Application of picoliter droplets for calibration and sample preparation in TXRF

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A thin film-thin deposit sample preparation is crucial to ensure an elemental analysis free of matrix effect in TXRF. The drying of large volumes in the microliter range produce unwanted "coffee rings" [1]. An alternative preparation with smaller volumes e.g. picoliter droplets, which usually yield homogenous specimens is achieved by "drop on demand" printing. The good reproducibility of the droplets and deposits allows its use as calibration method [2]. Besides, the picoliter residues have also been used to the study physical interactions of X-rays with the sample [3,4]. Picoliter residues could serve as reference to study various aspects of instrumental performance in TXRF and other techniques e.g. determination of detector signal in dependence of specimens position. This has been studied using microliter volumes [5].

To use picoliter deposits as reference, it is necessary to characterize their performance in terms of: volume per droplet; deposited mass per droplet; contamination effects and precision. Quite a number of parameters have an effect on the volume in each droplet: viscosity; surface energy and boiling point of the solvent. Within a defined matrix, we found the pipette to reliably deliver volumes of 130 – 140 pL. The delivered masses then only depend on the elemental concentration inside the nozzle, which is determined by the initial formulation and the time between two printed droplets referred to as quiettime [6].

In this work a picoliter printer consisting of a commercially available ink-jet cartridge with multiple linear stages and 3d-printed construction parts was build. This composition is capable of printing single droplets and user-defined pattern with defined quiettimes. The performance of the picoliter printer with respect to precisely deliver elemental amounts was evaluated using a table top TXRF instrument (S4 T-Star, Bruker Nano, Berlin, Germany).

Via optical microscopy and atomic force microscopy, a uniform spot-like morphology of the picoliter dried deposits was found. These results are in-line with previous investigations [2]. After the successful characterization of the deposits, they were used with respect to determine the relative sensitivity for a TXRF instrument.

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