Proposal of a new calibration strategy for LA-ICP-MS based on residues of individual picoliter droplets.

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Motivation

Hyphenating laser ablation (LA) to inductively coupled plasma mass spectrometry (ICP-MS) has evolved to a major technique in direct elemental analysis with high spatial resolution. However, strong matrix effects, elemental fractionation and the lack of available standard reference materials strongly limitate an accurate calibration for quantitative analysis in many applications.

Concept

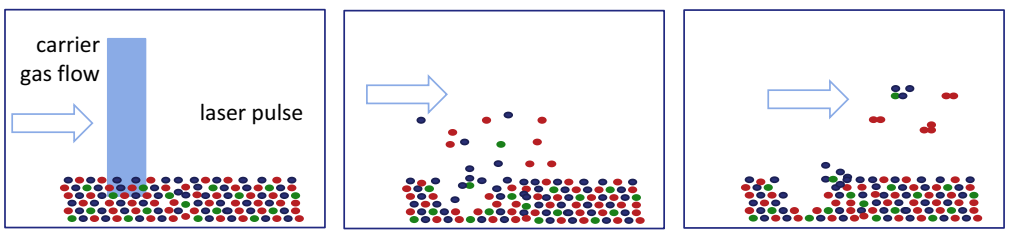

Figure 1: Schematic description of a conventional calibration based on laser ablation of solid standard reference materials.

- Conventional calibration (Fig. 1) is based on different, available solid standard reference materials. If possible, these materials have to match in both, matrix and analyte concentration, to provide the same ablation mass and obtained aerosol characteristics. Furthermore, a high homogeneity has to be guaranteed which is especially of importance for small ablation sites in high spatial resolution.
- The proposed new calibration strategy (Fig. 2) is based on the total ablation of dried residues from picoliter droplets with known volume of standard solutions[1]. 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.

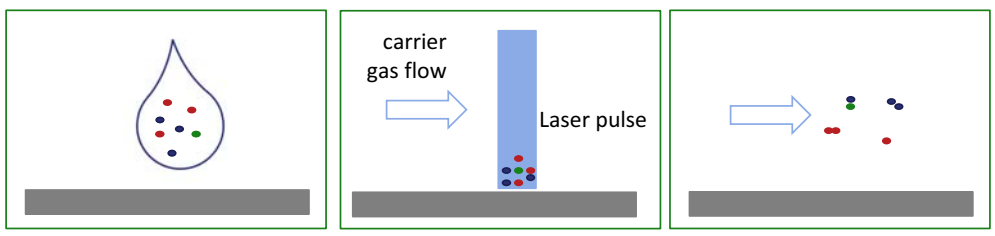

Figure 2: Schematic description of the novel calibration strategy based on laser ablation of dried residues of picoliter droplets from liquid standard solutions.

Design of the DOD generators

For dosing of individual picoliter droplets a so called "'Drop-on-Demand"' (DOD) generator has been developed. It consists of a microcontrolled electric pulse generator, which is able to drive modified thermal inkjet cartridges (so far the types: HP 29, 45 and 49). Furthermore, the system contains a PC Interface (LabJack U12, LabView 8.2) for controlling the dosing frequency and the number of dosing repetitions. The cartridge is mounted above an x,y,z translation stage, the dosing process is monitored by a microscope for targeting and an oscilloscope for appropriate pulse length and voltage.

AFM investigation

By using atomic force microscopy (AFM: JPK, NanoWizard) we could demonstrate that our DOD-generator is capable of reproducible transferring sample volumes with reproducibility < 10% (Fig. 3).

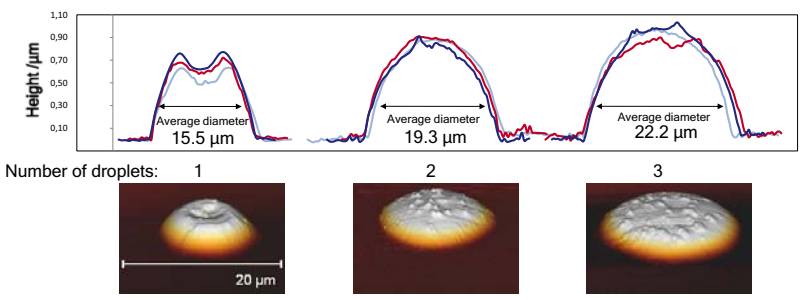

Figure 3: Characterization of the shape of dried residues depending on the number of dosing repetitions: (top) cross-sections, (below) AFM images.

