Understanding, Measuring and Regulating Sub-23 nm Particle Emissions from Direct Injection Engines Including Real Driving Conditions

Deliverable No. 2.2	
Author(s): Emmanouil Daskalos (APTL/CERTH), Christos Softas (APTL/CERTH), Anastasios Melas (APTL/CERTH)	
Quality control: Nickolas Vlachos (APTL/CERTH), Peter Morten Moselund (NKT Photonics)	
Version: 1.0 [final]	**Version date**: 31.03.2018
Project: SUREAL-23 (http://sureal-23.cperi.certh.gr)	**Project number**: 724136
Duration of the project: 01.10.2016 – 30.09.2019 | 36 months	
Project coordination and contact on behalf of SUREAL-23: Aerosol and Particle Technology Laboratory/CPERI/CERTH 6th Km Charilaou-Thermi, 57001 Thermi – Thessaloniki, Greece Contact: helen@cperi.certh.gr	

Acknowledgement

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Deliverable	**D2.2 Tunable UV photoelectric setup**
Associated WP	WP 2 Technology development
Associated Task	T2.2 Tunable UV laser photoelectric charger composition-specific aerosol charging
Due Date	31.03.2018
Date Delivered	31.03.2018
Prepared by (Lead Partner)	NKT Photonics
Partners Involved	APTL/CERTH
Dissemination Level	Public

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Introduction

The focus of SUREAL-23 is on the particulate emissions from contemporary light duty direct injection (DI) internal combustion (IC) engines (Diesel and gasoline) that will be addressed by homologation standards beyond Euro-6, especially for nanoparticles smaller than the current regulation cut-off diameter of 23 nm, with a threshold of at least 10 nm.
Within this context, the objectives of SUREAL-23 are:

- to complement existing standard instrumentation by introducing extensive size and composition characterisation of exhaust particles especially for sizes below 23 nm,
- to support future emissions compliance through technical development in real driving emissions measurement,
- to fully characterise the nature of the particulate emissions which potentially evade current emission control technology and regulations,
- to contribute to future definitions of particulate emissions limits of the “Super Low Emission Vehicles”.

The aim of WP2 is the development of technologies that:

- enable the understanding of PN sub-23 nm emissions with the introduction of in-situ, real-time characterization of particle composition,
- offer precise measurement of sub-23 nm particles number or size distribution allowing both ambient and hot temperature sample measurements with the potential for on-board use.

This report documents the delivered demonstrator “D2.2 Tunable UV photoelectric setup”, a prototype instrument developed in the frame of WP2 of the SUREAL-23 project. It describes the current state of the art, the innovation and the principle of operation of the developed setup and it presents some preliminary results performed with an aerosol generated by a propane diffusion flame. This prototype will continue to undergo improvements and will be available for sub-23 nm combustion aerosol characterisation in the SUREAL-23 project.

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Abbreviations list

APTL	Aerosol and Particle Technology Laboratory
CAST	Combustion Aerosol Standard
D	Deliverable
DMA	Differential Mobility Analyzer
EP	Electrostatic Precipitator
EC	European Commission
EU	European Union
FHNW	University of Applied Sciences Northwestern Switzerland
IC	Internal Combustion
M	Month
PN-PEMS	Particle Number-Portable Emissions Measurement Systems
PAH	Polycyclic Aromatic Hydrocarbon
RDE	Real Driving Emissions
SMPS	Scanning Mobility Particle Sizer
SoA	State-of-the-Art
UV-PEC	Ultra-Violet Photoelectric Charger
WP	Work Package

