Sample Introduction in Atomic Emission Spectrometry (AES)

Different Pneumatic Nebulizers at Comparable Operating Conditions

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Abstract
The atomic emission spectrometry (AES) is a commonly used method to analyse chemical trace elements. The introduction of the liquid sample occurs usually with pneumatic nebulizers. Because only droplets with diameters smaller than 10 µm are valid for this analytical method, the nebulizer must generates a comparatively fine aerosol.

An investigation has been carried out to compare three in AES frequently used pneumatic micro nebulizers (Concentric Nebulizer, V-Groove Nebulizer and Cross Flow Nebulizer [1]) together with two in our laboratory miniaturized pneumatic nebulizers (Prefilming-Swirl-Nozzle (PFDD) and Pneumatic Extension Nozzle (PEN)). The orifice diameter d_O of the five nebulizers varied in a range of 190 µm ≤ d_O ≤ 250 µm. The droplet sizes from the five different nebulizer designs were measured by a Laser-Diffraction-Spektrometer (LDS) and additionally by a Phase-Doppler-Analyser (PDA). It is illustrated that the PEN generated a nearly 3.5-fold larger mass fraction of desired droplets with diameters D < 10 µm as the CPN that is commonly applied in AES. Therefore, an enhanced spectroscopical analysis is expected due to the improved sample introduction by means of the PEN.

Introduction
The AES is currently one of the most capable methods applied for chemical analysis besides chromatography. The atoms of the sample are excited in a high temperature plasma. Thereby, light is emitted from the atoms. This light has a wave length spectrum, that is characteristic for each substance.

The liquid samples are introduced into the excitation source (high temperature plasma e.g.) mostly as an aerosol using pneumatic nebulizers. In order to prevent serious disturbance of the analytical signal the sample has to evaporate completely within the excitation source. Therefore, droplets larger than 10 µm in diameter may not reach the excitation source. Using commonly nebulizers only 10 to 20 percent of the generated aerosol mass have utilizable droplets with diameters smaller than D = 10 µm. Therefore, larger droplets must be removed from the aerosol before introduced into the excitation source. For this purpose a separation chamber is switched between the nebulizer and the excitation source. Finally, only 1 to 2 percent of the sprayed sample mass reaches the excitation source due to the small part of suitable droplets produced by the nebulizer and due to the insufficient separation effect of the chambers.

Aim of the project
The aim of the project is a more effective sample introduction by the enhancement of the atomisation process. I.e. the part of suitable droplets with D < 10 µm has to be increased. Then, a higher mass flux of sample can be introduced into the excitation source after the aerosol passes the separation chamber. This should lead to a shift of the detection limit towards lower concentrations and provides the opportunity of a higher resolution of the analytical signal.
In order to achieve this aim nebulizer designs that are quite new for sample introduction in AES should be established. Therefore, two different nebulizers were miniaturized in our laboratory. The first type is shown in Fig. 1. Based on a work of Glaser [2] the geometry of this modified and thus quite simply to miniaturize Prefilming Swirl Nozzle (PFDD) was first-ever presented in [3,4]. Compared to other pneumatic nebulizers, Prefilming nozzles exhibit a relatively high degree of efficiency at low pressure drops. Prefilming nozzles were intensively investigated by Lefebvre [5] and Wittig [6] e.g.. As shown in Fig. 1, the PFDD is composed of two parts. The swirl chamber is considered as the central unit i.e. comp. No. 2. The liquid is fed from a hole of 200 µm in diameter within comp. No. 1 into the centre of the swirl chamber. Due to the two tangential enties of the gas a

rotating gas flow is generated inside the swirl chamber. The liquid is taken up by the rotating gas flow and is collected on the wall of the swirl chamber as a gas driven wavy film. Below the nozzle orifice with diameter of d_O = 200 µm the liquid film is disintegrated into droplets that are comparatively small to the orifice diameter.

