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A Low-Cost, Normally Closed, Solenoid Valve for Non-Contact Dispensing in the Sub-µL Range

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Abstract: We present a disposable, normally closed, non-contact dispensing valve for the sub-µL range. The miniaturized solenoid valve (diameter: 8 mm, height: 27.25 mm) is compatible to standard Luer-Lock interfaces. A highly dynamic actuation principle enables opening times down to 1 ms. The dispensing performance was evaluated for water (η = 1.03 mPas) and a 66% (w/w) glycerol/water solution (η = 16.98 mPas), at pressures varying from 200 to 800 mbar. The experimentally determined minimal dispensing volume was 163 nL (CV 1.6%) for water and 123 nL (CV 4.5%) for 66% (w/w) glycerol/water. The low-cost polymer valve enables high precision dispensing of liquid volumes down to the lower end of the sub-µL range comparable to high-end non-disposable micro-dispensing valves.

Keywords: non-contact dispensing; solenoid valve; normally closed; disposable

1. Introduction

Valves are common fluid flow control components which are used in many macro- and microfluidic applications. They are used to regulate and switch liquid flows in continuous flow devices [1,2] or for ejection of droplets or jets in non-contact dispensing applications [3]. Such dispensing valves are facing demanding requirements in terms of minimal volume and volumetric precision and accuracy [3,4]. Especially for biomedical applications, dispensing valves usually need to be normally closed, requiring rather complex closing or return mechanisms. Additionally, the avoidance of cross-contamination is crucial giving preference to non-contact dispensing systems that transfer liquids as free flying jets or droplets. To eject free droplets or jets of small volume, the dispensing valve needs to feature high dynamics to overcome surface tension and viscous dissipation.

Piezo actuated or solenoid dispensing valves are the preferred technologies to address these requirements, due to their highly dynamic and precise behavior [5,6]. Most of the commercially available systems feature complex and expensive designs, materials and actuation mechanisms and therefore need to be cleaned and reused many times. Such washing procedures are expensive, decrease throughput and increase the risk of cross-contamination.

We have developed a dispensing valve addressing these requirements and overcoming the limitations described above. That is to say, we developed a highly dynamic and precise dispensing valve which features a very simple (*i.e.* disposable) normally closed design. The solenoid actuation principle features opening times down to 1 ms, depending on the viscosity of the liquid to be dispensed and is therefore well-suited for non-contact dispensing of small volumes. The valve is normally closed by a simple and effective ferromagnetic closing mechanism. Due to the simple design and the low-cost materials, the valve presented hereafter can be considered as a disposable enabling carry-over free liquid dispensing without expensive and time-consuming washing steps.

2. Working Principle

The disposable part of the solenoid valve consists of the main elements as sketched in Figure 1: A valve body containing a ferromagnetic plunger that can engage with a valve seat to close the nozzle. The valve is normally closed, *i.e.* when no electrical current is applied to the actuating coil the ferromagnetic ring magnet attracts the ferromagnetic plunger and pulls it downwards to close the valve (see left hand side of Figure 1). The inlet of the valve is pressurized at a constant actuating pressure level of typically 200 to 1000 mbar, which are typical values to drive dispensing valves. This actuating pressure is released when the valve is opened. Opening is achieved by moving the ferromagnetic plunger upwards to open the upper end of a metal capillary, which forms the valve seat. To achieve this, an electrical current is applied to the actuating coil which induces a magnetic field to overcome the attractive force of the two permanent magnets to open the valve (see right hand side of Figure 1).

The electrical current has the form of a peak and hold signal [7], as depicted in Figure 2, to reduce energy consumption and Joule heating of the valve. The signal starts with a peak current (I_{peak} = 10 A), which is reduced to a hold current (I_{hold} = 2.7 A) after t_{peak} = 5 ms. For actuating times smaller than 5 ms no hold current is applied.

