Measurement of Mass of Single Inkjet Drops with a Quartz Crystal Microbalance QCM

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Abstract

Monitoring inkjet performance requires control of parameters such as drop velocity, direction and drop volume. Present methods to determine drop volume utilize optical vision systems or calculation of an average drop mass from large numbers of drops on a precision balance.

An alternative technique based on QCM (Quartz Crystal Microbalance) was assessed to measure the mass of single drops. Low-cost plano-convex 6 MHz AT-cut quartz resonators were used to measure single inkjet drops. Since the footprint of these ink drops is of the order 100 µm the QCM detector was used in a 'localized spot' measurement mode in contrast to the typical large area detection mode. The sensitivity of an inner 0.5 mm circle was determined to be 5.46 x 10^{-10} g/Hz for solid silver films.

Single drops of an oil-based ink of 50 pL nominal volume were jetted using a Xaar126 piezo inkjet printhead onto the QCM target area and produced signals with a SNR better than 70:1. This paper presents the technical challenges relating to liquid droplet volume measurements using higher frequency oscillators.

Introduction

Inkjet printing showed to be a viable alternative to commonly used coating and deposition techniques, due to its low volume nature in combination with high ejection frequencies, its high efficiency especially with respect to precious materials and its full digital nature. While drawbacks, such as lateral resolution as well as throughput are counteracted by appropriate waveform design as well as stacking concepts, drop volume and respectively also droplet velocity consistency was only lately considered with respect to cross-talk phenomena [1], originating from the structural design and the fluidic crosstalk resulting from the share manifold design used in printheads with high nozzle density.

While the effect of varying droplet volumes ejected from a nozzle were not yet considered highly critical, emerging applications are narrowing the specifications, as the application of biological tracers or semiconducting materials calls for ever lower amounts of functional material with higher accuracy. QCM measurements offer the possibility to provide the data for both scenarios, the droplet volume ejected from the printhead and the material loading after evaporating the carrier needed for the adaptation to the viscosity requirements of the printhead.

Measuring liquids was discussed in the literature with respect to fully immersed crystals or droplet measurements utilizing several µL of fluid samples, in order to investigate viscoelastic properties of the fluids, wetting characteristics relating to surfactants or the adsorption of molecules. Measuring the dried functional material on the surface of a crystal was extensively studied in the literature.

Localized Quartz Crystal Microbalance (LQCM)

It was recently [2] demonstrated that the mass sensitivity of any mass measuring device depends on the acceleration acting on the measured mass. By associating the acceleration with the field intensity the mass sensitivity will be related to the intensity of the field acting on the measured mass. In case of the quartz crystal microbalance a harmonic inertial field is created at the crystal surface during vibration. The maximum value of the acceleration of the harmonic motion is million times higher than the gravitational acceleration and, thus, the intensity of the harmonic inertial field is million times higher than the intensity of the gravitational field.

On the surface of a quartz crystal resonator the field intensity has a Gaussian distribution with the maximum at the centre of the quartz resonator disk. The localized quartz crystal microbalance is using only a very small area at the centre of the quartz resonator disk in order to achieve a higher sensitivity on the location with the highest intensity of the harmonic inertial field. The local mass sensitivity can be experimentally measured by vacuum deposition of a small spot of metal. Using common AT-cut resonators, plano-convex, 14 mm in diameter with a fundamental frequency of 6 MHz, the measured localized sensitivity was k=5.45776x10^{-10} g/Hz for a spot diameter of 0.5mm and k=7.853982x10^{-10} g/Hz for a spot diameter of 1mm. When the entire mass sensitive area with a diameter of about 6mm is coated the mass sensitivity is k=6.1988x10^{-9} g/Hz. It results that the mass sensitivity can be an order of magnitude higher than the theoretical sensitivity of 6.1988x10^{-9} g/Hz, when it is used only within a small diameter of about 0.5 mm on the central part of the quartz resonator.