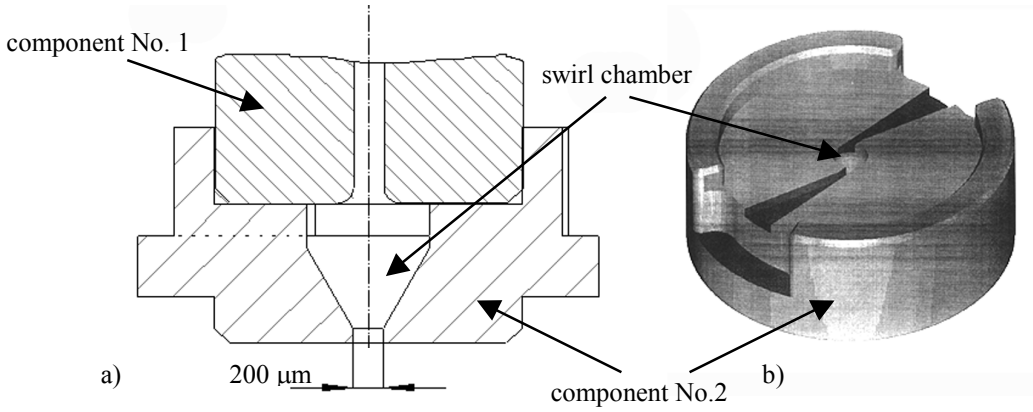

Figure 1. a) 2-D sketch of the modified PFDD; b) 3-D sketch of component No. 2

In addition to the PFDD a further pneumatic nebulizer was miniaturized in our lab. A prototype of this pneumatic extension nozzle (PEN) is shown in Fig. 2b. In the case of PEN a liquid jet emerges from a capillary of d_C = 200 µm in diameter into a chamber pressurized by the gas. The gas discharges from the chamber through an orifice of d_O = 200 µm together with the liquid. Due to the aerodynamic forces of the accelerated gas the liquid jet is constricted and has a structured surface. Within the chamber the jet already disintegrates into ligaments and finally comparatively small droplets are formed. To clarify the flow behaviour an enlarged model of the PEN was operated under similar flow conditions. Fig. 2c shows a spray pattern at the PEN.

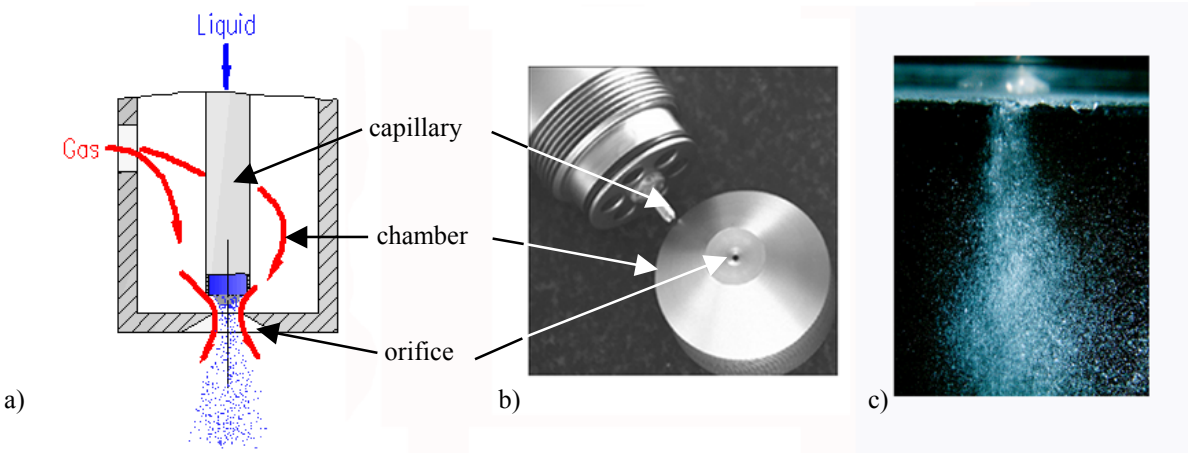

Figure 2. a) Scheme of the PEN; b) Photo of the PEN prototype; c) spray pattern below an enlarged model of the PEN with d_C = 6 mm under hydrodynamic similar flow conditions

A similar method has been already applied in 1966 by Walz [7] to produce rock and glass wool. In order to produce a monodispersed aerosol Gañán-Calvo and Barrero [8] examined laminar capillary microjets, that are disintegrated by the Rayleigh mechanism. Therefore, they have applied a nozzle type similar to the PEN.