Figure 1. Working principle of the dispensing valve. Left: In its normally closed state, the ring magnet attracts the plunger and the valve seat is closed. Right: The actuating coil overcomes the attractive force between the ring magnet and the plunger to open the valve.
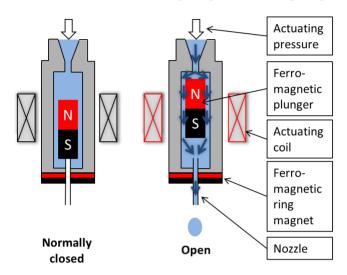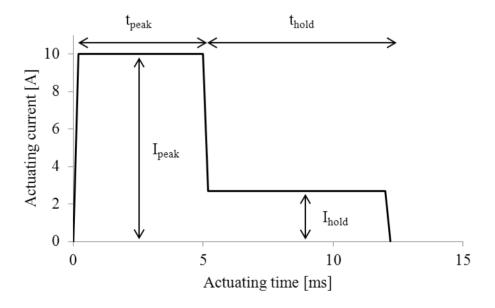

Figure 2. Scheme of the peak and hold actuation pulse, adapted from [7]. The peak current is 10 A and the hold current is 2.7 A. The duration of the peak current does not exceed 5 ms.

Applying a high peak current at the beginning of the actuation pulse allows for a dynamic movement of the plunger. This elevated peak current is important especially at the beginning of the pulse, where the inductivity of the solenoid in addition to the attractive force of the magnets needs to be overcome. The lower hold current reduces heat coupling effects that can lead to heating of the reagent, decreasing its viscosity, which results in higher flow rates and thus a reduced accuracy and precision.
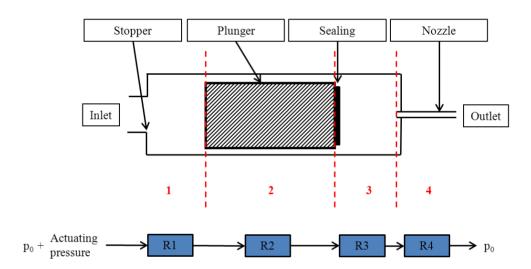
It should be mentioned that the actuation time (*i.e.* the time the coil is energized) does not necessarily equal the opening time of the valve. Especially for very small actuation times (e.g. <10ms),

the precise control of the time delay between the electrical actuating current and the actual opening time of the valve can be very difficult as described by Shvets *et al.* [8]. The effects described hereafter all have this problem of reproducibly defining the actual opening time of a valve in common.

A first source of uncertainty concerning the exact control of the opening time is the soft sealing layer between the plunger and the valve seat (see Figure 3). Since the sealing is compressed while the valve is closed, a movement of the plunger away from the valve seat does not open the valve immediately but with a small but hardly reproducible time delay.

Secondly, the time delay between actuation and opening time depends on the viscosity of the liquid since the liquid has to be displaced for moving the plunger. The viscosity in turn depends critically on the temperature of the liquid. Thus, temperature variations due to e.g. heat coupling effects of the coil (described above) influence the actual opening time also.

Figure 3. Scheme of the different subsections of the dispensing valve and the corresponding fluidic resistances. The total fluidic resistance equals the sum of the individual resistances R1 to R4.

Additionally, the plunger might bounce when hitting against the stopper (valve opens) or the valve seat (valve closes) [8]. Both bouncing movements can affect precision negatively. For a confined range of actuation time, the bouncing of the plunger off the stopper can decrease the actual volume (*i.e.* accuracy) significantly. The bouncing against the stopper imparts a momentum to the plunger which decreases the valve's actual opening time. Accordingly, the bouncing against the valve seat can increase the actual volume and accuracy by opening the valve for an additional amount of time.

Lastly, for very small actuation times, the position of the plunger is very hard to predict or control since it does not move far enough to come at rest against the stopper. Again, this behavior makes a reproducible control of the opening time difficult which diminishes dispensing precision.

The effects described above become more significant for small actuation times or target volumes since the relative timing inaccuracies increase for small actuation times [8].

A vital characteristic of a dispensing valve is its fluidic resistance since it substantially determines the valve's flow rate, *i.e.* the volume which is dispensed per unit of time when the valve is opened. In

order to investigate the effects of mechanical tolerance on the dispensing performance an approximate formula for the flow rate is derived in the following.

