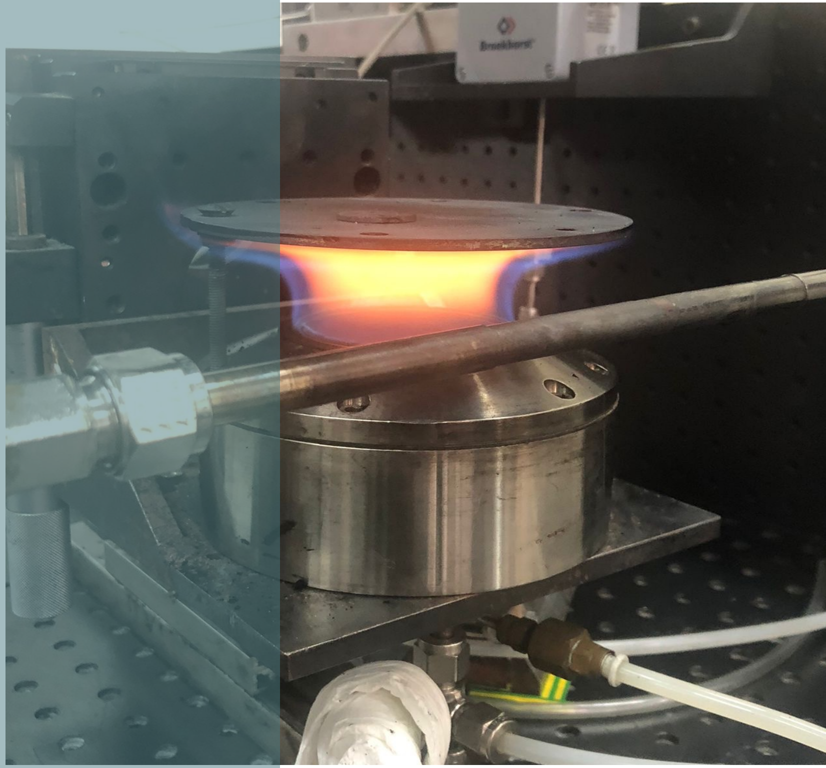
26th Nanoparticles Conference – ETH

Formation, Growth, and Photochemical Aging of Laboratory-Generated Nanoparticles



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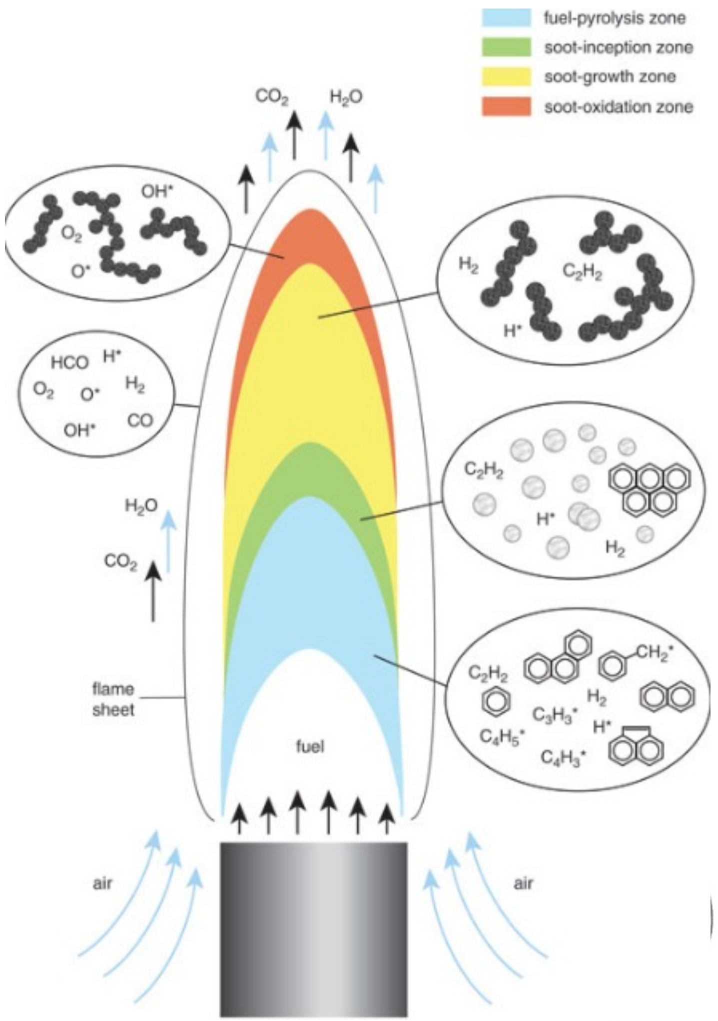
** Centro Servizi Metrologici e Tecnologici Avanzati, Università degli Studi di Napoli Federico II, Napoli, 80146, Italy

† Dipartimento di Ingegneria Chimica. dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Napoli, 80125, Italy

‡ Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili, CNR, Napoli, 80125, Italy