Commonly used nebulizers in AES

The mostly used nebulizer is shown in Fig. 3. This Concentric Pneumatic Nebulizer (CPN) is applied in almost 90 percent of all AES devices [9]. The liquid sample is fed to a fine capillary of d_C = 250 µm in diameter at the outlet position. The gas flows coaxial to the liquid through an annular slot with an average width of 20 µm at the outlet position. With the aid of an enlarged and transparent model of the CPN with a capillary diameter d_C = 10 mm the spray formation at the outlet position was observed. A typical spray pattern produced by a CPN is shown in Fig. 4b.

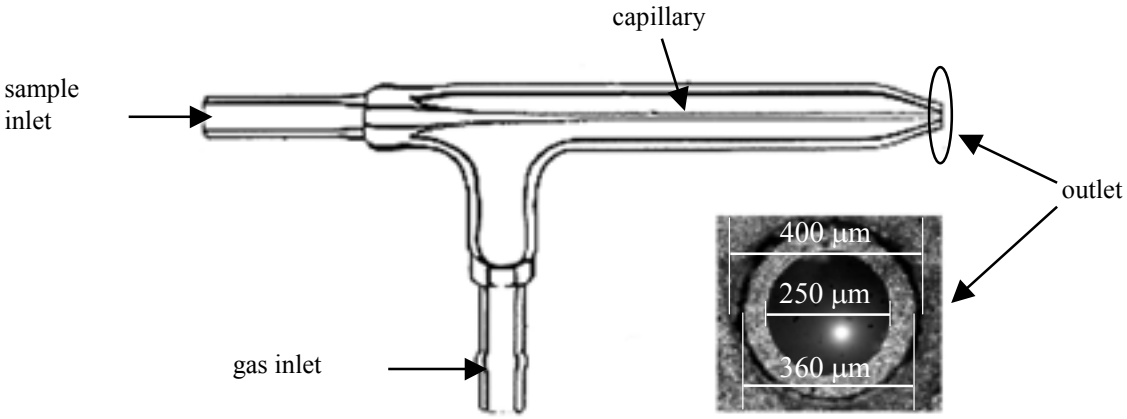

Figure 3. Concentric pneumatic nebulizer CPN most frequently applied in AES

Due to the high gas velocity at the end of the annular slot, and the consequentially induced torus shaped secondary gas flow, the liquid is spread out on the capillary wall, whereby a cyma originates. Therefore, the liquid is discharged from the capillary in comparatively thin ligaments. After a short distance of approximately $L_C \approx d_C$ the ligaments collide centrically below the capillary. This spray pattern produced by an CPN was also observed by Sharp [9]. Apparently, the coalescence of the ligaments leads to an increase of droplet diameter and thus indicates thesubsta ntial drawback of the CPN.

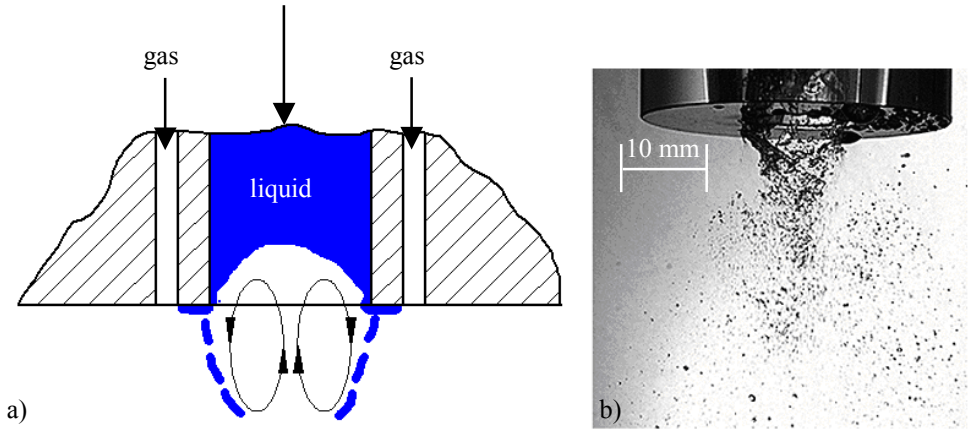

Figure 4. a) CPN with torus-like gas vortex; b) Photo of the spray pattern below the enlarged model of the CPN with capillary diameter d_C = 10 mm at hydrodynamic similar mean flow conditions

Further nebulizers applied for sample introduction in AES are shown in Fig. 5 and Fig.6. The V-groove nebulizer has two drill holes with different diameters, as illustrated in Fig. 5a. The liquid emerges from the larger drill hole into a V-shaped groove and is atomized by the gas discharged from the smaller hole of 190 µm in diameter.

