Development and characterization of a *drop-on-demand* aerosol generator for the introduction of small sample volumes in plasma spectrometry

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Introduction of liquids in plasma-spectrometry - Disadvantages and possible solutions

One recent and major trend in current Analytical Chemistry is related to down-scaling analytical methods an the miniaturization of analytical instrumentation. Among other tasks which have to be addressed in this context, the accurate handling of small reagent and sample volumes is of particular importance, not only in the field of (miniaturized) plasma spectrometry. Hyphenated techniques, based e.g. on the combination of capillary electrophoresis (CE) and plasma mass spectrometry, require additional make-up solvent flows to meet the specifications of conventional systems used for sample introduction into the plasma source.[1] To avoid sample dilution, to minimize the risk of contamination and the degradation of chromatographic resolution a new strategy for direct and flexible introduction of liquid samples is desired.

Prior investigations have shown, that commercially available thermal-inkjet printers can be successfully used for precise handling of small sample volumes.[2] However, such available systems are software-dependent and limited to fixed parameter settings, which is still disadvantageous regarding e.g. flexible volume flows and adjustable droplet diameters.

We present here the development of a microcontrolled stand-alone ink cartridge with full access to all important parameters to the process of droplet generation.

Development of a suitable microcontroller

Usage of self-assembled controllers to drive thermal-inkjet cartridges, offers several advantages compared with conventional inkjet printing systems. One major point is the free access to essential parameters of the droplet formation process, with which the discontinous operation of conventional printing heads (return at the end of line) can be avoided. Tab. 1 shows the four available parameters and their operational ranges of the engineered controller.

Table 1: Free accessible parameters for dosing controller

Dimension	Symbol	Description	Range
time-to-life	TTL	Time between start and stop of the relay	$0.2 - 12\ s\ /\ \infty$
voltage	U	voltage of amplifiing module	12 - 30 V_{DC}
frequency	f_s	resonant frequency of the *Schmitt-Triggers* → drop-frequency	$0.07 - 7.9\ kHz$
pulse width	t_2	width of electric pulses , adjustable independent from frequency	$0.96 - 14.4\ \mu s$ $0.08 - 2.1\ \mu s$

Fig. 1 shows the setup used for driving a stand alone ink cartridge in continuous and time-limited mode.

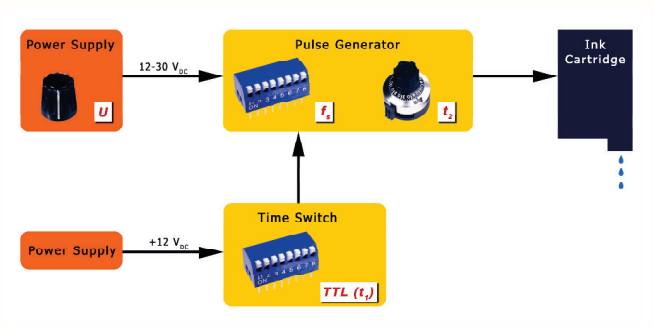

Figure 1: Scheme of the controller, setup for driving a stand alone ink cartridge

Linearity and average droplet volume $\bar{V}_D$

Droplets were generated with the described controller (Fig. 1) using a 1.0 g/L Zn-solution, which was dosed under univariant conditions.

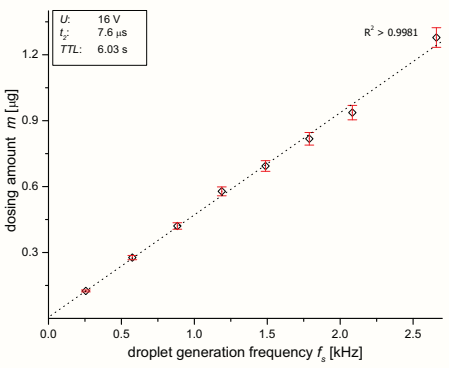

Figure 2: Absolute dosing amount m versus droplet generation frequency f_s

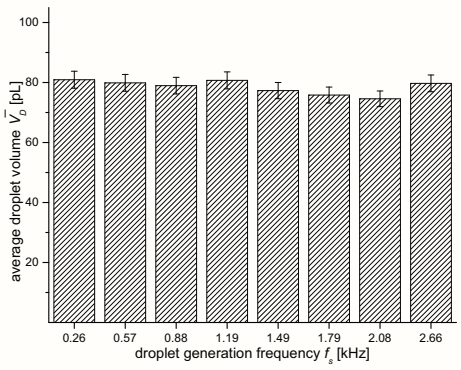

Figure 3: Average droplet volume $\bar{V}_D$ versus droplet generation time f_s

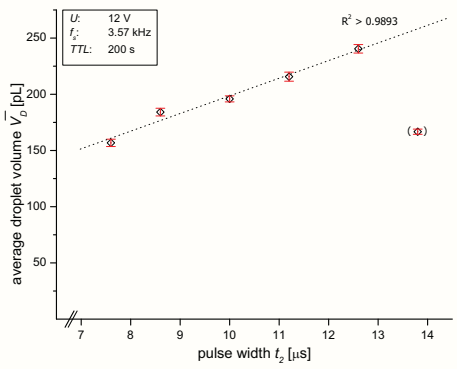

Figure 4: Average droplet volume $\bar{V}_D$ versus pulse width t_2

Fig. 2 shows the linearity between the selected dosing frequency f_s and transfered sample amount m.

