Graz University of Technology

Diplomarbeit

Characterization of a Particle Generator for the Validation of Particle Number Measurement Systems

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Graz, 28.01.2013

Preface

First of all I want to thank Prof. Stefan Hausberger, Dr. Barouch Giechaskiel and DI Herwig Jörgl for their support and mentoring of my diploma thesis.

My thanks also goes to my working colleagues that have helped me with words and deeds during the experiments for my diploma thesis.

A special thank goes to my girlfriend Katrin, for her love and her support on every day we have been together as well as during my whole study and to my family for their financial and morally support without whom my study would not have been possible.

Furthermore I want to thank all my friends and colleagues from the university who have shared their experience and knowledge with me.

Eidesstattliche Erklärung

Ich erkläre an Eides statt, dass ich die vorliegende Arbeit selbstständig verfasst, andere als die angegebenen Quellen/Hilfsmittel nicht benutzt, und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Roman Davok

Graz, 28.01.2013

Abstract

Euro 5b vehicle emissions regulation introduces a particle number limit. The particle number emissions are measured with a device that consists of a dilution system, where the exhaust gas is diluted with air and volatile components are removed and a condensation particle counter (CPC or PNC). According to legislation an annual device calibration is mandatory to ensure a high quality of the measurement. However, if the annual calibration fails it is not always easy to determine the time at which the device started to deviate. Thus it can be difficult to execute a back correction of the values and in the worst case the measurements have to be repeated.

For that reason the demand for a check of the systems in more frequent intervals are necessary. According to the legislation a monodisperse aerosol is required (i.e. particles of specific sizes). However, to achieve such an aerosol expensive test equipment and radioactive sources are necessary. For this reason, the AVL List GmbH designed an instrument that generates particles that can be used for the checks of the devices using a polydisperse aerosol (i.e. without the need for classification) easily and relatively fast.

This thesis initially gives the legislation background and explains the need of a generator. Then various particle generators were compared, in order to get an impression of the existing devices regarding repeatability and stability. The components of the AVL Particle Generator (APG), that consists of a burner unit and a dilution system and a dilution bridge stage were analyzed in more detail. In addition important parameter that affect the size distribution, more specific the diffusion flame and the soot formation of the APG were explained. Finally the applications of the APG for on-site checks of particle number devices was demonstrated.

Kurzfassung

Mit der Einführung der Euro 5b Abgasnorm wurde neben der Partikelmasse (PM) auch die Partikelanzahl (PN) im Light- Duty Bereich reglementiert. Ein System zum Messen der Partikelanzahl besteht aus einem Verdünnungssystem, in dem das Abgas verdünnt wird und flüchtige Komponenten entfernt werden, und einem Kondensations Partikelzähler (PNC bzw. CPC). Um eine hohe Messqualität zu gewährleisten sieht die Gesetzgebung eine jährliche Kalibrierung dieser beiden Hauptkomponenten mit einem monodispersen Aerosol vor. Wird bei der jährlichen Kalibrierung festgestellt, dass das Messgerät nicht mehr korrekt misst, ist der Zeitpunkt ab welchem eine Abweichung auftrat oftmals schwer nach zu vollziehen. D.h. im schlimmsten Fall müssen eine Vielzahl von Messungen wiederholt werden. In Bezug auf die Gesetzgebung wird zur Kalibrierung ein monodisperses Aerosol benötigt, d.h. aus einer Größenverteilung wird eine spezifische Größe für die Messungen heraus geschnitten. Zum Generieren eines solchen Aerosols ist einerseits teures Mess-Equipment, eine stabile Aerosolquelle sowie eine radioaktive Quelle erforderlich. Aus dieser Situation heraus entstand für die AVL List GmbH die Motivation ein Gerät bzw. ein Tool zu entwickeln, mit welchem schnelle und einfache Überprüfungen des Messsystems ohne der Notwendigkeit einer radioaktiven Quelle, durchgeführt werden können. Hierzu wird anstelle eines monodispersen ein polydisperses Aerosol verwendet. Im Rahmen dieser Diplomarbeit wurde zu Beginn die Gesetzgebung und die Notwendigkeit eines Überprüfungstools erarbeitet. Des Weiteren wurden Messungen mit verschiedenen Aerosolgeneratoren durchgeführt um einen Eindruck über bereits vorhandene Systeme bezüglich Stabilität und Wiederholbarkeit zu erhalten. Danach wurden dann die einzelnen Komponenten des AVL Particle Generators, welcher aus einer Brennereinheit und einer Verdünnungseinheit entsteht, untersucht sowie im Detail analysiert. Damit konnten wichtige Einflussfaktoren auf die Rußgenerierung bzw. auf die Partikel Größenverteilungen festgestellt werden, welche im Weiteren für einzelne Anwendungen von höchster Bedeutung sind. Abschließend wurden noch die Applikationen in Kombination mit einem AVL Particle Counter durchgeführt.

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Abbreviations

APC	AVL Particle Counter
APG	AVL Particle Generator
CAST	Combustion Aerosol Standard
CPC	Condensation Particle Counter
DBS	Dilution Bridge Stage
DF	Dilution Factor
DMA	Differential Mobility Analyzer
EC/OC	Elemental Carbon/ Organic Carbon
ET	Evaporation Tube
FSD	Flame Safety Device
HEPA	Filter High Efficiency Particulate Filter
MFC	Mass Flow Controller
MFM	Mass Flow Meter
PCRF	Particle Concentration Reduction Factor
PM PEMS	Particulate Matter Portable Emission Measurement System
PM	Particulate Matter
PN	Particle Number
PNC	Particle Number Counter, is equal to the CPC
PND	Particle Number Diluter
SMPS	Scanning Mobility Particle Sizer
VPR	Volatile Particle Remover

1 Introduction

The motorization rate in the European Union increased in the last years quickly. In the ranking of the number of passenger cars per 1000 persons, Austria is on the fifth position with 517. Leader in this ranking is Luxemburg (659 cars) followed by Italy (606 cars), Cyprus (575) and Malta (573). In order to decrease the environmental pollution, emission limits e.g. of carbon monoxide, NO_x, hydrocarbons and particulate matter for passenger cars and for heavy duty engines, have been already introduced in the 60s of the last century. In addition, recently, the particle number emissions were limited for passenger cars with diesel engines certified starting with Euro 5b (2011); passenger cars with gasoline engines certified with Euro 6 (in 2014) and heavy duty engines certified with EURO VI (in 2014) will follow. For this reason the demand of particle number measuring systems increased in the past years and will increase also in the future.

The particle number measurement systems are very sensitive. To ensure a high accuracy and reliability of the measurements, legislation requires an annual system calibration when the devices are used for engine certification measurements. When the yearly calibration fails, i.e. due to a difference to the calibrated factors of >10%, in most of the cases it is difficult to find the moment at which the system started drifting. Thus, back corrections of the results cannot always be applied. In the worst case the measurements have to be repeated. Consequently the demand for tools to ensure the stability and accuracy of the systems between the yearly calibration interval increases. In the current legislation expensive equipment with a radioactive source is required. Special training for the user is also needed for these kind of checks. Furthermore a particle generator which has to produce a stable aerosol is required.

This diploma thesis, 'Characterization of a particle generator for the verification of particle number counting systems', is the result of a project performed at the AVL List GmbH. Aim is to develop and to characterize a system that can be used for fast and reliable checks of particle measurement systems without the need of an additional expensive equipment and a radioactive source. The device should be easy to use and the results easy to interpret. Not only the system but also the applications to conduct on-side checks will be described in the course of this work.

In the first section (Chapter 2) the legal requirements and the legislation background for a PN system calibration are described to provide an overview about the current situation. Also the principle of particle number counting and the used particle number (PN) counting systems like an AVL particle counter (APC), a PNC from TSI and a differential mobility analyzer (DMA), to classify particles for a monodisperse aerosol, are explained.

Chapter 3 of this thesis deals with different particle generating systems like the Palas spark soot generator, the combustion aerosol standard (CAST), evaporation and condensing techniques and atomizing principles. Here the Palas generator was analyzed in detail, especially the settings and respectively the parameters that affect the generated aerosol regarding particle size and number concentration are investigated. Also the theoretical background behind combustion and soot formation will be discussed. Especially the formation of polycyclic aromatic hydrocarbons (PAH), the soot formation process and the characteristics of a diffusion flame are described in detail.

Chapter 4 and 5 contain core elements of this work. Here the components and their functional principle of the AVL particle generator (APG), the effects of various parameters and settings on to the aerosol and the results of repeatability and stability measurements are discussed in detail.

The last chapter deals with the application of the APG. Here the following three on-side checks are described in detail: the cut-off check, the linearity check and the PCRF check. The summary and the main conclusion of this thesis are given in the final chapter.

2 Legislation Background (1) (2)

A particle number (PN) measurement system consists of two main components, the volatile particle remover (VPR) and the particle number counter (PNC)[1]. The VPR includes a primary hot dilution at 150°C, an evaporation tube at 300-400°C and a cold secondary dilution. The VPR has two functions, the removal of the volatile components and the dilution of the aerosol, so that particle number concentrations less than 10^4 particles per cm^3 are achieved at the inlet of the PNC (this is the maximum concentration current PNCs can measure in single count mode). The calibration and validation procedures of the PNC and the dilution system (VPR) will be described below.
Furthermore an overview of the used particle measurement systems regarding number concentration and particle size is provided.

2.1 Calibration of the PNC

The calibration of the PNC includes two tests, the counting efficiency and the concentration linearity. In both cases the device to be calibrated is compared with a more accurate system, e.g. an aerosol electrometer (reference standard). The results have to be included in the calibration certificate. The calibration setup requires a differential mobility analyzer (DMA) to achieve a monodisperse aerosol. The two systems are connected parallel to the DMA to measure the number concentrations, refer to (3).

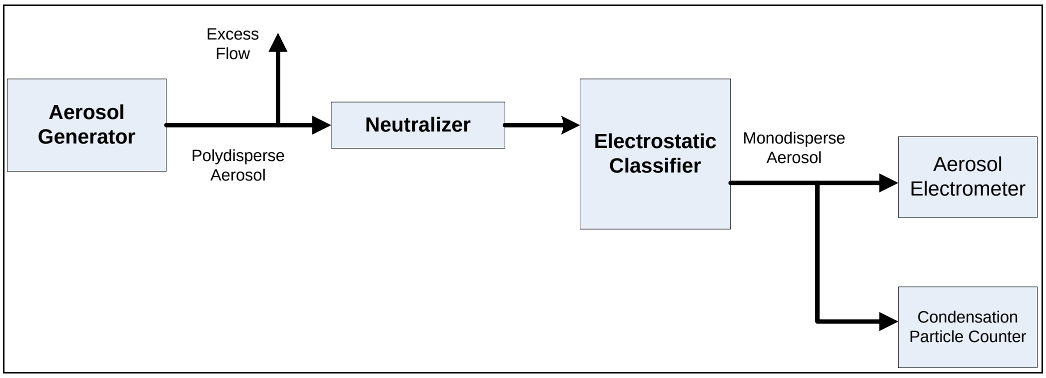

Figure 2.1: Setup for validation measurements of a PNC

2.1.1 Counting efficiency

For the verification of the counting efficiency, the lower detection limit is determined. Therefore the device to be calibrated and the electrometer are measuring sized aerosols in parallel. Subsequently the readings of the PNC are compared with the readings of the electrometer and the results are calculated in percent. For the PNC, legislation requires a 50% (±12%) counting efficiency for particles with an electrical mobility diameter of 23 nm (this is the definition for the cut point) and >90% for particles larger than 41 nm.
Following figure shows an exemplary result of a counting efficiency measurement with the mentioned tolerances.

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[1] Also called condensation particle counter (CPC)

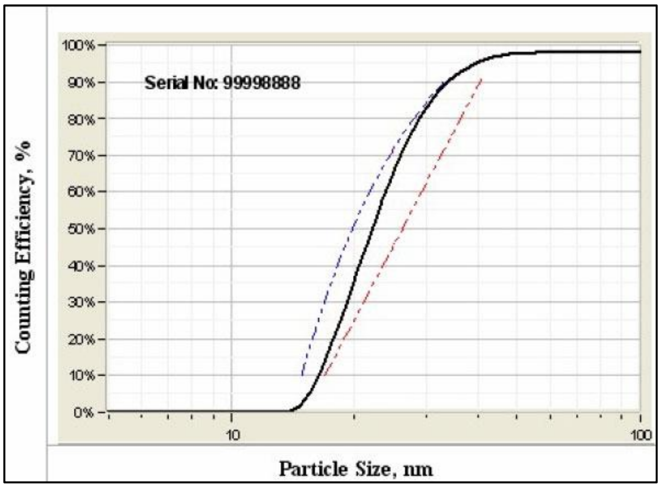


Figure 2.2: Results of a counting efficiency measurement **(1)**

2.1.2 Concentration Linearity

In comparison to the counting efficiency, where different particle sizes are measured, an aerosol with at least 5 various particle number concentrations has to be produced for the linearity verification. Therefore a monodisperse aerosol with a particle diameter of 50nm is classified by a DMA and diluted with e.g. a dilution bridge. Following figure shows an exemplary graph and the linearity of the PNC readings and the electrometer readings. According to the legislation the linear slope should be within 0.9 - 1.1 and the linear regression should be $R^2 > 0.97$.

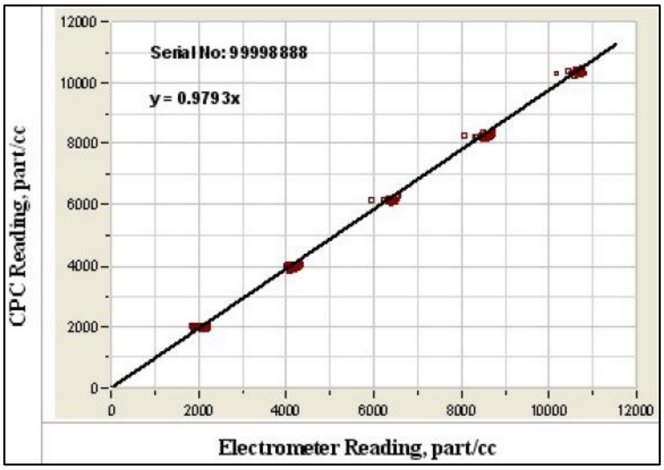


Figure 2.3 Results of a concentration linearity measurement**(1)**

2.2 Calibration of the dilution system (VPR)

The calibration or validation of the VPR dilution factor (more specific: PCRF) requires three different monodisperse aerosols at 30, 50 and 100nm. For each aerosol a reference device measures the particle number concentration up- and downstream the VPR. Then the mean PCRF of the three particle diameter is calculated. This calculated PCRF is compared with the set dilution ratios and the deviation is corrected by a calibration factor (see equitation below).

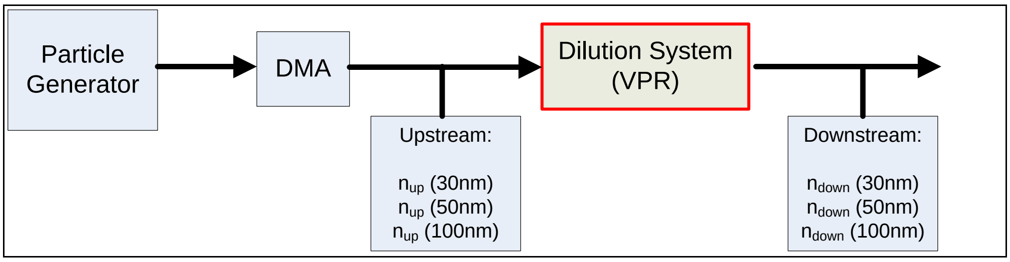


Figure 2.4: Up- and downstream measurement of a VPR for PCRF calibration, acc. to **(1)**

$$PCRF_{mean} = \frac{1}{3}\left(\frac{n_{up,30}}{n_{down,30}} + \frac{n_{up,50}}{n_{down,50}} + \frac{n_{up,100}}{n_{down,100}}\right) \quad \text{(Equ. 1)}$$

For the restriction of particle losses in the VPR, it is required that the PCRF ratio for 30 and 50 nm is <1.3 and <1.2 times than the PCRF at 100 nm, refer to equitation below.

$$\frac{PCRF_{30}}{PCRF_{100}} < 1.3 \text{ (Equ. 2)s}$$

$$\frac{PCRF_{50}}{PCRF_{100}} < 1.2 \text{ (Equ. 3)}$$

It can be summarized that the calibration or the verification of PN devices is a complicated procedure thus trained personal and the appropriate equipment is required. Additionally as mentioned before when a calibration fails it is not always possible do determine the moment at which the system started to drift and in the worst case many measurements have to be repeated, which can be a time and money consuming process. Based on this situation, the motivation for AVL arises to develop an approach to conduct onsite checks with a polydisperse aerosol that is produced by a particle generator with specific pre-calibrated operating points. This means to create a tool with which the volatile particle remover (more specific the PCRF) and the PNC (regarding the cut-point and the linearity) of a particle number counting system can be checked, ensuring a high accuracy and reliability of the PN measurements. Aim is to simplify the whole testing procedure. The advantage of checks with a polydisperse aerosol is, that no expensive test equipment or a radioactive source is required. Aim of the on-site checks is to reduce the probability of a failed annual calibration.

In the following chapter the principle of particle number counting and used devices, this means the measurement systems that are required for a PN system calibration, are explained. An open issue is the particle generation respectively the generators, which will be discussed in chapter 3.

2.3 Particle Number Counting and Devices

In the following section the used particle counting systems, like a condensation particle counter from TSI or the AVL Particle Counter, and the functional principles of the systems will be explained.

2.3.1 Condensation Particle Counter

The Condensation Particle Counter (CPC), also called Particle Number Counter (PNC), uses a light scattering method to count particles. That the laser is able to detect particles they have to grew by a condensing vapor, e.g. of an alcohol like butanol.

In general condensation is defined as the transfer from a gaseous or vaporous state to a liquid phase. It can be distinguished into a **heterogeneous** and into a **homogenous** condensation. Whereby a heterogeneous condensation needs an external condensation nucleus, e.g. dust, as trigger. A homogenous condensation, also called self-nucleation, starts due to supersaturation and spontaneous nuclei formation. That means if the supersaturation is too high, condensation will even start without the presence of any particles because molecules from the vapor phase form clusters due to van der Waals forces and the motion of the gas. As a consequence droplets can be formed, that probably may be detected by the laser diode although no aerosol passes the laser (4) (3).

The quotient of the actual vapor partial pressure and the saturation vapor pressure is defined as the saturation ratio φ:

$$\varphi = \frac{P}{P_s}\ , supersaturation\ for\ \varphi > 1 \quad \text{(Equ. 4)}$$

The condensation of vapor onto a particle requires a minimum particle size that is also called the Kelvin diameter d, which can be described with following equitation:

$$\varphi = \frac{P}{P_s} = exp\left[\frac{4\gamma M}{\rho R T d}\right] \quad \text{(Equ. 5)}$$

where: γ ...surface tension of the condensing fluid
M ...molecular weight of the condensing fluid
ρ ...density of the condensing fluid
R ...universal gas constant
T ...absolute temperature
d ...Kelvin diameter

That means by increasing the saturation ratio φ the Kelvin diameter decreases. To avoid homogenous condensation the CPC operates under the supersaturation ratio.

2.3.1.1 Functional Principle of the CPC (3)

The functional principle of the CPC is explained in the following based on the flow schematic of the CPC 3775.

A vacuum pump takes constantly 1.5 liters per minute (lpm) in. The flow through the detector is constant 0.3 lpm thus depending on the setting, the device can sample either 0.3 lpm or 1.5 lpm, a bypass line has to be activated.

The aerosol enters the heated saturator, 39°C, where butanol saturates from a soaked wick and mixes with the sample. Now the flow consists of the aerosol and butanol vapor. Subsequently the flow enters the cooled condenser, 14°C, where a heterogeneous condensation of the vapor starts onto the particles. Thus the particles are enlarged and enter the counting unit via a nozzle. To avoid condensation onto the lens surface the wall temperature of the optics is higher than the saturator temperature. The flow through the counting unit is kept constantly by a critical orifice and monitored by a difference pressure measurement.

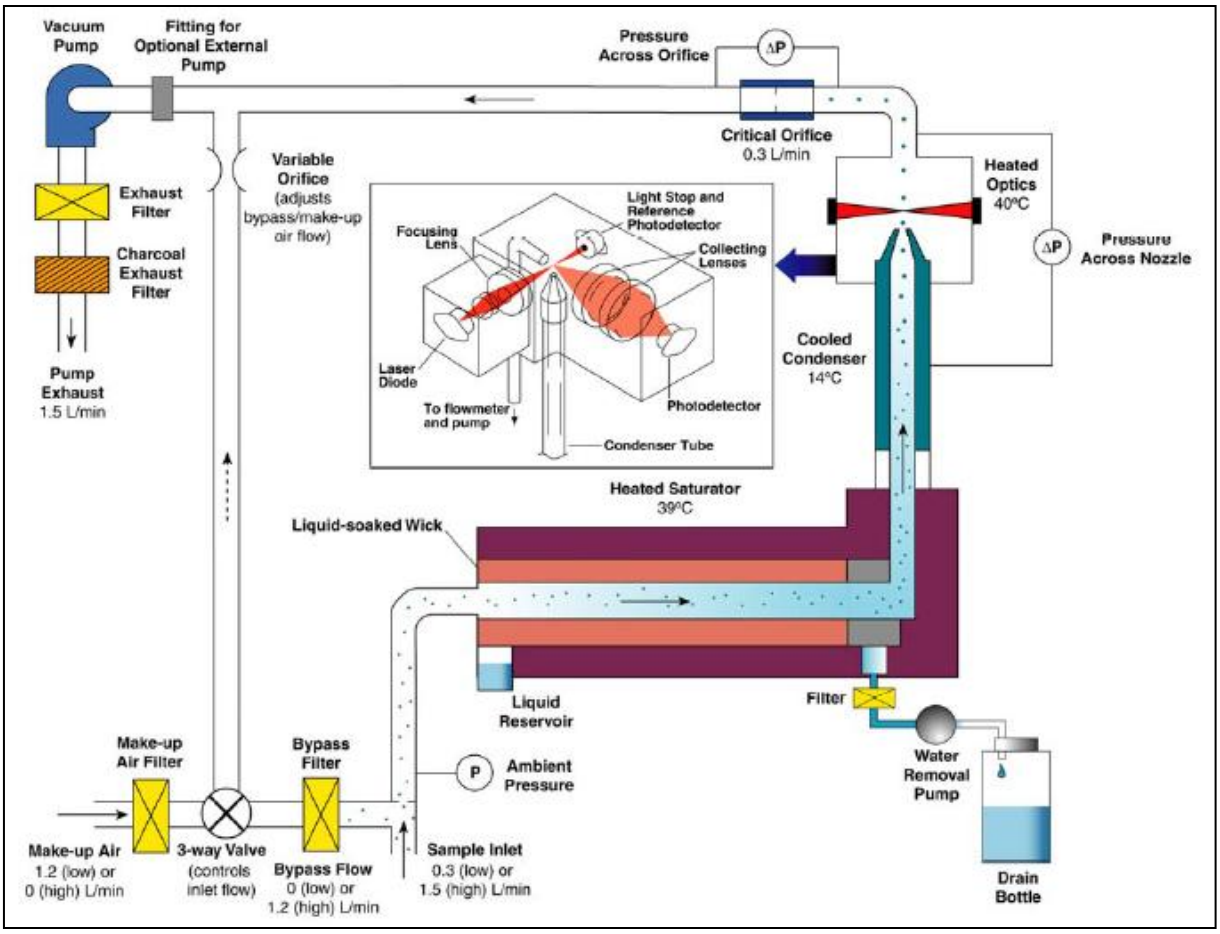


Figure 2.5: Flow Scheme of a condensation particle counter (CPC) from TSI, model 3775 **(3)**

Following Table 1 shows the specifications of the two used condensate particle counters:

Table 1: Specifications of CPC 3775 and 3790 from TSI **(3) (5)**

	Model 3775 CPC 	Model 3790 CPC 
Particle Size Range Min. detectable particle Max. detectable particle	D_{50}: 4.0 nm >3µm	D_{10} efficiency 16nm ± 1nm D_{25}efficiency 18nm ± 2nm D_{50} efficiency 23nm ± 3nm D_{90} efficiency 37nm ± 4nm >3µm
Particle Concentration Range	<u>Single Particle Counting:</u> 0 to 50,000 particle/cm^3 with continuous live time coincidence correction <u>Photometric:</u> 50000 - 10^7 particle/cm^3	0 to 10^4 particles/ cm^3
Particle Concentration Accuracy	±10 % at ≤ 50,000 particle/cm^3 ±20 % at ≤ 10^7 particle/cm^3	±10 % at ≤ 10^4 particle/cm^3
Flow Rate	Inlet, low flow 0.3±0.015 lpm Inlet, high flow 1.5±0.015 lpm	1 ± 0.05 lpm
Operating Temperatures Saturator Condenser Optics	39°C±0.2°C 14°C±0.2°C 40°C±0.2°C	38.3°C±0.2°C 31.0°C±0.2°C 40.0 °C±0.2°C
Environmental Operating Conditions	Indoor use Altitude up to 2000m Inlet Pressure 75 to 105 kPa Operating Temperature 10 to 35 °C Safe Temperature Range 5 to 40 °C Storage Temperature -20 to 50 °C Ambient Humidity 0 to 90%	

2.3.2 Scanning Mobility Particle Sizer (SMPS)

A Scanning Mobility Particle Seizer consists of two main components, an electrostatic classifier and an condensation particle counter. The classifier filters several particle sizes out of an aerosol. That means the device processes a polydisperse aerosol, from the inlet, and provides a monodisperse aerosol at the outlet.

Combined with a condensation particle counter the classifier scans a range of particle sizes and the CPC delivers the corresponding particle concentration that leads to the result of a particle size distribution of an aerosol (6) (5).

The CPC and the functional principle is explained in the chapter before, in the following the electrostatic classifier and the appropriate components are described.

2.3.2.1 Electrostatic Classifier (Series 3080)

The Classifier consists of a Differential Mobility Analyzer (DMA) and additional subsystems listed below:

- Impactor: Acts as a pre-selector and removes particles above a selected particle size.
- Sheath Air Flow Controller: Monitors the flow rate through the sheath flow loop and controls the desired flow by a pump.
- Neutralizer: Charges the particles of the aerosol with a known distribution using a Krypton 85 neutralizer. Afterwards the aerosol enters the DMA
- High Voltage Controller: Monitors the charge of the DMA high voltage rod and controls the desired values entered at the front panel.

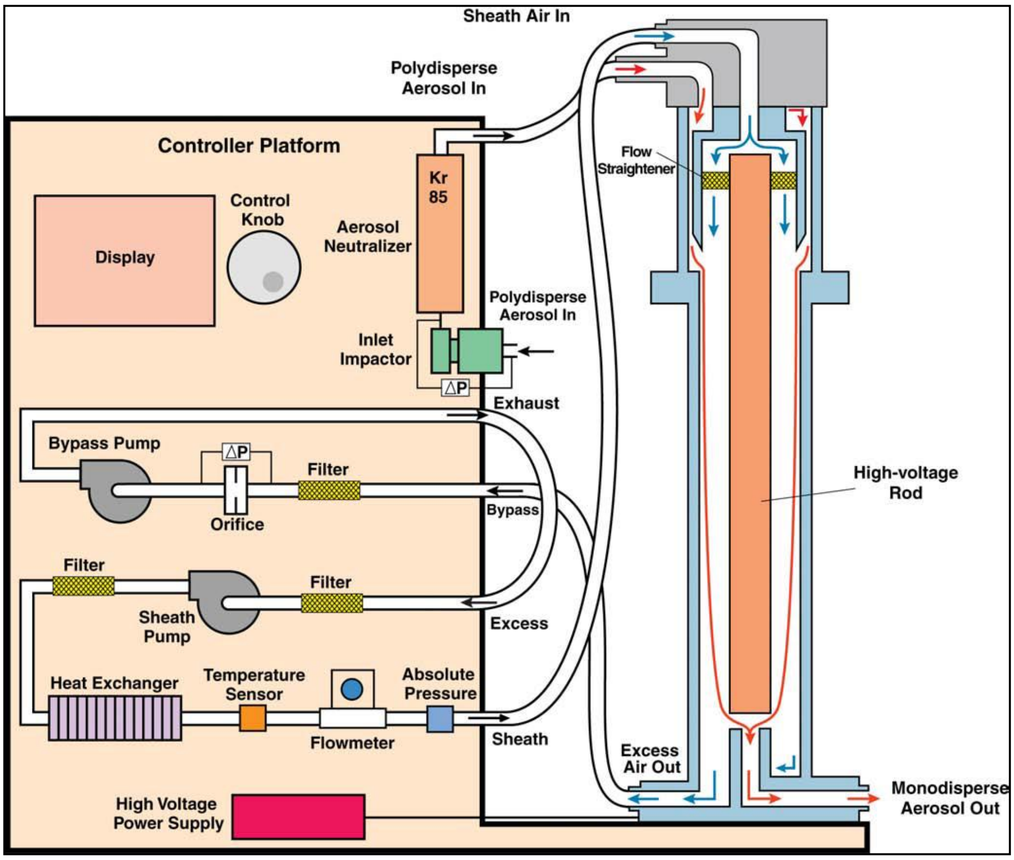


Figure 2.6: Flow Scheme of an electrostatic classifier from TSI (model 3080) utilizing a long DMA **(6)**

2.3.2.2 Differential Mobility Analyzer (DMA)

For the SMPS application a long DMA is used, so the functional principle will be explained for this device.