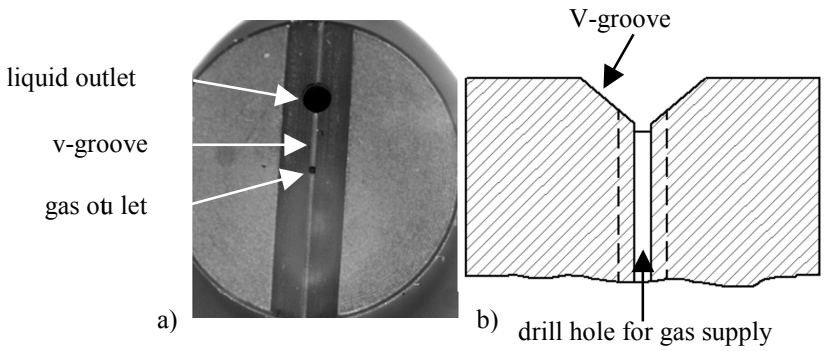

Figure 5. a) top view on the V-groove nebulizer; b) drafted side cut view of the V-groove nebulizer

The cross flow nebulizer operates quite similar to the V-groove nebulizer. But, the liquid is supplied by discharge from a glass tube positioned in straight angle to the gas stream, as shown in Fig. 6.

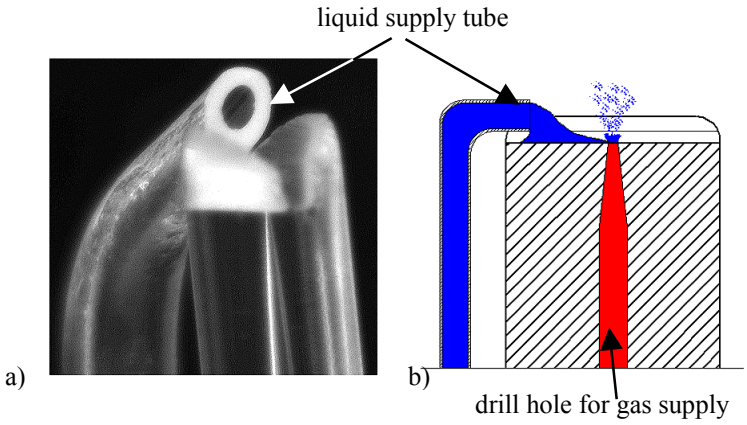

Figure 6. a) photograph of a cross flow nebulizer; b) sectional drawing of a cross flow nebulizer

In AES the V-groove and the cross flow nebulizer are not as relevant as the CPN. Therefore, they are rarely used for sample introduction. Since the V-groove and the cross flow nebulizer provide comparatively wide flow cross-section areas for the liquid, they are mainly applied for liquids of high salt contents in order to avoid plugging.

Experiments

In order to classify the efficiency of the five above presented nebulizers an investigation was carried out. For that purpose the drop size distributions of the different nebulizer designs were measured with a Laser-Diffraction-Spektrometer (LDS) and additionally a Phase-Doppler-Analyser (PDA). In order to operate the nebulizers under comparable conditions, three characteristic values were utilized that are significant for pneumatic atomisation. The Gas-Laplace-number Δp_g*, the liquid to gas flow ratio μ, and the Ohnesorge-number were kept constant for all nebulizer designs. The Gas-Laplace-number is deduced from the Weber-number (We_g) and is defined as:

$$\Delta p_g * = \frac{\Delta p_g \cdot d_{ch}}{\sigma} = \frac{We_g}{2} \tag{1}$$

In order to consider the clogging behaviour the smallest diameter the liquid had to pass was chosen as the characteristic nozzle diameter d_{Ch}. The liquid to gas flow ratio is given by:

$$\mu = \frac{\dot{m}_l}{\dot{m}_g} \tag{2}$$

The Ohnesorge-number primarily characterises the material properties of the sprayed liquid, e.g. the viscosity in combination with the nozzle size scale. It is defined as:

$$On_l = \frac{\eta_l}{\sqrt{d_{ch} \cdot \sigma_l \cdot \rho_l}} \tag{3}$$

During the whole investigation the Ohnesorge-number was maintained at a constant value of $On_l = 0.008$.