Conversion via absolute number of droplets generated, leads to an average droplet volume $\bar{V}_D$, which is plotted in Fig. 3 versus the frequency f_s.

The average droplet volume is independent from the droplet generation frequency f_s (Fig. 3), but is adjustable in contrary to conventional inkjet printers via pulse length t_2 (Fig. 4).

Achievable dosing rate of liquids

To compare the developed system with conventional pneumatic nebulizers, the achievable dosing rate was determined. Therefore, several univariant series of measurements were performed (Fig. 5). The sample amount was converted via the known number of droplets and time of droplet generation TTL into dosing rate Q_L (Tab. 2), which is comparable to the liquid flow rate of pneumatic nebulizers.

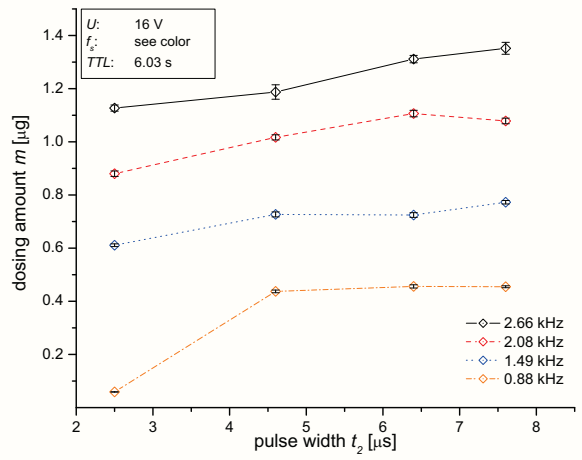

Figure 5: Range of achievable dosing amounts

As Fig. 5 and Tab. 2 show, that a combined variation of pulse length t_2 and frequency f_s, enables access to dosing rates Q_L over a wide range of the μL/min-region. The achievable dosing rates could be maximized by simultaneous usage of mutliple nozzles, up to approx. 0.7 mL/min. The minimal dosing rate is only limited by selected frequency, which has to be an even multiple of the reciprocal integration time of the detecting system, to avoid periodic signal fluctuation. Hypothetically, using a spectral repetition rate of 10 Hz and a droplet generation frequency f_s of 100 Hz with minimal pulse width t_2, will lead to dosing rates Q_L in the nL/min-range.

Table 2: Total achievable range of liquid dosing rates

Settings (c = calculated or m = measured, f_s, t_2)	Dosing rate Q_L [μL/min]
single-nozzle, very low frequency (c, 66 Hz, 4.6 μs)	**0.33**
single-nozzle, medium frequency (c, 0.57 kHz, 6.1 μs)	**2.91**
single-nozzle, moderate frequency (m, 0.88 kHz, 4.6 μs)	**4.35 ± 0.05**
single-nozzle, high frequency (m, 2.66 kHz, 6.1 μs)	**13.5 ± 0.2**
50 nozzles, moderate frequency (c, 0.88 kHz, 4.6 μs)	**217**
50 nozzles, high frequency (c, 2.66 kHz, 6.1 μs)	**675**

Conclusion and Outlook

With the developed microcontroller, droplet diameter and total dosing rate are adjustable. The frequency of droplet generation is tunable over a wide range down to single droplets. Linearity and reproducibility were demonstrated by using ICP-QMS.

The developed microcontroller is capable of driving a stand-alone thermal-inkjet cartridge for *drop-on-demand* generation of very small sample volumes. Particularly, because of the width of the accessible dosing rate over four magnitudes, this system is most suitable for further development of sample introduction systems in coupling techniques from very low to medium flow rates of liquid samples.

Extensive investigations on noise spectra will be performed, as well as the ability for direct aerosol generation avoiding drawbacks well known from pneumatic nebulizers such as e.g. liquid flow rate dependent aerosol formation efficiency and peristaltic pump-based signal fluctuations.

References

[1] Taylor, K., Sharp, B., *et al.*, Design and characteristaion of a microconcentric nebuliser interface for capillary electrophoresis-inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* **1998**, *13*, 1095-1100.

[2] 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.

[3] Massmann, J., Entwicklung und Charakterisierung eines neuartigen *drop-on-demand*-Zerstäubers für die Zuführung kleinster Probenvolumina in der analyitschen Atomspektrometrie, *Diplomarbeit*, Universität Hamburg, **2009**.