Short Project Overview

A large proportion of the total number of particles emitted from direct injection engines are below 23 nm and although the EU aims to regulate those emissions and impose limits for new light-duty vehicles, this is not yet possible due to the absence of accurate quantification methods, especially under real driving conditions. The main reason for this is the absence of adequate knowledge regarding the nature of sub-23 nm particles from different engine/fuel combinations under different operating conditions. SUREAL-23 aims to overcome such barriers by introducing novel measurement technology for concentration/size/composition measurements. The recently established supercontinuum laser technology will be coupled to photoacoustic analysis and will also be employed for photoelectric ionization aerosol charging to achieve real-time, composition size-specific analysis of the particles. In parallel, state of the art aerosol measurement techniques will be advanced for better compatibility with sub-23 nm exhaust particles as well as onboard use. The developed instrumentation will assess sub-23 nm particle emissions from both Diesel and GDI vehicles accounting for effects of the fuel, lubricants, after-treatment and driving conditions for existing and near-future vehicle configurations. The most suitable concepts will be developed for PN-PEMS applications and evaluated accordingly. The project will provide measurement technologies that will complement and extend established particle measurement protocols, sustaining the extensive investments that have already been made by industry and regulation authorities. The project will deliver systematic characterization of sub 23-nm particles to facilitate future particle emission regulations as well as to assess any potential trade-off between advances in ICE technology towards increased efficiency and emissions. The consortium consists of European and US organizations, which are leaders in the field of aerosol and particle technology.

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1 STATE OF THE ART (BRIEF REVIEW)

Aerosol particle composition is most commonly determined ex-situ, using various physical or chemical analysis methods on filter-collected particle samples. These methods include microscopy (i.e. SEM, TEM) techniques with Energy-Dispersive X-ray Spectroscopy (EDS), Thermogravimetric Analysis (TGA), chemical analysis for Soluble Organic Fraction (SOF) and Polycyclic Aromatic Hydrocarbons (PAHs), FTIR-Raman spectroscopy etc. The ex-situ particle composition characterization presents obstacles in the understanding of sub-23 nm engine/vehicle exhaust aerosol, due to the difficulties to study transient phenomena arising during cold start, filter regeneration or short high-power bursts of the engine.

Over the last years on-line/in-situ optical composition detection techniques are being developed mainly based on advances achieved in incoherent light (lamp) sources as well as in coherent (laser) sources. A widely used on-line/in-situ composition analysis technique is photoelectric ionization based on the photoelectric effect. Accordingly, when an aerosol is irradiated with ultraviolet (UV) light of energy below the threshold for ionization of the carrier gas molecules but above the photoelectric threshold of the particles, photoelectrons may be emitted from the particles which aquire a positive charge [1]. UV photons in the range of 4 – 7 eV are typically required to photo-ionize nanoparticles and combustion aerosols [2]. The fraction of aerosol particles charged at different light wavelengths is strongly material dependent and gives important information on the chemical fingerprint of condensed matter on the exhaust particles [3].

Photoemission has been described in the literature with a four-step model [1] : i) absorption of a photon and excitation of an electron, ii) movement of electron to the surface, iii) overcoming of the surface potential, and iv) escape of the electron from the surface of the particle. The emitted electrons may rebound back to the particle and recombine with the positive charge left behind. However, the possibility of such back-diffusion is small for sub-23 nm particles due to their small size compared to the exhaust gas mean free path. The positively charged exhaust particles are subsequently detected either by an electrometer or by a Differential Mobility Analyzer (DMA). It is important to note that internal particle material does not contribute to photoelectric emission – only substances present at the particle surface.

Photoelectric ionization shows a great potential in detecting and/or classifying combustion-generated particles from different hydrocarbon combustion sources (smoke/fire , diesel vehicle exhaust, etc.) due to the PAHs adsorbed on their surface. It is well-established that PAHs generate a high photoelectric yield compared to other particulate components in ambient air, permitting the selective charge of particles that originate from incomplete combustion [4]. Photoelectric charging has been also proposed as an alternative to traditional charging methods which are based on diffusion charging [5], potentially overcoming their inherent charging efficiency drop-off for smaller aerosol diameter. Additionally, it provides a probe of surface activities of nanoparticles that offers information on the transition of properties from atoms to bulk materials.

