LA-ICP-MS based on dried residues of individual picolitre droplets

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Introduction

Laser ablation in combination with plasma source mass spectrometry has evolved to a mature tool in the field of spatially-resolved elemental analysis of solid samples. However, accurate calibration is still difficult, since it is hampered by elemental fractionation and the lack of available standard reference materials.
The proposed novel calibration strategy is based on the ablation of dried residues from small droplets with known volume of standard solutions. Therefore, a novel single-drop-on-demand generator based on thermal inkjet technology was designed for the reproducible transfer of minute amounts of sample mass onto various sample targets. The so called "drop-on-demand generator (DOD)" is micro controlled, uses a modified "stand alone" printer cartridge for droplet generation and is capable to dose sample volumes in the picoliter-range. The droplet diameter is adjustable. It is possible to create droplets in both individual and continuous modes, allowing a variable droplet generation frequency. Furthermore, different sample reservoirs and an individual number and thus positions of the used dosing nozzles can be selected out of 3x16 available nozzles, which is potentially advantageous e.g. in the case of standard addition.

Experimental Setup

DOD generator: An electrical pulse generator has been designed to apply a single pulses of 12 V (DC) for 4 μs to the dosing nozzle of a modified inkjet HP 49 printer cartridge. To speed up rinsing of the nozzles higher frequency (variable) pulses can be selected.
Sample target: To minimize the diameter of the transferred droplets, hydrophobic microscope glass slides were used. Therefore the slides were 1. heated to 60 °C, 2. dipped for 5 min in a solution containing 5 vol. % dichlorodimethylsilane (99 %, Acros Organics) in hexane, 3. washed with methanol and 4. dried at 60 °C)

Figure 1: Modified cartridge.

Dosing: The target was placed on a x,y,z translation stage approximately 2 mm below the cartridge. Indium ICP standard solution (Alfa Aesar, 1.0 g/l) was used as a sample. The cartridge was rinsed three times by applying a dosing frequency of 1.3 kHz before use. Then a sequence of a single, a double and a triple dosage was applied without drying the individual layers. The dried residues were investigated by atomic force microscopy (AFM; JPK NanoWizard).

Previous Studies

Such print cartridges have successfully been used for analytical purposes in total reflection x-ray fluorescence (TXRF) and laser ablation ICP-MS.[1] In such studies they where controlled by a modified inkjet printer, which leads to various limitations:

- the dosing nozzle is selected by the printer software on the basis of the pixel scheme to be printed
- the dosing nozzles are moving and as a result precession worsens with the number of printed layers.

Experimental: Using a modified HP500C Inkjet printer, pL droplets (1.0 g/L Ga solution) were dosed onto acrylic glass sample carriers. After each dosing step the droplets were dried (except Fig. 2-B2). The diameter of dried residue ranged between 20 and 75 μm.

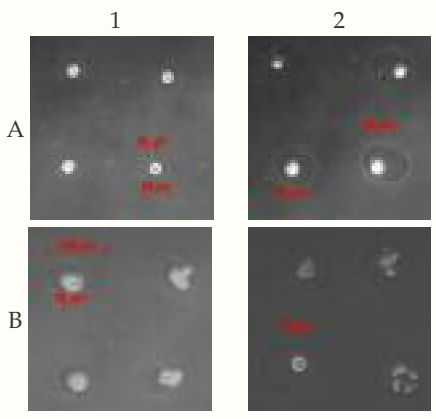

Figure 2: pL droplets printed by a modified HP500C Inkjet [2];
printed mass of Ga: 130 pg, single dosing (A1); 390 pg triple dosing (A2); 650 pg quintuple dosing (B1); 650 pg quintuple dosing without drying the individual layers (B2).