The fluidic resistances of the various subsections inside the valve are outlined in Figure 3. Subsection one is located in-between the inlet of the valve and the movable plunger. The fluidic resistance of subsection two is determined by the gap in between the plunger and the body of the valve. Subsection three is located in between the plunger and the upper end of the nozzle. The fluidic resistance of the nozzle equals the fluidic resistance of the last subsection. However, due to the small radius of the nozzle of 100 μm, the total fluidic resistance of the dispensing valve is mainly dominated by the fluidic resistance *R4* of the nozzle, which is given by [9]:

$$R_4 = \frac{8\eta h}{\pi r^4} \tag{1}$$

where *h* and *r* represent the length and the radius of the nozzle and *η* represents the viscosity of the reagent (see also the nomenclature at Table 1). The flow rate *q* is inversely proportional to the fluidic resistance:

$$q \propto (R)^{-1} \propto r^4 \tag{2}$$

which indicates a very strong effect of the geometrical tolerances of the radius of the nozzle on the flow rate and therefore on the volumetric dispensing accuracy as discussed further in the Results section.

Table 1. Nomenclature of the symbols used throughout this paper.

Symbol	Description	SI Base Unit
η	Dynamic viscosity	Pa·s
h	Length of the nozzle	m
I_{peak}, I_{hold}	Amplitude of the peak and the hold current	A
Intra-Run CV	Volumetric dispensing precision within one run	%
L	Number of tips (*i.e.* valves) under evaluation	-
N	Number of single aliquots per run	-
OD	Outer diameter of the nozzle	m
p_0	Ambient pressure	Pa
q	Flow rate	$m^3 \cdot s^{-1}$
r	Inner radius of the nozzle	m
R	Fluidic resistance	$Pa \cdot s \cdot m^{-3}$
Tip-to-Tip CV	Volumetric dispensing precision across different tips	%
t_{peak}, t_{hold}	Duration of the peak and hold current	s
V_n	Volume of one individual aliquot *n*	m^3
$\overline{V}$	Mean volume of a run of *N* consecutive aliquots	m^3
$\overline{V}_{T2T}$	Mean volume of all runs performed with *L* Tips	m^3

3. Design

The valve's modular low-cost design consists of "dry parts" which are not in contact with the reagent and "wet parts" which are contaminated by the liquid to be dispensed (see Table 2).

Table 2. List of components of the dispensing valve, including the approximate material costs.

Component	Source	Application	Approx. Costs
Valve body	Printed (Project HD300, 3D Systems)	Wet part: Contaminated	≈1 $
Plunger	IBS Magnet	Wet part: Contaminated	0.6 $
Sealing	RALICKS	Wet part: Contaminated	0.1 $
Nozzle	Nordson EFD	Wet part: Contaminated	0.8 $
Ring Magnet	IBS Magnet	Dry part: Reused	0.3 $
Coil	Imetron	Dry part: Reused	≈2 $

The dry parts comprise the actuating coil (2.2 Ω, 0.47 mH) and the ring magnet (hard ferrite, 380–400 mT), which functions as a normally closing magnetic attraction mechanism (see Figure 1). The control electronics generating the peak and hold actuating current is custom made with an integrated circuit "LM1949" [10] from Texas Instruments, Inc. as a key element.

The wet parts consist of a two-part valve body, a ferromagnetic plunger and a metal capillary. The valve body is fabricated by 3D printing (material "Visijet EX 200") but is designed to be injection-moldable. It consists of two separate parts which are connected by a thread enabling the insertion of the plunger for an easy manufacturing process of the valve. Beams on the inner wall of the body work as guiding structures for the movement of the plunger which has a travel of 2.3 mm (see Figure 4). The beams allow fluid to flow around the plunger through ducts separating the beams. The gap in between the plunger and the wall of the valve body is 0.45 mm. The inlet of the valve body is equipped with a Luer-Lock thread providing a standard interface for straight forward connections of the valve to e.g. commercial syringes.
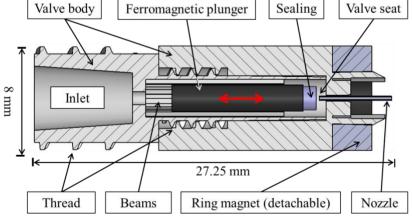
Figure 4. Cross-section through the dispensing valve with the movable plunger (red arrow).
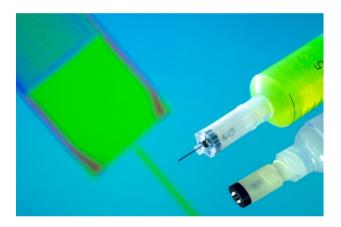