Light sources that have been used for aerosol photoionization are excimer lamps, deuterium lamps and lasers. Excimer lamps offer a high intensity, narrow band source of UV light. A well-established, commercially available photoelectric sensor is the Photoelectric Aerosol Sensor (PAS 2200CE, EcoChem) which uses an excimer lamp to detect ultrafine carbon aerosols in real-time. The lamp photon energy (dominant wavelength) is selected so that only

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carbonaceous particles are ionized and the resulting aerosol electrometer current provideses a signal which is proportional to the concentration of elemental carbon and/or surface PAH. Deuterium lamps are low-pressure gas-discharge sources having a wider and continuous spectrum in the UV region, typically 185-400 nm. Coupled with an optical filter they provide a narrow UV wavelength. Lasers may generate wavelengths in the UV region either directly (UV laser diodes, solid-state bulk UV lasers etc.) or based on a visible/infrared laser, i.e. with a longer wavelength, and one or several nonlinear crystals for nonlinear light frequency conversion. The UV spectrum obtained depends on the selected technology being narrow but also continuous. To our knowledge, there are no commercially available photoelectric sensors that use a deuterium lamp or a UV laser.

2 Tunable UV photoelectric charger DESCRIPTION

2.1 Innovation

In the frame of SUREAL-23 project requirements, a variable wavelength UV photoelectric charger (UV-PEC) setup was designed and constructed for the study of sub-23 nm particulate emissions from contemporary light duty direct injection (DI) internal combustion (IC) engines (Diesel and gasoline). The proposed setup introduces two major developments for the needs of SUREAL-23:

- a multi-wavelength light source with an output wavelength that can be selectedover the entire middle UV region (200 to 300 nm),
- advanced combustion/engine exhaust conditioning systems and instrumentation developed in SUREAL-23 project.

The requisite UV light spectrum is achieved by using two different light sources: (1) the SuperK Compact® super-continuum laser source in combination with the SuperK Extend-UV® unit (NKT photonics) which is a tunable deep-UV supercontinuum spectral extension unit for a number of NKT's supercontinuum laser sources, and (2) a deuterium UV lamp (Newport) in combination with dielectric coating based UV spectrum filters. The wide and tunable spectrum available by these two sources offers the possibility of investigating the nature of sub-23 nm particles, which, in terms of surface composition, may be solid (amorphous or graphitized carbon, metal oxides etc.) or liquid (adsorbed hydrocarbons and sulfur species).

The advanced instrumentation developed in SUREAL-23 project that will be tested in tandem with the UV-PEC are the advanced Half-Mini DMA (HM-DMA) and a high flow catalytic stripper developed within the project. The HM-DMA system is a supercritical differential mobility analyser, with a 2 cm working section, initially developed at Yale University and subsequently improved – within SUREAL-23 – by SEADM (Boecillo, Spain) able to classify combustion aerosol particles (including molecular ions) in the size range 1-30 nm with high resolution and fast acquisition frequency [6]. The placement of the HM-DMA downstream the photoelectric charger will offer a high resolution size-selective analysis of the charged aerosol fraction. The high-flow catalytic stripper was developed by APTL and is able to remove heavy hydrocarbon and sulphur particles while the solid particle penetration is larger than 75% down to 10 nm. The use of the catalytic stripper upstream of the photoelectric charger will permit the detailed assessment of the effect of particle conditioning, typically applied at engine exhaust, on the particles' composition.

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2.2 Principle of Operation

The multi-wavelength UV photoelectric exhaust particle detectorsystem consists of the following parts:

- electrostatic precipitator
- tunable UV Source
- ionization Chamber

Figure 1 shows the schematic of the developed photoelectric charger setup.