Experimental: An In standard solution (Alfa Aesar, 1.0 g/L) was dosed using a modified HP 49 cartridge. Sample target was a silanized microscope slide. It was found that timing plays an important role when transferring individual or multiple droplets onto the target, i. e. the delay before and between dosing the first and the following droplets, respectively. At the time of these experiments, no software control was available, so the delay was controlled manually (approx. 10 s before first and 300 ms between the following droplets).

TXRF investigations

For further investigation of the influence of the delay between two dosing events on the transferred mass, a computer interface to control the dosing repetitions and dosing frequency has been set up. A Ga standard solution (Alfa Aesar, 1.0 g/L) was dosed onto quartz discs and the residues were analyzed by total X-ray fluorescence (TXRF: Bruker AXS: S2 PICOFOX, integration time: 1000 s) (Fig. 4).

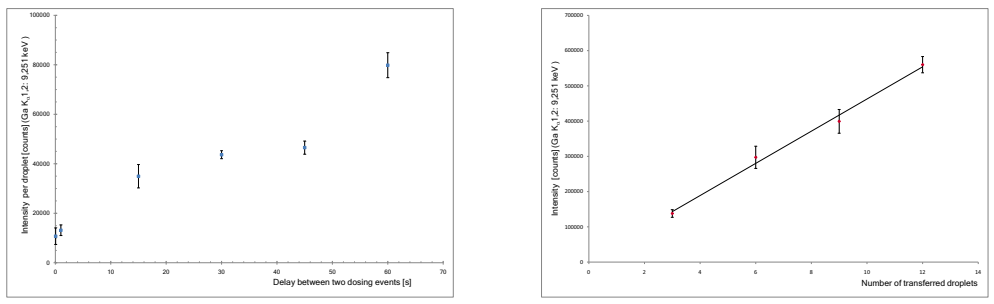

Figure 4: (left) TXRF-signal intensity per dosing event (9 replica) versus the delay between two events; (right) TXRF calibration curve: intensity versus number of transferred droplets (delay time 45 s).

It turned out that the transferred mass is strongly depending on the dosing frequency (Fig. 4, left). For delays > 10 s it was possible to remove the first droplets of the dosing process manually. Also good linear correlation between measured intensity and number of droplets could be observed (R^2=0.993) (Fig. 4, right).

Reference system: Microliter pipette

For comparison of the obtained results and standardization for TXRF measurements an electronic microliter pipette (Biohit, ePet, 0.2-10 µL) has been mounted above an x,y,z translation stage and was slightly modified to allow remote control. First TXRF data obtainted from residues containing 50 pg Se (0.5 µL droplet) demonstrate good applicability for standardization in TXRF (integration time: 2000 s). For 18 measurements a standard deviation of 5.1% could be achieved.

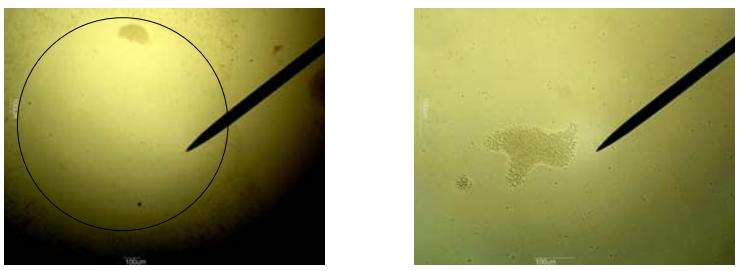

Figure 5: Microscopic images of dried residues dispensed by a microliter pipette (500 nl droplets, transferred mass: 500 pg Se).

However, high spatial resolution can not be achieved with this system. For transferring picogram masses, low concentrated solutions have to be used. The location of the dried residue within the formally wetted area (diameter ca. 1200 µm) is unpredictable (Fig 5). However, this approach is suitable for a calibration of the used TXRF-instrument, as the beam with is about 7 mm.

Conclusion

- Dried residues of DOD system show dimensions and shape applicable for standardization in laser ablation
- DOD generator allows precise mass transfer, proportional to number of droplets
- Microliter pipette is not suitable for application in LA-ICP-MS

Outlook

- Modification of the DOD-system for fast, automatic removal of first droplets
- Quantification of transferred mass by TXRF and ICP-MS
- Investigation of dried residues by LA-ICP-MS
- Investigations of the influence of different target materials and matrix additives of the solution and the qualtity of the dosing process.

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Literature

[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.