Measuring fluidic samples is further complicated by the dissipation of energy in the fluid, which introduces an exponential decay of the shear wave amplitude with increasing penetration into the liquid sample. As a result only a small portion of the sample will mathematically respond to the shear motion introduced at the crystal-liquid interface. The fraction resonating can be represented by the decay length given by

$$\delta = \sqrt{\eta_l / (\pi f_q \rho_l)} \quad (1)$$

where δ is the decay length, η_l is the dynamic viscosity of the fluid, ρ_l is the density of the sample and f_q is the frequency of the crystal. Using η_l of 10 mPa.s, ρ_l of 1 g/ccm and f_q of 6 MHz results in a decay length δ of 728 nm, which implies that most of the deposited volume lies outside the penetration depth and will not be reflected directly by the measurement

Experimental

The experiments presented were performed using a Xaar126-50 pL printhead utilizing an unpigmented oil ink (Toyo, US). Printing was carried out on an X-Y-stage performing with 1 µm positioning accuracy. Alignment was carried out using a DinoLite digital microscope. In order to discriminate single droplet events, jetting frequencies were kept below the readout frequency of the system. This, furthermore, allowed the suppression of deviations such as *second-drop-slow*-phenomena and in-channel crosstalk.

A QCM system comprising an AT-cut, plano-convex resonator with a diameter of 14 mm and a fundamental frequency of 6 MHz (QCMLab, Järfälla, Sweden) was mounted on the moveable stage, connected to a designated resonator/frequency counter circuit. The readout system was designed to have a frequency of 1 Hz. The frequency data was supplied to a custom program to be analyzed for the frequency shifts introduced by the droplet deposition.

Results

Crystal Current

Single droplets of 50 pL nominal volume were applied to the crystal center at a repetition frequency of 0.05 Hz. Figure 1 shows the dependence of the apparent detection of a droplet as a function of time *versus* the crystal current supplied to the system. It was shown that low crystal currents resulted in fuzzy droplet detections with varying frequency shifts even though the same mass/volume was applied. The variance of the system, furthermore, did not allow for a correct detection of droplets. The variance of the detected signal was clearly related to the applied current, as this correlated to the *acceleration* of the crystal surface in contact with the fluid. It, therefore, modulated the amplitude of the shear wave at the top surface and did alter the conditions described by Equation (1).

All of the experiments showed a similar initial detection phase, which was characterized by a fairly linear decay during the first 10 deposited droplets. Towards higher currents the detection stabilized, resulting in more reproducible measurements up to 0.75 µA, which is the maximum current applicable in the system. Using this setting a stable measurement was established, showing a strong linear decay, followed by what appeared to be a resonance at a deposited volume of approximately 500 pL and a stable frequency shift up to 80 droplets before the trace became more noisy and decreased towards a zero frequency shift.

Repeatability and Time-Dependent Behavior

Figure 2 shows an overlay of 10 measurements using a crystal current of 0.75 µA and a repetition frequency of 0.1 Hz. The initial phase of the detection showed good reproducibility with a linear decay of the frequency shift with 5.78 Hz per droplet (cf. Figure 1 (a)). Beyond this initial phase the course of the frequency shift deviated reproducibly from the expected behavior. While the increasing fluid volume available for dampening of the crystal motion as well as departure from the high sensitivity mass region in the center of the crystal, would suggest a decrease in the

