Development and Characterization of a Drop on Demand (DOD) Generator for a Novel Calibration Strategy for LA-ICP-MS Based on the Ablation of Dried 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

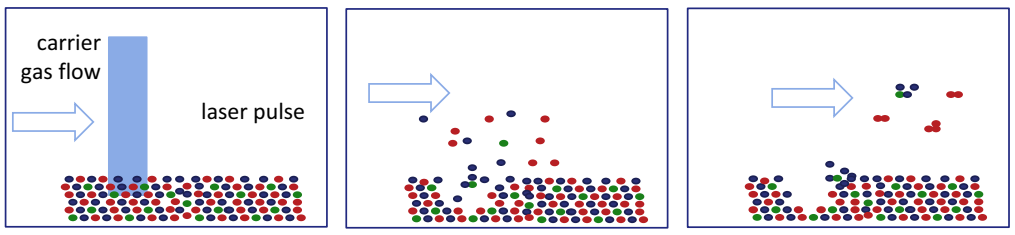

Figure 1: Schematic description of a conventional calibration based on laser ablation of solid standard reference materials.

- 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.

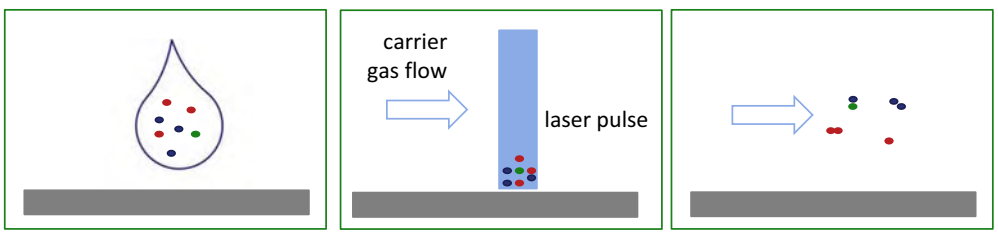

Figure 2: Schematic description of the novel calibration strategy based on laser ablation of dried residues of picoliter droplets from liquid standard solutions.

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.

Previous investigation and novel developments

It was demonstrated in previous studies using the HP 49 cartridge that dried residues of well defined mass and morphology can be obtained through dosing elemental standard solutions by using the above described DOD-generator. The diameter of the residues[2] are in the lower-to-mid µm range and therefore comparable to spot sizes commonly used in LA-ICP-MS. This DOD technique was also found to be suitable for calibration in TXRF - thus in principle also for LA-ICP-MS either by using different concentrations of solution to be sampled onto the solid target or preparing an increasing number of layers of residues through consecutive transfer of an increasing number of droplets stemming from a single standard solution[3]. In the latter case, the delay timer between repeated dosing events was found to strongly influence the amount of mass transferred onto the target, as it was also reported for other non-commercial thermal inkjet devices[4].
The results outlined in this presentation are based on the first use of a more recent HP 45 cartridge. The general aim of this study is to investigate to what extend the observed effects are depending on different types of cartridge used for DOD experiments.

Conclusion

- Results for transferred masses determined by TXRF and ICP-MS are consistent
- Increased precision of the DOD-generator by different cartridge type
- Microliter pipette is not suitable for application in LA-ICP-MS
- Dimensions of residues of pL droplets transferred by novel DOD generator suggest application of thermal inkjet printing techniques in LA-ICP-MS

Outlook

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

Determination of the transferred mass

For detailed study on the influence of the delay time (see above) on average transferred sample mass per droplet, ICP-MS and TXRF measurement were performed. Both experiments, i.e. transferring the sample solution onto a target for TXRF analysis and into a vial for ICP-MS measurements, were performed in parallel to guarantee comparable air humidity, which was found to significantly influence the dosing accuracy. Sr solution (MERCK CertiPUR, 1.0 g/L) was used throughout this study.