OUTLINE

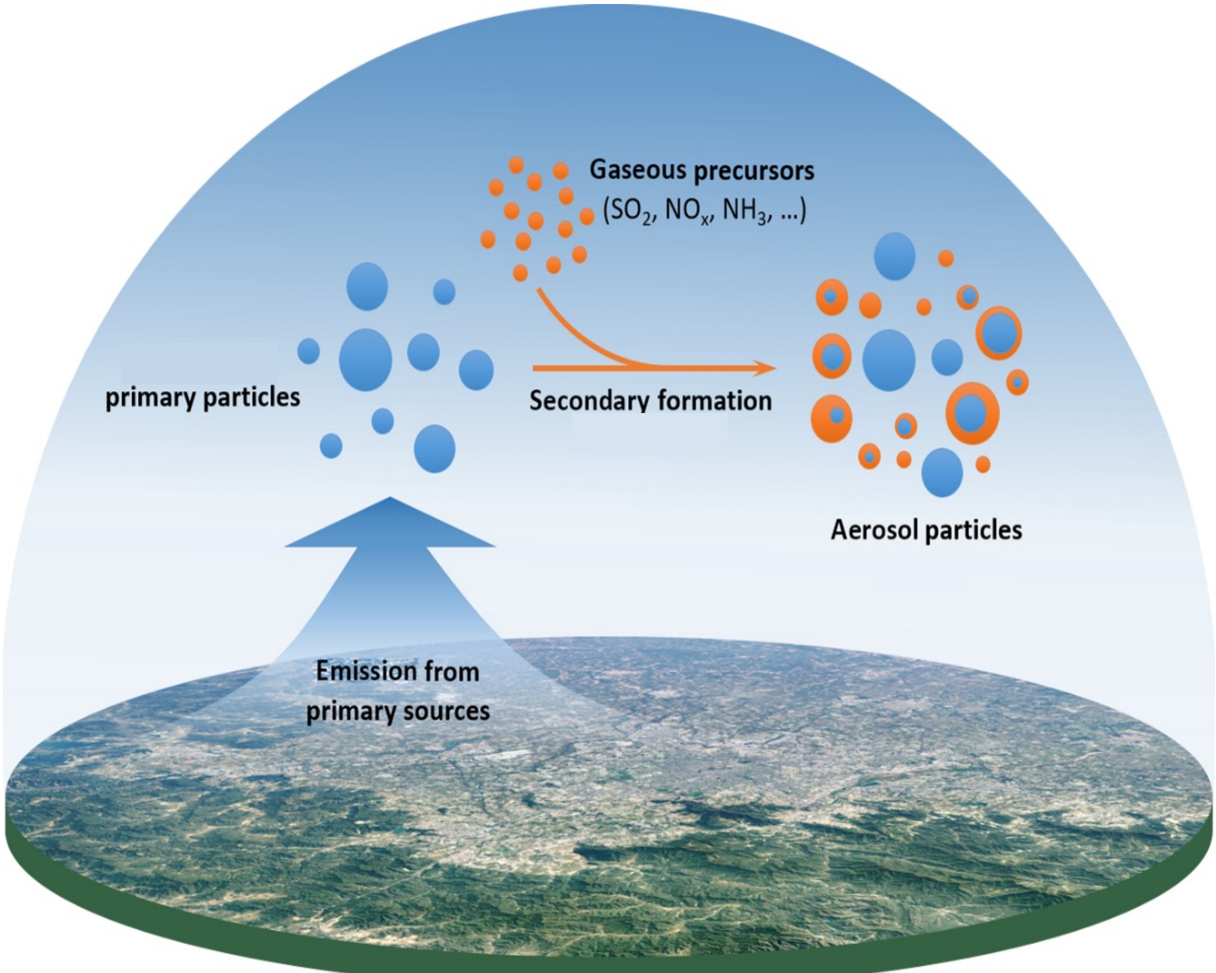
- Introduction: atmospheric aerosol and aim of this study;
- Experimental Setup;
- Results Discussion;
- Conclusions.



ATMOSPHERIC AEROSOL

Atmospheric aerosols are suspensions of liquid, solid, or mixed particles with highly variable chemical composition and size distribution (*Putaud et al. 2010*)

- **Primary Aerosol**
  - Directly emitted by the source
- **Secondary Aerosol**
  - Generated in the atmosphere
    - From gaseous precursors by condensation of vapours on pre-existing particles
    - Formed by nucleation of new particles



ATMOSPHERIC AEROSOL

Atmospheric aerosols are suspensions of liquid, solid, or mixed particles with highly variable chemical composition and size distribution (*Putaud et al. 2010*)

Direct scattering and absorption of incoming solar radiation	Variation of the Surface Temperature and the Earth's energy balance
Trapping of outgoing long-wave radiation	Increase of extreme atmospheric phenomena
Formation of clouds and precipitation	Alteration of cloud optical properties
Health Damages	Increment of cancers, cardiovascular diseases and inflammatory cases

PROPOSED ANALYSIS

In this study an investigation on the aerosol generated by an ethylene/air flame doped with ethanol is proposed.