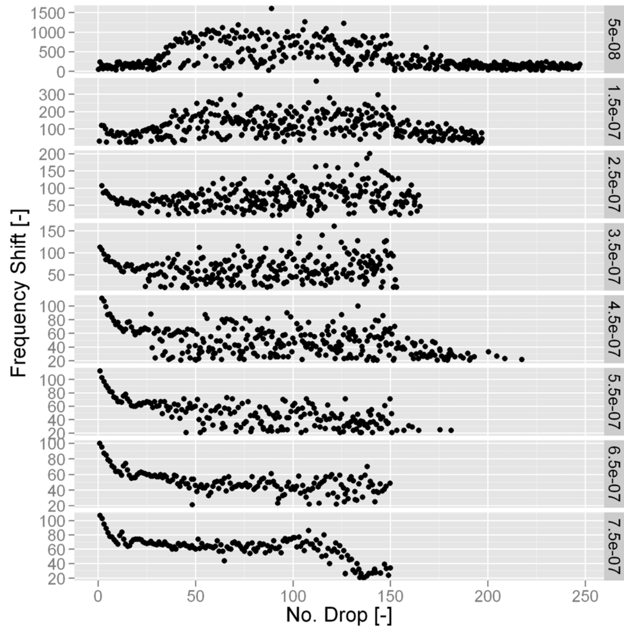

Figure 1: Influence of the crystal current on the consistency of the droplet detection

frequency shift intensity, i.e. lower detected mass values, two subsequent local maxima were detected, which were reproducible for all the measurements. This first maximum was found at approximately 1 nL droplet volume and exhibited a rather low increase of the frequency shift value of 10 Hz. The second maximum was found at a deposited droplet volume of 5 nL and represents the peak of a continuous increase from 100 to 160 Hz without increasing the volume supplied from the printhead. Subsequently the detected mass linearly decreased towards zero and provided no further information.

Altering the repetition frequency during the experiments yielded the graphs in Figure 3. The values were normalized to the signal of the first droplet applied to emphasize the changes. Low repetition frequencies showed a less steep reduction during the initial phase, indicating the spreading dynamics of the droplet being a driving force for the deviating characteristics. As the time between droplet depositions was increased, wetting phenomena allowed for further spreading of the droplet before deposition of the subsequent droplet. The larger area wetted by the previous droplets may give rise to a stronger dissipation of the kinetic energy of the impinging droplet and therefore reduce the advancement of the contact line. The location of the maxima appeared also to be influenced by the droplet application frequency. The number of droplets needed for the generation of a maximum was inversely proportional to the ejection frequency of the printhead and showed saturation towards 0.0125 Hz.

The second maxima was absent in the experiments with repetition frequencies of 0.0125 and 0.025 Hz. 0.05 Hz showed a slight increase with higher noise towards at droplet counts higher than 100.

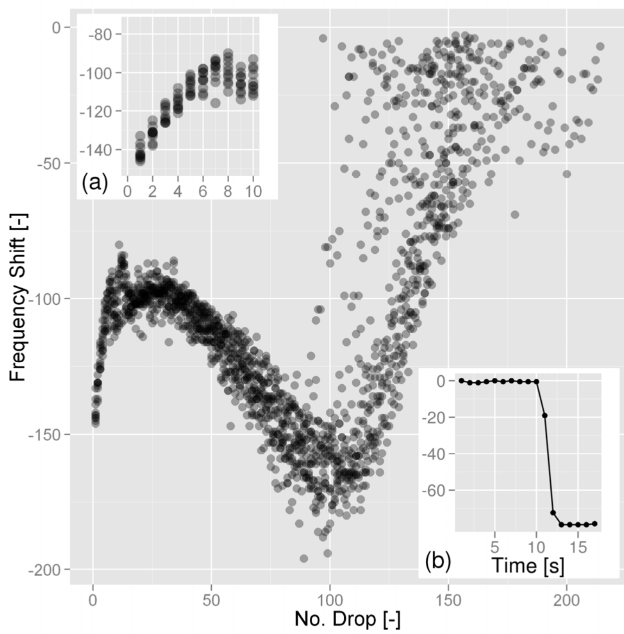

Figure 2: Repeatability of a QCM detection of 50 pL droplets ejected every 10 seconds [nominal number 150 droplets, 10 repetitions] - inset: (a) repeatability of the measurements for the first 10 droplets; (b) time dependent signal for a single droplet detection)