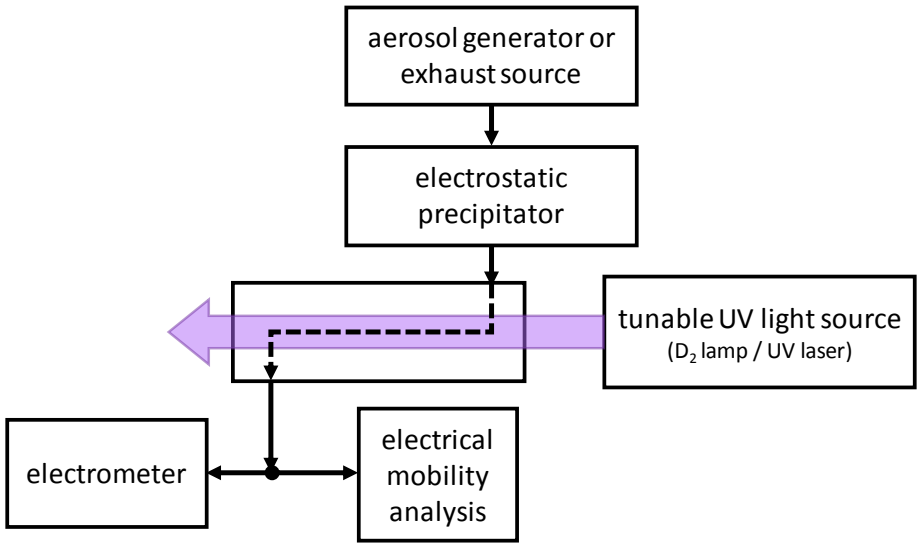

Figure 1. Schematic of themulti-wavelength photoelectric aerosol analysis system.

The primary components of the multi-wavelength aerosol photoionisation system are described below.

2.2.1 Electrostatic precipitator

Almost invariably, a fraction of combustion-generated particles are naturally charged (pre-charged) while the total charge and its distribution vary widely with combustion conditions. In order to utilise the photoelectric charging to explore the nature of the exhaust aerosol it is necessary to pre-treat the exhaust sample to ensure a charge-free aerosol sample. This is achieved by using the electrostatic precipitator, an aerosol pre-treatment device that retains pre-charged particles through the use of a strong electric field across a pari of electrodes, perpendicular to the aerosol flow. The applied voltage needs to be below 30 kV/cm to avoid air ionization and the associated electrical arcing.

The electrostatic precipitator (EP) as well as the high voltage control unit to be employed with the exhaust aerosol photoionization system were developed at APTL/CERTH. The control unit is comprised of off-the-self electronic components and a custom built printed circuit board. The

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EP consists of two concentric cylinders with the high voltage being applied in the resulting annular gap. Gap voltages up to 7KV can be achieved via a variable DC voltage supply device. The electric field created is directed radially outward from the inner cylinder to the outer cylinder while the aerosol flow travels perpendicularly to it. Figure 2 shows an image of the developed EP setup.