The ferromagnetic plunger (NdFeB, 1170–1250 mT) has a diameter of 2.0 mm and a length of 10.0 mm. It is coated with Parylene C to ensure biocompatibility. A circular piece of silicone or EPDM (ethylene propylene diene monomer (M-class) rubber, OD × h = 1.8 × 1.0 mm) is attached to the lower end of the plunger forming the sealing layer at the valve seat. The durometer of the sealing can be varied between 50A to 70A depending on the specific dispensing application. The best results were obtained with a durometer of 60 A. The ring magnet at the very end of the valve is attached to the

valve body by a simple clipping fixture (see Figure 4). It is therefore detachable and can be reused since it is not contaminated by the liquid.

The metal capillary has an inner diameter of 0.2 mm and a length of either 16.5 mm or 5.5 mm (see Figure 5). The shorter nozzle is the standard nozzle which is also suitable for dispensing high viscosity fluids (up to *ca*. 30 mPas). The longer nozzle is suitable for dispensing e.g. low viscous fluids or is used when aspiration of liquid is desired. The upper end of the metal capillary protrudes beyond the valve body by 0.5 mm and forms the valve seat. The lower end functions as the nozzle of the valve.

Figure 5. The dispensing valve with its black ring magnet attracting the inner plunger to its normally closed position. Foreground: two valves mounted on commercial syringes. Upper valve: long nozzle (16.5 mm) and external ring magnet fixture. Lower valve: short nozzle (5.5 mm) and ring magnet attached by clamping fixture. Background: a screenshot of numerical simulations of the fluid dynamics within the valve as presented in [11].
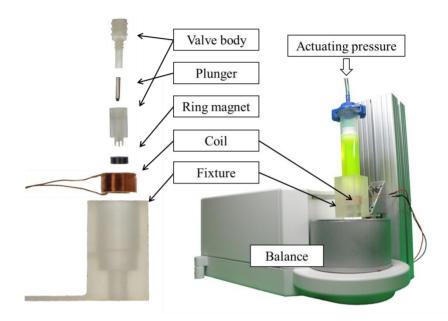

4. Experimental Trials

4.1. Experimental Set-up

Experiments presented hereafter were performed with a nozzle of the length $h = 5.5$ mm and with EPDM (durometer 60A) as the sealing material. We used a polymer syringe from Nordson EFD Deutschland GmbH [12] as the liquid reservoir in combination with a pressure connection as shown in Figure 6. Due to the standard Luer-Lock thread at the inlet of the valve, the valve can be connected easily to such commercial components and utilized straightforwardly.

Figure 6. Left: exploded view of the dispensing valve and the fixture for the valve. Right: the gravimetric measurement set-up with a commercial polymer syringe as the liquid reservoir.

The dispensing performance has been characterized with water (η = 1.03 mPas) and 66% (w/w) glycerol/water solution (η = 16.98 mPas). The pressure was set to 200–400 mbar for water and 800 mbar for glycerol to compensate for the higher viscosity.

The dispensed volume was measured gravimetrically using the "Gravimetric Regression Method (GRM)" as described by Liang *et al.* [13]. The measurement method compensates for evaporation of liquid during the measurement on the basis of a linear regression analysis of continuously monitored gravimetric results. We used a XP2U/M micro balance from Mettler Toledo, Inc. (see Figure 6.) which provides readability down to 0.1 µg corresponding to a droplet volume of 0.1 nL for water at standard conditions. The GRM has an evaluated measurement uncertainty at standard conditions of <13.4 nL [13] for the target volume range of the experiments presented hereafter.