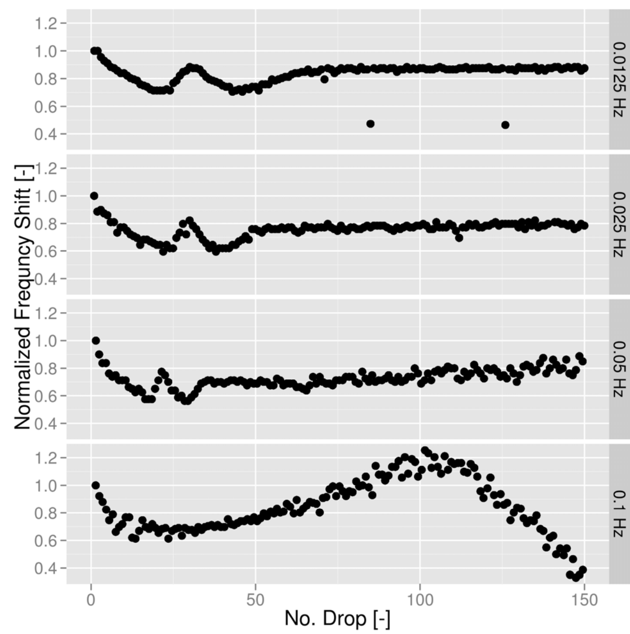

Figure 3: Influence of the repetition frequency on the frequency shift introduced by a 50 pL droplet

As the clear dependency on the time between two subsequent droplet impacts was observed, the resulting effect may be attributed to the intermediate wetting of the crystal and, hence, the conformation of the resulting droplet. The lateral as well as the height conformation of the droplet may be of importance for the interpretation of the phenomena. König et al. [3] described the temporal evolution with respect to the complex frequency shift $\Delta f + i\Delta\Gamma$ and showed that the change in contact area may trigger changes in $\Delta f/\Delta\Gamma$ and thereby time dependent frequency shifts. McKenna et al. [4] additionally attributed certain resonances as a result of interference of compressional waves resonating inside the droplet, with the height of the droplet affecting the constructive or destructive interference pattern.

Conclusion

The basic applicability of localized quartz crystal microbalance measurements for the assessment of droplet consistency in functional deposition was investigated. The very high relative measurement accuracy (cf. Figure 2 (b)) was shown to be available for volume monitoring. The absolute mass accuracy, however, could currently not be exploited due to the shear wave dissipation in the fluid and the resulting detection limits of the system.

It was established that high crystal currents allow for reproducible measurements due to the increased shear wave amplitude, which counteracts the strong damping from the applied liquid. Repeatability was studied and found to be within ±10% for the first 50 droplets deposited.

Multi-droplet measurement greater than 10 droplets was found not to be linear but time and volume dependent. While the repeatability study concedes the application due to a defined effect, precise reasons for this behavior were not yet fully understood.

References

[1] W. Voit, "Evaluation of Crosstalk Effects in Inkjet Printing with Xaar 1001", Proc. NIP27 (IS&T, Minneapolis, MN, 2011).

[2] V. M. Mecea, Is quartz crystal microbalance really a mass sensor? Sensors and Actuators A, 128 (2006) 270-277.

[3] A. M. König et al., "Measurements of Interfacial Viscoelasticity with a Quartz Crystal Microbalance: Influence of Acoustic Scattering from a Small Crystal-Sample Contact", Langmuir (22), (2006).

[4] L. McKenna et al., "Compressional acoustic wave generation in microdroplets of water in contact with quartz crystal resonators" J. Appl. Phys. (89), (2001).

Author Biography

Ingo Reinhold graduated in micromechanics-mechatronics with emphasis on print- and media technology from Chemnitz University of Technology in 2008. After joining Xaar's Advanced Application Technology group in Järfälla, Sweden, he focused on advanced acoustic driving of piezo-type inkjet printheads alongside with pre- and post-processing of functional materials in digital fabrication. He is currently enrolled as a PhD student within the iPack VINN Excellence Center at the Royal Institute of Technology (KTH) in Stockholm, Sweden.