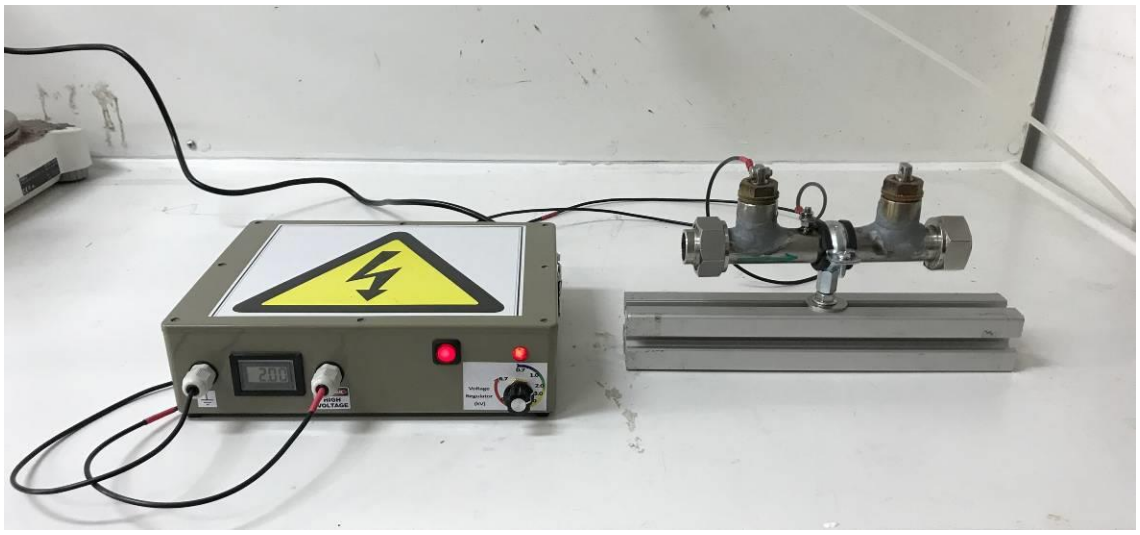

Figure 2: Electrostatic precipitator and high voltage control unit (without exhaust sample inflow-outflow lines).

The EP was evaluated with particles generated by a propane diffusion flame burner (CAST). Three different CAST setpoints were used to generate particles in a wide size range from 10 nm up to 350 nm. Before entering the device, the EP particles are passed through a Kr-85 neutralizer (TSI Inc., model 3077) to obtain a known charge distribution. Downstream of the EP, a Scanning Mobility Particle Sizer (SMPS) measures the charged particle size distribution without further aerosol charging applied.

The EP's charged particle removal efficiency was found to depend on the particle size, the aerosol flow, and the applied voltage. The EP was able to remove 100% of particles up to 350 nm for an aerosol flow Q=1.5 lpm, and with applied voltage V=5500 V. Smaller particles, in the sub-23 nm size range were completely removed with voltages down to V=1500 V, and so the EP constructed was deemed adequate for current purposes.

2.2.2 Tunable UV Source

The specifications of the UV sources have been chosen in close collaboration between FHNW, NKT, and APTL. Two different UV sources were used in the developed setup; the supercontinuum laser based SuperK extend-UV (NKT photonics) unit and a compact deuterium UV lamp (Newport).

The SuperK COMPACT (NKT Photonics) laser is a low cost supercontinuum white light source delivering diffraction limited light in the entire 450-2400 nm region with a brightness orders of magnitude larger than that of incandescent lamps and with far greater bandwidth than ASE (amplified spontaneous emission) sources or SLEDs (superluminescent emitting diodes). The supercontinuum light is delivered in a single mode fiber terminated with either a standard FC/PC connector or a compatible collimator. The SuperK EXTEND-UV (NKT Photonics) is a deep-UV supercontinuum spectral extension unit for NKT's SuperK EXTREME and

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COMPACT supercontinuum lasers that produces UV light from a robust fiber laser source with 265-480 nm range and 2-80 μW output power. The features of the laser are:

- pulsed deep UV output
- tunable in the 265-480 nm range
- short pulses down to 20 ps (superK EXTREME source)
- 2-12 nm bandwidth

Deuterium lamps are arc lamps filled with deuterium gas at near ambient pressure. The arc in D_2 lamps emits high intensity ultraviolet radiation down to 160 nm, making them ideal for UV spectroscopy. Deep UV radiation, below 180 nm, can be selectively discarded by using suitable window materials (UV glass), in order to avoid ionisation of sample gas components (e.g. O_2 oxidation to ozone) which would be problematic for current purposes. The deuterium lamp used (by Newport Corporation) is an ozone-free type lamp that is housed in an enclosure equipped with a beam collimator. The features of the Deuterium lamp are:

- 185-400 nm spectral range
- 30 W light output power
- 33 mm diameter collimated output beam

The small size of the light-emitting arc (typically 1 mm) is one of the factors permitting an intense colimated beam from this setup. Wavelength selection is achieved via UV bandpass filters (dielectric coating type) mounted on a manually acruated filter wheel.