At first, the aerosols produced by the five nebulizers were measured by LDS. The Gas-Laplace-number and the liquid to gas flow ratio were varied in a range of $500 \leq \Delta p_G* \leq 700$ and $0.5 \leq \mu \leq 3.0$. Fig. 7 illustrates the related sauter mean diameter D_{32}/d_{ch} as a function of μ at $\Delta p_G* = 600$ and $On_l = 0.008$. Fig. 7 shows that the cross flow and the V-groove nebulizers generate relatively large aerosols compared to the three other nebulizers. The examination of the cross flow nebulizer had to be interrupted when the spray started to pulse at $\mu < 1.5$. In the investigated operation range of $0.5 \leq \mu \leq 3.0$ and $500 \leq \Delta p_G* \leq 700$ the smallest D_{32}/d_{ch} values were achieved by using the Pneumatic Extension Nozzle (PEN). At operation conditions of $\mu = 0.5$ and $\Delta p_G* = 600$ the related sauter mean diameter D_{32}/d_{ch} of the CPN could be approximately halved.

In lower regions of μ the PFDD produced comparatively large droplets. This can be explained by the relatively high amount of larger droplets produced by the PFDD, as shown in Fig. 8.

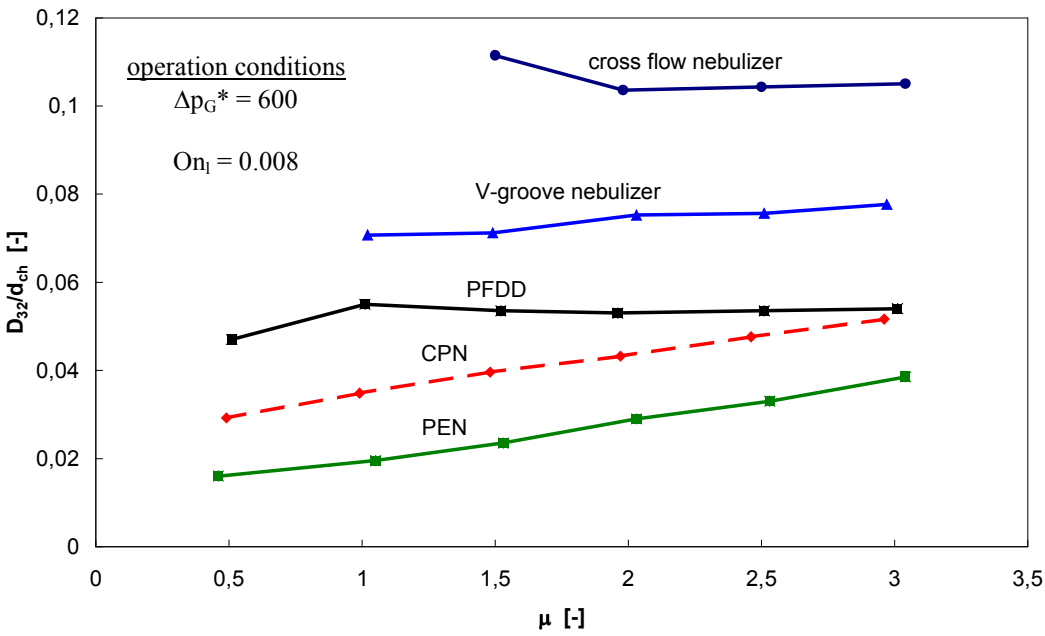

Figure 7. Related sauter mean diameter D_{32}/d_{ch} as a function of μ at Δp_G* = 600 and On_l = 0.008, measured by LDS (Malvern)

For the application in AES only droplets with diameters smaller than 10 µm are suitable for introduction into the excitation source. Therefore, the fraction of suitable droplets with diameter of D < 10 µm within the aerosol should be as large as possible. Fig. 8 shows the cumulative droplet size distributions of the PEN, PFDD and CPN at operation conditions of Δp_G* = 600, μ = 0.5 and On_l = 0.008.