4.2. Performance Parameters

The dispensing valve was characterized on the basis of performance parameters, as proposed by Bammesberger *et al.* [3]. Each data point of Figures 7 and 8 represents the mean volume $\overline{V}$ of one run of $N = 24$ individually measured aliquots V_n:

$$\overline{V} = \frac{1}{N}\sum_{n=1}^{N} V_n \tag{3}$$

The "*Intra-Run CV*" [3] of the respective run:

$$Intra-Run\,CV = \frac{\sqrt{\frac{1}{N-1}\sum_{n=1}^{N}(V_n - \overline{V})^2}}{\overline{V}} \tag{4}$$

represents the coefficient of variation (CV) of the volume of N aliquots of a run. The variation across $L = 4$ different dispensing valves is evaluated by the "*Tip-to-Tip CV*" defined as [3]:

$$Tip - to - Tip\, CV = \frac{\sqrt{\frac{1}{L-1}\sum_{l=1}^{L}(\bar{V}_l - \bar{V}_{T2T})^2}}{\bar{V}_{T2T}} \tag{5}$$

whereby $\bar{V}_l$ represents the mean volume of one run with one valve l and $\bar{V}_{T2T}$ represents the mean volume of all runs performed with $L = 4$ valves. The *Tip-to-Tip CV* measures the volumetric precision of the different valves' mean volume if all parameters (actuation time and pressure) are kept constant. Thus, it evaluates the influence of the fabrication tolerances, in particular variations of the inner diameter of the nozzle, on the dispensing accuracy of the individual valves as described in Section 2.

5. Results and Discussion

5.1. Volume Range and Linearity

The actuation time of the coil (*i.e.* $t_{peak} + t_{hold}$; see Figure 2) was varied between 1 to 100 ms. The measured volume ranged between 163 nL to 11.4 μL for water and 123 nL to 6.6 μL for 66% (w/w) glycerol. The correlation of the measured volume to the actuation time was very linear for the complete volume range with $R^2 = 0.9957$ for water and $R^2 = 0.9917$ for glycerol as shown in Figure 7. For actuation times <10 ms (see Figure 8) the coefficient of determination was $R^2 = 0.8395$ for water and $R^2 = 0.9977$ for glycerol. The decrease of linearity for water at small actuation times can be attributed to the challenge of defining the actual opening time precisely. Especially the reduced actual volume in-between 2 to 6 ms could result from the plunger bouncing off the stopper as described above. The linearity of glycerol is not affected since the bouncing movement is dampened significantly by the higher viscosity.

5.2. Intra-Run CV

The dispensing valve showed a highly precise dispensing performance with *Intra-Run CVs* prevalently below 1.0% for volumes >2 μL (see Figure 7) and prevalently below 8% for volumes in the range of 0.1 to 2 μL (see Figure 8 and Table 3).

Two outliers in terms of a high *Intra-Run CV* at 280 nL (*Intra-Run CV* = 22.0%) and at 157 nL (*Intra-Run CV* = 24.2%) can be explained by the absence of the very first aliquot for the respective runs, *i.e.* no liquid was ejected in these first dispenses at all.

The *Intra-Run CVs* at the smallest volumes were 1.6% for water at 163 nL and 4.5% for glycerol at 123 nL. Hence, the dispensing valve enables high precision dispensing of liquid volumes down to the lower end of the sub- μl range comparable to high-end non-disposable micro-dispensing valves [3].

5.3. Tip-to-Tip CV

The *Tip-to-Tip CV* of four different tips was 14.7% or 150 nL (at a mean volume of 1.02 μL, see Table 3) revealing considerable variations of the flow rate for different valves due to fabrication tolerances of the nozzles.