Φ	Air [L/min]	Ethylene [L/min]	Ethanol [L/min]	Ethanol [%]	Heights Above the Burner (HABs) [i.e. Residence time]
2.010	14.570	2.051	-	-	8, 10 and 14mm
2.010	14.570	1.846	0.205	10%	8, 10 and 14mm
2.010	14.570	1.641	0.410	20%	8, 10 and 14mm

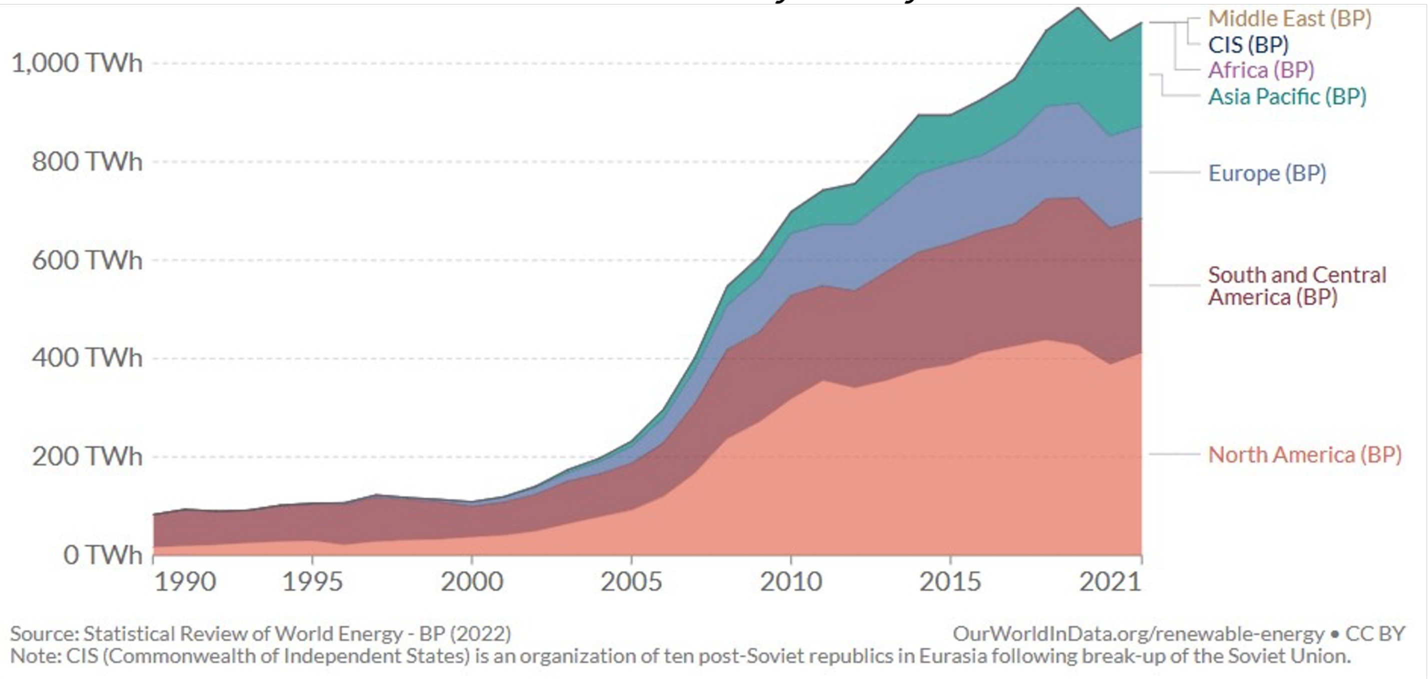
Constant Φ

$$\Phi = \frac{(^{C}/_{O})}{(^{C}/_{O})_{stoic}}.$$

Three Ethanol Concentrations

WHY ETHANOL?