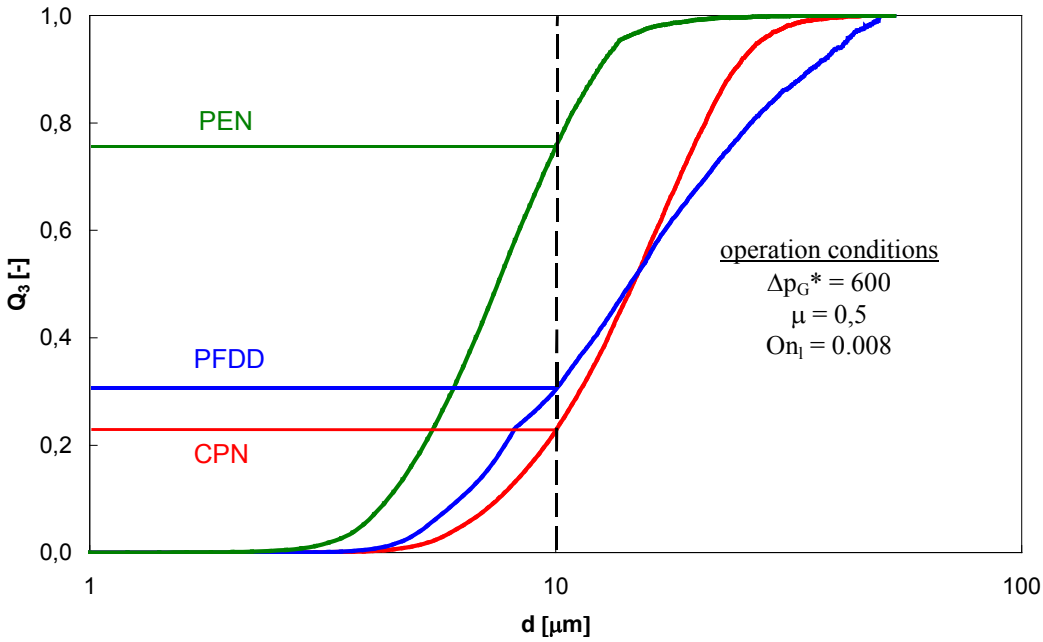

Figure 8. Cumulative droplet size distribution Q_3 for three different nebulizers at Δp_G* = 600, μ = 0.5 and On_l = 0.008, measured using PDA

The droplet size distributions of the V-groove and cross flow nebulizer were not illustrated because Fig. 7 already indicates that both nebulizers produce comparatively larger droplets. The CPN generates an aerosol mass fraction of droplets with D < 10 µm of approximately 23 %. This value can be enhanced up to 31 % by means of PFDD. Whereas, the PEN create an aerosol containing 78 mass percent of suitable droplets. Thus, the PEN provides a nearly 3.5-fold larger mass fraction of useable droplets as the CPN commonly applied in AES.

An enhanced spectroscopical analysis can be expected due to an improved sample introduction by means of PEN. This will be verified by upcoming spectroscopical investigations that will be carried out in cooperation with the Institute of Spectrochemistry and Applied Spectroscopy (ISAS-Dortmund).

Nomenclature

D_{32}	sauter mean diameter, µm	Δp_g	gas pressure difference; Pa
D	droplet diameter, µm	$\dot{m}_l$	mass flux of liquid; g/min
d_O	orifice diameter, µm	$\dot{m}_g$	mass flux of gas, g/min
d_C	capillary diameter, µm	σ_l	surface tension of liquid, N/m
d_{Ch}	characteristic nozzle diameter, µm	ρ_l	density of liquid, kg/m^3

$$\Delta p_g * = \frac{\Delta p_g \cdot d_{ch}}{\sigma}$$ Gas-Laplace-number, [-]

$$\mu = \frac{\dot{m}_l}{\dot{m}_g}$$ liquid to gas flow ratio, [-]

$$On_l = \frac{\eta_l}{\sqrt{d_{ch} \cdot \sigma_l \cdot \rho_l}}$$ Ohnesorge-number, [-]

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