

# PICOLITER DEPOSITION FOR MXRF CALIBRATION AND QUANTIFICATION USING PROTOTYPE THERMAL INKJET TECHNOLOGY

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Modified ink jet printers have been used for various purposes, where reliable jetting of small volumes is needed<sup>1</sup>. Just recently this technology has been adapted for analytical chemistry using a modified HP DeskJet printer<sup>2</sup>. In this study an HP picoliter pipette prototype was used called the Thermal Inkjet Pico-Fluidic System (TIPS). Its design allows for easy exchange of solutions for deposition. The device comes with either single volume tips or multiple volume tips. The volume can be software selected in discrete steps between 2 and 220 pL. There are no apparent memory effects from the reservoir tip, yet it can easily be exchanged if this is a concern. In this work different characteristics of the spotted drops and dried residues were examined including volume, diameter of dried droplets and the mass of delivered metal ions. The aim is to show to the extent this device can be used for calibration and quantification purposes in MXRF.

Aqueous single element and multi-elemental standard solutions were used. The droplets were jetted on polypropylene film. An x,y,z stage was used to adjust the distance from substrate to the TIPS and to generate patterns. Two different tip designs were tested, a single volume tip of 220 pL with 16 nozzles and a multiple volume tip with 35 pL, 10 pL, 5 pL and 1 pL with 4 each nozzles.

The actual volume of the droplets was determined by weighing multiple jetted droplets. The diameter of the dried residues was determined with a light microscope and the delivered elemental amounts were determined using MXRF.

The results show that the delivered volumes vary from the nominal given values, for example  $31 \pm 0.5$  pL were found instead of 35 pL and  $199 \pm 16$  pL instead of 220 pL. The diameter of the dried residues covered a size range from  $13 \pm 0.6 \mu\text{m}$  to  $58 \pm 4.9 \mu\text{m}$  using a 10 g/L Ni solution with varying droplet volume. The results from the MXRF analysis show a linear correlation between the count rate and most of the measured volumes with a relative standard deviation between 6 and 12%. The actual mass measured directly by the MXRF is in the 50 pg range for single droplet of 5.3 pL. Preliminary detection limit calculations are 706 fg ( $10^{-15}$ g) for a dried spot size of 19 micrometers and a 100 live second acquisition time using an EDAX Eagle III with a polycapillary optic and excitation spot size of nominally 50 micrometers. A dried spot which would be closer to the excitation spot size would be expected to result in a higher signal-to-noise and therefore potentially lower detection limit.

Additional work is being done to explore different solution depositions along with direct deposition onto a variety of substrates to create direct calibration spots on specimens for quantitative analyses.

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<sup>1</sup> De Gans, B.-J. et al. *Adv. Mater.* (2004), 16, 203-213.

<sup>2</sup> Fittschen, U. E. A. et al. *Anal. Chem.*, in press, 2008.