In the DMA the real separation of the particle size from the polydisperse aerosol takes place. The DMA consists of two coaxial aligned cylindrical electrodes made of polished stainless steel, that are insulated from each other by two spacer at the top and at the bottom.

The sheath flow, filtered and particle free air, enters the DMA at the top and flows downwards between the two electrodes. After passing a flow straightener the sheath flow is mixed smoothly with the polydisperse aerosol and transports it to the bottom. Then depending on the electrical mobility and the electric field between the center (negative charged) and the outer electrode, positive particles are pulled with various strong forces in to the direction of the center axis. Particles with a high electrical mobility are pulled to the center electrode earlier then particles with a smaller electrical mobility.

Only particles with a narrow range of electrical mobility can leave the DMA through radial arranged slits in the center electrode. Thus a monodisperse particle flow exit the DMA.

Negative charged particles stick at the outer electrode and neutral are transported by the sheath flow to the bottom of the DMA. (6)(5)

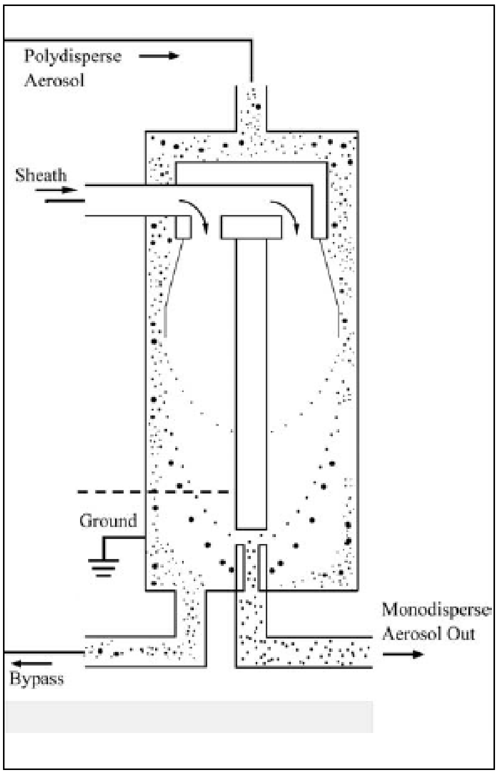


Figure 2.7: Flow Scheme of a DMA **(5)**

Figure 2.8: Long DMA from TSI, model 3081 **(6)**

Following Table 2 shows the specifications of the controller platform and of the Electrostatic Classifier:

Table 2: Specifications of the DMA from TSI, model 3080 **(6)**

3080 Controller Platform:	
Mode of Operation	Bipolar charge neutralization and differential mobility analysis
Flow Rates Aerosol Sheath Flow Bypass Flow	0 to 3 lpm 0 to 15 lpm (Single Blower Mode) 0 to 20 lpm (Dual Blower Mode) 0 to 15 lpm (Single Blower Mode) None (Dual Blower Mode)
Aerosol Temperature Range	10 to 40 °C
Charger/ Neutralizer	Bipolar, Kr-85, 10 millicurie, half life of 10^7 years
Aerosol Pressure Range	70 to 120 kPa
Environmental Conditions	Indoor Use Altitude 3000m Ambient Temperature 10 to 40 °C Ambient Humidity 0-90%
3080L Electrostatic Classifier	
DMA	Long (Model 3081)
Particle Type	Solids and nonvolatile Liquids
Particle Size Range	Adjustable from 10 to 1000nm
Maximum Input Concentration	10^8 particles/cm^3
Voltage	10 to 10,000 VDC

2.3.3 AVL Particle Counter (1)

The AVL Particle Counter (APC) measures particle number concentration of an exhaust gas and can be installed either at a CVS tunnel or tailpipe. The device consists of following components:

- Chopper Diluter
- Evaporation Tube
- Secondary Dilution
- Particle Number Counter

The Particle Number Counter (PNC) counting limit is at a number of 10^4 #/cm^3. In order to provide an aerosol where the PNC inlet concentration is below the limit a dilution system that decreases the concentration by a defined dilution is necessary. The chopper diluter, also called primary diluter, the evaporation tube and the secondary diluter built such a dilution system which is contained in the APC.

2.3.3.1 Chopper Diluter:

One of the components of the chopper diluter is the rotating disk. The disk consists of bore holes that are constantly arranged over the circumference. The disc is mounted on a shaft which is cranked by a stepper motor with a defined frequency.

At one site of the disk dilution air with 150 °C flows through the bore holes, at the other exhaust gas. When the disk starts rotating exhaust gas is transported to the side of the air flow and diluted.

Following figure shows the components of the PND1.

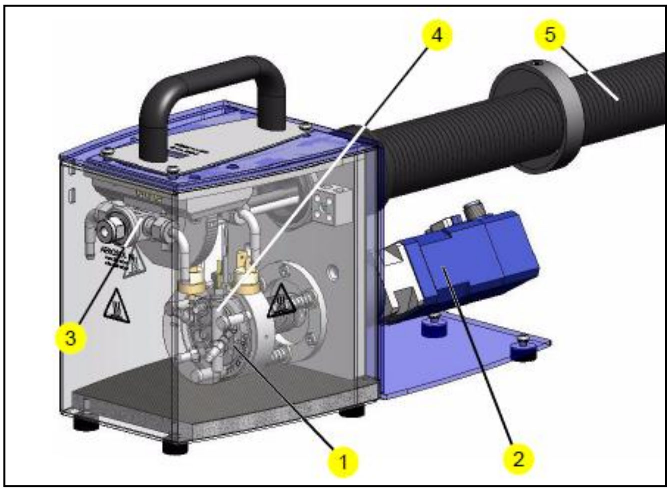


Figure 2.9: Copper Diluter of an APC: Perforated Disk (1), Stepper Motor (2), Ball Valve (3), Heating Cartridges (4), Heated Hose (5), **(1)**

2.3.3.2 Evaporation Tube and Secondary Dilution

The maximum of the evaporation tube (ET) heating power is at 400°C. Under these conditions the volatile and semi-volatile components of the hot diluted aerosol are evaporated. After the ET the flow is mixed a second time with dilution air at ambient temperature in a porous tube diluter, also called Particle Number Diluter 2 (PND2).

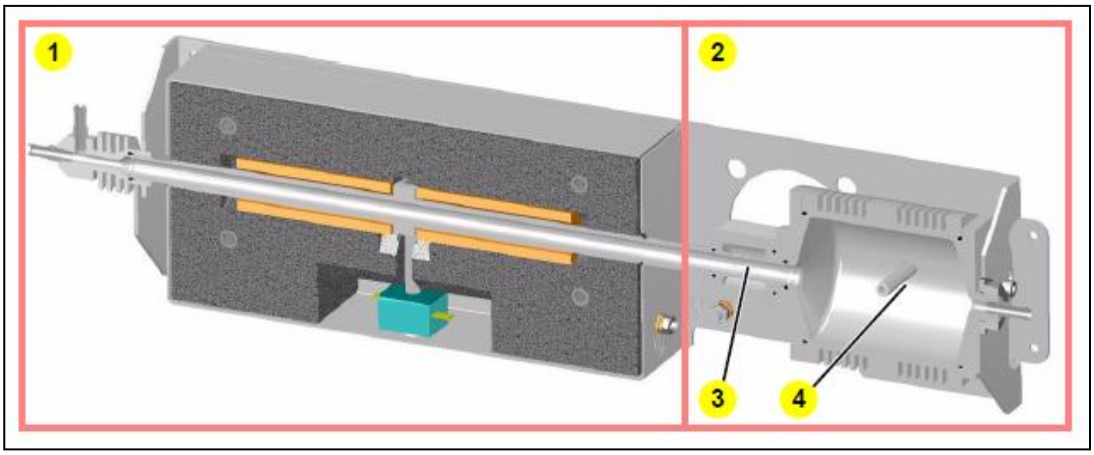


Figure 2.10: VPR components of an APC: Evaporation Tube (1), Secondary Diluter (2), Porous Tube Diluter (3)m Stabilization Chamber (4), **(1)**

3 Particle Generators and different Principles:

The particle generating principles that will be explained in the following are a spark generator, an atomizer, evaporation and condensation techniques and a diffusion flame generator. Also the details about combustion of hydrocarbons, the soot formation and the characteristics of a diffusion flame are discussed.

3.1 Spark Soot Generator (7) (8)

The spark soot generator (from Palas) utilizes two graphite monolithes to produce a condensation aerosol.

Two graphite electrodes are charged with high voltage. The result is a flashover between the electrodes and a high temperature which leads to an evaporation of the carbon, see Figure 3.1. The flashover is not a constant electric arc but a single flash with a frequency of a few kHz. It can be controlled by varying the energy and the current of the device. Depending on the material of the two electrodes different aerosols can be generated, e.g. silver or gold can be used as well.

A nitrogen or argon flow transports the vaporized carbon out of the chamber, cools it down and agglomerates of carbon are formed. Afterwards the aerosol is diluted with an air flow that can be regulated by a mass flow controller. The dilution may have effects on to the particle size of the generated aerosol.

The distance between the two electrodes (1) has to be constant to guarantee a stable aerosol flow, if not the gap would increase and affect the particle formation. To avoid that a threaded spindle is used to adjust the electrodes automatically to the needed position.

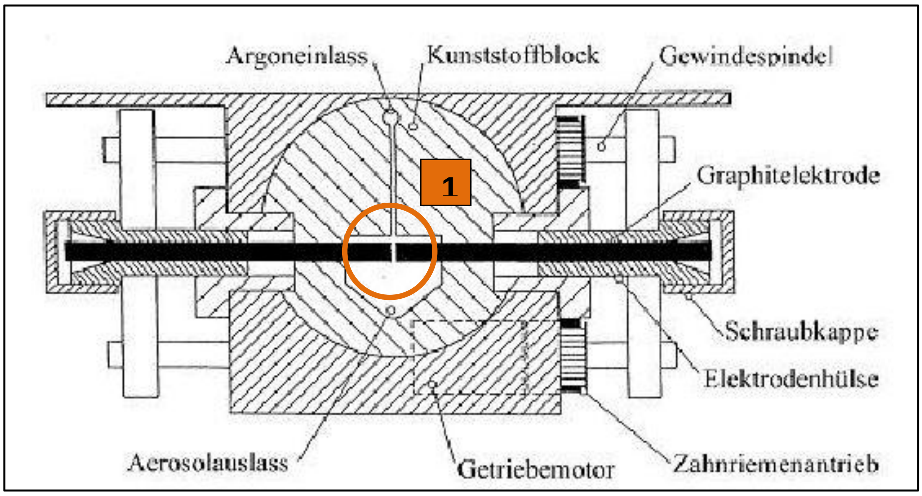


Figure 3.1: Configuration of a Palas sparking soot generator **(7)**

The following Table 3 shows the specifications of the Palas DNP 3000 sparking soot generator, which was examined in this thesis:

Table 3: Specifications of the Palas sparking soot generator DNP 3000 **(7)**

Particle Material	Carbon
Carrier Gas	Nitrogen
Volume Flow	4-6 lpm
Pressure	4-6 bar
Dilution Gas	Particle free and dry pressurized air
Volume Flow	0-40 lpm
Pre-pressure	4-6 bar
Number Concentration	>10^7
Mass Flow	Approximately 0.06 - 7 mg h^{-1}
Primary Particle Size	3-5 nm
Agglomerates	Approximately 20 - 150 nm

3.1.1 Parameter that affect the Aerosol

Different parameters affect the particle formation at the sparking soot generator. In the following the values that can be modified by the user are investigated. Table 4 below shows the influencing factors and corresponding limits for the values that can be modified:

Table 4: Parameter of the Palas sparking soot generator DNP 3000 **(7)**

Parameter	**Limits**
Energy	Low 2.5 kV Medium 3.0 kV High 3.5 kV
Current	0.5 – 7.3 mA
Air Flow	2 – 50 lpm
N_2 Flow	3 – 20 lpm
Distance between the Electrodes	Constant
Material and purity of the Electrodes	Not investigated

3.1.1.1 Current

As mentioned earlier the energy and the current affect the frequency of the flashover between the two electrodes. Following figure shows the results of varying the current value with a constant energy of 3.5 kV (high). The total particle concentration increases, which is equal to the area under the size distribution, and the distribution is shifted to the right. By enlarging the current the frequency of the flash over between the electrodes is increased, which results in more primary particles that can agglomerate subsequently.

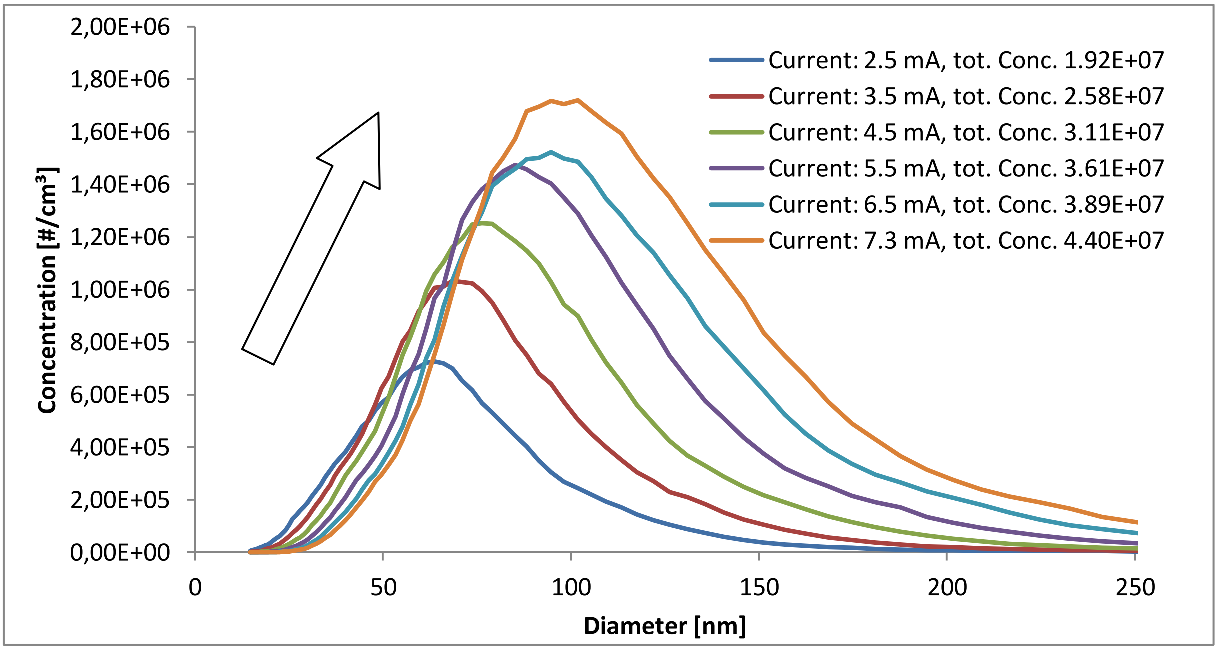


Figure 3.2: Effects of the Current on to the aerosol size distribution

3.1.1.2 Nitrogen Carrier Flow

The nitrogen flow has the function to transport the vapor out of the chamber where the electrodes are located and to freeze the generated particles.

The nitrogen flow affects the coagulation of the particles, this means for larger flows the total concentration remains high because of less coagulation, compare to Figure 3.3.

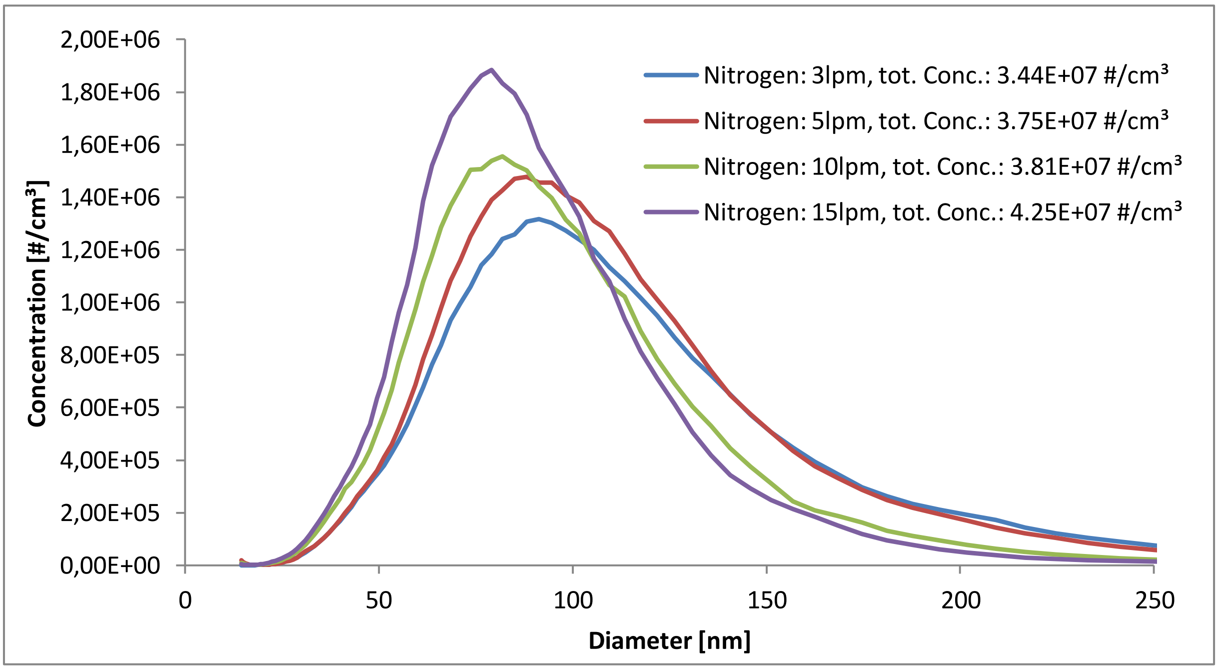


Figure 3.3: Effects of the nitrogen carrier flow on to the aerosol size distribution

3.1.1.3 Dilution Air Flow

An increase of the dilution air flow decreases the particle concentration due to dilution The agglomeration after dilution is affected by the dilution flow and the particle diameter remain small for large dilution ratios, compare to Figure 3.4.

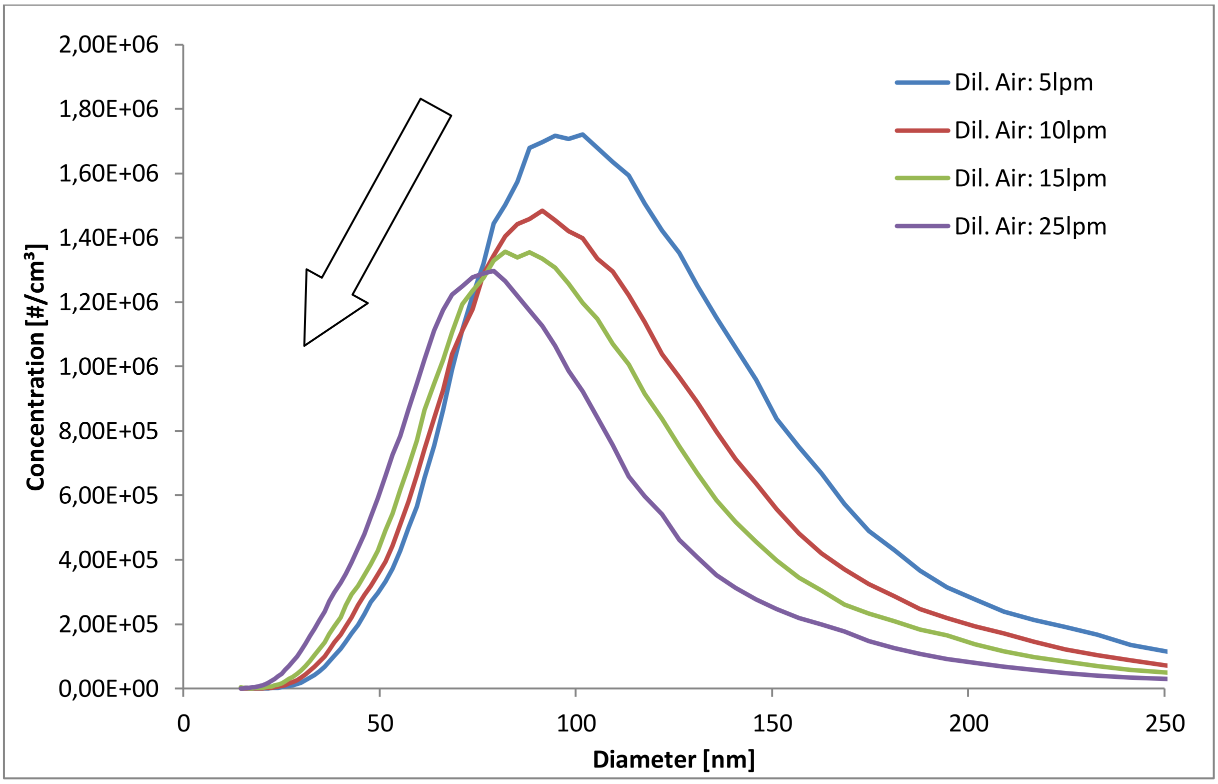


Figure 3.4: Effects of the dilution air flow on to the aerosol size distribution

3.2 Evaporation and Condensing Technique

As an example for the evaporation and condensation techniques the aerosol generator according to Scheibel and Pörstendorfer can be mentioned. Sodium chloride is filled into a pipe, made of e.g. glass or stainless steel. This pipe is placed into a tube furnace that is heated up. At temperatures of approximately 600°C the salt starts evaporating. To transport the vapor out of the cylinder a nitrogen flow acts as the carrier gas. After leaving the furnace the gas cools down, the nucleation starts and salt particles are formed. Compared to diesel soot the chemical potential to form droplets in a condensation particle counter (CPC) is different as well as the stability of the aerosol if it´s heated up in an evaporation tube (9).

3.3 Atomizer (10)

As an example for an atomizer the liquid nebulizer for suspensions from Palas (model AGK 2000) will be mentioned. With this device liquids and potassium chloride solutions can be atomized to generate a size distribution with particle sizes in the range of 5 nm to 15 µm, depending on the solution concentration and the particle material. A binary nozzle that is supplied with pressurized air generates under pressure. With this under pressure liquid is sucked out of the liquid reservoir and an aerosol cloud is produced. Subsequently the aerosol enters a cyclone separator where larger particle are removed due to centrifugal forces and only smaller particles can leave the cyclone via the outlet. Thus this component plays an important role for affecting the required size distributions, more than the binary nozzle does. Following Figure 3.5 shows a schematic drawing of the AGK 2000 from Palas.

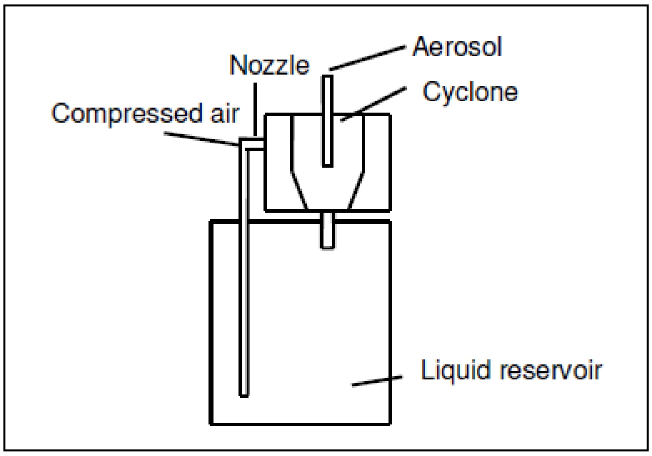


Figure 3.5: Schematic Drawing of the AGK 2000 **(11)**

3.4 Combustion Aerosol Standards (CAST) (12)

This principle utilizes a laminar propane co-flow diffusion flame that is coated with oxidation air to produce soot particles. Compared to the sparking soot generator a fuel gas for the combustion is needed. This type of flame produces soot particles within the combustion zone, where a lot of different oxidation reactions result a high temperature (hence the typical yellow center) and the oxygen supply is insufficient that a soot formation can occur. In the surrounding of this zone the largest number of soot particles is located whereas outside the flame no or only small numbers can be found because they are burnt off by diffusing through the oxidation layer of the flame. Thus to win soot particles the reaction has to be interrupted by quenching the flame.
Details about combustion and the soot formation process are given below.

3.5 Theoretical Background of Combustion

This chapter deals with the theory of the combustion, especially the reaction of hydrocarbons, the formation of poly aromatic hydrocarbons as intermediates of the soot formation, the soot generation and the combustion scheme of a diffusion flame, especially in which zones soot is generated.

3.5.1 Combustion

Combustion is the chemical reaction of a combustible substance, with oxygen. In most of the cases ambient air is used as oxygen medium. The combustion is an exothermic reaction, this means the chemical bounded energy of the fuel is converted to thermal energy which is then released to the ambience. The thermal energy can be used e.g. in a steam generator or as mechanical energy in a piston engine or as kinetic energy in aircraft engines (13). In the content of this thesis the combustion of hydrocarbons in a diffusion flame is used as soot source.

To start the oxidation, the ignition temperature of the fuel has to be reached at any point of the flame or the combustion is started with an external igniter respectively. If the temperature is not reached the reaction is stopped and the flame will be extinguished (14).

3.5.1.1 Combustion of Hydrocarbons

3.5.1.1.1 Fuels (15) (16)

Most of the technical important fuels consist of carbon and hydrogen which are the main energy source for the combustion. Depending on the purity of the fuel additional components, e.g. sulfur can be involved in the reaction. In the following some chemical hydrocarbon compounds are explained.

Alkyl Compounds:

- Paraffins (Alkane):
  Alkanes consist of single hydrocarbon compounds. In general alkane can be described with following structural formula: C_nH_{2n+2} and the ending -ane (Alk-**ane**).

  Referring to Figure 3.6 the first possible alkane is methane (CH_4) followed by ethane (C_2H_6), propane (C_3H_8), etc.

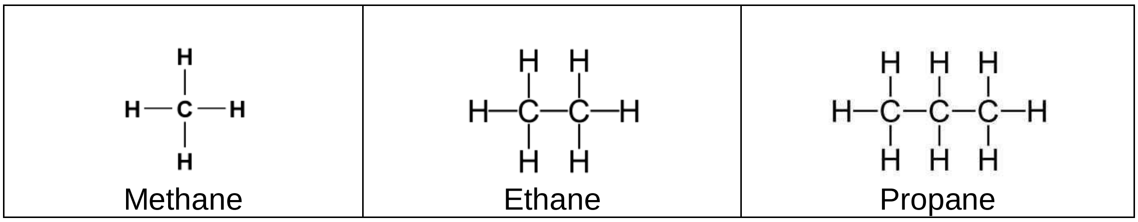

Methane Ethane Propane

Figure 3.6: Chemical Structure of the first three alkanes

- Olefins (Alkene):
  Alkenes consists of at least on double hydrocarbon compounds.
  Structural Formula: C_nH_{2n} and the ending with -ene (Alk-**ene**). The simplest alkene is ethylene, see Figure 3.7.

- Acetylenes (Alkyne):
  Alkynes consists of triple hydrocarbon bonds.
  Structural Formula: C_nH_{2n-2} and the ending –yne (Alk**-yne**). E.g. Ethyne (C_2H_2), see Figure 3.7.

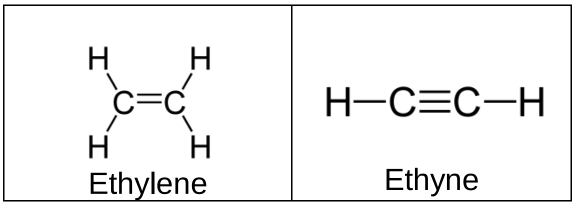

Ethylene Ethyne

Figure 3.7: Chemical structure of ethylene and ethyne

Aromatic Hydrocarbons:

Aromatic Hydrocarbons consists of hydrocarbon compounds which structure is based on a benzene ring, 6 C-atoms with 3 double bonds. E.g. benzene, has many different structures, thus it is very stable, see Figure 3.8.

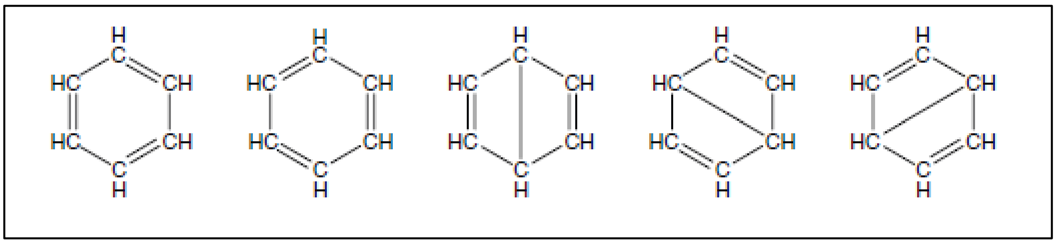


Figure 3.8: Various chemical structures of benzene

Alcohol:

Alcohol is an organic compound that contains a hydroxyl group (-OH). E.g. Ethanol (ethyl alcohol, Figure 3.9).

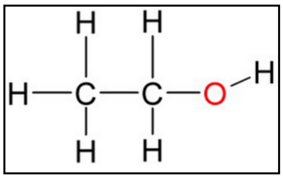


Figure 3.9: Chemical structure of ethanol

Aldehydes:

Aldehydes are chemical compounds that contain of a characteristic formyl radical group, see Figure 3.10:

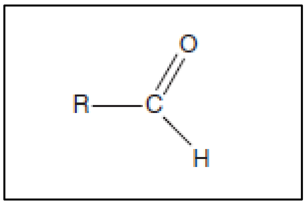


Figure 3.10: General chemical structure of an aldehyde

The radical group R can be a hydrogen atom or an organic radical, see following Figure 3.11.

