Development of a calibration strategy based on the dosing frequency of a *drop-on-demand* aerosol generator for micro-volume sample introduction in analytical atomic spectrometry

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Introduction

Conventional pneumatic nebulization is the most common way of introducing liquid samples into excitation sources in atomic spectrometry, but it is still a major bottleneck due to considerable losses. Well-known drawbacks from the use of these pneumatic nebulizers such as e.g. liquid flow rate dependent aerosol formation efficiency and peristaltic pump-based signal fluctuations are limiting further enhancements. This is especially the case if only minute amount of sample material is available and down scaling of the instrumentation becomes necessary.

The novel approach outlined in this work is based on the development of a micro controlled drop-on-demand (DOD) aerosol generator, which employs a modified thermal inkjet cartridge, offering full access to all parameters important for the droplet generation process of minimum sample volumes. As shown before, our developed system is most suitable for external calibration, while providing improved sensitivity compared to established low-flow nebulizers such as the MicroMist™.[1,2]

DOD/Nebulizer Comparison: Experimental

The developed DOD-system was compared to state-of-the-art pneumatic nebulizers. The used setup details are listed in Tab. 1.

Table 1: Key data of compared systems.

Dual-DOD (HP™-45 cartridge)

- Lab-built aerosol transport chamber, dual gas inlet
- Lab-built dual micro controller with full access to all parameters of droplet generation
- Liquid flow rate (depending on droplet generation frequency): 0.02 - 2.64 µL min^{-1}
- Dual sample design provides dosing of two different solutions at two different flow rates
- Minimum droplet volume: 16 pL

MicroMist™

- Cyclonic spray chamber
- Self-aspirated
- 40-70 µL min^{-1} liquid flow rate

EnyaMist™

- Lab-built total consumption chamber
- sample feed through syringe-pump
- 0.2-50 µL min^{-1} flow rate

DOD/Nebulizer Comparison: Results

The in Tab. 1 described systems were characterized with respect to the achievable absolute sensitivity, detection limit and signal stability (Fig. 1).

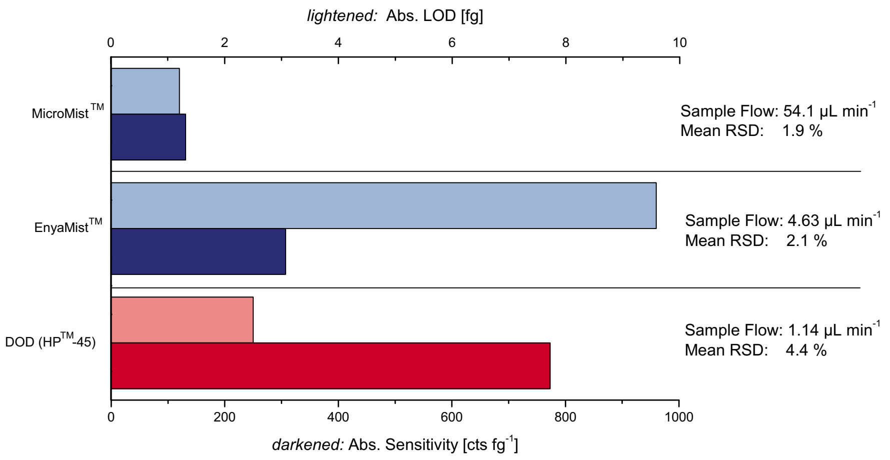

Figure 1: Comparison of analytical figures of merit of different pneumatic nebulizers and the DOD-System as introduced in Tab. 1.

Analysis of CRM: Applicability of DOD-System

To evaluate the applicability of the developed DOD-System a certified reference material (drinking water, CRM-TMDW, High Purity Standards, Charleston, USA) was analyzed employing both, pneumatic nebulizer and the novel DOD-System. The CRM was diluted 1:10 with 2 % nitric acid, the total cation content was 5.7 mg/L, V and Mo were selected as analytes.

Tab. 2 shows the applicability of the novel DOD-System for the analysis of a certified drinking water sample. The achievable precision is of the same order as it is in the case of the used MicroMist nebulizer.

conc. [µg L^{-1}]	^{51}V	^{98}Mo
certified	3.00± 0.02	10.0± 0.05
MicroMist	2.89± 0.24	10.5± 0.70
DOD (I.S.)	2.83± 0.34	10.0± 1.01

Table 2: Analysis of drinking water sample.

Dosing frequency-based calibration: Principle

In contrast to conventional external calibration (Fig. 2), the precise handling of two different sample flow rates through two independent nozzles enables access to a calibration strategy employing only one standard solution.