Figure 7. The dispensed volume in dependence of the actuation time for water (blue squares) and glycerol (red crosses). Each data point represents one run of 24 individually measured aliquots. Percentages and corresponding error bars (too small to be visible in this figure) state the respective *Intra-Run CV*.
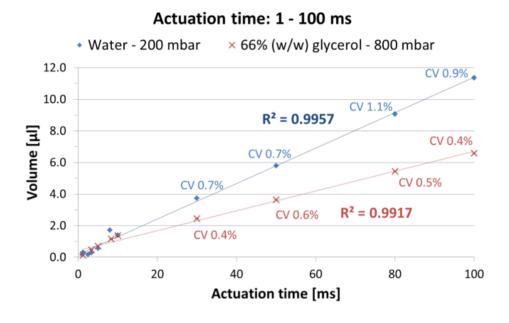

Figure 8. Detail of Figure 7 for actuation times ≤10 ms. The measured minimum volume was 163 nL for water (*Intra-Run CV* 1.6%) and 123 nL for glycerol (*Intra-Run CV* 4.5%).
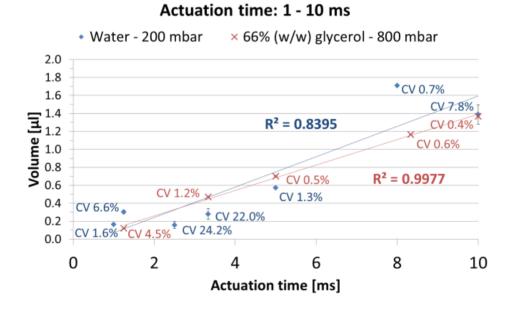
Table 3. Tip-to-tip experiments with $L = 4$ different valves. The runs were performed with water at a pressure of 400 mbar with an actuating time of 5 ms. The mean volume of all four valves is 1.02 μL, with a *Tip-to-Tip CV* of 14.7%.

	Valve $l = 1$	Valve $l = 2$	Valve $l = 3$	Valve $l = 4$	*Tip-to-Tip CV*
Volume $\overline{V}_l$ (μL)	1.16	1.07	0.83	1.02	$\overline{V}_{T2T} = 1.02$
Intra-Run CV	1.9%	2.4%	5.7%	2.2%	**14.7%**

The diameter of the used nozzles is specified with fabrication tolerances of ±10 μm. According to Equation 2, this corresponds to an expected variation of flow rate in between $q_{min} = -18.6\%$ to $q_{max} = +21.6\%$, which matches well with the experimental *Tip-to-Tip CV* of 14.7%. Thus, the volumetric variation across different valves is mainly attributed to the mechanical tolerance of the nozzle diameter. The dispensing accuracy could be improved e.g. by injection molded nozzles with low tolerances or by individual calibrations of each valve.

5.4. Variation of Nozzle Length

For some applications, e.g. for the aspiration of reagents out of Microtiter plates, an elongated nozzle length can be necessary. Equations 1 and 2 imply that the flow rate q is expected to be inversely proportional to the nozzle length h. In Table 4, the flow rate of water for a nozzle length of $h = 16.5$ mm is compared to a nozzle having a third of the length ($h = 5.5$ mm). The experiments are in good accordance with the theory. Hence, the characteristics of the valve in terms of its flow rate and functionality can be adjusted to specific applications by varying the length of the nozzle according to Equation 2. Nevertheless, the results of Subsection 5.3 and 5.4 indicate that each valve must be calibrated individually in order to dispense a specific liquid accurately.

Table 4. Experimental evaluation of the flow rate q of water at different nozzle lengths h, and actuating pressures.

	$h = 16.5$ mm	$h = 5.5$ mm
Pressure: 0.2 bar	$q = 48$ μL/s	$q = 125$ μL/s
Pressure: 0.4 bar	$q = 88$ μL/s	$q = 232$ μL/s

It should be noted, that due to the linear increase of the fluidic resistance for a longer nozzle, the required minimal actuating pressure for dispensing high viscous liquids increases also. For 66% (w/w) glycerol solution the minimal pressure required for ejecting a free droplet increased from 0.7 to 1.3 bar when the nozzle length was increased from 5.5 mm to 16.5 mm.