2.2.3 Ionization Chamber

The ionization chamber is the compartment that facilitates the charging process of the sub-23 nm particles by means of exposing the particles to the highly energetic photons produced by the relevant light source (spectrally extended supercontinuum laser or filtered deuterium UV lamp). During its realization several design factors were considered in order to ensure the key attributes of the unit: high charging efficiency, continuous/long-term operation, low particle losses as well as the protection of optical windows/mirrors. Such factors were length, diameter, flows and geometries concerning the specific site, the relative angles and the type of sample/protective flow ports. CFD analysis was employed to support the design of the ionization chamber, with primary objectives: (a) to optimise the exposure of the aerosol to the centrally passing UV light beams and (b) to prevent deposition of exhaust particles (as well as condensible vapors) on the optical elements at the chamber ends (quartz window at the light inlet end, flat UV mirror at the other end). Example results from this effort are shown in Figure 3 below.

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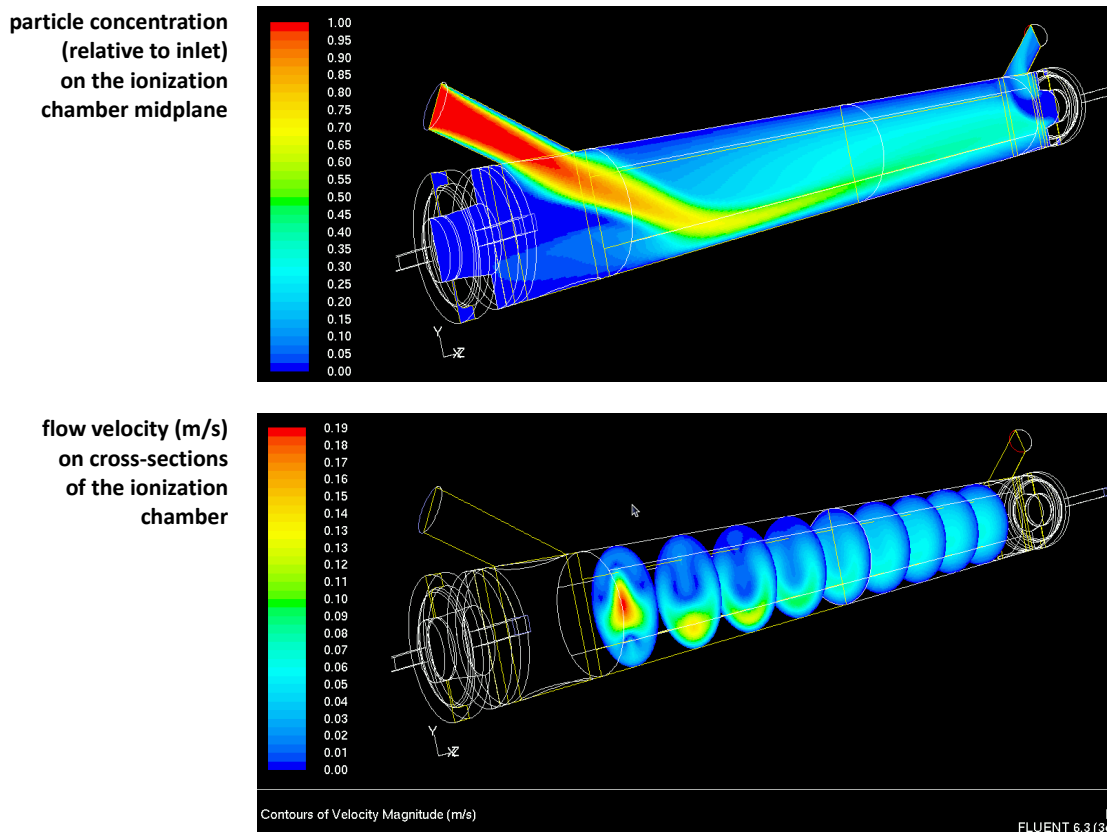

Figure 3. Example results from CFD analysis performed for the design of the ionization chamber.