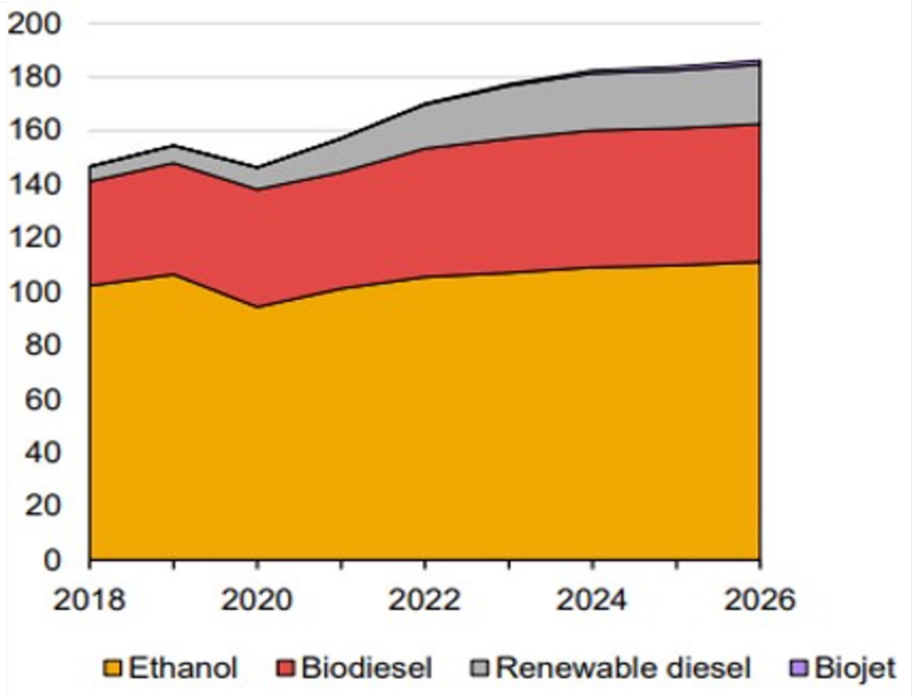
Biofuel Production by Country



Reference: bp Statistical Review of World Energy 2022, BP p.l.c., 2022

Since 1990, biofuel consumption has drastically risen.

Biofuel Demand By Fuel



Ethanol (EtOH) represents a valid alternative to petroleum-based fuels.

References: *Renewables 2021*, International Energy Agency, 2021;

INTRODUCTION

Ethanol Use has several advantages:

Costs	Availability	Equipment Flexibility	Further Investigations
Reduced production Costs with respect to other biofuels	Ethanol can be obtained from sugarcane, corn, grain or indirectly from paper waste.	Possibility of using Ethanol for already existing vehicles; Better Combustion performances due to oxygen presence.	Energy Density of Biofuels; Effects of the produced compounds on Human Health

INTRODUCTION

antages:

Costs

Reduced production Costs with respect to other biofuels

Availability

Ethanol can be obtained fro sugarcane. c grain or indirectly fro paper waste.

Equipment Flexibility

Possibility of

Further Investigations

Energy Density

due to oxygen presence.

	Ethanol Production Costs [USD/Lge]*	Biodiesel Production Costs [USD/Lde]*
Brazil	0.54-0.62	0.73-0.98
United States	0.51-0.58	0.76-0.86

*Lge=liters of gasoline equivalent; Lde=liters of diesel equivalent

References: *Renewables 2018*, International Energy Agency, 2018;

INTRODUCTION

Ethanol Use has several a

Costs

Reduced production Cos with respect to other biofuels

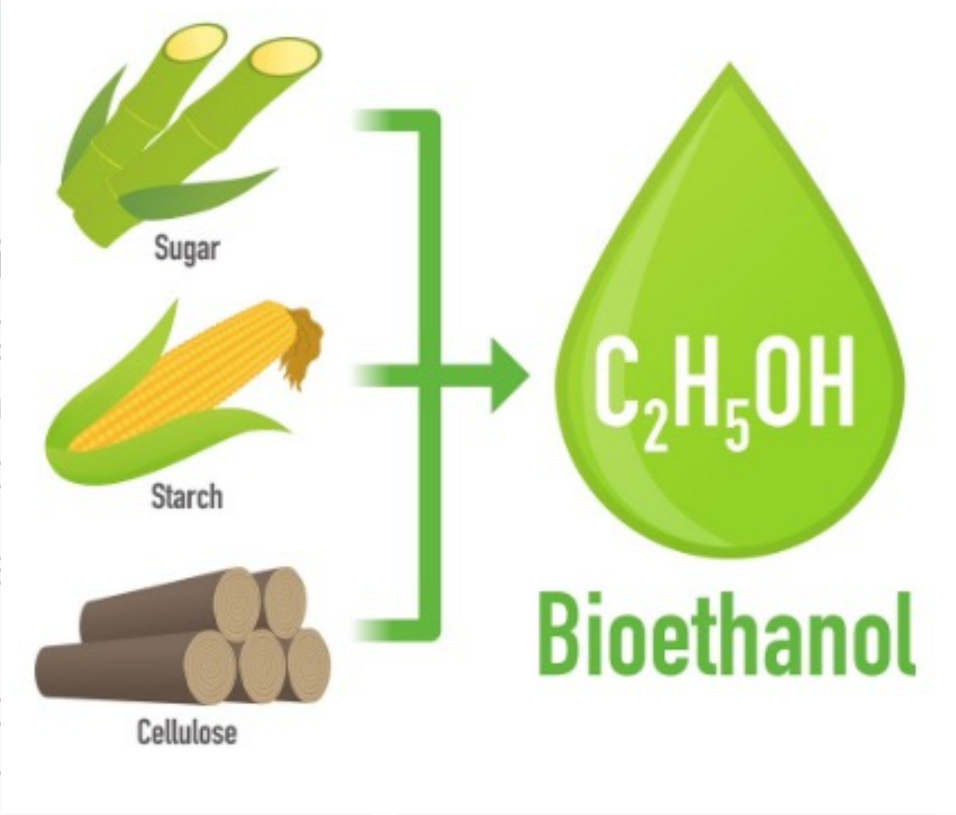
Availability

Ethanol can be obtained from sugarcane, corn, grain or indirectly from paper waste.

Equi Flex

Possi using alrea vehic

Bette Com perf due presence.