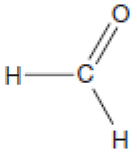
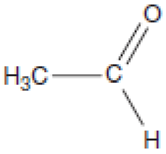
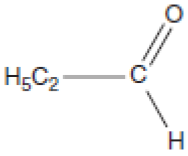
 Formaldehyde	 Acetaldehyde	 Proprionaldehyde

Figure 3.11: Illustration of aldehydes with different radical groups

3.5.1.2 Explosion Limits and Auto ignition: (17) (16)

Auto ignition, also called self- or spontaneous ignition, is a process at which a combustible fuel- oxidizer mixture starts to react without an external energy supply as it is needed for a normal ignition of a flame. Either auto ignition occurs by a premixed fuel oxidizer mixture or by a non-premixed composition, at which the separated elements react simultaneously.

High order hydrocarbons, especially propane and higher, oxidize much more slower than hydrogen.

In general compositions of hydrocarbons and oxygen, or air respectively, react slowly at temperatures around 200°C. When the temperature increases CO and H_2O are the predominating components in the product. At 300-400 °C often a weak light appears that is followed by one or more blue flames, which are called cool flames. That light emissions can be followed by explosions. Due to that fact explosion limits for hydrogen – oxygen mixtures exist. Following Figure 3.12 shows hydrogen explosion limits in general for the first three hydrocarbons.

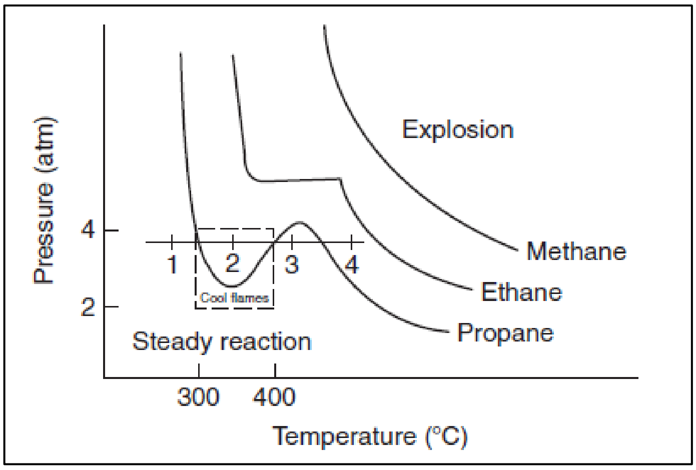


Figure 3.12: General explosion limits of hydrogen-air mixtures **(16)**

The larger the hydrogen molecules the lower is the temperatures and the pressure at which the auto ignition process starts. An explanation for that may be due to the increasing size of the hydrogen it is easier to break down the molecules and the intermediates by intermolecular collisions, which leads to the formation of radicals that are starting a fast reaction.

If the pressure remains constant usually an explosion occurs by increasing the temperature from point 1 to point 2. By increasing the temperature further the explosion limit is passed a second time, which is called ‘multiple ignitions’. In the case of propane a two stage ignition exhibits that may be related to the cool flame phenomenon.

As an example the auto ignition temperature and the flammable range of two hydrocarbons mixed with air at 20 °C are mentioned in following Figure:

Table 5: auto ignition temperature of methane and propane **(18)**

	Vol.-%	Ignition Temp.
Methane	5.1 – 13.5	645 °C
Propane	2.1 – 9.5	470 °C (DIN 51974)

3.5.1.3 Stoichiometric Combustion (19) (20)

For a complete combustion of an element a minimum amount of oxygen is necessary. This value can be determined by stoichiometric equations, in consideration of the composition of air that consists of 21 vol.- % Oxygen and 79 vol.- % Nitrogen.

$$L_{min} = \frac{1}{0{,}21} * O_{2,min} = 4{,}76 * O_{2min} \text{ (Equ. 6)}$$

Used units for L_{min} and O_{2min} are $kmol_{O2}/kmol_{fuel}$ or Nm^3_{O2}/Nm^3_{fuel}. The air requirement is called stoichiometric air requirement, because this is the amount of oxygen that is required for a complete combustion.

Often the more air is supplied than required, then the stoichiometric value leads to following ratio:

$$\lambda = \frac{L}{L_{min}} \text{ (Equ. 7)}$$

where λ is called the air/fuel ratio. For a complete combustion λ has to be greater than 1, λ less than 1 leads to an incomplete combustion.

3.5.1.4 Oxidation of High Order Hydrocarbons (20) (16)

At a complete combustion the C_xH_y are formed into carbon dioxins CO_2 and water in form of steam, typical products of an incomplete combustion are carbon monoxide and soot. In general this reaction can be described with following equitation:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow x\, CO_2 + \frac{y}{2} H_2O \text{ (Equ. 8)}$$

This equitation, also called gross elemental equation, is the result of many single reactions, e.g. the combustion of methane consists of 400 different elemental reactions.

The oxidation of aliphatic hydrocarbons is a complicated process. Following figure shows a simplified general overview.

Fristom and Westernberg (21) distinguished two thermal zones. The primary zone, in which the hydrocarbons are reduced to products (carbon monoxide, hydrogen water), radicals (hydrogen, oxygen, hydroxide) and intermediates. The formed intermediates depend on the fuel, e.g. for propane: olefins (ethene, propene) and paraffins (methane, ethane) are built. In the secondary zone CO and H_2 are completely oxidized to carbon dioxin and water in form of steam. In this zone most of the heat is released.

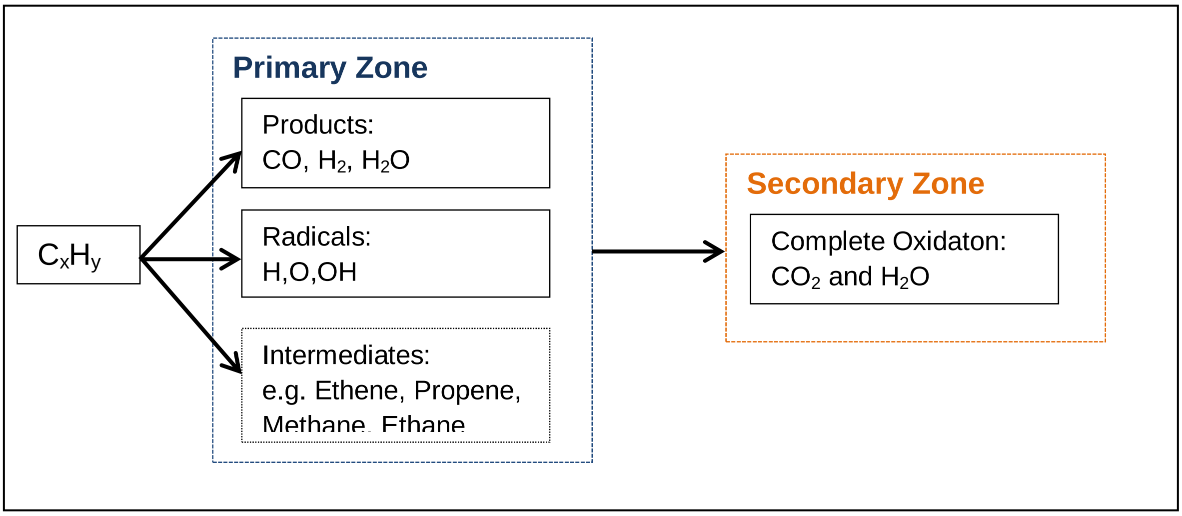


Figure 3.13: Simplified overview of two reaction zones during combustion

3.5.2 Formation of Polycyclic Aromatic Hydrocarbons and soot

In the following a description of how soot is formed will be given. First it starts with a general overview of particle generation and then an explanation of two different reactions that lead to the formation of poly aromatic hydrocarbons, which are intermediates in the soot generating process, is provided. At the end the soot formation in general will be described.

3.5.2.1 Particle Formation in General

According to today's knowledge the particle formation can be described with following strongly simplified schematic explanation (22)(23):

Due to thermal conduction from the flame front C-H and C-C compounds are split and among other components a high quantity of ethyne is formed, which is an important component for the soot formation. Due to the reaction between ethyne and radicals of alkenes and alkynes, aromatic hydrocarbons are formed, which coagulate to larger molecules and PAH´s subsequently. Plane PAH´s build spatial soot nuclides with a diameter of approximately 1nm.

Surface growth and coagulation of the soot nuclides form primary soot particles with diameters around 20-30 nm.

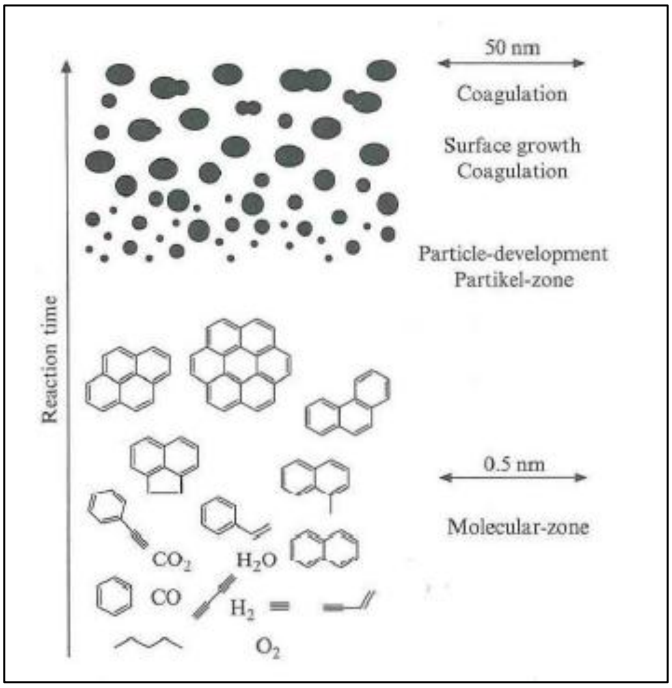


Figure 3.14: Simplified process of soot formation **(24)**

3.5.2.2 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons, PAH´s, are organic compounds that consist of minimum two aromatic ring systems. As example the simplest PAH is naphthalene, see Figure 3.15.

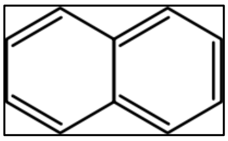


Figure 3.15: Chemical structure of naphtalene

When polycyclic aromatic hydrocarbons are arranged in a spatial configuration, instead of a plane one, soot particles are formed.
The formation of the first benzene ring can be described with different reactions, which depends on the combustion procedure and the used fuel. In the following the Ethyne- and the Ion Path Reaction are explained.

3.5.2.2.1 Ethyne Path Reaction:

In a first step the ethyne reacts with a vinyl radical (C_2H_3) to C_4H_5. Then depending on the local temperature two reaction paths are possible, for each path an additional ethyne molecule is needed to close the benzene ring (25). At high temperatures a phenyl, at low temperatures a benzene ring is formed.

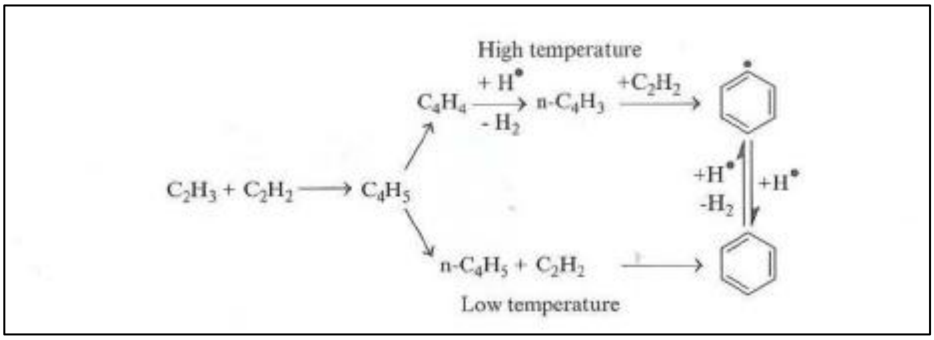


Figure 3.16: Reaction path in the formation of benzene rings, acc. to Frenklach and Wang (1994)

3.5.2.2.2 Ion Path Reaction (26):

First the ethyne molecules react with CH- or CH_2- groups and form C_3H_3-ions. With a relocation of H-atoms two C_3H_3-ions form PAH rings, refer to Figure 3.17.

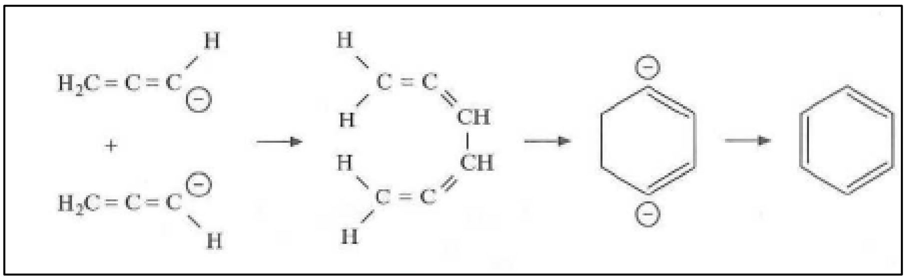


Figure 3.17: Development of benzene rings, acc. to Warnatz et al (2001),

Due to an increasing level of H-abstraction and C_2H_2 addition PAH rings are formed, see Figure 3.18.

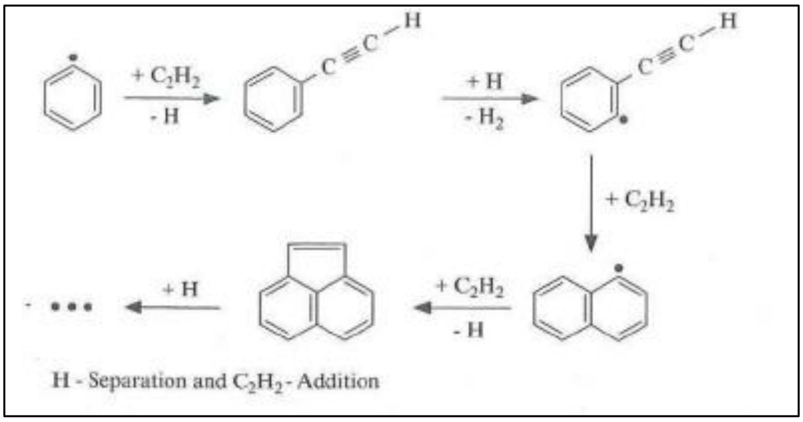


Figure 3.18: H-Separation and C_2H_2 Addition

A second possible way to build ring compounds is that benzene rings directly unite, see Figure 3.19.

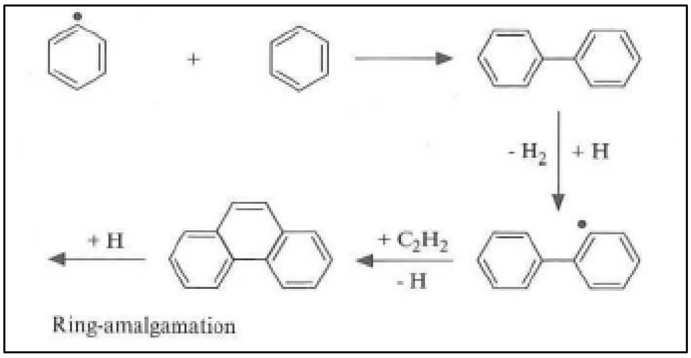


Figure 3.19: PAH growth, acc. to Frencklach and Wang (1994),

3.5.2.3 Soot Formation (22) (20)

The word soot is often used for a wide range of carbonaceous solid materials that contain hydrogen or other elements which can be found in fuels.
Some characteristics that are described by Palmer and Cullis (27) will be mentioned:

- The carbon formed in flames generally consists of at least 1% by weight of hydrogen
- under an electron microscope the carbon appears to consist of spherical particles that looks like a necklace
- the diameters of these "pearls" vary from 100 to 2000 Å
- X-ray diffractions show that each particle consists of a large number (10^4) of crystallites
- Electron diffraction shows that each crystallite consists of 5-10 sheets of carbon atoms
- based on calculations an "average" spherical particle contains of 10^5 to 10^6 carbon atoms

The formation of polycyclic aromatic hydrocarbons (PAH) is the base of the soot formation. Typically the term soot can be used when PAH`s are arranged spatially due to the collision of two PAH molecules or more. When the size of the aromatic structures is large enough they can build soot nuclei. The diameter of such formed carbon particles is around 1-2nm. Molecules from the gas phase, as example PAH´s that condensate on to the soot particles, enlarge them.
Then the growing particles coagulate and primary soot particles are formed. As mentioned before the particles exhibit a chain-like structure. Parallel to the formation process soot oxidation occurs and gaseous products are formed. Both, the formation (pyrolisis) and the attack (oxidation), are depending on high temperatures, thus the influence of the temperature regarding an overall soot formation process is hard to standardize.

Palmer and Cullis had investigated whether the type of the flame plays an important role during the soot formation process (27): *"With diffusion flames and premixed flames investigations have been made of the properties of the carbon formed and of the extent of carbon formation under various conditions. In general, however, the properties of the* *carbon formed in flames are remarkable little affected by the type of flame, the nature of the fuel being burnt and the other conditions under which they are produced."*

The soot formation is not a homogenous process. Thus particles have different rates of growth, of oxidation, of condensation and of coagulation so that a distribution of different particle diameters occurs. This size distributions play an important role for possible applications the soot source can be used. Important parameters that affect the soot formation will be described later.

3.5.3 Combustion Scheme of a Diffusion Flame (28) (24)

It can be distinguished into following three flame types (29):

- **Premixed flame**
  The fuel and the oxidizer (reactants) are mixed before they are reaching the flame front. As example a Bunsen burner can be mentioned.

- **Diffusion flame**
  The reactants are not pre-mixed and the flame front is located where the fuel and the oxidation air meet. E.g. the flame of a lighter or a candle

- **Partially premixed flame**
  This kind of flame occurs when the reactants are injected a few centimeters before the flame front and the time between the injection and the combustion is too short to pre-mix the components completely. This type of flame is used in most of the modern gas turbines.

Figure 3.20: Diffusion flame (left), partally pre- mixed flame (center) and a pre-mixed flame (right) **(29)**

At a diffusion flame the cold fuel is heated up due to the diffusion of warm combustion elements that are located nearby at the flame front. The increasing temperature combined with a high deficiency of oxygen leads to a thermal dehydration, Figure 3.21-area 1. During this process a big part of the available hydrogen is split from the hydrocarbons and ethyne (C_2H_2) is formed. Due to a high level of diffusivity and a low convective velocity the hydrogen reaches the sidewise delivered oxygen first and creates then the reaction zone at the base of the flame area 2. To that effect the OH radical concentration is high in this area.

Around area 3 ethyne reacts with oxygen first to carbon monoxide and then to carbon dioxide. The conversion of CO to CO_2 is a highly exothermic process.

$$C_2H_2 + \frac{3}{2}O_2 \rightarrow CO + H_2O + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O \text{ (Equ. 9)}$$

The blue luminous effect, area 2, results from chemiluminescence of carbon monoxide (indication that hydrogen oxidizes).
The rest of the ethyne diffuses to the flame core, area 4, and leads to the formation of polycyclic aromatic hydrocarbons (PAH). The formation of PAH´s with a sufficient residence time leads to the formation of soot. The following parameters affect the soot formation:

- the quantity of the formed ethyne,
- the residence time within an insufficient oxygen zone
- an adequate high temperature for the reaction and
- the residence time of the formed soot in zones with sufficient oxygen supply and high temperatures (T_{crit} > 1400K), thus soot burn off will start.

With an increasing flame height the availability of hydrogen decreases, that leads in reaction with hydrocarbon compounds to carbon dioxides. In area 5 the soot particles begin to burn off. The flame burns orange which is an indication that carbon is combusted. Due to soot radiation, the temperature decreases, the soot burn off stops and soot is released from the diffusion flame. Thus soot can be won by cooling the reaction in an earlier phase of the combustion.

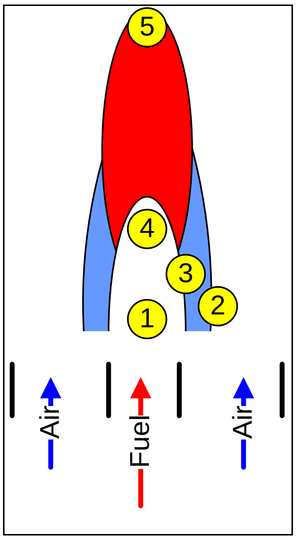


Figure 3.21: Reaction zones in a Diffusion Flame

3.5.4 Particle Losses and Dynamics (30)

The particles of an aerosol are affected by different mechanisms. As a result the particle mass or/and the particle concentration can be changed due to the effects explained in the following.

3.5.4.1 Basic Definitions of Particle Losses, Dynamics and Transformation

Following Figure 3.22 shows the most important mechanisms of particle losses, dynamics and transformation that may have effects on to the particle size distribution regarding number and mass concentration.

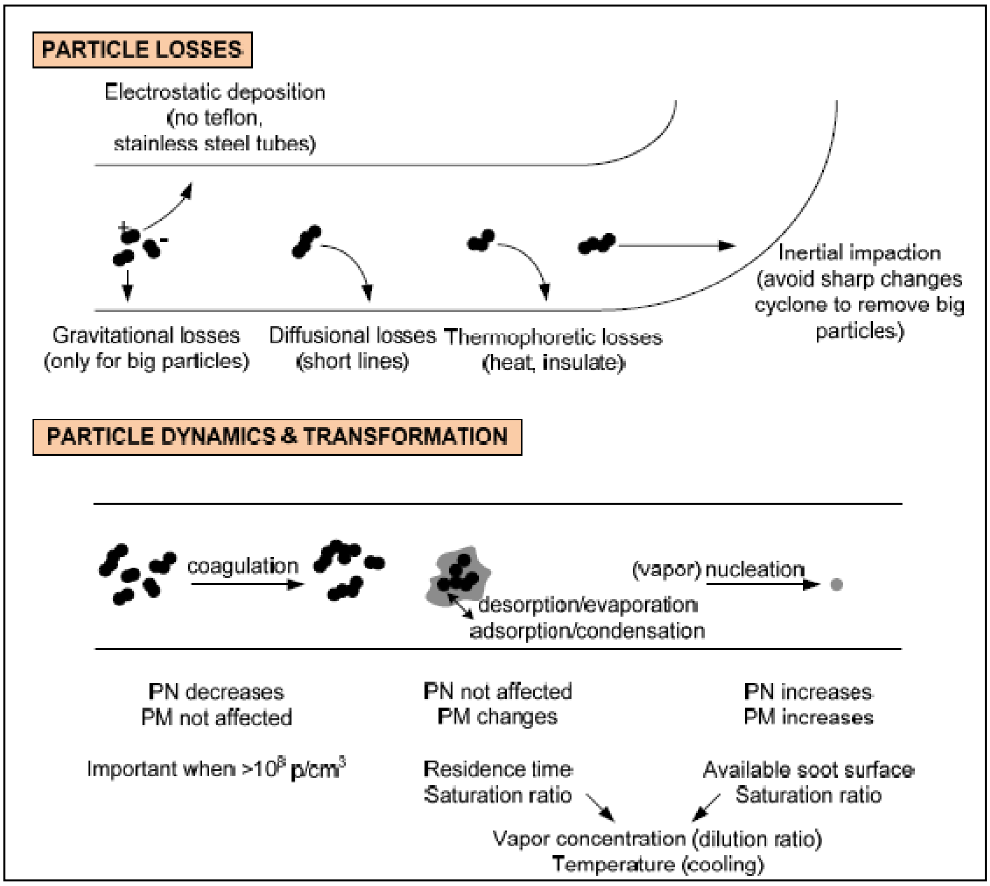


Figure 3.22: Mechanisms that affect the particle mass and/or the concentration **(30)**

Electrophoresis:
Electrophoresis is the motion of charged particle induced by an electric field (30). This mechanism can occur in tubes or pipes that are produced of a material which can be electrically charged. For 100 nm around 30% of the particles are charged positively, approximately 30 % negatively and the rest neutral due to the processes of an internal combustion. This means when a non- conductive tube material is used the electric field may cause a motion and a deposition of the particles at the wall.

Gravitational Losses:
This effect occurs for larger particles, <1µm. For smaller particles this mechanism is negligible small.

Inertial Impaction:
As a result of sharp changes and bends it is possible that particles are not able to follow the flow lines anymore due to their inertia. Thus they will deposit at the wall and the particle concentration is affected. This effect is negligible small for particles <1µm.

Thermophoresis:
A temperature gradient between the aerosol (hot) and the wall (cold) results in a motion of particles and their deposition. To avoid this effect the tubes can be heated to reduce the gradient.

Coagulation:
Coagulation of particles is a process wherein aerosol particles collide with one another due to a relative motion between them and adhere to form larger particles. As example the collision of primary soot particles can be mentioned to form agglomerates.

This definition does not distinguish between liquid or solid particles. In the case of solid particles, the coagulation process is also called agglomeration and the resulting particle clusters are known as agglomerates respectively.

Coagulation affects the particle size and of course the number concentration of the aerosol but does not change the particle mass concentration.

4 AVL Particle Generator

The AVL Particle Generator (APG) consists of a Burner Unit (MiniCAST, Model 6203C), a Volatile Particle Remover (VPR) and a Dilution Bridge Stage (DBS). The burner produces soot particles during the combustion of propane and the VPR thermally pre-treats the aerosol by removing volatile and semi-volatile components.
With an additional Dilution Bridge Stage the particle number concentration can easily be set to low values, e.g. which are necessary for a PNC linearity check, by using a needle valve. Referring to Figure 4.1 three sample outlets are available. The first one directly after the burner provides the highest particle mass- and number concentration but the particles contain volatiles. At the second sample outlet (VPR out) the volatile portion is removed and the aerosol is diluted twice. At the third outlet (dilution bridge out) the soot particle are diluted a third time.

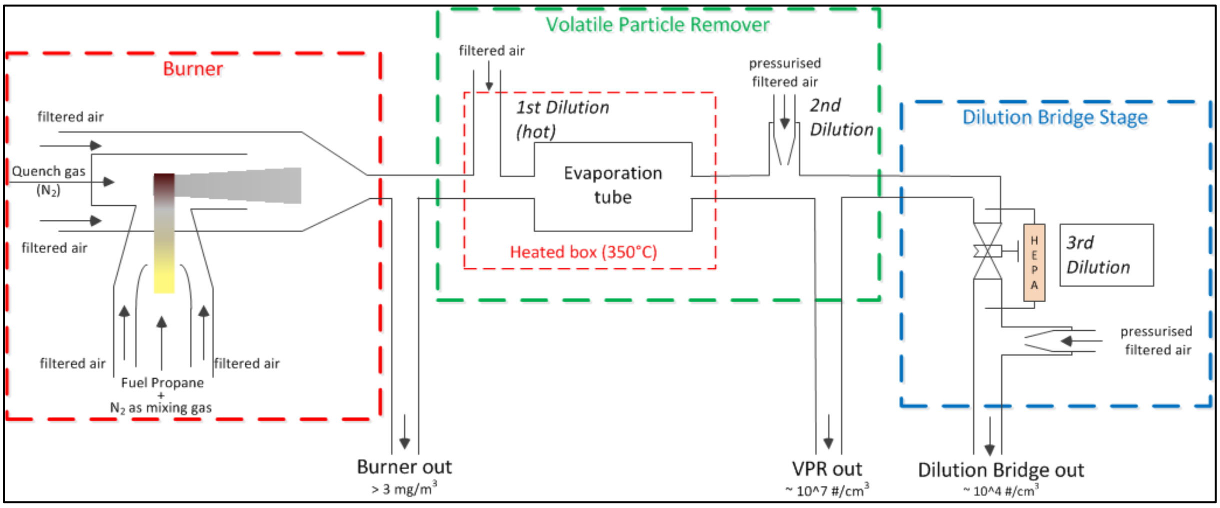


Figure 4.1: Main components of the AVL particle generator

To avoid throttling effects at the sample outlets due to overpressure, additional outlets for an excess flow are installed after every component. Due to the thermal condition and the various dilution stages the APG can be used for a wide range of applications:

- Particle number counting (PNC) device checks like the lower counting limit and the concentration linearity
- Particle concentration reduction factor (PCRF) check of a PN system
- PM and PN relative measurements
- Calibration of a PN system like an AVL Particle Counter (APC)

In the following the separate components and the functional principle of the APG will be described in detail.

4.1 Burner Unit (MiniCAST)

The MiniCAST uses a diffusion flame to generate soot particles via pyrolisis. As described earlier soot is generated in areas at which the oxygen supply is insufficient. That means, to use this type of flame as a soot source a further oxidation of the soot particles that are formed within the flame has to be stopped.

4.1.1 Functional Principle

The functional principle of the burner can be explained with following Figure 4.2. The burner uses a co-flow diffusion flame to generate soot particles. The propane fuel and the N_2 mixing gas are led to the burning chamber. The oxidizer, in that case filtered air, coats the flame, compared to the pre-mixed flame in which the fuel and the oxidizer are mixed together before entering the burning chamber. In the surrounding of the flame no or only a small number of soot particles can be found due to soot particle oxidation.
In order to generate soot with this type of flame a further oxidation of the particles is stopped by cooling the reaction with an inert gas like nitrogen. Quenching the flame freezes the reaction and soot particles are released. For a dilution, air is added to the exhaust flow subsequently.