The ionization unit consists of a main pipe with a diameter large enough to avoid any shadowing effects from its sub-features (flow inlets, electrodes) on the collimated light beam. Light enters the chamber, coaxially with the main flow, through a fused silica window of high optical transmissivity in the UV region. Subsequently, it interacts with the aerosol particles and, after minor absorption, reaches the other end of the pipe, where a UV-enhanced aluminum coating mirror is installed in order to redirect the remaining UV light towards the particles and enhance the charging efficiency. The aerosol inlet and outlet (3⁄8" diameter tube) are symmetrically positioned close to the ends of the exposure chamber pipe, forming a shallow angle (≈30°) with respect to the main axis of the unit in order to keep the aerosol as much as possible in the chamber center. The aerosol flow is further focused toward the central axis of the unit by using an auxiliary gas jet (supplied by a smaller flow inlet) and adjustable ring-shaped baffles, to deflect/direct the particle-laden flow away from the chamber walls. Furthermore, along the second half of the exposure chamber pipe, ion trap electrodes are installed, consisting of two parallel flat plates – outside the UV beam path – that can be (optionally) employed to form an alternating electric field in order to deplete the charged aerosol from ejected photoelectrons that could reattach to the UV-charged particles (recombination), leading to a reduction of the charging efficiency. This function is expected to be required for higher (>10^5 #/cm³) exhaust particle concentrations. Finally, in order to protect the optical elements from particle deposition and prolong the operating time of the unit before cleaning is needed, two protective, annular air curtains are injected through peripheral slits near each pipe end. All values for critical dimensions, flows and positions have been defined after a parametric study in order to reach a satisfactory balance between all set goals. The ionization chamber constructed (without flow connection lines) can be seen in Figure 4.

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Figure 4: The protoype of the UV ionization chamber (without flow connection lines or the light source)

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3 TECHNICAL SPECIFICATIONS

The table below presents the technical specifications of the tunable UV particle photoelectric analyser setup:

NKT Photonics SuperK COMPACT light source	
Wavelength	450-2400 nm
Total output power	> 110 mW
Dimensions	93 x 221 x 332 mm
Weight	3.8 kg
SuperK Extend-UV Supercontinuum Extension Unit	
Output wavelength	265-480 nm
Dimensions	287,0 x 211,5 x 67,6 mm
Weight	5.9 kg
Compact deuterium lamp source (Newport Corp.)	
Wavelength	185-400 nm
Beam power	30 W
Dimensions	127,0 x 165,0 x 214,0 mm
Electrostatic Precipitator	
Maximum Voltage	7000 V
Length	200 mm
Diameter	20.5 mm
Aerosol Flow Rate	1 - 3 lpm
Ionization chamber	
Length	650 mm
Diameter	57 mm
Aerosol sample flow rate	1 - 3 lpm
Auxiliary flows required	up to 3 lpm, clean air or N_2

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4 CONCLUSIONS

A prototype tunable UV photoelectric charger system has been designed and constructed for the puprose of on-line/in-situ characterization of sub-23 nm particulate emissions with respect to photoelectrically determined composition. The main novelty of the setup lies in its ability to expose the exhaust aerosol of interest to a tunable UV light wavelength spectrum, thereby allowing one to probe the surface composition of the exhaust particles. This function is expected to benefit also from the combined use of the UV photoionization system in tandem with new SUREAL-23 instrumentation for sub-23 nm particles size classification and conditioning.

Preliminary experiments were performed with CAST-generated particles to characterize the electrostatic precipitator performance and the optimal operation settings were found. The UV light sources were specified accordingly to cover all the middle UV region (200-300 nm). Finally, the ionization chamber was optimised for high charging efficiency, continuous/long-term operation, and low particle losses. Further evaluation of the tunable UV-PEC in different testing platforms for the needs of SUREAL-23 will give the necessary feedback for possible improvements.

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