INTRODUCTION

Equipment Flexibility

- Possibility of using Ethanol for already existing vehicles;
- Better Combustion performances due to oxygen presence.

INTRODUCTION

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Costs

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Equipment Flexibility

Possibility of using Ethanol for already existing vehicles;

Better Combustion performances due to oxygen presence.

Further Investigations

Energy Density of Biofuels;

Effects of the produced compounds on Human Health

INTRODUCTION

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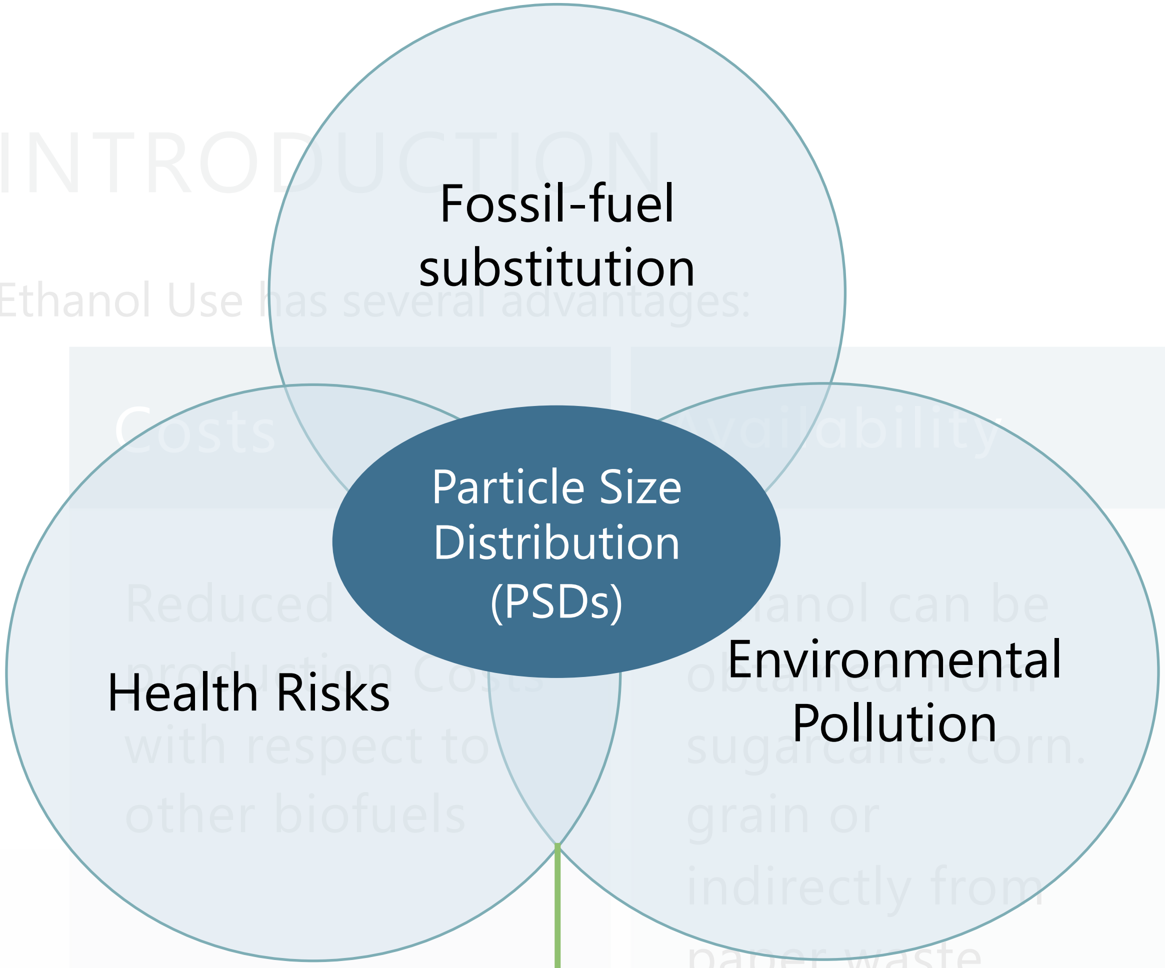
Further Investigations