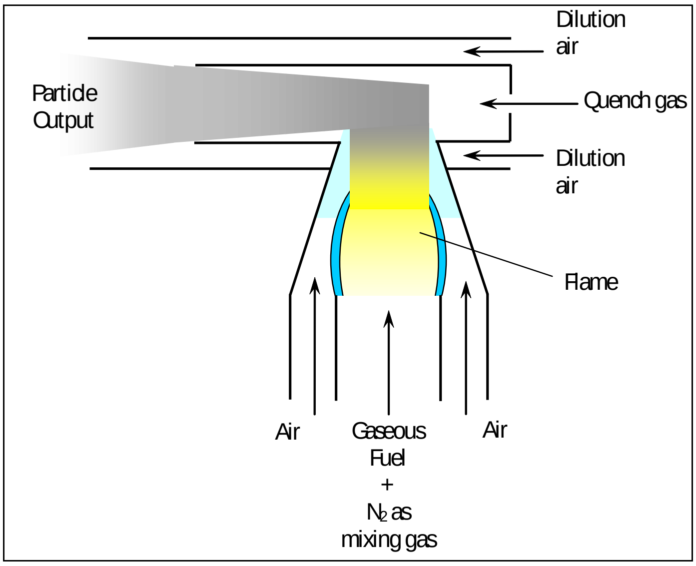


Figure 4.2: Functional principle of the MiniCAST burner **(28)**

For particle inception and growth the vertical axis plays an important role, refer to Figure 4.3. Low in the flame small soot nuclei are formed that start coagulating with other primary particles to larger particles by moving up the vertical axis. Higher in the flame or at the side where the oxygen supply is larger, soot oxidation occurs and the previously formed coagulates are burnt. Thus the concentration decreases but the diameter of the soot particles increases due to larger agglomerates.

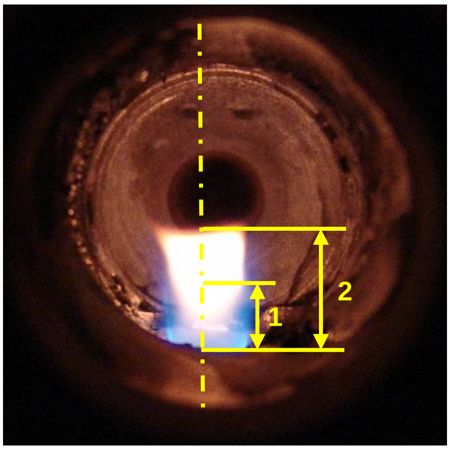


Figure 4.3: View into the MiniCAST burner outlet on to the propane diffusion flame

When a low quenching position (position 1) is chosen, soot particles with a small diameter are released accordingly a high quenching position (position 2) releases larger sized particles. In order to change the quenching position one should change the geometry of the quenching position either by moving the nitrogen inlet or by moving the bottom of the flame. With respect to the MiniCAST burner the geometry is fixed, that means setting the quench height requires the movement of components. Alternatively the size of the flame, which leads to different quenching positions, can be changed by varying the propane flow. A high gas flow will effect a large flame and the quench process is conducted in an earlier phase of the reaction, while a low fuel flow leads to a small flame and large particles.

The quenching of the flame with nitrogen acts also as a dilution of the exhaust gas thus no water condensation occurs at room temperature (28).
As mentioned before the fuel gas can be mixed with a mixing nitrogen flow that will result smaller particles by increasing the mixing gas flow.
Depending on the settings, the MiniCAST burner can produce soot particle concentrations in the range of 10^7 - 10^8 particles per cm³. Most of the applications need particle concentrations with lower values. For this reason the exhaust gas flow can be diluted with filtered air before the flow is released to the exhaust pipe.

Summarizing five mass flow controllers are necessary to control the diffusion flame and the soot production/ formation respectively:

- Fuel gas flow
- Nitrogen mixing gas flow
- Nitrogen quenching gas flow
- Oxidation air flow and
- Dilution air flow

The effects of these parameters are discussed in chapter 4.1.2.2. Following figure shows the flow diagram of the MiniCAST model 6203C that is used in the APG.

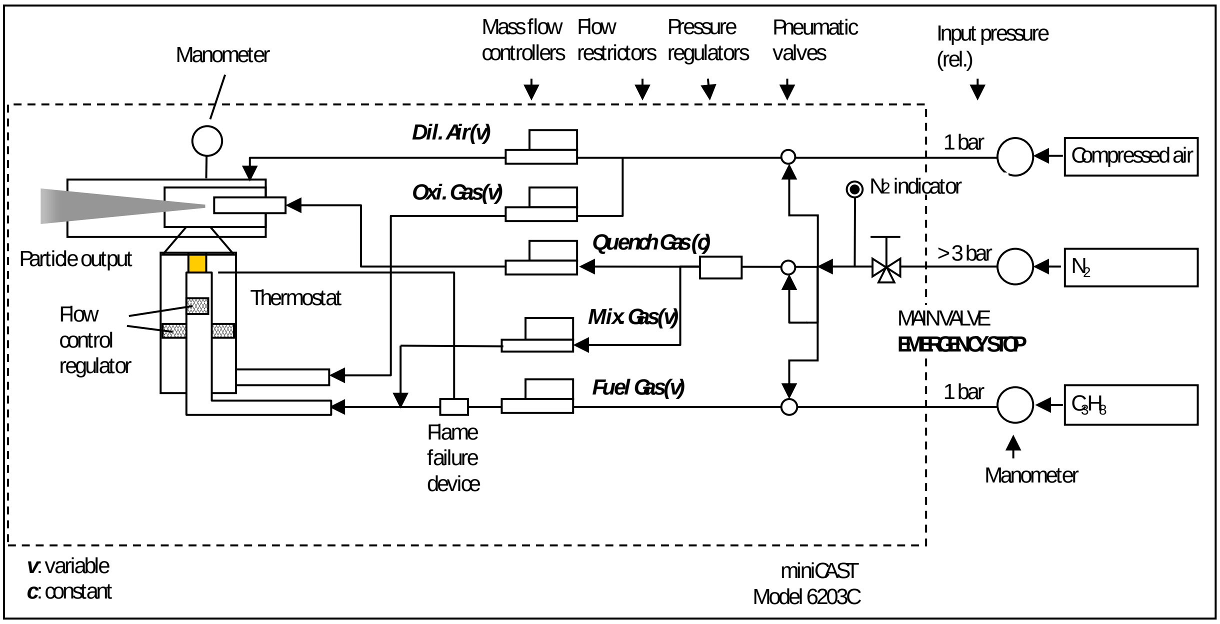


Figure 4.4: Flow scheme of a MiniCAST, model 6203c from Jing **(28)**

With the main valve the nitrogen flow can be controlled. The nitrogen flow causes the opening of the pneumatic valves if the pressure is at least 3 bar (relative pressure) or higher. By opening the pneumatic valves the mass flow controllers are exposed with the respective flow. When the main valve is closed the valves are switched off and the gas supply for each controller is stopped. Thus the main valve has the function of an emergency stop.

4.1.1.1 Safety Features

To prevent an active flow of propane if the flame is not ignited or got extinguished an additional flame safety device got used. A thermo couple, installed in the burning chamber, generates a voltage due to thermo electric- or the Seebeck effect respectively. The voltage opens a small magnetic valve and the propane line to the burning chamber is opened. The thermo couple requires a high temperature to work, this is the case when the flame is ignited and burning. If the flame got extinguished the voltage decreases the valve closes and the propane supply is stopped. Thus the release of propane to the ambience is avoided.

In order to avoid that a flammable propane air mixture is released to the environment, the nitrogen mass flow controller is set to a constant value of 2 liters per minute. This means in the case the valve of the flame safety device stuck open the mixed composition is under the explosion limit thus the flow at the outlet of the burning chamber cannot even be ignited by a lighter.

Summarizing the propane supply flow is stopped mechanically if the flame is extinguished and even if the valve is broken the propane is mixed with nitrogen and oxygen resulting a mixture that is under the explosion limit.

The AVL Particle Generator utilizes a MiniCAST series 6203c soot generator from Jing. Following Table 6 shows the specifications of the device (31):

Table 6: Specifications of a MiniCAST model 6203c from Jing **(31)**

Particle	Combustion Soot Particle
Particle Size Range	20-200 nm
Concentration Range	Up to 10^8 # cm^{-1}
Smoke Exhaust Gas	30 lpm (1.h m^3 h^{-1})
Mass Output	20 (30nm) - 500 (200nm) mg h^{-1}
Aerosol Temperature	80 - 140 °C
Accuracy	± 5% for mass and number concentration ± 2 % for Particle Size (± 3 nm)
Repeatability	± 5%
Quench Gas	Inert Gas (N_2) or ambient air
Fuel Requirement	Oil free, purity < 99%

4.1.2 MiniCAST Components

In following section the separate components of the MiniCAST, their functional principle and influencing factors on to the aerosol are discussed.

4.1.2.1 Burner of the MiniCAST

In order to generate a co-flow diffusion flame, refer to chapter 4.1.1, the fuel gas flow has to be coated with the oxidation air. In the following the realization for the MiniCAST burner unit will be explained. The figure below shows the components of the burner. The first three components, from the left, built the lower part (1) and the remaining component the upper part (2) of the burner. Figure 4.6 shows the view into the lower part (A-A) and Figure 4.8 shows the view into the upper part where the propane is combusted and the diffusion flame is located (B-B).

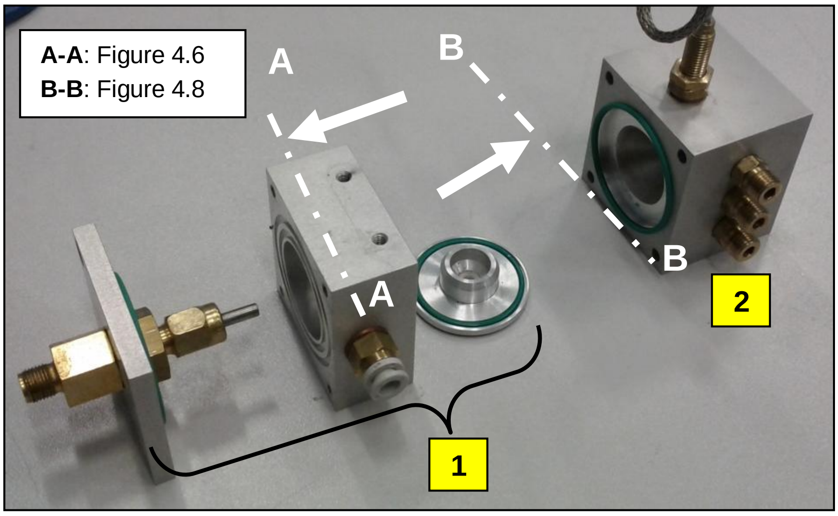


Figure 4.5: Main components of the burner

The propane and the mixing gas inlet is located at the bottom side of the burner. The mixture flows through an orifice and a short metal tube and then enters the burning chamber (Figure 4.6, red arrow), that is the upper part of the unit. At the side the oxidation air inlet is located (1). The air flows to a stabilization chamber and then through the round disk (Figure 4.7) to the burning chamber, that is located at the upper part of the burner, refer to Figure 4.5 (2). The oxidation air flow is then parallel to the propane flow (blue arrows).

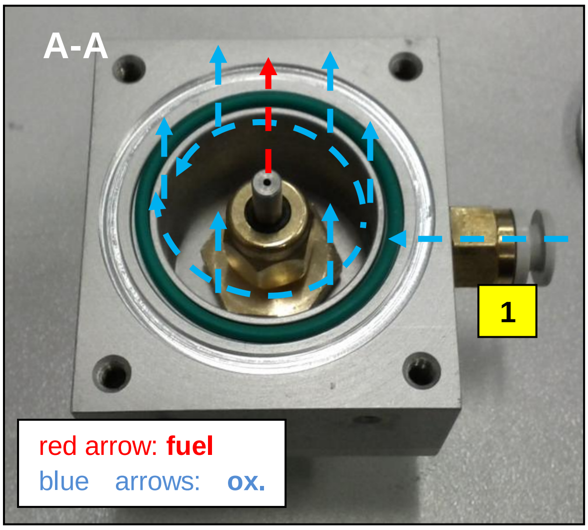


Figure 4.6: Lower part of the burner

Figure 4.7: Cover plate of the oxidation air chamber

Figure 4.8 shows the inlet into the burning chamber of the fuel and oxidation air (see view B-B). The orange arrow indicates the flow of the quench gas that is merged with the diffusion flame in a 90° angle. The quench flow carries the aerosol out of the burning chamber (red arrow) . The connectors for the dilution air are on the same side as the connector for the quench gas is, thus the dilution air flows through the block (see Figure 4.8, blue arrows) and is than mixed at the outlet of the burner with the exhaust gas flow (see **Figure 4.9**, blue arrows). Detail (1) shows the thermo couple of the flame safety device that touches the flame.

Figure 4.9 shows the view into the burning chamber from the exhaust outlet. The fuel gas and the oxidation air enter this part of the burner from the bottom side (red arrow). At position (2) the nitrogen flow quenches the flame. Subsequent the exhaust flow is mixed with the dilution air through the supply holes (blue arrows).

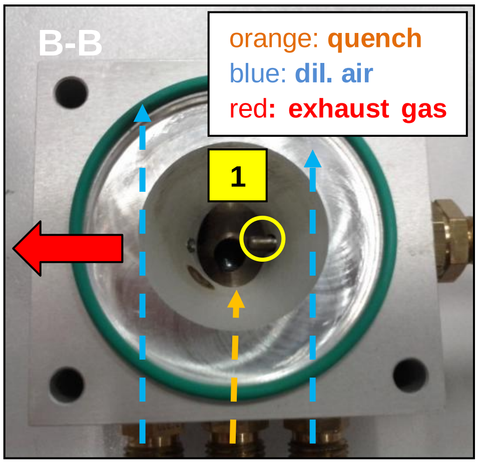


Figure 4.8: Inlet of the gasses to the burning

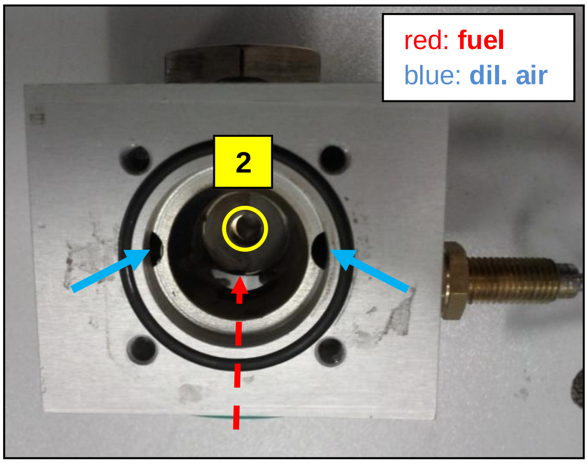


Figure 4.9: View into the burning chamber outlet

4.1.2.2 Parameters that affect the generated size distributions

The size distribution of the generated aerosol can be affected, as mentioned before, by the mass flows of the respective supply flows, more specifically:

- The C/O (carbon to oxygen) ratio, or the air to fuel ratio or the lambda. This can be achieved by modifying either the fuel or the oxidation air flow.
- The quenching position: This cannot be achieved by physically moving the position but indirectly by changing the flows of fuel and oxidation air (even for keeping the same lambda).
- Dilution: Dilution after quenching further affects the agglomeration process and the final concentration.

In the following the effects of each flow on to the size distributions and the aerosol will be discussed. For the measurements, a SMPS that consists of an electrostatic classifier from TSI (model 3080) and a TSI condensation particle counter (model 3775) are used, see Figure.4.10.

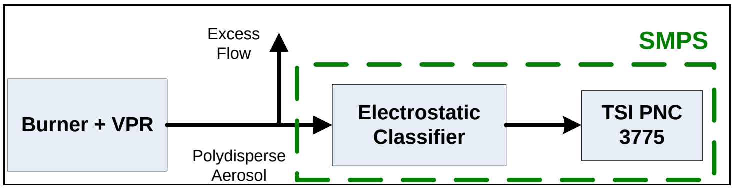


Figure.4.10: Setup for measuring the aerosol size distributions

The ranges of each mass flow controller are limited and respectively depending on the dimensions of the burner unit. Following table shows the used controller with the respective limit and effects:

Table 7: Parameter of a MiniCAST model 6203 from Jing

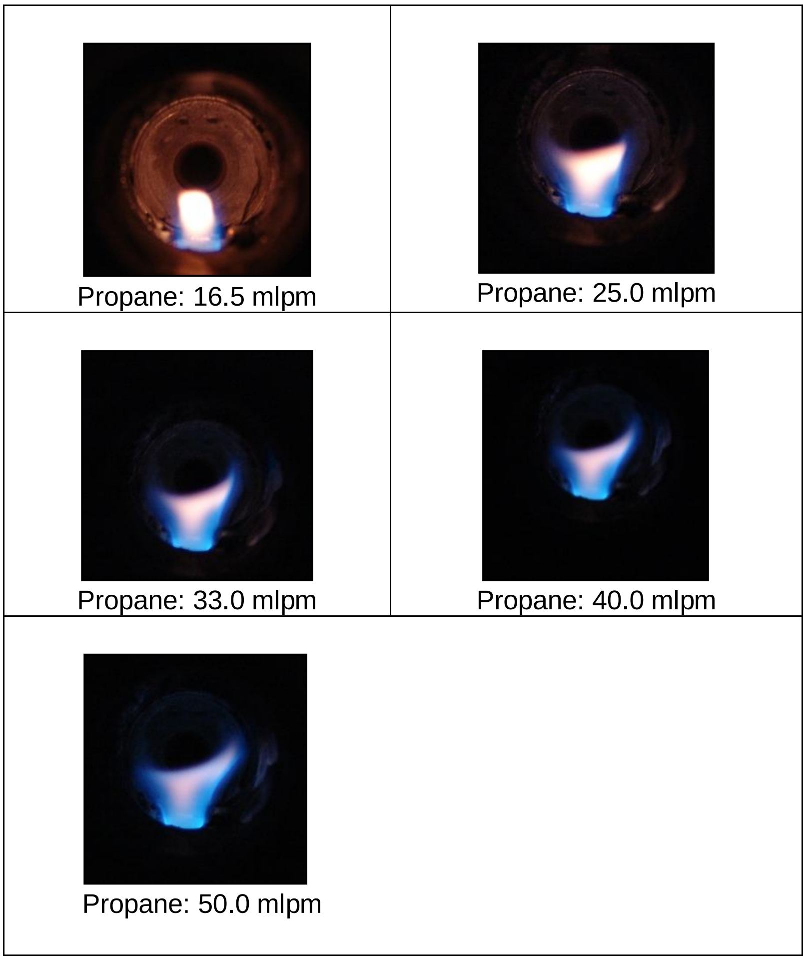
MFC	Limit	Effects on to:
Fuel Gas C_3H_8	50 mlpm *	Quench position, Concentration, Size
N_2 Mixing Gas	60 mlpm *	Concentration, Size
Oxidation Air	1.0 lpm **	Concentration, Size
N_2 Quench Gas	2.0 lpm **	Concentration, Size
Dilution Air	10.0 lpm **	Concentration, Size

* mlpm...milliliter per minute

** lpm liter per minute

4.1.2.2.1 Fuel Gas

Following pictures provide a view, against the quench gas flow direction, directly into the burner of the MiniCAST. At low propane flows (16.5 mlpm) the quenching position is high relative to the flame. By increasing the mass flow of the fuel the lambda decreases and the flame grows, so that the tip of the flame forms a sickle (see Figure 4.11 – propane flow 25 to 50 mlpm). In this case the quench position relative to the flame height is lower.


Propane: 16.5 mlpm

Propane: 25.0 mlpm

Propane: 33.0 mlpm

Propane: 40.0 mlpm

Propane: 50.0 mlpm

Figure 4.11: Effects on to the flame by changing the propane flow

Figure 4.12 shows the size distributions of the different propane flow rates. The propane flow rate affects both number concentration and mean size of the distribution. The higher

the flow rate, the higher the total number concentration. This is reasonable as more fuel is available for combustion. However higher flow rate results in smaller size too.
For example, see Figure 4.12 (1) and (2). A lower propane flow results in a smaller flame (Figure 4.11 - 16.5 mlpm), thus the quench flow touches only the tip of the flame and the orange center in the flame is unaffected resulting larger agglomerates, refer to Figure 4.12 (1). With a fuel flow of 25 mlpm the flame is larger and the quench flow intrudes into the flame more in the orange center, see Figure 4.11 – 25 mlpm. Referring to Figure 4.12 (2) the particle size decreases and the particle number concentration increases due to a higher amount of propane.

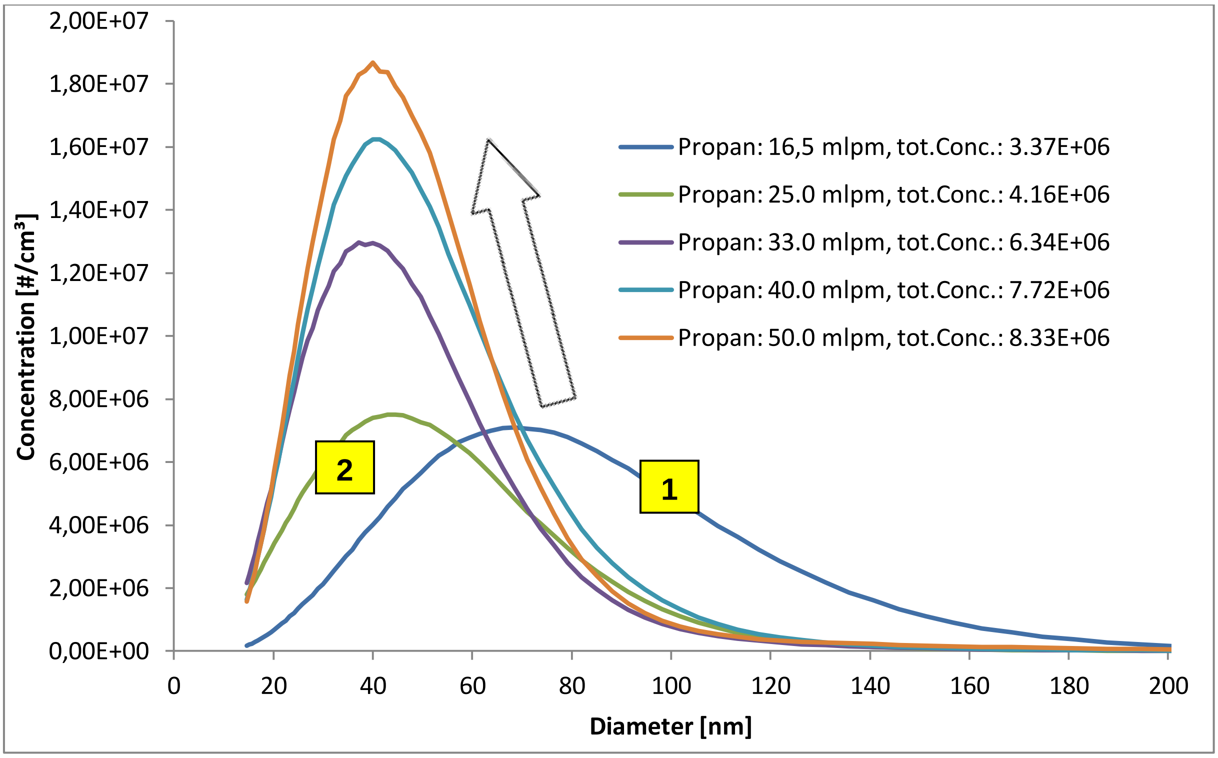


Figure 4.12: Effects on to the size distributions by changing the propane flow with an oxidation air flow of: 1.0 lpm

4.1.2.2.2 Oxidation Air

As described earlier in chapter 4.1.1 the fuel is combusted in a co-flow diffusion flame where the oxidation air supply at the outer side of the flame is sufficient and at the center insufficient, thus soot will be generated there. In this section the influence of the oxidation air respectively the lambda are investigated.

Table 8 shows three different propane flows (18, 20 and 25 ml/min), each with 4 different oxidation air amounts (400, 600, 800 and 1000 ml/min) and the measured mode diameter. For each setting the respective lambda is calculated.
It can be concluded that for settings where λ < 1 (the air supply is not sufficient enough that a “complete” diffusion flame can be formed), smaller particles are produced and for a λ >> 1 larger particles are generated

Table 8: Effects of different lambda on to the mode diameter

λ	C_3H_8 [ml/min]	Air [ml/min]	Mode [nm]
0.91	18	400	10.1
1.37	18	600	20.9
1.83	18	800	42.9
2.28	18	1000	57.3
0.82	20	400	10.6
1.24	20	600	17.5
1.64	20	800	34.6
2.06	20	1000	46.1
0.66	25	400	11.8
0.99	25	600	18.8
1.3	25	800	25.9
1.64	25	1000	35.9

At the flame of a candle the extraneous oxidation air supply is sufficient when the combustion takes place in a free ambience. The flame can built the typical diffusion flame zones. At the MiniCAST burner the different reaction zones of the flame can be affected by modifying the oxidation air flow or the lambda respectively as explained before. This means by supplying the diffusion flame with a more or less insufficient coating air flow, e.g. 0.3 mlpm (λ<<1), only a small, blue flame will be built. By increasing the oxidation air flow the typical orange zone in the center starts to be formed (λ>>1), compare to Figure 4.13, 0.4 mlpm and higher.

 Oxidation air flow: 0.3 lpm	 Oxidation air flow: 0.4 lpm
 Oxidation air flow: 0.5 lpm	 Oxidation air flow: 0.7 lpm
 Oxidation air flow: 0.9 lpm	

Figure 4.13: Effects on to the diffusion flame by changing the oxidation air flow

In respect to the formation and the size of the orange center explained above, the particle size and number concentration is affected as Figure 4.14 shows. By increasing the coating oxidation air flow respectively the lambda, the particle diameter grows but the number concentration decreases. It seems that this could be a result due to the sufficient formation of the flame zones. Thus primary particles have a higher chance to agglomerate when the orange center is larger (longer residence time), but the soot burn off will increase due to a sufficient air supply which causes a smaller number concentration.

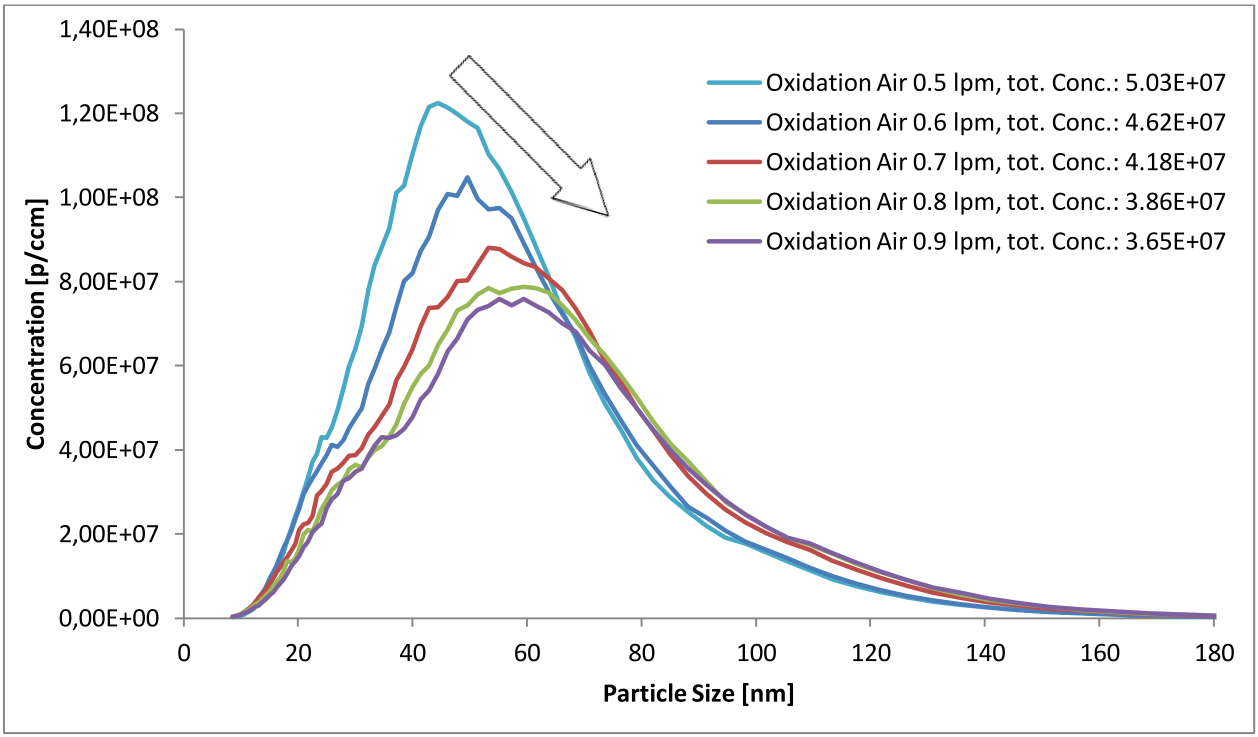


Figure 4.14: Effects on to the size distributions by changing the oxidation air flow [2]

Following figure shows the effects of the quenching position relative to the flame height for the same lambda. As explained earlier a larger propane flow results in a lower relative quenching position and smaller particles are formed whereas for lower flows the reaction is stopped at a higher flame level and larger particles are produced.

 Propane flow: 33.0 mlpm Oxidation air flow: 1.0 lpm λ = 1.25 Mode Diameter: 37.2 nm	 Propane flow: 20.0 mlpm Oxidation air flow: 0.6 lpm λ = 1.25 Mode Diameter: 53.3 nm

Figure 4.15: Different quenching position and the effects for the same lambda

Following equitation shows the chemical reaction of propane with oxygen at stoichiometric conditions, thus the C/O ratio is 0.3 (1 C_3 related to 5 O_2), see (equ. 10).

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \text{ (Equ. 10)}$$

Comparing to other literatures (32) the richer the flame the higher the amount of PAH´s is. Thus smaller size distributions include more PAH´s than larger distributions.