Results - Novel SINGLE-DOD-System

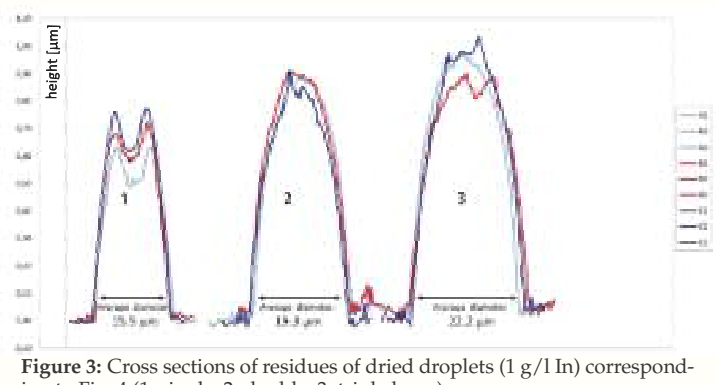

Figure 3: Cross sections of residues of dried droplets (1 g/l In) corresponding to Fig. 4 (1: single, 2: double, 3: triple layer).

Table 1: Volume of the residues (calculation based on cross section).

	1	2	3
A	74 μm^3	136 μm^3	196 μm^3
B	70 μm^3	149 μm^3	206 μm^3
C	75 μm^3	134 μm^3	215 μm^3

The formation of nearly circular residues with very reproducible diameters and cross section profiles was observed. The diameter is smaller than in previous studies[1]. Multiple sample transfer can be performed without drying the individual layers, due to high spatial layer-to layer reproducibility. However a comparison with the spot diameter of residues, achieved by multiple layer droplet transfer and inter layer drying has to be performed. Tab. 1 shows the volume of to residues calculated on the basis of the cross sections and indicates a linear correlation between volume and number of transferred layers.

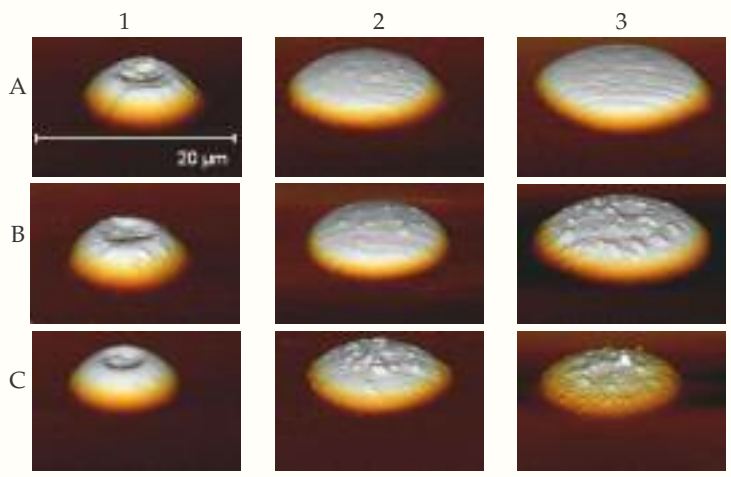

Figure 4: Array of AFM images of residues of dried droplets (1 g/l In)
1: single, 2: double, 3: triple layer.

Conclusion

- A DOD generator was developed to dose single droplets onto solid targets
- This novel device was successfully used to transfer metal standard solutions onto glass slides
- High layer to layer reproducibility
- Smaller and more symmetric dried residues compared with previous techniques

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] Bings, N.H. and Kiera, A., *Winter Conference on Plasma Spectrochemistry* , Temecula (USA), **2008**

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Outlook

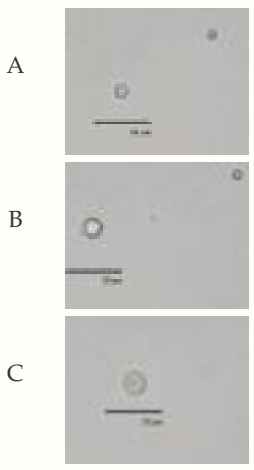

Figure 5: Light microscopic images of dried residues from smallest (so far) possible droplets.

- Extensive statistics on the shape and volume of the dried residues of the transferred droplets
- Investigations with TXRF and LA-ICP-MS
- Study on the influence of different concentrations of the used sample solutions
- Smallest (so far) possible droplets can be achieved by using a modified HP 45 cartridge (Fig. 5, A: single, B: double, C: triple dosing). However, satellite droplets can be observed most likely due to the Plateau-Rayleigh instability when using smaller nozzles for ejection of liquids. This might become negligible, depending on the nozzle-to-target geometry.
- The system's potential for reproducible transfer of ultra-low sample volumes on various solid surfaces has to be studied.