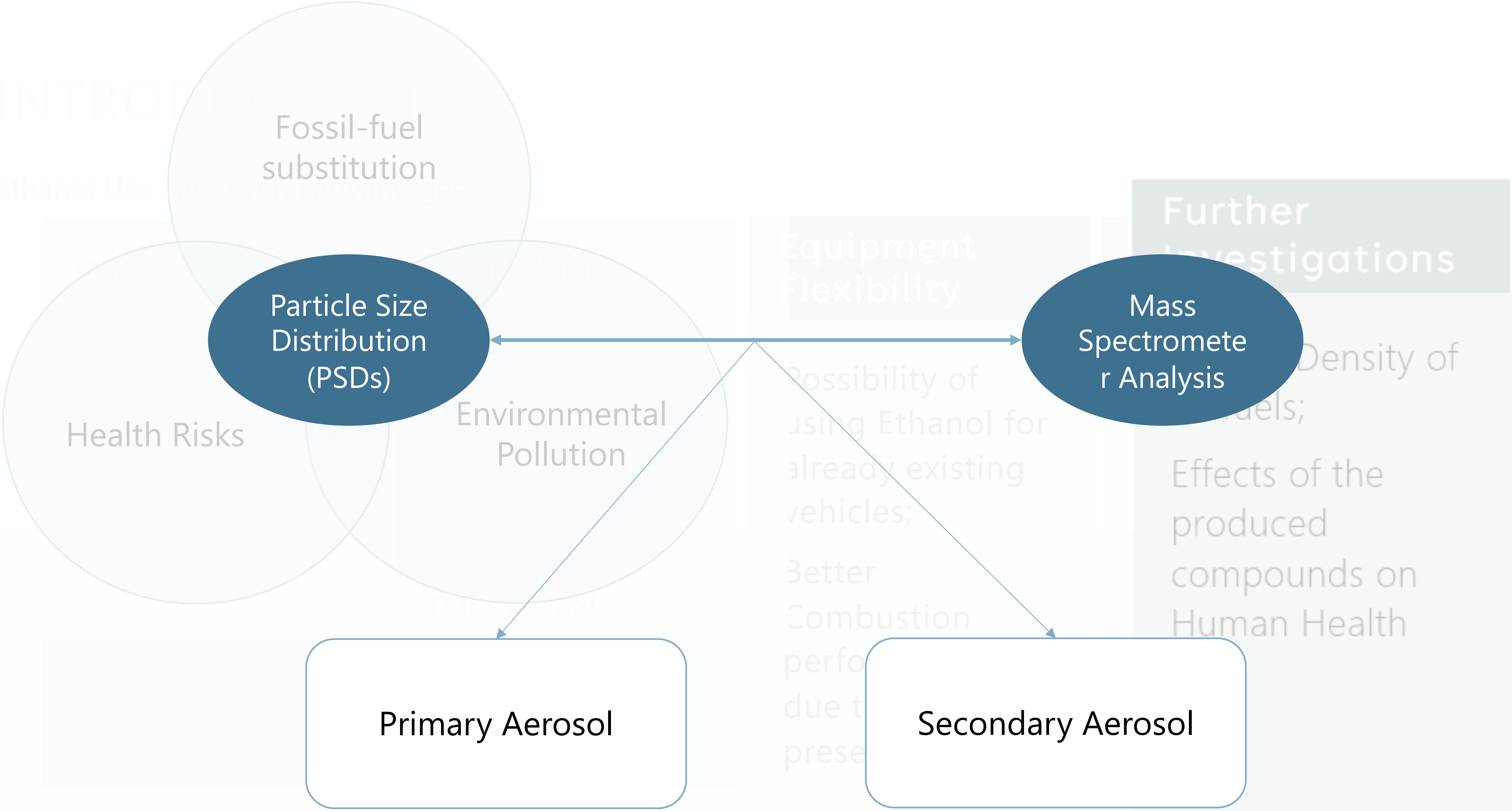
Energy Density of Biofuels;