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[2] Results refer to following settings: propane - 20mlpm, ox. air - xx, dil. air burner - 2lpm

4.1.2.2.3 Nitrogen Mixing Gas

Mixing nitrogen to the fuel gas affects the particle size. Figure 4.16 shows the effects on to the generated size distribution. Increasing the nitrogen mixing gas flow results in smaller particle size distributions. The modification of the nitrogen flow should be conducted in small steps to avoid a sudden extinction of the flame.

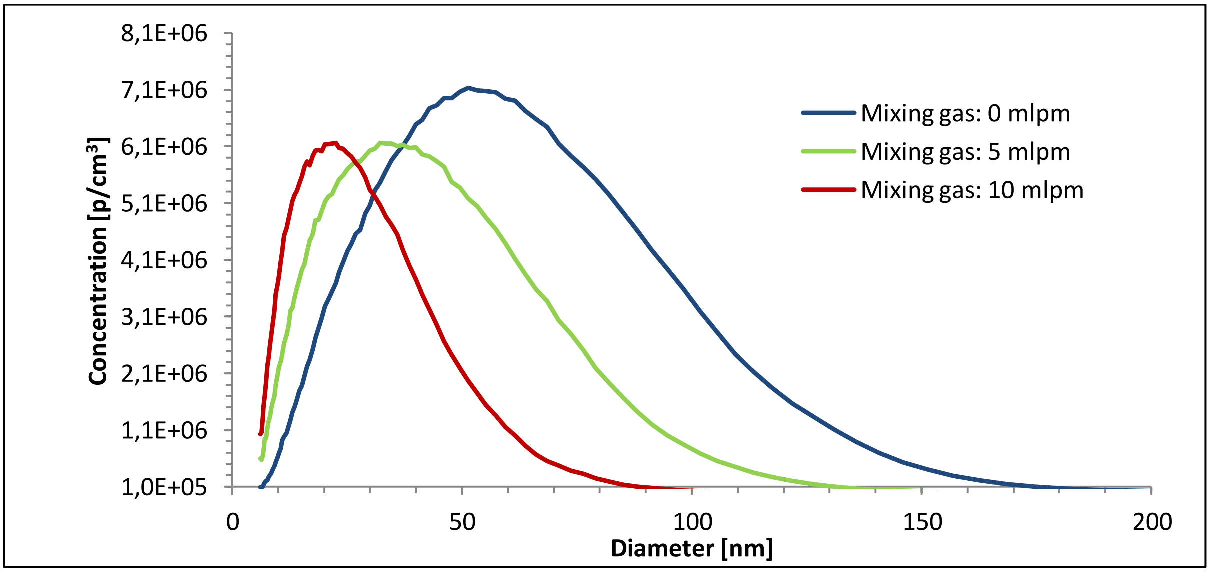

Figure 4.16: Effects of mixing nitrogen to the fuel gas; settings: 18mlpm propane, 0.8 lpm ox. air

4.1.2.2.4 Quench Gas

As described earlier the flow of the nitrogen quench gas is set to a constant value of 2 liter per minute due to safety reasons. For the following measurements the quench flow is the variable. However, in the normal operating mode a modification of the value is disabled.

Referring to Figure 4.17 an increase of the nitrogen quench gas flow causes higher number concentrations but smaller particle sizes. Probably this result is based on more effects: By increasing the flow the soot burn off is stopped earlier, because a higher flow to cool the flame is provided, which causes higher number concentrations. This means the reaction is stopped at a lower level. However, due to a higher nitrogen flow the dilution ratio increases as well, but it seems that the first effect has a stronger influence because all in all the concentration is enlarged. Additionally due to a higher dilution directly in to the upper part of the flame the agglomeration is affected and smaller particles are produced.

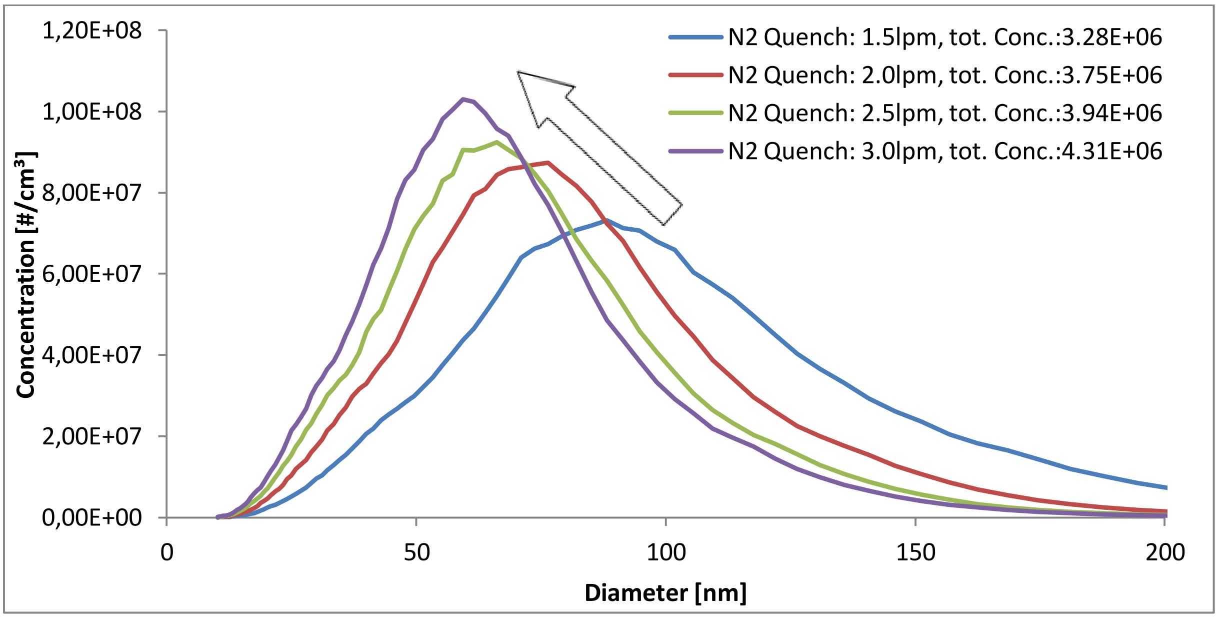

Figure 4.17: Effects on to the size distributions by changing the nitrogen quench flow

4.1.2.2.5 Dilution Air

In order to decrease the particle number concentration a dilution air flow can be mixed with the generated aerosol. Figure 4.18 shows the size distributions of different dilution air flows. As expected the higher the flow the lower the concentration. However, it seems that the air influences the agglomeration because by increasing the flow the particle diameters get smaller.

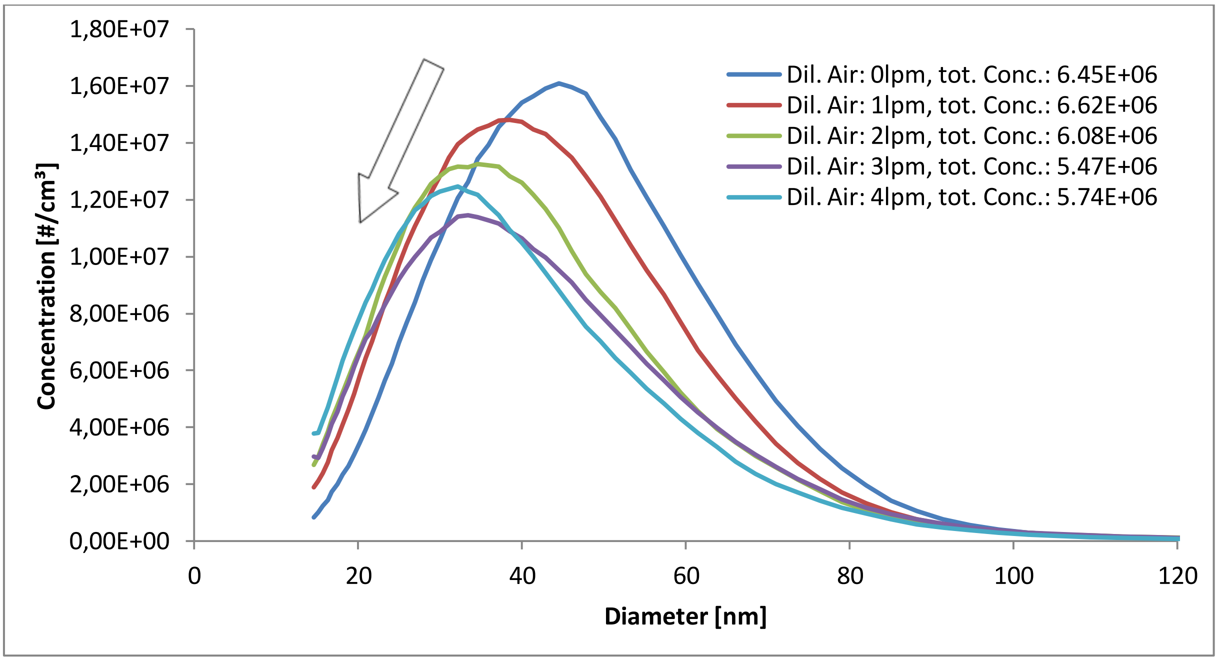

Figure 4.18: Effects on to the size distributions by changing the dilution air flow

That would imply that further agglomeration takes place after the burning chamber outlet. Referring to chapter 8.1, thermal coagulation is a spontaneous and ever present process, then the distance between the sample probe and burner outlet should be an additional factor which affects the aerosol. For further investigation the following measurements are conducted.

4.1.2.3 Distance between Burner Outlet and Probe Position

To determine possible effects of the distance between the burner outlet and the position where the volatile particle remover (VPR) samples from the exhaust pipe (see Figure 4.19), the VPR is connected at two different positions, x_1= 150 mm and x_2= 370 mm. Downstream the VPR a SMPS is measuring the respective size distribution. Additionally to the two distances the oxidation air supply will be varied to see if possible effects depends on the state of the flame, e.g. small air flow leads to a more or less blue flame.

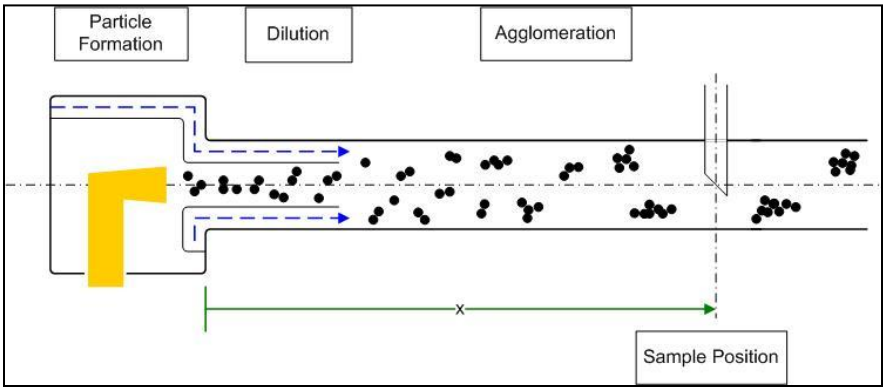

Figure 4.19: Dilution and agglomeration after the burner outlet, the length x describes the distance between the burner outlet and the sampling position

Independent from the oxidation air flow the size distributions are shifted to the right for a longer agglomeration line. The change of the number concentration is also similar, for each oxidation air supply an decrease about 26 % can be determined, except the first one which results from an unstable flame due to the flow conditions, refer to Figure 4.20.

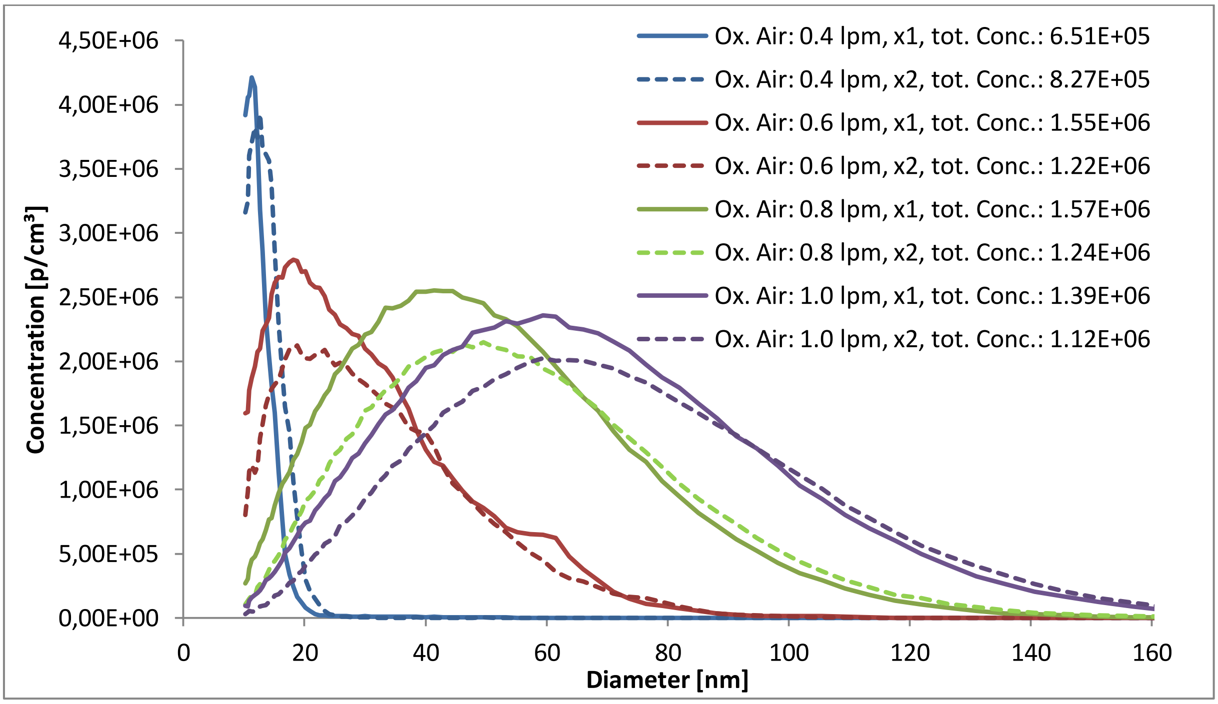

Figure 4.20: Size distributions of different distances between the burner outlet and the sampling position at different oxidation air levels. x_1=150mm and x_2 370 mm after the burner outlet. [3]

Thus it can be concluded that a consequence of a shorter distance between burner outlet and sampling position, is a higher total number concentration but smaller particle sizes due to an influence of the agglomeration. This means a longer distance affects positively a further agglomeration of the particles.

4.2 Mass Flow Controller

In order to control the respective flows that are necessary to regulate the diffusion flame, mass flow controller from the Vögtlin red-y smart series are utilized.

This type of mass flow controller uses the principle of the thermal radiation and the heat transport in a medium that is in motion. Compared to volumetric principles temperatures and pressure measurements are not necessary due to one of the big advantages that this principle is largely independent of these two state functions. The mass flow controllers are calibrated to standard volume (e.g. liter per minute) to provide values that can be compared to the results of other principles, but the output of the thermal principle is normally related to a mass (e.g. g/s). Important parameters are the specific heat and the standard density related to standard conditions, 0°C and 1013,25 mbar. Figure 4.21 shows the required components. Between two temperature measurement positions a heater is located. When the flow is zero position T1 and position T2 measure equal temperatures. By increasing the flow position T2 measures higher temperatures then position T1, thus a ΔT occurs that is direct proportional to the mass flow (see Figure 4.22). The reason that T1 measures a smaller temperature is that the sensor is cooled by forced convection, subsequently the flow carries the heat of the source to position T2 and the temperature increases there.

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[3] Results refer to following settings: propane - 18mlpm, ox. air - xx, dil. air burner - 2lpm

The sensor provides the actual value which is compared with the set value, subsequently a solenoid valve regulates the flow (33).

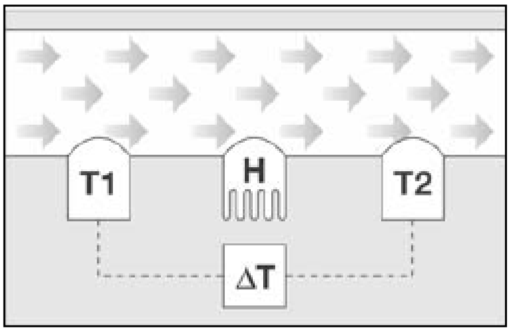

Figure 4.21: MFC Measurement principle**(33)**

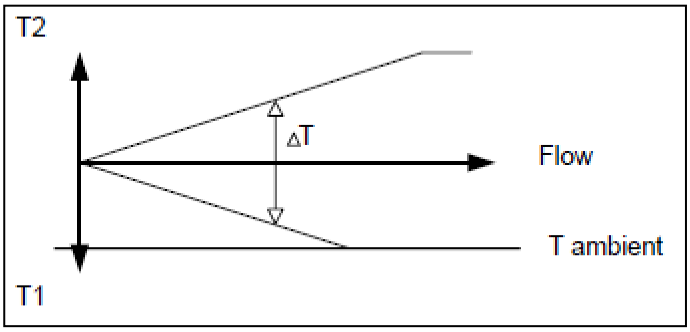

Figure 4.22: Temperature difference as a function of the flow**(33)**

4.3 Venturi Pump

In order to generate a flow through the volatile particle remover and through the dilution bridge venture pumps are utilized, see figure Figure 4.24 and Figure 4.31. The Venturi pump, also called ejector utilizes the Venturi effect which is a particular case of the Bernoulli principle. When a fluid is accelerated, as example by expanding a flow in a nozzle, the pressure decreases, that means pressure energy is converted into kinetic energy in the form of velocity and a low pressure zone is built that entrains a fluid. Subsequently the motive fluid and the entrained fluid, which can be, liquid or a dust laden gas as example, are mixed and decelerated. Thus velocity energy is converted back into pressure energy. The motive liquid can be steam, a liquid or any other gas (34)(35).
In the application with the particle generator compressed air, with 1 bar overpressure, is utilized that entrains a soot aerosol. A typical Venturi pump consists of a motive fluid nozzle and a converging nozzle and/or a diverging diffuser that builds the outlet.

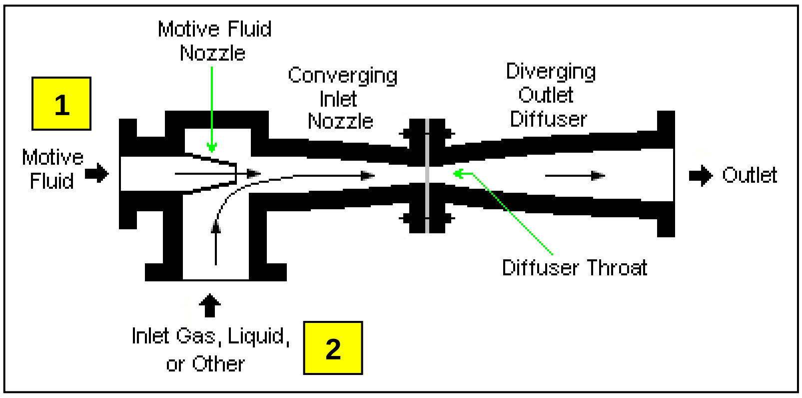

Figure 4.23: Components and functional principle of a venturi pump **(36)**

By changing the diameters either of the inlet nozzle or of the diffuser the inlet and the outlet flow can be adjusted. Thus the dilution ratio can be modified. Following Table 9 shows the effects of different component diameters. The dilution ratio is equal the quotient of Q_{out} to Q_{in}.

Table 9: Different diffuser and orifice diameter of a venturi pump and the effects on to the dilution ratio

Q_{in} [mlpm]	Q_{out} [lpm]	$d_{Orifice}$ [mm]	$d_{Diffuser}$ [mm]	p_{Inlet} [mbar]	Dilution Ratio
3110	12,0	0,9	1,4	-145	3,9:1
2560	15,0	1,0	1,4	-139	5,9:1
1240	15,8	1,1	1,4	-70	12,7:1
70	16,4	1,2	1,4	-	234,3:1
4660	14,6	0,9	1,6	-226	3,1:1
4470	17,0	1,0	1,6	-218	3,8:1
3850	18,4	1,1	1,6	-202	4,7:1
3250	19,4	1,2	1,6	-169	5,9:1

The values shown in the table above are measured at a venturi pump that is designed and used in an AVL Particle Generator, the motive gas flow has an overpressure of 1bar, refer to Figure 4.23 (1).

To analyze the effects of different orifices the diffuser remain constant, first with a diameter of 1.4 and then with 1.6mm, and the orifice is changed in 0.1mm steps. Then the flows up- and downstream of the venturi pump are measured with a mass flow meter (from Vögtlin) and then the dilution ration is calculated.

With the first used components, 0.9mm orifice and 1.4mm diffuser, the inlet flow is 3110 mlpm and the outlet flow is 12.0 lpm, that is equal a dilution ration of approximately 4 to 1. The inlet pressure is the corresponding underpressure to the inlet flow at position (2), referring to Figure 4.23. By enlarging the orifice diameter the inlet flow decreases, as well as the inlet pressure, and the outlet flow also increases. This means with larger orifice diameters, higher dilution rates can be achieved.

Using the same procedure with a diffuser diameter of 1.6 mm results larger inlet as well as outlet flows. This means expressed with values, using a 1.6 mm with a 0.9mm orifice leads to a dilution rate of 3.1 to 1. Compared to the 1.4 mm diffuser the dilution rate is smaller and increasing the orifice diameter affects smaller differences between the dilution ratios compared with the 1.4mm diffuser.

Summarizing this means with the diffuser diameter the range of the outlet flow can be modified. Compare the flow range using a 1.4mm diffuser, 12.0 to 16.4 lpm, to the larger diffuser, 14.6 to 19.4 lpm. A similar effect occurs for the change of the orifice diameter, but here the range also depends on the diffuser diameter, this means between 3110 and 70 mlpm for the smaller and 4660 and 3250mlpm for the larger diffuser.

4.4 Volatile Particle Remover

The Volatile Particle Remover of the APG consists of following three components:

- a primary hot dilution,
- an evaporation tube and
- secondary dilution at ambient temperature (Venturi Pump).

Figure 4.24 shows the flow scheme of the volatile particle remover. The dilution air (1) and the soot aerosol (2) flow pass two tubes at the outer side of this component, subsequently the flows are mixed together, see detail (3), and the diluted aerosol flow passes the inner tube with a larger diameter, which is the evaporation tube (4) at 350°C.
The VPR utilizes the principle of thermo-dilution (37) to remove the volatile and semi-volatile species from the aerosol. Due to a hot dilution the vapour pressure of the volatiles is reduced and no nucleation will appear during the cooling. An evaporation tube is required to evaporate all volatiles.
Another effect of the secondary dilution is to decrease thermophoretic losses. For this dilution stage a venturi pump, which has a constant dilution ration of 4:1 at operating temperature of the VPR at 350 °C, is utilized.

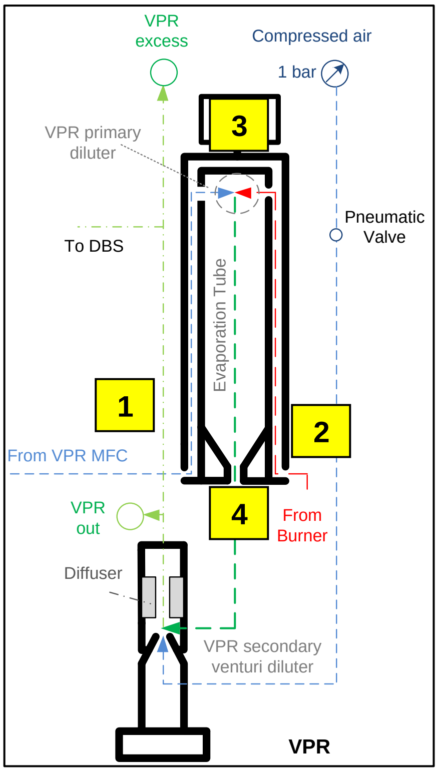

Figure 4.24: Flow scheme of the VPR used in an APG

The primary dilution flow is regulated by a mass flow controller, thus the primary dilution factor can be varied by changing the values of the MFC in a range between 0 - 5 lpm. Increasing the primary dilution air affects that the flow, sucked through the VPR by the venturi pump, is decreased. As example this means when the flow, sampled by the venturi pump, is constant 4.5 lpm without a primary dilution the inlet flow is equal 4.5 lpm. A VPR air flow of 1 lpm will affect that the inlet flow decreases to around 3.5 lpm because the venturi pump is still sampling 4.5 lpm constantly but 1 liter is provided by the dilution air. When using high dilution flows, e.g. 5 lpm, the intake flow of the venturi pump should be considered. As example the pump sucks 4 lpm and the air flow is set to 5 lpm, an overflow at the dilution air inlet will occur, thus the direction of the flows will change and no soot aerosol will be sucked through the evaporation tube. Typical venturi pump inlet flows are around 4 lpm, in order to avoid before mentioned effect typical used dilution air flows are in the range between 0 - 3 lpm.

4.4.1 Effects of the VPR on to the Size Distribution

The VPR removes volatile and semi-volatile components and dilutes the aerosol. To determine the effects of the removal on to the particles and their size distribution a SMPS was used downstream of the particle generator VPR, first with a temperature of 23°C (no effect on to the aerosol except dilution), than with operating temperature of 350°C (removal of volatiles expected). Also the flows are measured to determine the temperature effect on to the dilution factor of the VPR. Two different settings are chosen, one produces a rather large (burner settings: 17-0-1.0-2-2[4]) and the other a smaller (20-0-0.52-2-2) size distribution. For the smaller operating point, more volatiles and accordingly for the larger settings less volatile components are expected.

The venturi pump uses air as motive flow, thus the inlet and the outlet flow are affected by the temperature of the evaporation tube because the pump is also heated up by the hot (350°C) aerosol. Referring to Figure 4.25 the dilution factor, which is equal to the ratio of the outlet to the inlet flow, with a "cold" VPR is 4.35 : 1 and increases due to the higher operating temperature to 4.65 : 1. A primary dilution flow of 2 lpm is used. Thus the dilution factor increases, between the "cold" and the "hot" operating state of around 7 %.

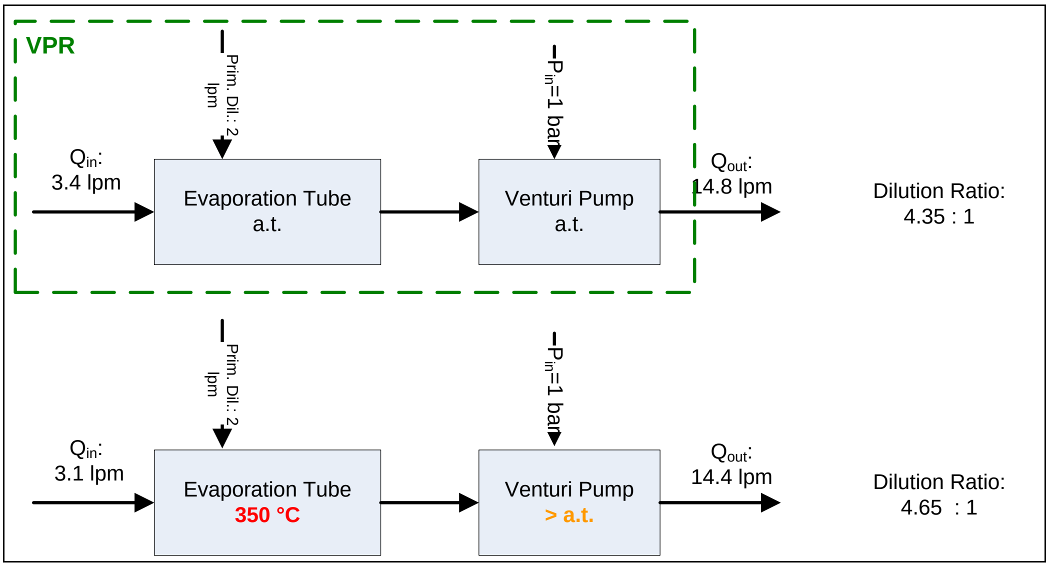

Figure 4.25: Effects of the VPR operating temperature on to the dilution factor

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[4] Burner settings refer to following flows: C_3H_8 [mlpm] - N_2 mixing gas [mlpm] - oxidation air [lpm] - dilution air [lpm] - primary dilution VPR [lpm]

Figure 4.26 shows the size distributions of the 2 different operating points measured downstream of the VPR, each at ambient- and at operating temperature as mentioned earlier. The mean diameter for the "larger" operating point (1) remain the same whereas for the "smaller" setting (2) the size distribution is shifted to the left, which is an indication that volatile components are removed.