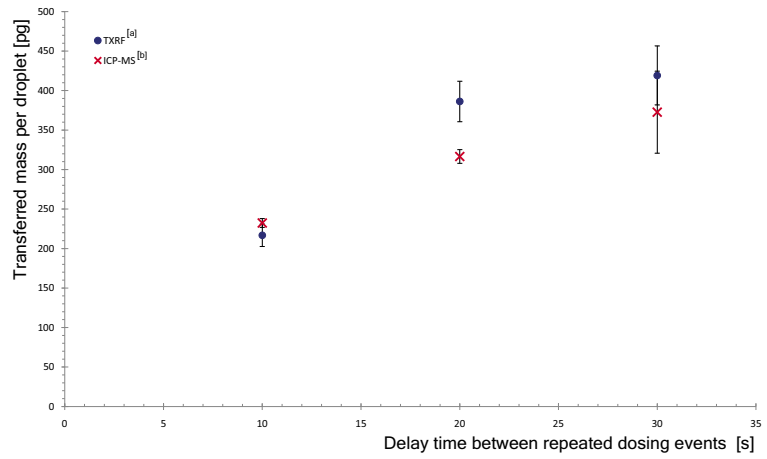

Figure 3: Determined transferred mass (Sr) per droplet (5 replica) versus the delay time between repeated dosing events; [a] 5 droplets per sample (quartz disc) ; [b] 50 droplets per sample diluted to 1 mL (1 µg/l Rh internal standard).

Instrumental: [a] (TXRF: Bruker AXS: S2 PICOFOX) Sample target: quartz disc, mass calculated from an internal standard (1 ng Se) transferred by an electronic microliter pipette (1µL,); [b] (ICP-MS: Agilent 4500) Mass calculated by calibration with internal standardization (Rh, 1 µg/l).
As observed for the HP 49 cartridge[3], also for the HP 45 cartridge the transferred sample mass strongly depends on the delay time between repeated dosing events (Fig. 3). The first 5 droplets of each dosing cascade were manually separated from the following droplets by ejecting them onto a dummy-target, since they were found to significantly differ in size compared to the following droplets and would therefore falsify the calculated mean mass transferred per droplet. Unfortunately, this additional step limits the minimum delay time to 10 seconds. Considering the achievable RSDs it can be concluded, that the reproducibility of the proposed dosing process can be improved by using the HP 45 cartridge (2-7 % RSD (HP 45), 6-15 % (HP 49)).

Reference system: Microliter pipette

An electronic microliter pipette (Biohit, ePet, 0.2-10 µL) was used as a reference system to judge the quality of the DOD dosing process in comparison with conventional, commercially available micro volume sampling systems. Therefore it was slightly modified to allow for electronic and vibration-free remote control and it was then mounted above an x,y,z-translation stage, carrying a quartz TXRF sample target. A sample volume of 1 µL of a solution containing 1 mg/L Se (MERCK CertiPUR) (1 ng Se absolute) were transferred onto a quartz disc and the dimensions of the resulting residues were than microscopically investigated. Also, the achievable RSD using this dosing process was determined by TXRF measurements.

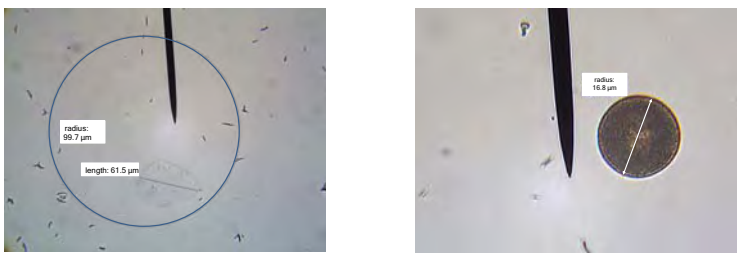

Figure 4: Left: Microscopic images of dried residues. Left: dispensed by a microliter pipette (1 µL droplet, 1 ng Se). Right: dosed by DOD-generator (see above) (5 droplets, delay time 10 s, approx. 1 ng Sr absolute mass).

It was found that the drying process of such relatively high volume of sample solution not just results in irreproducible sizes and locations of the residues but also in irreproducible number of individual residue "island" within the area formally wetted by the droplet (diameter approx. 1.2 mm). Thus, this technique is not recommended for sampling in LA-ICP-MS due to much smaller laser spot sizes combined with corresponding difficulties in localizing the residue (Fig. 4). However, an RSD of 2.8 % was achieved for TXRF analysis because of a much wider x-ray beam diameter of about 7 mm making this approach suitable for calibration in TXRF. In contrast, the precise transfer of pL volumes onto solid targets and the creation of well defined residues regarding their volume and location - as prerequisites for LA-ICP-MS - are also demonstrated in (Fig. 4). The novel DOD generator is therefore suggested as a dosing device for sample preparation in all fields of surface analysis with high spatial resolution, such as LA-ICP-MS.

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.

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