Effects of the produced compounds on Human Health

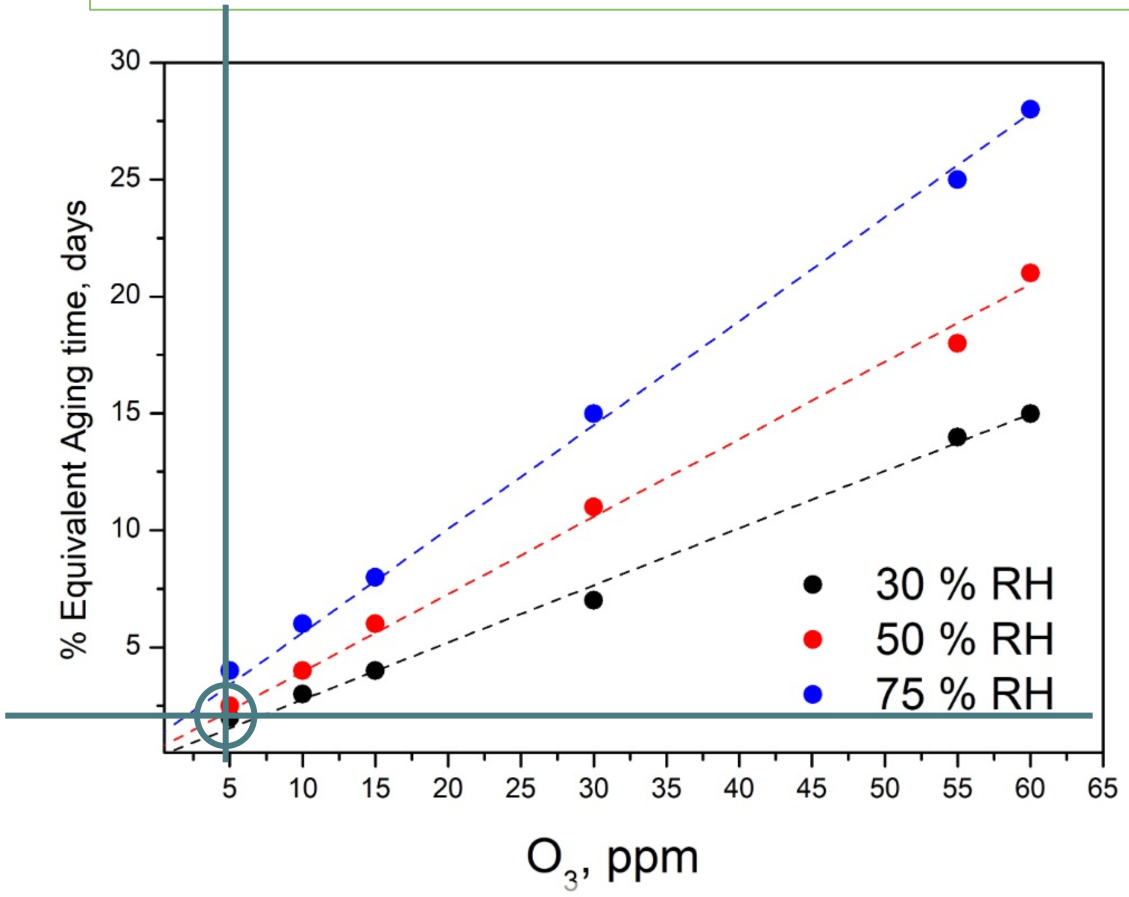


PSDs Analysis reveals to be crucial because it has been demonstrated that **Particle Toxicity** strongly depends on:

- Particle size;
- Number concentration.


Fossil-fuel substitution
Health Risks
Environmental Pollution
Particle Size Distribution (PSDs)
Mass Spectrometer Analysis
Primary Aerosol
Secondary Aerosol
Further Investigations
Effects of the produced compounds on Human Health

In order to simulate the atmospheric oxidative conditions and to study secondary aerosol formation, primary particles collected were exposed to an **ozone flux** able to replicate atmospheric aging processes.



A Concentration of **5ppm** was used, corresponding to c.a. **2 aging days** in the atmosphere.

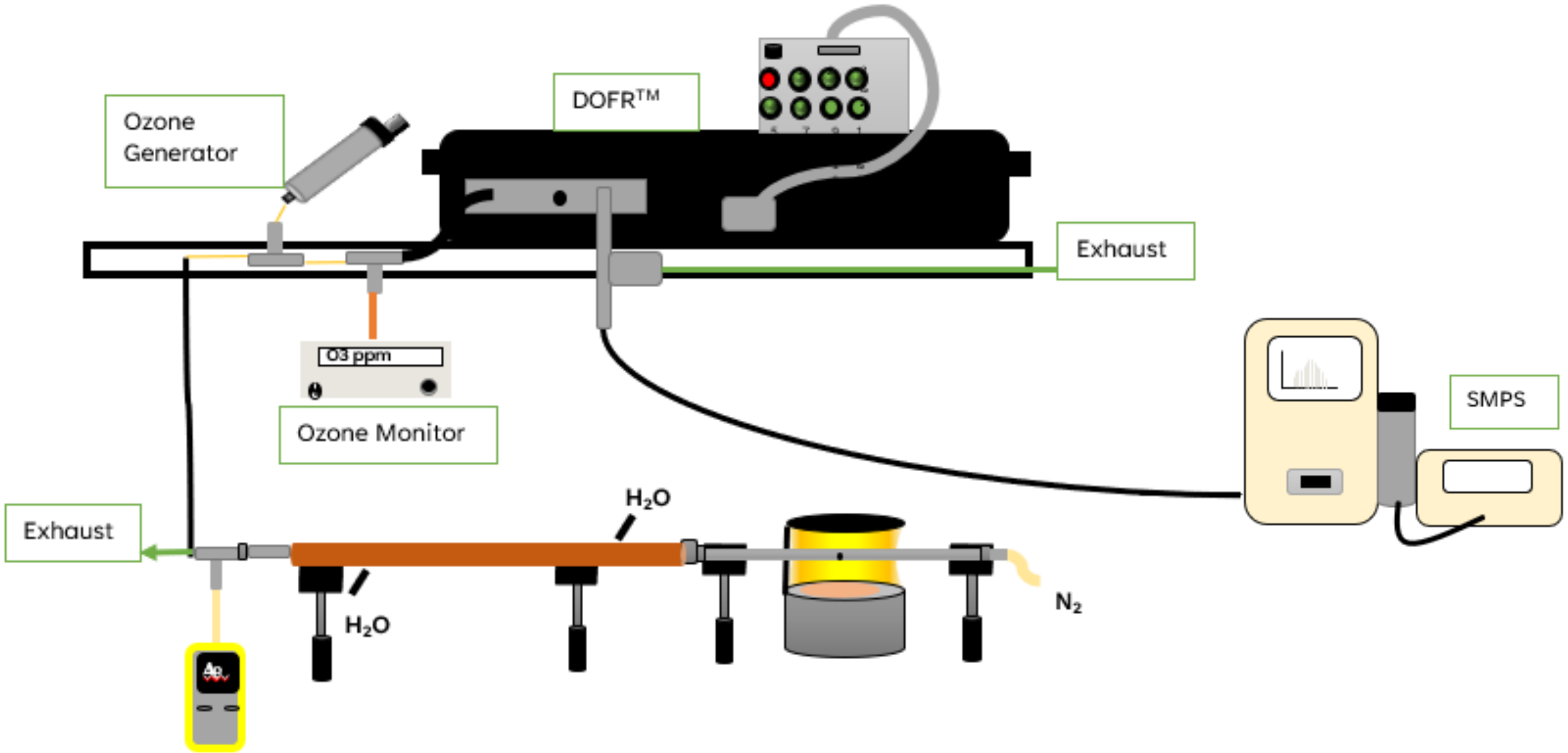
Aged particles are responsible of oxidative stress of the cells, higher inflammatory response, DNA damages .