As the dosing frequency dictates the transferred amount of analyte per time, a calibration function is accessible through varying the dosing frequency. To avoid plasma load effects, a second liquid flow containing purified water is used (Fig. 3). This principle simplifies the calibration process, as e.g. washing steps are no longer needed.

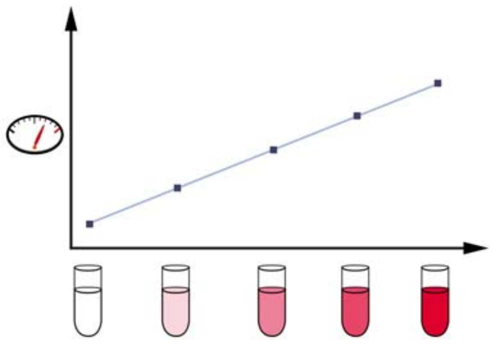

Figure 2: Principle of conventional external calibration: Different standard solution with constant sample flow rate.[3]

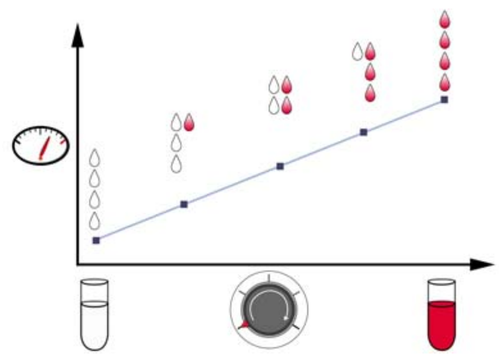

Figure 3: Principle of dosing frequency-based calibration (DFC): Only one standard solution at various flow rates.[3]

Dosing frequency-based calibration: Results

To demonstrate the applicability of the novel calibration strategy a 10 µg L^{-1}solution of Indium was chosen and smapled using various frequencies, while a blank solution was added through a second nozzle to maintain a constant total liquid flow rate.

A clear and linear dependency of the obtained ^{115}In signal on the dosing frequency was achieved (Fig. 4). The recovery rates of solutions spiked with In are examplarily shown in Fig. 5. No systematic deviation was found and the analytical data agree well with the expected values. However, the RSD are slightly higher in case of the DOD-system, as already shown in Fig. 1.

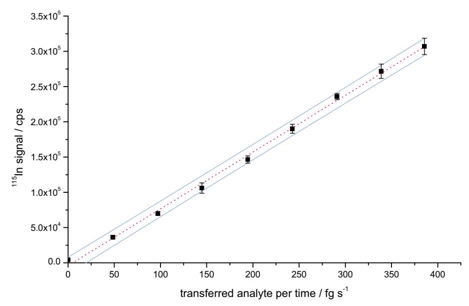

Figure 4: Calibration curve achieved via dosing only one standard solution at different dosing frequencies.

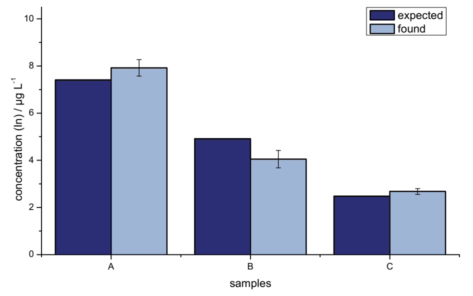

Figure 5: Recovery rates of spiked samples quantificated via dosing frequency calibration.

Conclusion

- The novel drop-on-demand aerosol generator is most suitable for ICP-MS analysis. Its overall performance can compete with state-of-the-art pneumatic nebulizers, while the achievable sensitivity has significantly improved.
- The matrix tolerance is comparable to miniaturized pneumatic nebulizers.
- In addition, our DOD-System is more flexible offering the independent dosing of two different solutions. Therefore novel calibration strategies, like the presented dosing frequency-based calibration are accessible.
- In addition to the improvement of long-term signal stability, further tasks will be the investigation of noise power spectra as well as the application of novel calibration strategies to samples with higher matrix load.

References

[1] Massmann, J.; Diplomarbeit, Universität Hamburg, **2009**.

[2] Massmann, J., Petersen, J.H., Schaper, J.N., Bings, N.H.; 2010 Winter Conference on Plasma Spectrochemistry, Fort Myers, USA (poster).

[3] Orlandini, A.; *Ausgewählte Illustrationen*, Universitätsmedizin Mainz, **2010**.

Acknowledgements

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