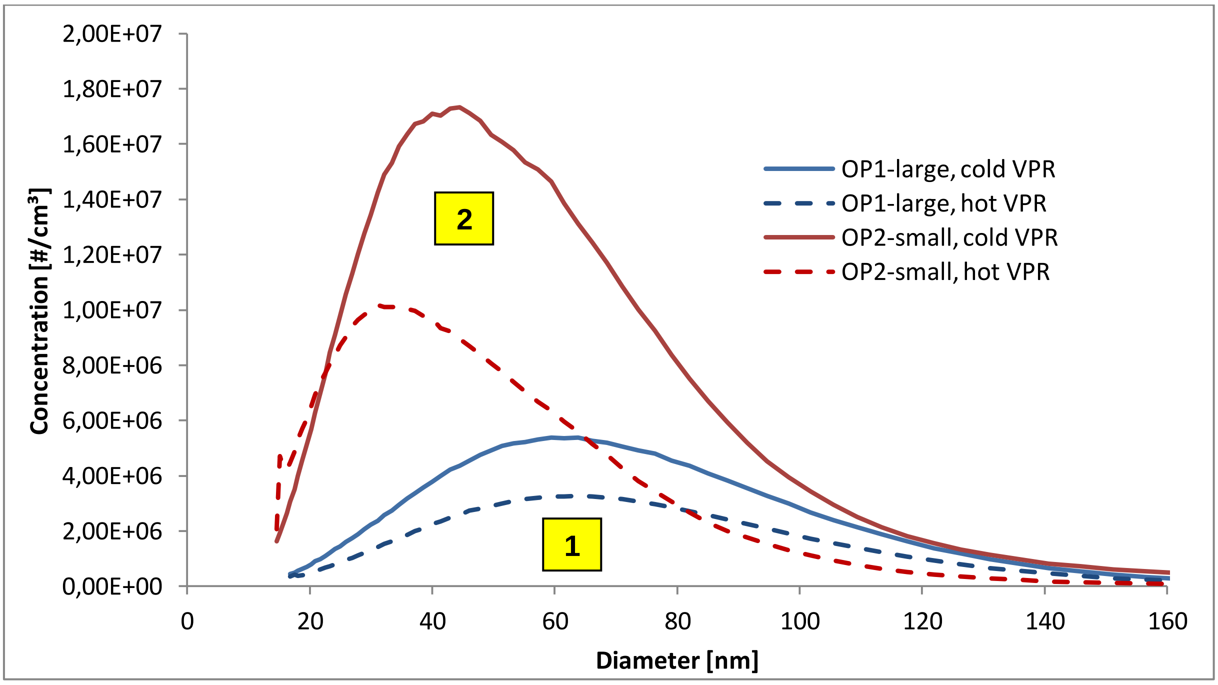

Figure 4.26: Effects on to the size distributions of a hot VPR

The volatile portion consists of e.g. organic carbon OC or polycyclic aromatic hydrocarbons PAH, that are intermediates of the soot formation process.

In respect to the *"EC/OC ratio of different mean particle sizes of a MiniCAST"* (38) the number of the elemental carbon EC increases for larger soot particles, refer to Figure 4.27. This is the result of following effects:

- As explained earlier smaller particles are generated when the combustion reaction is stopped in an early state of the soot formation, this may cause that PAH´s, which are intermediates of the formation remain in the aerosol and do not further react.
- A second effect of a larger OC portion is that after the formation "zone" the soot burn off "zone" follows where particles become smaller and a part of the soot is not completely oxidized but reduced to PAH´s (liquid) again (38).

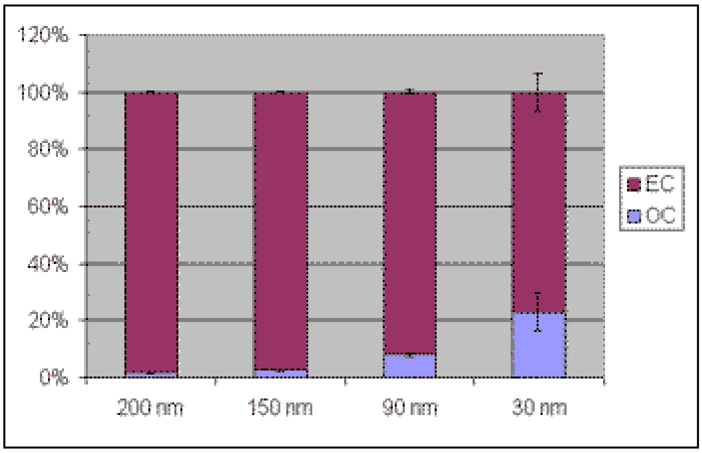

Figure 4.27: EC/OC ratio of soot with different mean particle sizes of a MiniCAST **(38)**

In respect to the effects of the VPR on smaller size distributions and the EC/OC ratios it can be concluded that the flow settings for smaller size distributions produce a higher fraction of volatile particles in the aerosol.

4.4.2 Particle Losses in the VPR

To get an estimation about the order of the particle losses in the VPR the size distribution first upstream, than downstream of the evaporation tube (ET) are measured. In order to achieve a thermally stable aerosol at the inlet of the APG VPR, an ALV Particle Counter is used, more specific the VPR of the APC. If no thermally stable aerosol is used, the losses cannot be determined because the concentration would change not only due to losses but also because of the removal of volatile components. To measure the size distributions a SMPS is connected up- and subsequently downstream of the ET, refer to Figure 4.28. This measurements are conducted with 6 different burner operating points accordingly different number concentrations and particle sizes. The primary dilution air flow of the VPR is set to zero in order to ensure only the losses of the ET are investigated.

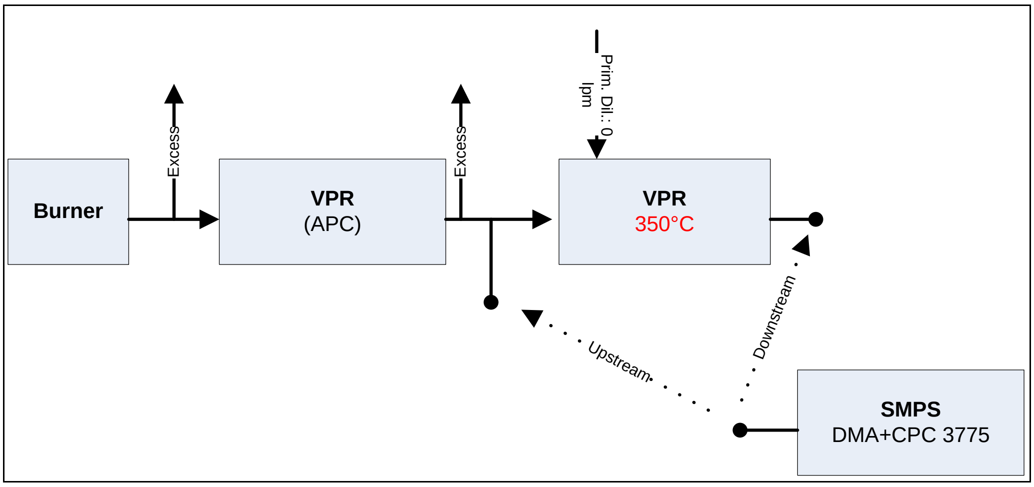

Figure 4.28: Schematic setup of the ET particle losses measurement

Figure 4.29 shows the measured up- and downstream size distributions of two operating points, one at around 45 nm and one at around 25 nm. The downstream distributions are not shifted, this is an indication that a thermally stable aerosol entered the evaporation tube, compare to chapter 4.4.1. Table 10 includes the corresponding results. The calculated difference between the up- and downstream concentrations provides an estimation of the losses. The average losses for the evaporation tube measured for these 6 operating points is around 14 %.

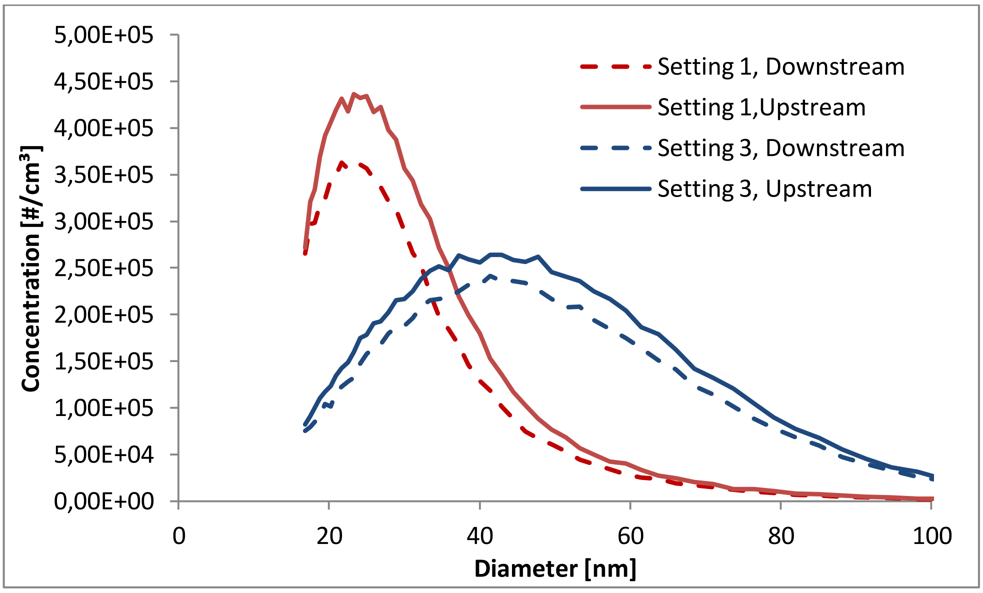

Figure 4.29: Up- and downstream size distribution measurements of the evaporation tube for two operating points

Table 10: Evaporation tube losses for different operating points

#	Setting	Concentration [#/cm³]		Difference	Mean [nm.]	
		Upstream	Downstream		Upstream	Downstream
1	20-0-0.5-3-0	1.54E+05	1.26E+05	22.66%	27.2	26.8
2	20-0-0.6-3-0	1.48E+05	1.31E+05	13.43%	39.0	38.7
3	20-0-0.7-3-0	1.37E+05	1.20E+05	14.55%	43.3	43.3
4	20-0-0.8-3-0	1.25E+05	1.12E+05	11.44%	44.4	45.3
5	20-0-0.9-3-0	1.21E+05	1.09E+05	10.53%	40.1	40.7
6	20-0-1.0-3-0	1.19E+05	1.07E+05	11.78%	43.2	43.7
				Average: 14.07%		

4.4.3 Parameters that affect the Dilution of the VPR

Different parameters affect the dilution ratio of the Volatile Particle Remover especially the venturi pump. In order to determine the effects following parameters are modified:

- the primary dilution air flow and
- the secondary dilution by varying the venturi pump motive flow pressure.

Referring to Figure 4.30 the primary dilution is increased in 1 lpm steps first with a "cold" at ambient temperature (1), than with a "hot" VPR (2) at operating temperature of 350 °C.

As expected by increasing the air flow at the primary dilution the total concentration of the size distributions drops and additionally the particle mean diameters remain stable, which is an indication that the particle agglomerates are not affected by modifying the dilution air at this position. Independent of the operating temperature the reduction of the total concentration exhibit a similar behavior at the "cold" and the "hot" VPR state.

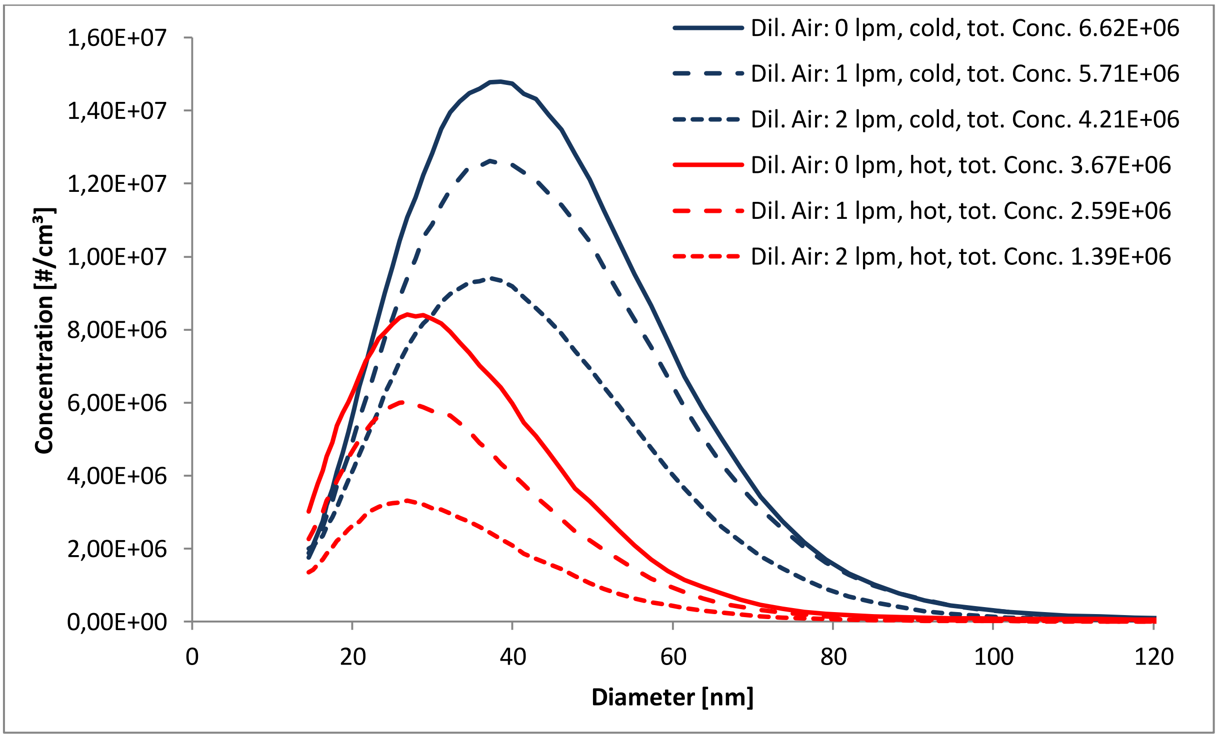

Figure 4.30: Various primary dilution ratios and the effects on to the size distributions

The secondary dilution can be modified by changing the pressures of the motive flow. Therefore the pressure is modified in 0.25 bar steps and the respective flows up- and downstream the VPR are measured. With these values the dilution factor for each pressure can be determined by:

$$Dilution\ Factor = \frac{\dot{Q}_{downstream}}{\dot{Q}_{upstream}} \text{ (Equ. 11)}$$

The dilution factor, also called dilution ratio indicates whether using different motive flow pressures may result different dilution behaviors. To have comparable values the change of the secondary dilution due to the enlargement of the pressure is conducted for two different primary dilution flows and the coefficient of variation is calculated for each flow by:

$$c_v = \frac{\sigma}{\mu} \text{ (Equ. 12)}$$

where: c_v... coefficient of variation
σ... standard deviation
μ... mean

Referring to the coefficient of variation for the primary dilution flow zero, see first three lines in Table 11, the dilution factor remain more or less stable for a pressure change. The results are also similar for the increase of the air flow to 1 lpm. Thus it can be concluded that the dilution ratio of the VPR varies within 5% for a motive flow pressure in a range of 1.0 ± 0.25 bar.

Table 11: Effects of the venturi pump motive flow pressure on to the dilution factor

Primary Dil. [lpm]	$P_{\text{motive flow}}$ [bar]	Q_{upstream} [lpm]	$Q_{\text{downstream}}$ [bar]	DF	CV
0	0.75	2.05	23.2	11.31	4,33%
	1.0	2.38	27.4	11.51	
	1.25	2.46	30.2	12.27	
1	0.75	1,14	23.2	20,35	4,40%
	1.0	1,44	27.4	19,03	
	1.25	1,61	30.2	18,76	

4.5 Dilution Bridge Stage

The dilution bridge stage (DBS) consists of a needle valve, a filter bypass and a second venturi pump, see Figure 4.31. This third main component of the APG has the function to achieve really low particle number concentrations. Low concentration values are required for e.g. particle number counter linearity or cut point checks, referring to chapter 6.
When the valve is completely open only a small flow enters the bypass and the majority of the aerosol passes through the valve. By closing the valve the flow through the filter bypass increases resulting a lower concentration until the valve is completely closed and the particle number downstream the DBS is zero. Subsequently the aerosol is diluted by a second venturi pump.

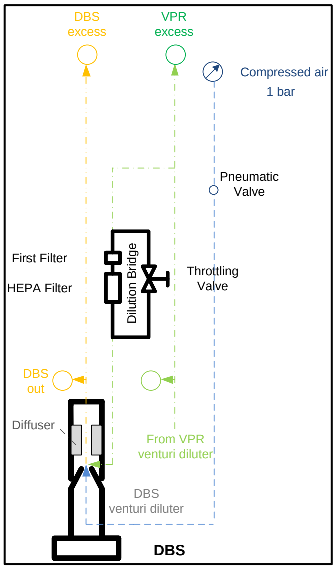

Figure 4.31: Flow Scheme of the Dilution Bridge Stage (DBS)

4.6 Calibration on the AVL Particle Generator

The Particle Generator can be used for the execution of various on-site verification checks of different particle measurement devices as described at the beginning of this chapter. One of the motivating ideas to develop such a device is to avoid an additional and expensive test equipment, as example a SMPS with an radioactive source, that are required due to the need of defined size distributions for the verification measurements, for a detailed description see chapter 6. Thus the AVL Particle Generator is calibrated once before it is shipped to the customer and then the device can be used to conduct onsite checks. In the following the calibration setup and the procedure of the calibration are explained in more detail.

4.6.1 Setup

Four calibrated operating points are available at the AVL Particle Generator. Three points (Cut Off, PCRF and Linearity) require the "VPR Out" or the "DBS Out" outlet in order to avoid volatiles and to achieve low enough concentrations. One point (MSS) utilizes the "Burner Out" outlet to provide an undiluted aerosol with a high particulate mass. To measure the size distributions a SMPS system, which consists of a Electrostatic Classifier (TSI model 3080 and model 3081) and a PNC (TSI model 3775) is used. Depending on the operating point either the SMPS is connected to the "VPR Out" or the "Burner Out" outlet. See Figure 4.32 for the setup.

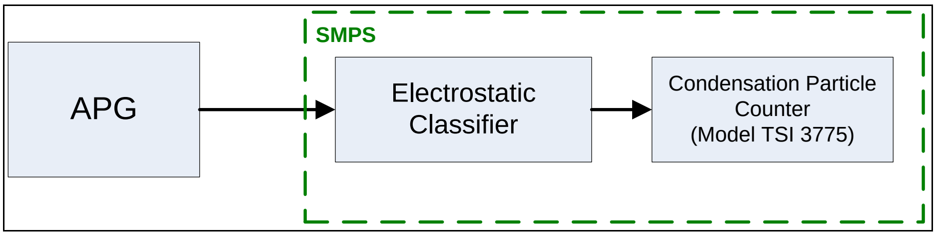

Figure 4.32: Schematic Setup of the APG Calibration

4.6.2 Calibration Procedure

In the following a description how to calibrate the burner flows to generate an aerosol with a specific size distribution, e.g. mean diameter at 50nm and a high number concentration, is described in general and not for the specific operating points mentioned before. It is more or less a trial and error procedure, this means in general one setting is used, then one parameter will be changed until the required distribution is found. Thus a little bit of experience can be helpful. After the calibration of specific operating points it is expected that the settings are similar for other APG. In order to get an estimation which parameter affects the distribution, a summary follows.

4.6.2.1 Conclusion of the Effects on to the Size Distributions

Different parameters have different effects on to the aerosol regarding the particle number concentration and the particle diameter. To provide a summary how the knowledge prepared in the chapters before can be applied to produce the requested size distributions, e.g. for an AVL Particle Counter calibration or other applications, two examples will follow how to generate a "large" and a "small" size distribution. It should be mentioned that similar size distributions can be produced with other settings as well, this means the following should just provide an example.

To generate a size distribution with "large" particles the following flow-parameter of the Particle Generator can be modified:

- Set the propane flow to relatively small values, e.g. 16 mlpm (max. = 50 mlpm) to reach a state that the quench flow penetrates the flame at the upper third shortly before the soot oxidation occurs, e.g. 16 mlpm.
- Set an relatively high oxidation air flow, e.g. 0.8 lpm (max. = 1 lpm) that the flame can built the typical orange center.
- Set an relatively small dilution air flow (max. = 10 lpm) to ensure that the agglomeration after the burner outlet will be the maximum, e.g. 0 or 1 lpm and use, if necessary the VPR primary dilution or respectively the dilution bridge to reach smaller particle number concentrations.
- Set the nitrogen mixing gas flow to 0 lpm.
- Choose a sampling position that is not directly after the burning chamber if possible. At the APG the distances between each connector and the burning chamber outlet are constant.

As a side effect of these flow settings also the particle number concentration decreases. To avoid this, the propane flow and the distance between the fuel outlet and the quenching position could be increased. However, for the specific CAST model (MiniCAST Model 6203c from Jing) the position and the flow of the quench gas are constant, thus the particle concentration is limited when larger particles are required.

To generate "smaller" size distribution the following flow settings and parameter can be modified:

- Use propane flow that the flame gets quenched and diluted more in the center, e.g. 20 mlpm.
- Set a relatively high oxidation air flow due to the same reason explained earlier, e.g. 0.9lpm
- For this distribution a high dilution air flow can be used in order to affect the particles not to form large agglomerates, e.g. 2 lpm or higher.
- If possible use small distances between sampling position and the burner outlet.

4.7 TEM Images

Following chapter is based on the work of a different project (cooperation between AVL and the institute of Electron Microscopy and Nanoanalysis at the TU Graz) which deals with the "Investigation of the formation of Carbon Nanotubes in Soot particles under a TEM"(39). In this section particles generated by the APG after the VPR, this means a thermally stable aerosol is achieved, are analyzed under a transmission electron microscopy (TEM). Two different particle sizes are under investigation one at 30 nm (small) and one at 100nm (large). Therefore burner settings are used that produce a size distribution with the maximum at 30 nm (25-0-0.8-2-2[5]) and at around 80 nm (18-0-1-2-1) respectively. In order to classify the 2 sizes a DMA is used after the APG.

Figure 4.33 shows two TEM Images of 30 nm and Figure 4.34 Images of 100 nm particles generated by an APG. The 30 nm as well as the 100 nm particles correspond with the selected size from the DMA. The smaller particles consist of a spherical structure whereas the larger agglomerates form a fractal structure, consisting of many primary particles.

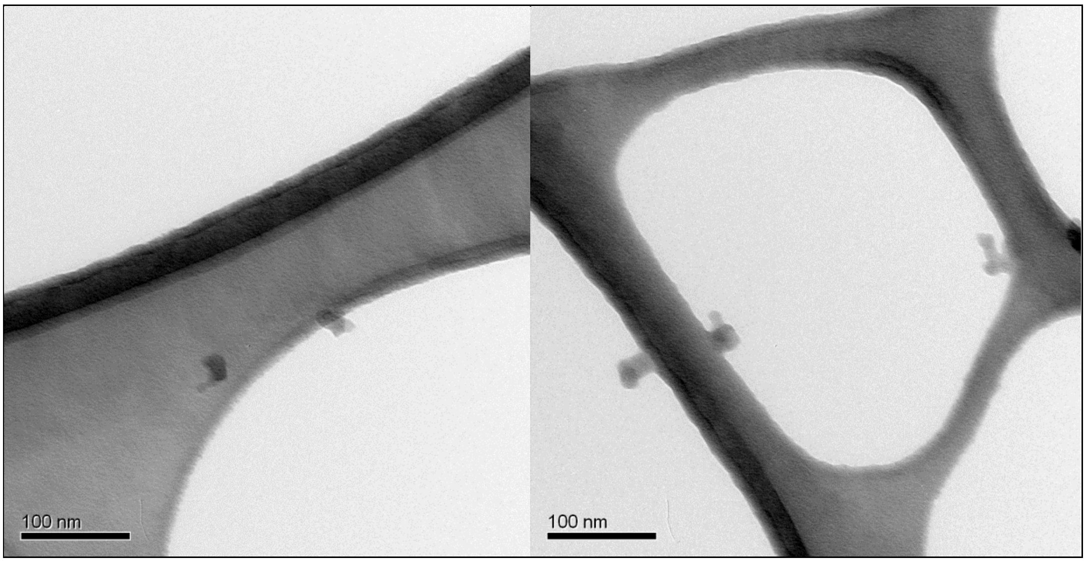

Figure 4.33: TEM Images of 30 nm particles generated by an APG

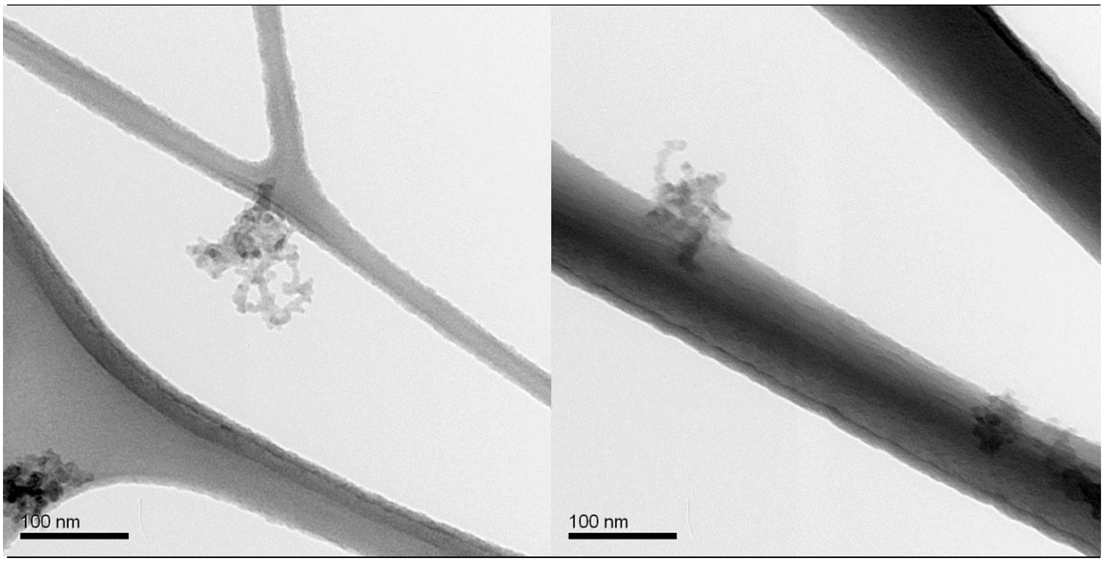

Figure 4.34: TEM Images of 100 nm particles generated by an APG

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[5] Burner settings refer to following flows: C_3H_8 [mlpm] - N_2 mixing gas [mlpm] - oxidation air [lpm] - dilution air [lpm] - primary dilution VPR [lpm]

4.8 The Final APG Design

As mentioned in earlier sections the measurements with the AVL Particle Generator were done with first prototypes, see Figure 5.7. This thesis is a part of a project where a complete device has been designed. Following figures show the final construction of the APG. Figure 4.35 shows the view from the front with an exploded drawing of the volatile particle remover (VPR) and Figure 4.36 shows the rear panel from the device.

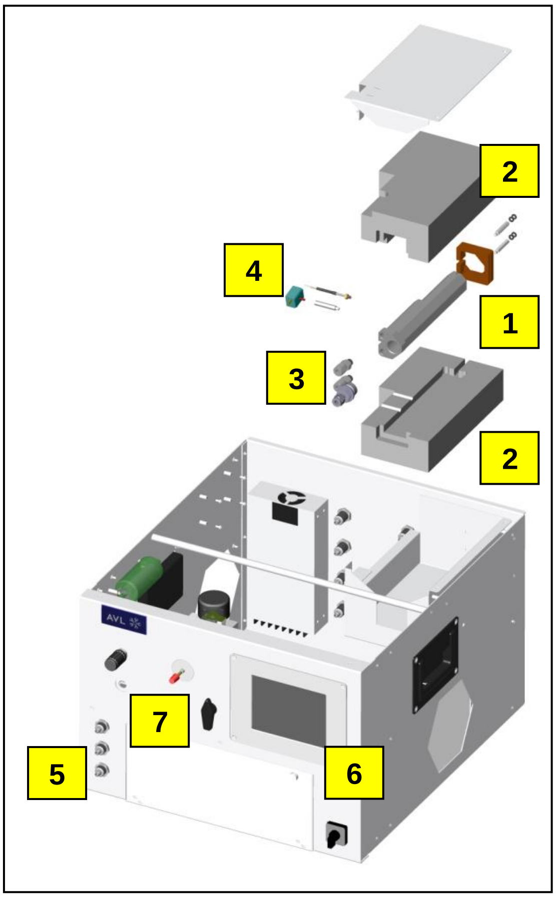

Figure 4.35: Front view with an exploded drawing of the VPR

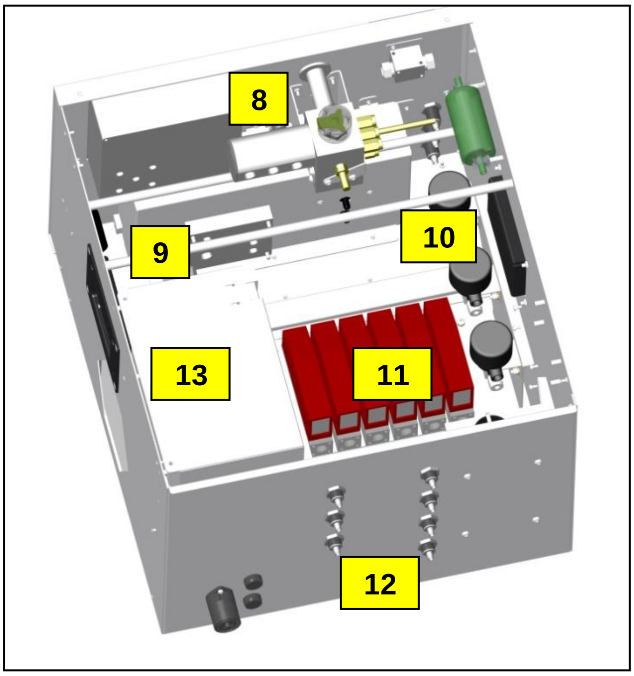

Figure 4.36: Rear view in to the APG

Front View:
1 ... Heated evaporation tube
2 ... Insulation
3 ... Connectors
4 ... Thermo Couple and Thermo Switch
5 ... Front Aerosol Outlets
6 ... Touchscreen Display
7 ... Burner Components

Rear View:
8 ... Burner Unit with stabilization chamber
9 ... Rear Side of the Venturi Pump
10 ... Pneumatic Valves
11 ... Mass Flow Controller
12 ... Rear Connectors
13 ... Heated VPR Box

5 Repeatability and Stability

In the following section the repeatability and the stability of the particle size distributions generated by the MiniCAST Soot Generator, the Palas Sparking Soot Generator and the AVL Particle Generator (MiniCAST + VPR) are investigated regarding the total concentration and the mean diameter.