6. Conclusions

We have presented a normally closed, non-contact, solenoid dispensing valve for the sub-μL range. Combining simple polymer parts (valve body) and permanent parts (electric coil) in a modular way, this valve has the potential to be used as a disposable valve while providing similar performance like high-end non-disposable valves. The *Intra-Run CV* primarily was below 1% for volumes >2 μL and below 8% for volumes in the range of 0.1 to 2 μL. The *Tip-to-Tip CV* was 14.7% at 1.0 μL, indicating

a strong influence of fabrication tolerances of the nozzle on the flow rate of the valve and the necessity to calibrate the valve for a specific application. However, such a dependency of the accuracy on mechanical tolerance applies to any dispensing valve design and is not specific to the presented valve only.

The modular injection moldable design allows for low-cost fabrication and disposable use of all liquid-contaminated components. Thus, elaborate washing procedures are obsolete and cross-contamination is prevented effectively. Its compact design (8 × 27.25 mm) and the standard Luer-Lock interface enable straightforward integration and microdispensing with high precision down to the sub-μL range for a wide range of applications such as for example reagent dispensing for medical diagnostic assay preparation.

Acknowledgments

References

1. Sia, S.K.; Whitesides, G.M. Microfluidic devices fabricated in poly (dimethylsiloxane) for biological studies. *Electrophoresis* **2003**, *24*, 3563–3576.
2. Oh, K.W.; Ahn, C.H. A review of microvalves. *J. Micromech. Microeng.* **2006**, *16*, R13–R39.
3. Bammesberger, S.; Ernst, A.; Losleben, N.; Tanguy, L.; Zengerle, R.; Koltay, P. Quantitative characterization of non-contact microdispensing technologies for the sub-microliter range. *Drug Discov. Today*, **2013**, in press.
4. Dunn, D.A.; Feygin, I. Challenges and solutions to ultra-high-throughput screening assay miniaturization: Submicroliter fluid handling. *Drug Discov. Today* **2000**, *5*, 84–91.
5. Niles, W.D.; Coassin, P.J. Piezo- and solenoid valve-based liquid dispensing for miniaturized assays. *Assay Drug Dev. Technol.* **2005**, *3*, 189–202.
6. Fanwei, K.; Zheng, Y.F.; Weidong, C. Automatic liquid handling for life sciences - A critical review of the current state-of-the-art. *IEEE Int. Conf. Robot. Biomim.* **2009**, 480–486.
7. Amirante, R.; Innone, A.; Catalano, L.A. Boosted PWM open loop control of hydraulic proportional valves. *Energy Convers. Manage.* **2008**, *49*, 2225–2236.
8. Shvets, I.; Makarov, S.; Shvets, A.; Osing, J. LIQUID DROPLET DISPENSING. U.S. Patent US 6,669,909 B2, 30 December 2003.
9. *Encyclopedia of Microfluidics and Nanofluidics*; Li, D.Q., Ed.; Springer: New York, USA, 2008.
10. LM1949 Injector Drive Controller, 2008. Texas Instruments, Inc. Web site. Available online: http://www.ti.com/lit/ds/symlink/lm1949.pdf (accessed on 13 November 2012).
11. Mutschler, K.; Dwivedi, S.; Kartmann, S.; Bammesberger, S.; Koltay, P.; Zengerle, R.; Tanguy, L. Multi physics network simulation of a solenoid dispensing valve. To be submitted for publication.
12. Nordson EFD Optimum Datasheet. Nordson Corporation Web site. Available online: http://www.nordson.com/de-de/divisions/efd/Literature/Brochures-Data-Sheets/Optimum/DE-Nordson-EFD-Optimum-DataSheet.pdf (accessed on 15 November 2012).

13. Liang, D.; Steinert, C.; Bammesberger, S.; Tanguy, L.; Ernst, A.; Zengerle, R.; Koltay, P. Novel gravimetric measurement technique for quantitative volume calibration in the sub-microliter range. *Meas. Sci. Technol.*, **2013**, 24, doi:10.1088/0957-0233/24/2/025301.