The repeatability provides a value that shows the difference of two or more measurement results taken at different times under following defined repeatability conditions (40):

- the same measurement procedure
- the same observer
- the same measuring instrument, used under the same conditions
- the same location
- repetition over a short period of time.

Stability in this context means that the behavior of a measurement value is investigated over a longer time period without an interruption in the same day. As example the result indicates whether the value strongly deviates or a significant drop occurs over the time.

In order to get comparable values the results of the repeatability and the stability measurements are expressed quantitatively with the coefficient of variation c_v, refer to equitation 8.

5.1 Stability Measurements

The stability of the generated aerosol has a high relevance for verification measurements of a PNC and Particle Number Systems (e.g. AVL Particle Counter) respectively. As example if a tolerance for the verification measurement of ±10% is required and e.g. a tolerance of 7% is calculated and the stability of the system is around 5%, then it is possible that the test fails due to the variability of the soot source. Thus it is hard to ensure whether the test passes or not. In order to have quantitative values the coefficient of variation is calculated for the measurement results. This means the smaller the coefficient of variation the easier it is to assess whether the test fails or not.

Verification measurements for PNC´s and PN systems is a part of the AVL Particle Generator application range. Thus it makes sense to conduct stability measurements with different particle generators to investigate the behavior of the repeatability and the stability of each generated aerosol.

In order to analyze the stability of the APG size distribution measurements with a SMPS are conducted over a defined time period. The values of interest are the total particle number concentration, that is equal the area under the particle size distribution, and the behavior of the mean diameter, that indicates whether the curve is shifted to smaller particles. The stability is expressed with the coefficient of variation.

5.1.1 Stability Measurement Setup

In this section the stability of the MiniCAST, the APG and the Palas soot generator are investigated. For the measurements, settings that produce size distributions with a maximum at around 30 nm, this means rather small sizes, are chosen. For each setup a SMPS system is connected to the respective generator and the produced size distributions are recorded every 6 minutes.

5.1.2 Evaluation and Interpretation of the MiniCAST and APG Results

In following the stability results of the MiniCAST and the APG are compared and discussed. The comparison between the Palas Generator and the APG regarding the stability follows in the next chapter.
As described before, the operating point is the same used for the two devices, first the MiniCAST alone and then the APG (MiniCAST thermal pre-treatment) are discussed.

5.1.2.1 MiniCAST

Figure 5.1 shows the measurements results of the total concentration and the mean diameter over a period of 6 operating hours. The measurement starts from a "cold" device state, this means there is no warming up time for the device before the measurements start. The MiniCAST needs a stabilization period of around 90 minutes for this operating point to reach a stable total concentration. This can result of the time period that is required until all the components (burning chamber, stabilization tube, etc.) are heated up. Expressed with the coefficient of variation, refer to Table 12, the stability of the MiniCAST is 7.39 % calculated for the total concentration including the stabilization time (range over the entire measurement) and 1.81% for the mean diameter.

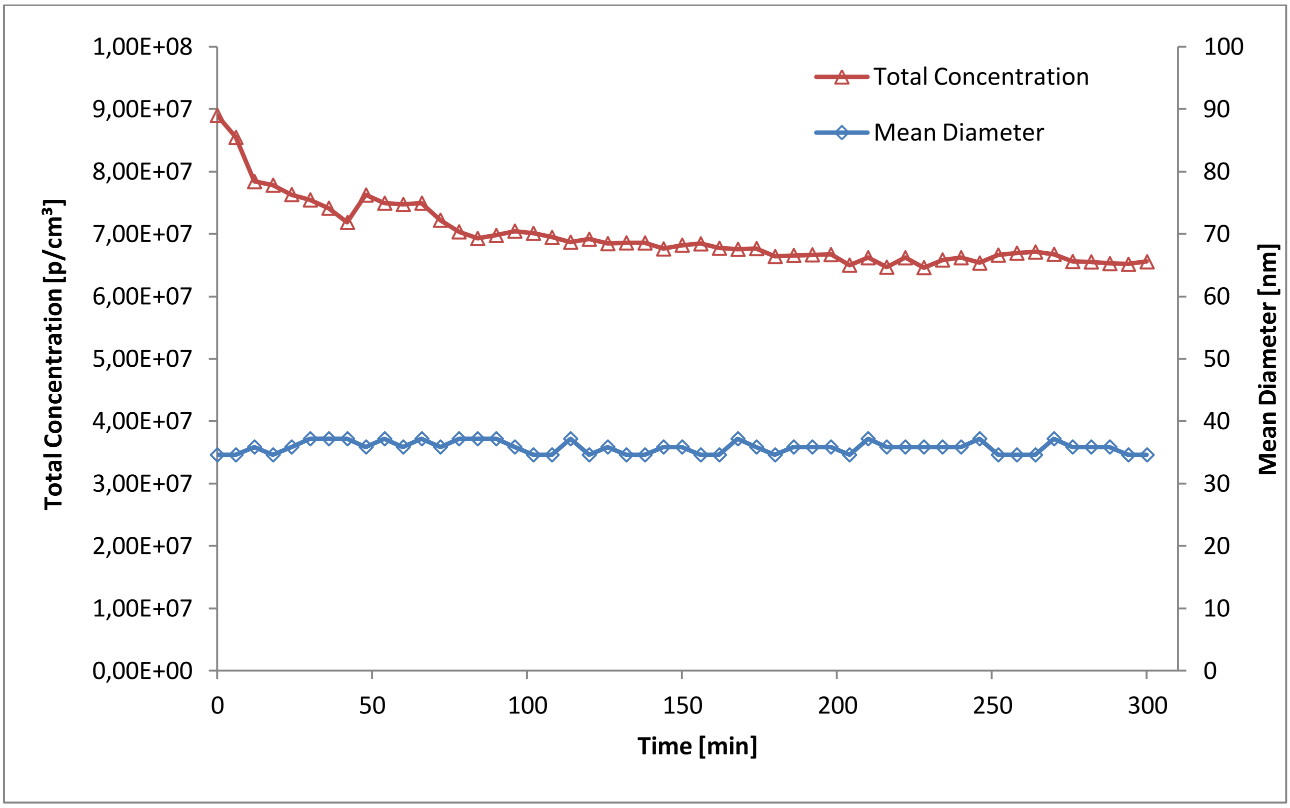

Figure 5.1: Stability measurements with the MiniCAST

Table 12: Coefficient of variation of the MiniCAST stability measurements

	Total Concentration [p/cm³]	Mean Diameter [nm]
Average	6,97E+07	35,795
Standard Deviation	5,15E+06	0,649
Coefficient of Variation	**7,39%**	**1,81%**

5.1.2.2 AVL Particle Generator

In the following two stability measurements of the APG are conducted. First at the VPR outlet and then at the dilution bridge stage outlet.

5.1.2.2.1 APG Outlet - VPR

For the stability measurements at the VPR outlet, every 10 minutes the size distributions over a period of approximately 6.5 hours are recorded. After the warming up phase of about 30 minutes, until the VPR reached the operating temperature of 350°C, the total particle concentration as well as the mean diameter reached stable values, see Figure 5.2. Expressed with the coefficient of variation this means the total concentration deviates with 3.84% after the VPR warming up process (time range between minute 30 until the end), which is approximately the half of the MiniCAST measurements related to the stability including the stabilization time, and the mode diameter with 2.51%. (refer to Table 13)

The difference between the average values of the concentrations, 6.97E+07 for the MiniCAST and 2.00E+06 for the APG, results from the dilution of the VPR and the removal of the volatile components, after the warming up process. Thus it can be summarized that using the MiniCAST in combination with a thermal pretreatment, which is equal the APG, leads to a faster achievement of a higher aerosol stability and facilitates an easier interpretation of the verification measurement results of particle number systems.

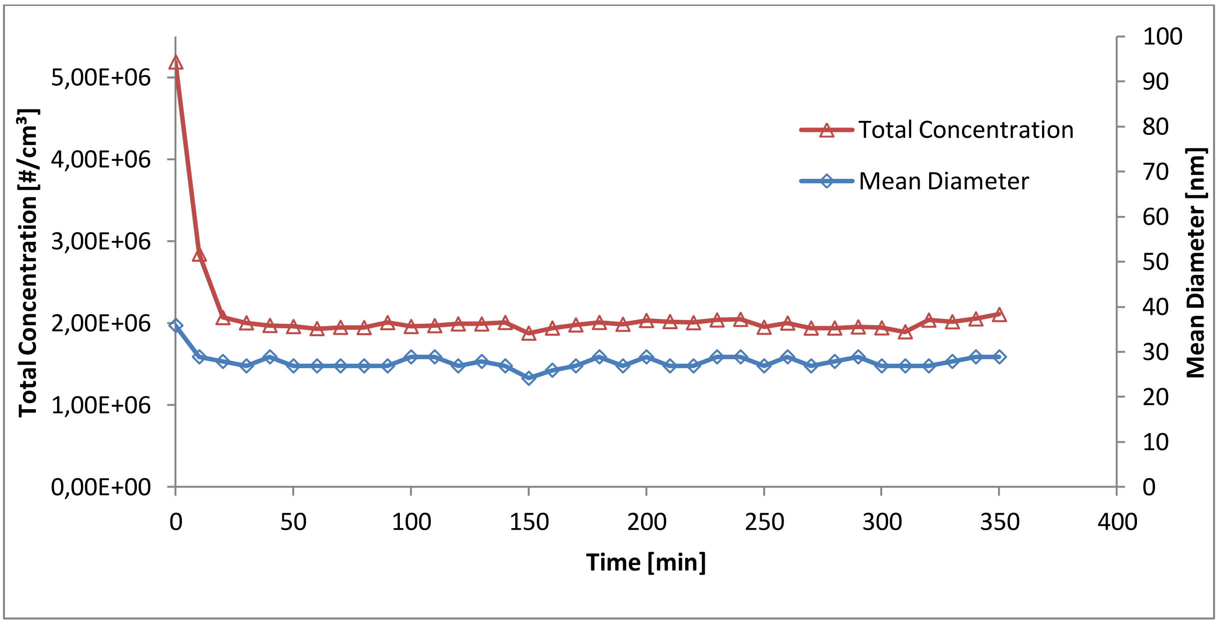

Figure 5.2: Stability measurements with the AVL particle generator at the VPR outlet

Table 13: Coefficient of variation of the APG stability at the VPR outlet

	Total Concentration [p/cm³]	Mean Diameter [nm]
Standard Deviation	7.68E+04	0.851
Average	2.00E+06	33.9
Coefficient of Variation	**3.84%**	**2.51%**

5.1.2.2.2 APG Outlet - Dilution Bridge Stage (DBS)

In order to generate really low particle concentrations the dilution bridge stage can be used. As example concentration of around 10 particles per cm³ can be required for a PNC linearity check, refer to chapter 6.2. For this measurement only a PNC and not a SMPS is used to determine the stability at the DBS outlet, resulting that only the particle concentration can be analyzed. Following Figure 5.3 shows the measured number concentration over a time period of 10 minutes (this is a typical length for a linearity check). Referring to Table 14 a coefficient of variation of 4.92% is calculated for the APG stability regarding then number concentration at the DBS outlet.

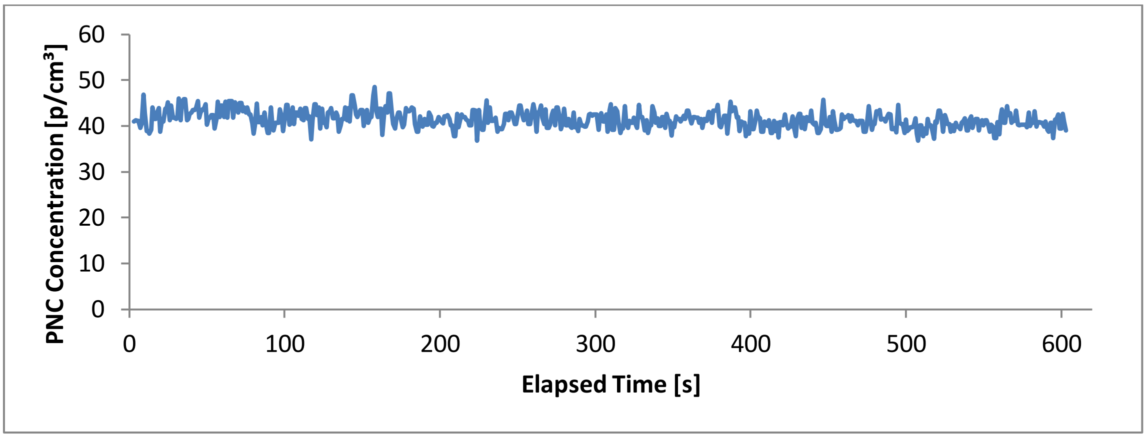

Figure 5.3 APG stability measurement at the DBS outlet

Table 14: Calculation of the APG stability at the DBS outlet

	Concentration [p/cm³]
Standard Deviation	2.03
Average	41.42
Coefficient of Variation	4.92%

5.1.2.3 Palas Spark Soot Generator

In this section the Palas Sparking Soot Generator regarding the stability of the total particle number concentration and the mean diameter of the generated size distributions are discussed. Therefore the setup remains the same used for the stability measurements of the MiniCAST and the APG. First the stability of the polydisperse aerosol and then the direct comparison of a monodisperse aerosol between Palas Generator and APG will be discussed.

Polydisperse Aerosol Stability

The size distributions of the Palas generated aerosol over a time period of 90 minutes is recorded. Following Figure 5.4 shows the results of the plotted total concentrations an mean diameters.

Referring to chap. 3.1 the distance between the two graphite electrodes has to be constant, thus the distance is adjusted automatically. It seems that this automated adjustment is the result of the concentration peak at minute 60 (1). Considering the mean diameter stability the adjustment affects this function as well.

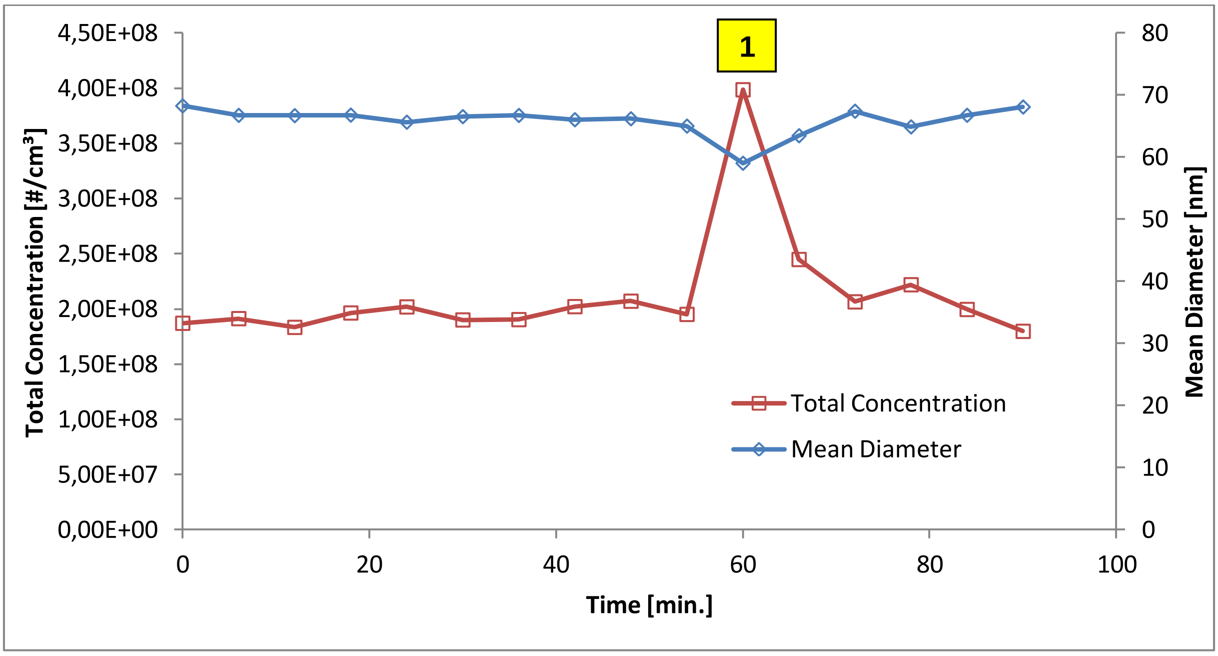

Figure 5.4: Stability measurements with the Palas sparking soot generator

As a result of this peak the stability of the total concentration expressed with the coefficient of variation is about 24.57%. By excluding the peak the value decreases to 8.19% for this operating point.

In summary the total concentration stability of the Palas generator is worse than the one generated by the AVL Particle Generator even when the value of the automatic adjustment is excluded. This means when this process occurs during a measurement it probably has to be repeated which increases the time effort for the execution of quality checks.

Table 15: Coefficient of variation of the Palas generator stability measurements

	Total Concentration [p/cm³]	Mean Diameter [nm]
Standard Deviation	5,22E+07	2,19
Average	2,12E+08	65,89
Coefficient of Variation	**24,57%** (8,19%)	**3,32%**

Monodisperse Short Term Aerosol Stability

For the execution of some applications, e.g. a calibration of an AVL Particle Counter, a monodisperse aerosol is required. This means after the respective particle generator, Palas or APG, an electrostatic classifier is connected to classify a required particle size, e.g. 100 nm for the following measurements. Thus two similar operating points regarding the maximum of the size distributions (Palas and APG) are used. Afterwards the monodisperse particle concentration is recorded by a particle number counter (model TSI 3790), refer to Figure 5.5.

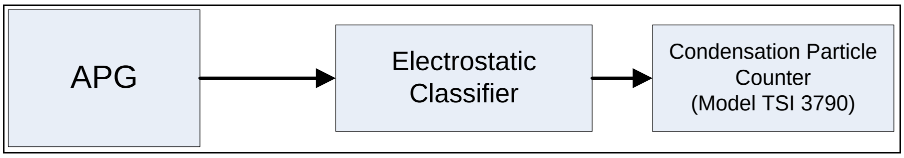

Figure 5.5: Schematic setup of the monodisperse stability measurement

In general this measurements are short term measurements, that is the reason why the stability of the aerosol is recorded only for 80 seconds. Figure 5.6 shows the results of the measurements. As expected, based on the data from the polydisperse aerosol stability, the stability, again described with the coefficient of variation of the APG is more accurate than the one of the Palas Soot Generator. Expressed with numbers the Palas Generator has a stability of 5.73% and the AVL Particle Generator of 1.11% for the short term measurements, refer to Table 16. This means using the APG for this kind of applications, provides more accurate measurement results due to higher stability.

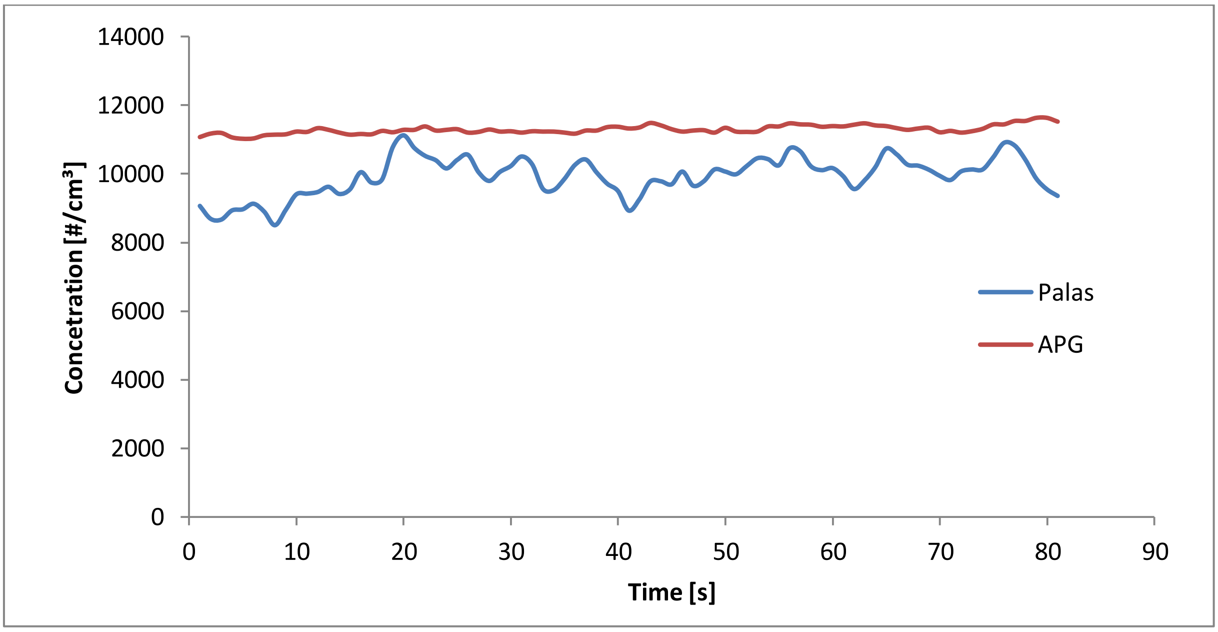

Figure 5.6: Comparison of the short term stability between the Palas generator and the APG with a monodisperse aerosol at 100nm

Table 16: Difference of a monodisperse short term stability measurement between the Palas generator and the APG

	Monodisp. Conc. Palas [p/cm³]	Monodisp. Conc. APG [p/cm³]
Standard Deviation	568,75	125,34
Average	9927,44	11291,36
Coefficient of Variation	**5,73%**	**1,11%**

5.2 Repeatability Measurements with the AVL Particle Generator

For the repeatability measurement a prototype setup was used: A MiniCAST (model 6203c from Jing) produced the aerosol, an exhaust pipe was mounted at it´s outlet and the VPR was sampling from this pipe. No dilution bridge stage was used in order to have high concentrations for the SMPS, refer to Figure 5.7. The same VPR dilution flow settings are used for each repeatability measurement. A primary dilution of 2 lpm and a venturi pump motive flow pressure (secondary dilution) of 1 bar is set. The sampling position at the exhaust tube and the tubing were the same over all measurements.
Three different burner operating points; one at 30nm, one at 50 and one at 70 nm, are used to determine whether different repeatability achieved for different particle size distributions.

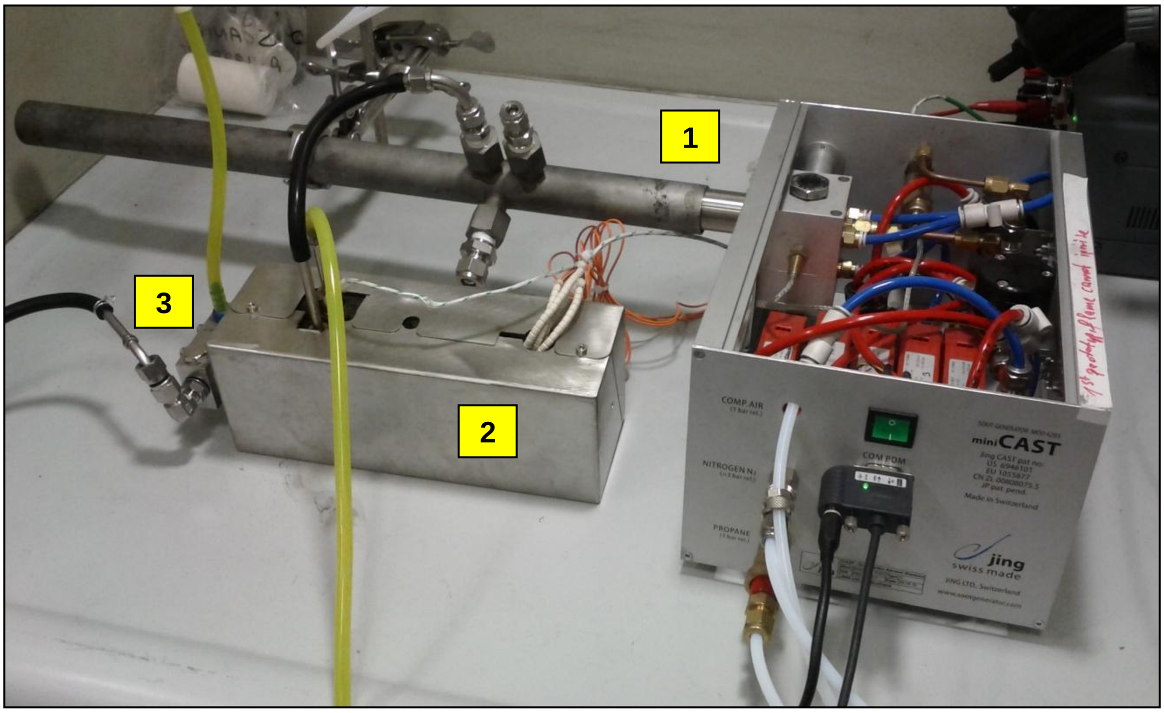

Figure 5.7: APG Testing Setup used for repeatability and stability measurements

In order to record the size distribution a SMPS; that consists of an electrostatic classifier, a long DMA and a CPC 3775, is installed after the venturi pump. The SMPS is connected to the VPR with a conductive silicon tube, length 1.7 meter. Not conductive tubes may increase the deposition of particles at the tube walls.

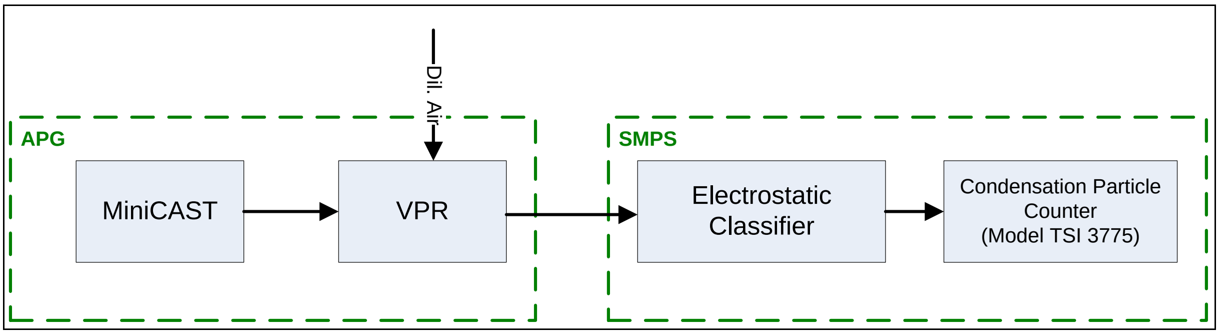

Figure 5.8: Schematic setup of the repeatability and stability measurements

5.2.1 Evaluation and Interpretation

The repeatability measurements were done on 4 different days within two weeks. Between each measurement the system was running for around 10 operating hours. Every size distribution measurement is done after the heating up process of the APG. Table 17 shows the total particle concentrations of the different operating points. The repeatability, expressed with the coefficient of variation, for the 50 and the 70 nm point regarding the total concentration is <4 %. For the 30 nm operating point it is 9.82% that results from the last size distribution which was much different compared to the days before. Without this size distribution the repeatability is 4.34%.
The deviation of the mean diameter of the size distributions, that indicates whether the distribution is shifted to the left (to smaller particles) or to the right (to larger particles), also expressed with the coefficient of variation, is smaller than 3 % for each operating point (Table 17).

Table 17: Total concentrations of 3 APG operating point repeatability measurements using a conductive silicon tube

Date of Measurement	Total Concentration [p/cm³]		
	OP 30 nm	OP 50 nm	OP 70 nm
2011-12-02	2.04E+06	1.65E+06	1.61E+06
2011-12-07	2.12E+06	1.72E+06	1.72E+06
2011-12-12	1.94E+06	1.64E+06	1.64E+06
2011-12-16	1.68E+06	1.56E+06	1.58E+06
Average	1.95E+06	1.64E+06	1.64E+06
Standarddev	1.91E+05	6.36E+04	6.01E+04
Coefficient of Variation	**9.82% (4.34%)**	**3.87%**	**3.67%**

Table 18: Mean diameter of 3 APG operating point repeatability measurements using a conductive silicon tube

Date of Measurement	Mean Diameter [nm]		
	OP 30 nm	OP 50 nm	OP 70 nm
2011-12-02	34.6	50.1	60.6
2011-12-07	34.4	48.6	64.4
2011-12-12	34.4	48.6	63.7
2011-12-16	32.4	48.5	64.8
Average	33.98	48.95	63.37
Standarddev	1.027	0.760	1.878
Coefficient of Variation	**3.02%**	**1.55%**	**2.96%**

Figure 5.9 shows the size distributions of the repeatability measurements for the three operating points. As the calculation shows, for the 50 and the 70 nm points the distributions are closer to each other.

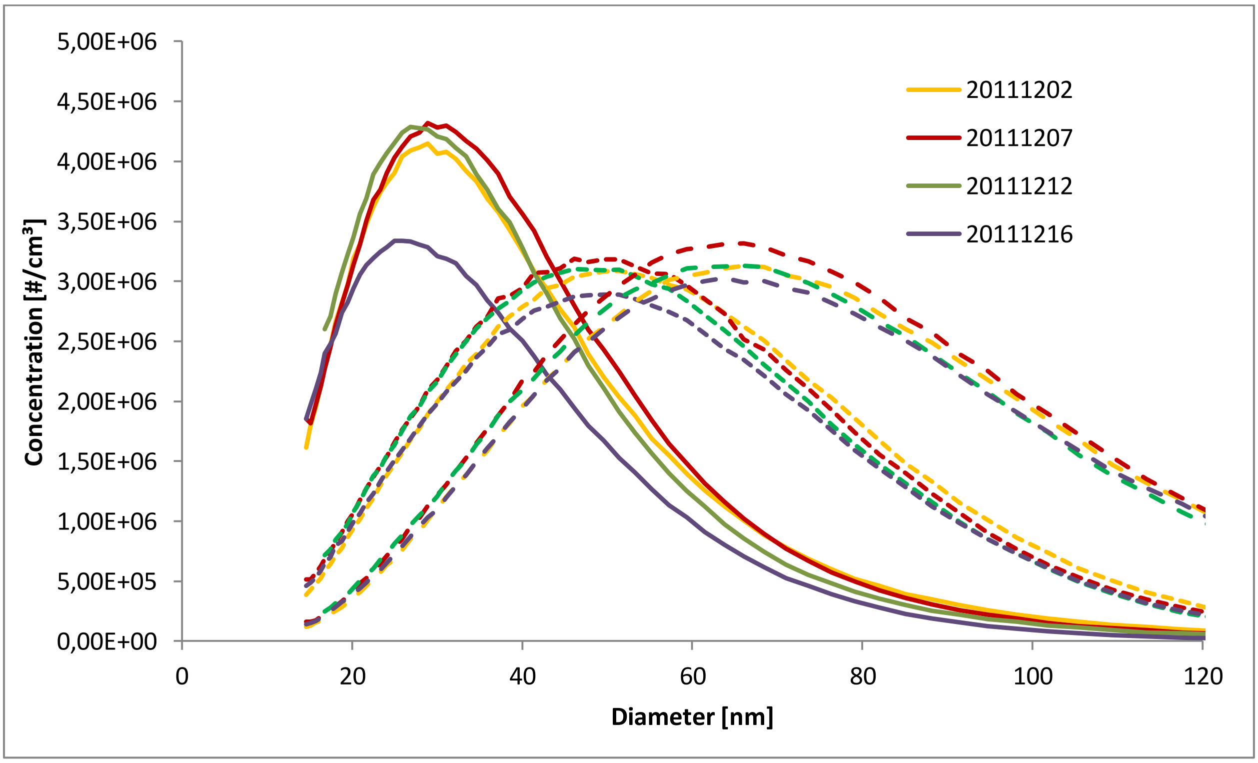

Figure 5.9: Repeatability measurements of 3 APG operating points

In addition to the repeatability calculations the concentration drop over the time can be determined easily by calculating the difference between the "start" and the "end" concentration, then relating the result to the "start" concentration. Afterwards this value can be related to the operating time of 41 hours. The result indicates the concentration drop per hour in per cent, see Table 19.

Table 19: Estimated particle concentration drop over 41 operating hours

Date of Measurement	Total Concentration [p/cm³]		
	OP 30 nm	OP 50 nm	OP 70 nm
2011-12-02	2.04E+06	1.65E+06	1.61E+06
2011-12-16	1.68E+06	1.56E+06	1.58E+06
Δ Concentration [p/cm³]	9.80E+04	8.81E+04	2.84E+04
$\frac{\Delta Concentration}{Concentration_{start}}$	4.80%	5.34%	1.76%
Concentration drop per hour [%/h]	**0.11%**	**0.13%**	**0.04%**

Summarizing a 0.5 to 1.5% drop of the total number concentration is expected every 10 hours of operation.

A decreasing trend of the total concentration over the time is the result of the contamination and particle depositions on to venturi pump components, e.g. nozzle and diffuser. This means the flow sampled by the venturi decreases due to contamination of the diffuser but the motive flow remain more or less constant, thus the dilution ratio of the secondary dilution increases and the total concentration after the VPR decreases. Figure 5.10 shows qualitative the difference between contaminated and new venturi components; nozzle and diffuser. The orange curve (1) shows the particle size distribution with contaminated venturi pump nozzle and diffuser after an operating period of around 30 hours. Then the components got exchanged, thus the dilution ratio of the secondary dilution decreases, due to a higher intake flow of the venturi pump, and the result is a higher total particle concentration (2). So it can be summarized that the cleaning or the exchange of contaminated venturi pump components should be considered to ensure a high repeatability.

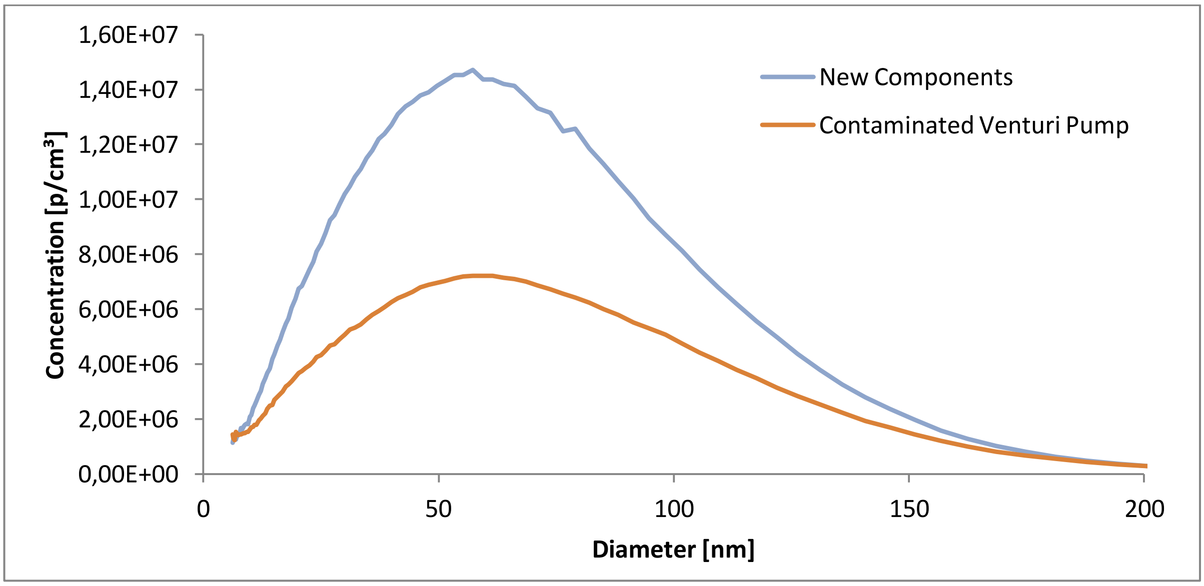

Figure 5.10: Difference between new venturi pump components and contaminated parts

5.3 Repeatability Measurements with the Palas Sparking Soot Generator

According to the definitions and conditions described in chapter 5.1, repeatability measurements regarding the size distributions, especially the total number concentration, of eight different operating points of the Palas generator were conducted. This means the setup, the test person, the instruments and the location remained the same over the testing period. In order to have comparable values between the measurement results of the APG and the Palas Generator the setups are the same except the respective particle generator. The measurement period is about 4 weeks and every week the measurements are conducted. With the 8 operating points a mean diameter size between 35 and 100 nm is covered, see Table 20 for a detailed description of the settings.

Table 20 : Palas generator settings for the repeatability measurements

Operating Point	Setting[6]	Approx. Size [nm]
1	High - 0.5 - 5 - 5	~ 35
2	High - 1.5 - 5 - 5	~ 50
3	High - 2.5 - 5 - 5	~ 60
4	High - 3.5 - 5 - 5	~ 70
5	High - 4.5 - 5 - 5	~ 75
6	High - 5.5 - 5 - 5	~80
7	High - 6.5 - 5 - 5	~ 85
8	High - 7.3 - 5 - 5	~ 100

Following Figure 5.11 shows the measurement results of each operating point at the 4 different testing days. As expected and as mentioned in chapter 3.1.1.1, the particle concentration grows by increasing the current due to a higher frequency of the flashover between the two electrodes. Referring to Table 21 it seems that the repeatability, again expressed with the coefficient of variation, correlates with the frequency as well. This means operating points with a higher current (compare to settings 6-8) have better repeatability's than points with a lower current (compare to settings 1 - 5).

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[6] Settings refer to: Energy: 3.5 [kV] - Current in [mA] - Air Flow in [lpm] - Nitrogen Flow in [lpm]

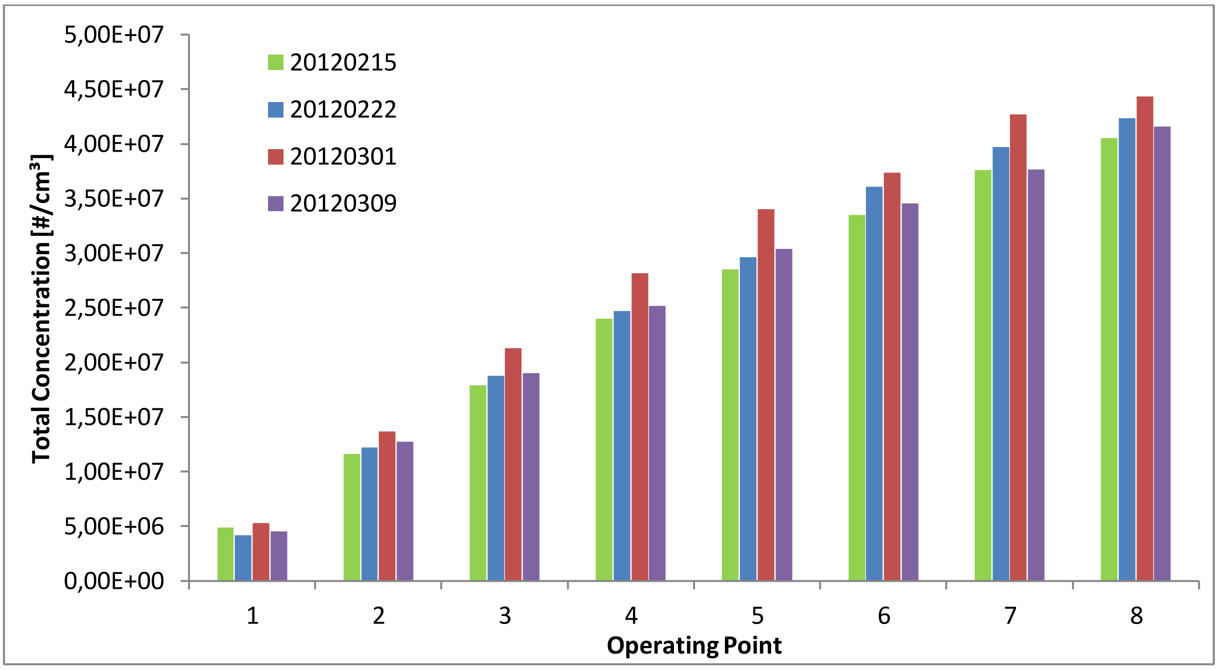

Figure 5.11: Total concentrations of the different repeatability measurement operating points

Table 21: Results of the Palas generator repeatability measurements

Operating Point	Standard Deviation	Mean	Coefficient of Variation
1	4,78E+05	4,73E+06	10,10%
2	8,72E+05	1,25E+07	6,94%
3	1,46E+06	1,92E+07	7,59%
4	1,82E+06	2,55E+07	7,16%
5	2,39E+06	3,06E+07	7,79%
6	1,70E+06	3,54E+07	4,82%
7	2,38E+06	3,94E+07	6,04%
8	1,63E+06	4,22E+07	3,85%

6 Applications of the APG

The AVL Particle Generator is a device for conducting on-site quality checks of particle measurement devices to ensure a high reliability and accuracy of the measurement results. Due to thermal conditioning of the aerosol and the three dilution stages, the APG can be used for a wide range of applications:

- On-site checks of particle number counting devices, e.g. an AVL Particle Counter (APC). This on-side checks include the cut off-, the linearity- and the PCRF check.
- Calibration of an APC
- Comparison measurements of two particle measurement systems, e.g. of two AVL Micro Soot Sensors or of two AVL Particle Counter

In the following the most common on-site checks in connection with a particle number counting system (an AVL Particle Counter) and a Particle Number Counter (PNC) are described. As discussed in earlier sections the APC consists of a dilution system (VPR) and a Condensation Particle Counter (CPC = Particle Number Counter), refer to chapter 2.3.3. So the first two checks described in the following, the Cut Off Check and the Linearity Check, focus on the CPC and the third check, the PCRF Check, concentrates on the dilution system (Volatile Particle Remover).

The checks using only an AVL Particle Generator with calibrated operating points and required size distributions does not calibrate a system, it is for a fast check whether the quality of the measurement device is high enough to ensure a high accuracy of PN measurements.

According to legislation (refer to chapter 2) the PNC calibration includes the verification of the lower detection limit and the concentration linearity. Both measurements as well as the VPR calibration require a monodisperse aerosol, thus a DMA to classify particle sizes has to be used. For the three APG applications described below a polydisperse aerosol is used. As a consequence that no DMA respectively a radioactive source is needed.

6.1 Cut Off Check

With the APG Cut Off Check the D50 of a PNC either standalone or included in a particle number counting system, e.g. an APC, can be checked without using a SMPS or a DMA system. The CPC and the reference device, that is measuring in parallel, only have to be connected to the APG, see Figure 6.1.

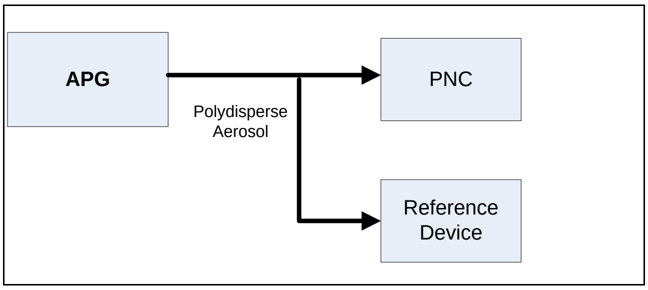

Figure 6.1: Setup of the Cut Off Check with an APG

For the tests a CPC 3790 from TSI is used which has a cut point at 23 nm, refer to Table 1 and Figure 6.2 (2). This D50 was chosen by legislation in order to measure all soot particles, that have in general diameter between 50 and 100nm, and to avoid the detection of particles from the volatile nucleation mode, that usually have diameters smaller than 20nm.

The APG generates an aerosol with the maximum of the size distribution at around 10 nm and small concentrations for larger particles, refer to Figure 6.2 (1). If the PNC under evaluation and the reference PNC are measuring similar concentrations for this example of <500 #/cm³ (total concentration of the size distribution is around $1x10^5$) the check passes. If the PNC to be evaluated detects higher concentrations than the reference device, e.g. in the order of 10³ #/cm³ and the reference is < 500 #/cm³, it indicates that the lower detection limit of the PNC has drifted to the left, this means to smaller particles and the check fails.

(1) ... APG operating point for the cut off check
(2) ... PNC counting efficiency for a PNC with a D_{50} at 23nm
(3) ... D50 at 23nm and D90 at 41nm

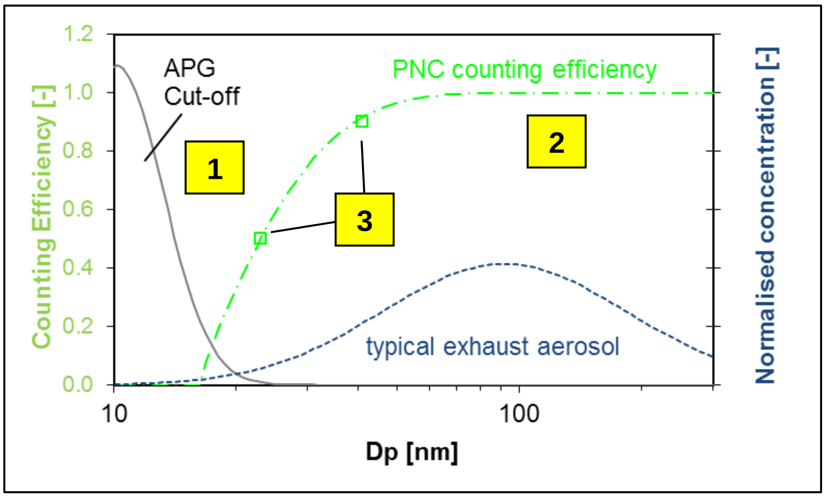

Figure 6.2: APG Cut Off size Check of a PNC **(2)**

6.2 Linearity Check

For the linearity check using an APG, the CPC under evaluation and the reference device are connected parallel to the generator. As mentioned earlier the APG should generate an aerosol with a mean diameter between 80 - 90 nm to ensure that the two PNC´s are measuring with their highest counting efficiency, as example for an operating point with a large amount of particles at 41 nm and smaller the readings of the devices can differentiate only due to various counting efficiencies although both devices are calibrated correctly.

The procedure of calculating the concentration linearity is the same as it is used for the PNC calibration, refer to chapter 2.1.2.

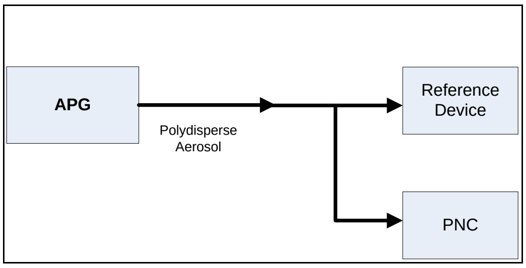

Figure 6.3: Setup for the APG linearity check

6.3 PCRF Check

The particle concentration reduction factor (PCRF) is the dilution factor of the APC dilution system (VPR). In the following section the on-site quality check using an AVL Particle Generator is described.

6.3.1 PCRF Check with an APG

The PCRF verification measurement using an APG consists of two checks that will be described in the following:

- Check of a “low” reference PCRF and the
- PCRF relative check

6.3.1.1 Check of a Reference PCRF

The first check is performed by measuring particle concentration up- and downstream of the dilution system, e.g. an AVL Particle Counter, for a “low” set PCRF. This means for dilution factors between 100 and 1000. The concentrations at the inlet and at the outlet of the dilution system are measured with a reference PNC (see Figure 6.4). For this verification measurement an operating point of the APG is set that the generator produces a size distribution around 50nm and the dilution bridge stage outlet is used in order to achieve upstream concentrations <1x10^4 [#/cm³].

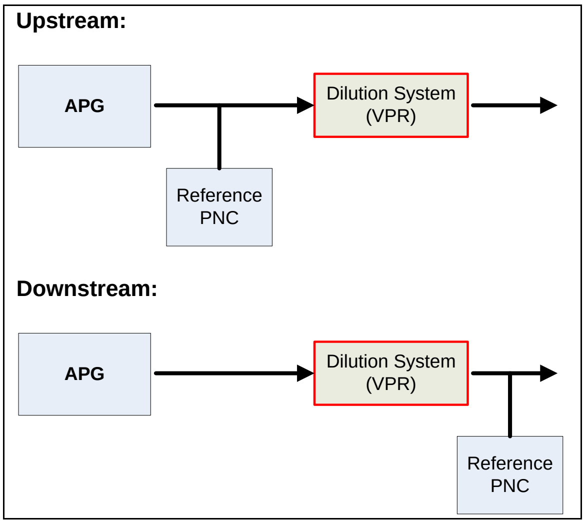

Figure 6.4: Setup for the APG reference PCRF check

With the averaged measured concentrations of the reference PNC the PCRF are calculated. The calculated PCRF is compared with the set dilution factor of the system. The difference has to be within a tolerance of ±10% that the check is passed.

$$PCRF_{calc} = \frac{n_{up}}{n_{down}}$$ (Equ. 13)

$$\Delta PCRF = \frac{PCRF_{calc}}{PCRF_{set}} = \pm 10\%$$ (Equ. 14)

6.3.1.2 Relative PCRF Check

With the verification of a reference PCRF only one dilution factor is checked. With the relative PCRF check the remaining PCRF´s are analyzed. For this measurement the reference PNC is connected downstream of the dilution system (APC), refer to Figure 6.4 downstream setup. The aerosol downstream the VPR under evaluation got diluted with a set PCRF of e.g. 100. The reference PCRF that was checked previously as example is 250, this means for the relative check all remaining PCRF´s are compared with this PCRF 250. For the evaluation the calculated number concentration corrected with the relative PCRF are compared with the results calculated with the reference PCRF.
The concentration generated by the APG should be set to a value so that the reference device is able to detect the particles (<1x10^4 #/cm³) at the lowest dilution factor of the VPR (PCRF 100) in order to avoid errors at the PNC. These measurements are performed with primary dilution low of the dilution system under evaluation (PCRF range 100 - 3000) and high (PCRF range 2000 – 20000). The calculated emissions at each PCRF related to the reference PCRF should be within a tolerance of ±10%, see Figure 6.5.

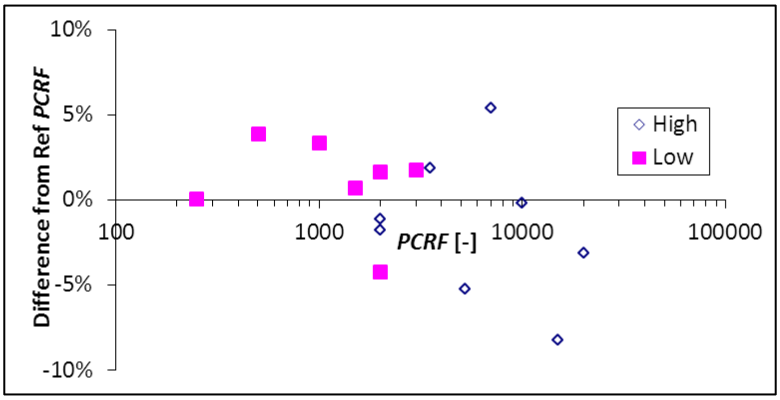

Figure 6.5: Tolerances of the relative PCRF check

7 Summary

Euro 5 legislation introduced a particle number (PN) limit. All PN measurement systems have to be calibrated annually. Furthermore on-site quality checks are recommended to ensure a high reliability as well as quality of the measurement results within the calibration interval. For the calibration of the systems a particle generator is necessary. In the content of this thesis a particle generator designed by the AVL List GmbH (APG) was characterized in detail. Not only the system itself was described, but also the applications in combination with a particle measurement system were explained.

The first section of this thesis dealt with the legislation background; especially the legal requirements for the calibration of a PN counting system. A PN device calibration can be distinguished into the PNC and the VPR calibration. Regarding the PNC calibration the counting efficiency, more specific the lower detection limit and the concentration linearity have to be determined. For the counting efficiency the device to be calibrated is measuring in parallel with an aerosol electrometer (reference standard) various sized (monodisperse) soot aerosols. In order to calculate the counting efficiency, the readings of the calibration device are related to the readings of the reference device. According to legislation a counting efficiency of 50% (±12%) for particles with an electrical mobility diameter of 23nm and >90% for particles >41nm should be achieved by the PNC.
In order to measure the concentration linearity, a monodisperse aerosol with particles of ≥ 50nm at various number concentrations is required. At least 5 different concentrations have to be measured. Then, similar to the evaluation of the counting efficiency, the readings of the two devices are compared resulting a linear correlation. According to legislation the linear regression has to be $R^2 > 0.97$ and the slope should be within the range of 0.9 and 1.1.
In addition to the legislation background the principle of PN counting and the used devices like the AVL particle counter, a particle number counter from TSI (model 3775 and 3790) and a differential mobility analyzer (model 3080 from TSI) are described.

In the next chapter different particle generating principles and particle generators like the spark soot generator, the combustion aerosol standard (CAST), evaporation and condensing techniques and an atomizer are discussed. In detail the Palas spark soot generator is investigated in detail because beside the CAST this is a well-known soot particle generator in the automotive industry. Especially different settings (relevant parameters are the current, the air flow and the nitrogen carrier flow) and the effects on to the generated aerosol are tested. It could be determined that increasing the current creates larger size distributions with larger concentrations, a higher nitrogen carrier flow results smaller particles and a larger amount of dilution air decreases the number concentration as well as the particle size.
This chapter includes also the theory behind combustion and soot formation. In detail the combustion of hydrocarbons, combustion under stoichiometric conditions, the formation of polycyclic aromatic hydrocarbons (PAH) and the soot formation are explained. At the end the diffusion flame, as the core element of the soot generation of the AVL Particle Generator is explained in detail. A diffusion flame occurs when the fuel and the oxidation air are not pre-mixed before the combustion takes place, e.g. a flame of a lighter or a candle. Thus the flame front is local positioned where the reactants meets. A bright red to orange spectrum indicates an incomplete combustion which is necessary for soot formation. At the upper part of the flame soot oxidation occurs and the concentration decreases. Thus soot particles can be extracted by cooling the flame, this means stopping further oxidation reactions, with a nitrogen quench flow. Depending on the settings, operating points that generate smaller size distributions contain more volatile components, e.g. PAH´s that are intermediates of the soot formation, than operating

points that produce large distributions. For this reason a volatile particle remover (VPR) is used to remove these volatile components and to stabilize the aerosol.

The next section dealt with the core of this thesis. Here the APG, the used elements, the parameter that affect the generated aerosol were discussed in detail. The APG consists of a burner unit (MiniCAST Model 6203c from Jing Ltd.), a volatile particle remover (VPR) and a dilution bridge stage to achieve low particle concentrations. At the APG the following 5 flow rates can be modified via mass flow controller: the fuel (propane), the nitrogen mixing, the oxidation air and two dilution air flows, one directly after the burner and one at the VPR unit (primary dilution). The nitrogen quench flow is set to 2 l/min constantly due to safety reasons.

Modifying the propane flow affected the height of the flame. Due to a constant position where the quench flow enters the burning chamber, different relative levels at which the nitrogen flow intrudes into the flame can be achieved. This means with a lower fuel flux the reaction is stopped at a higher relative position resulting larger particles and vice versa. A disadvantage of the fixed quench flow position at the burning chamber is that the concentration for larger particles is limited because by increasing the fuel (higher flow results higher concentrations), the quench of the oxidation occurs earlier and smaller particles are formed.

Changing the oxidation air amount modified the flame characteristics. A low oxidation air flow led to a small instable flame, where no or only a small orange center occurred. After increasing the amount of the air the diffusion flame grew and formed the typical orange zone resulting larger particles and number concentrations.

The dilution air flow directly after the burning chamber affects the number concentration as well as the particle size. Lower flow amounts result a smaller dilution, this means larger number concentrations and particle sizes due to higher agglomeration after the burner. The dilution air flow at the VPR does not affect the particle size but only the number concentration because at the VPR inlet the aerosol regarding agglomeration is more or less stable.

Chapter 5 examined the stability and repeatability of the generators. For the stability measurements following devices are under investigation: the APG, the MiniCAST and the Palas generator. Operating points that produce smaller size distributions (around 30nm) are used because here higher fluctuations regarding the stability of the concentration and mean diameter are expected. For the chosen operating points the stability expressed with the coefficient of variation (CV) of the APG is 3.8% for the number concentration and 2.5% for the mean diameter for a time scale of a few minutes. The other two generators achieved a stability regarding the number concentration of 8% (MiniCAST) and 8% (Palas), and 1.8% (MiniCAST) and 3.2% (Palas) concerning the mean diameter.

For the repeatability measurements the size distributions of the APG and the Palas spark soot generator are measured on 4 different days within 2 and a half weeks. For the APG three operating points and for the Palas eight operating points with different number concentrations and particle sizes are under investigation. The APG achieved for the three operating points an average repeatability (again expressed with the CV) regarding the concentration of around 4% and concerning the mean diameter of around 3%. Referring to the results of the Palas generator the repeatability correlates with the current respectively the particle size. For low current (smaller particles) the Palas achieved a repeatability of 10% and for a higher current (larger particles) 4% regarding the number concentration.

Chapter 6 discussed the most common applications of the APG. One is to use it for the calibration of the PN systems as described in the legislation. The other is to check the system on-site without the need of the radioactive source.
The cut point of the PNC e.g. at 23 nm for a CPC 3790, can be checked by generating a really small particle size distribution (around 10nm). The PNC under investigation should measure very low concentrations.
For the linearity check the internal PNC is compared with a reference PNC. Therefore a size distribution that produces large particles (>70nm) is required. The number concentration at the inlet of the two PNC´s varies within a range of 10 to 10.000 particles per cm³ for this application.
The Check of the PCRF of the volatile particle remover (VPR) can be determined with a reference PNC and comparison to the calibrated values. For this application the APG should produce a size distribution of around 50 nm.

Summarizing the APG is an appropriate tool for an easy and fast execution of these applications based on the combination of the volatile particle remover and the calibrated operating points, in which the knowledge of the required thermally stable size distributions to perform these applications is included.
In future the application of the APG with additional particle measurement devices, as example an AVL Micro Soot Sensor or an AVL PM PEMS, will be investigated to possibly extent the current application range.

8 Appendix

8.1 Definitions

In the following section some not common used phrases will be explained for an easier understanding.

Aerosol
An aerosol is a suspension of solid or liquid particles in a gas. The term aerosol includes both, the particles and the suspending gas, which is usually air. Particle size ranges from about 0.002 to more than 100µm can be included (41) .

Pre-mixed Flame:
In a pre-mixed flame the fuel and the oxidizer are mixed in the supply line. Afterwards this flammable mixture is combusted in a burning chamber (24).

Diffusion Flame:
In comparison to a pre-mixed flame the burner is supplied with the fuel and the oxidizer separately (24).

Brownian Motion
The Brownian Motion results from irregular collisions of the permanent movement of atoms and molecules. The variation of the number, the impulse strength and the impulse direction the gas molecules are executing, affects a random movement of an aerosol particle (41).

Mean Diameter (42)
The mean diameter that is used for the evaluation of the particle size distributions is defined as:

$$\frac{\sum_{l}^{u} \boldsymbol{n} * \boldsymbol{D_P}}{\boldsymbol{N}}$$

Where: n…number weighted concentration per channel
D_p…particle diameter (channel midpoint)
N… total number concentration
l…lower channel boundary
u… upper channel boundary

Chemiluminescence :
Luminous effect that occurs during a chemical reaction (24).

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