SECONDARY AEROSOL

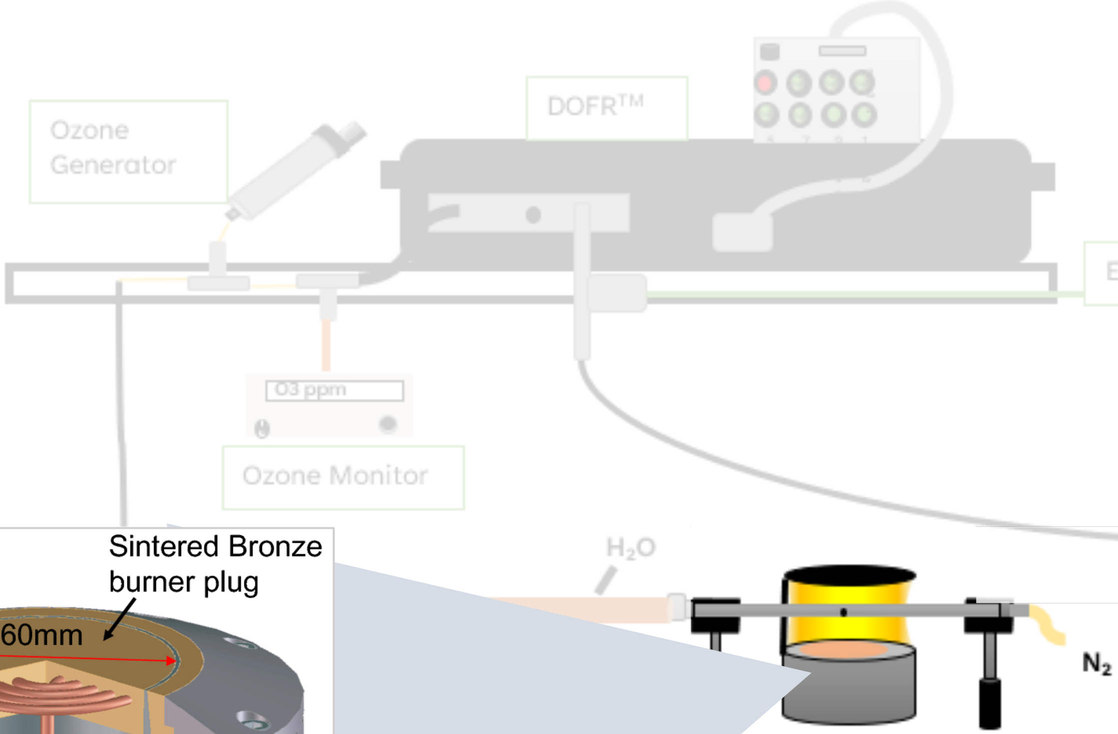
And oxidative atmospheric conditions simulations

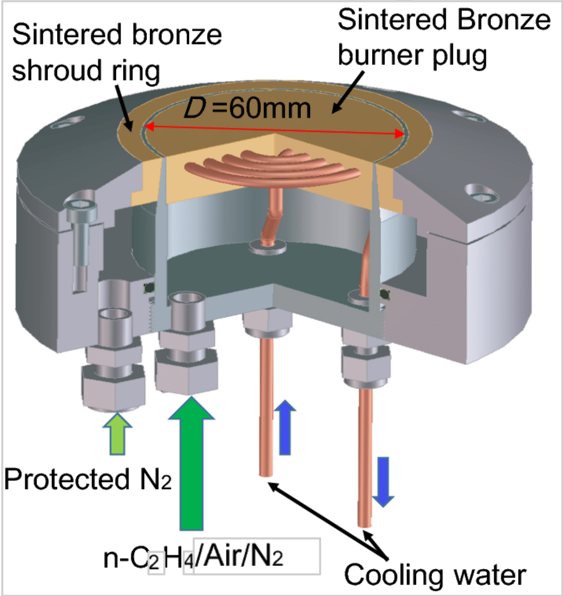
Reference: Dekati Oxidation Flow Reactor

EXPERIMENTAL SETUP



EXPERIMENTAL SETUP



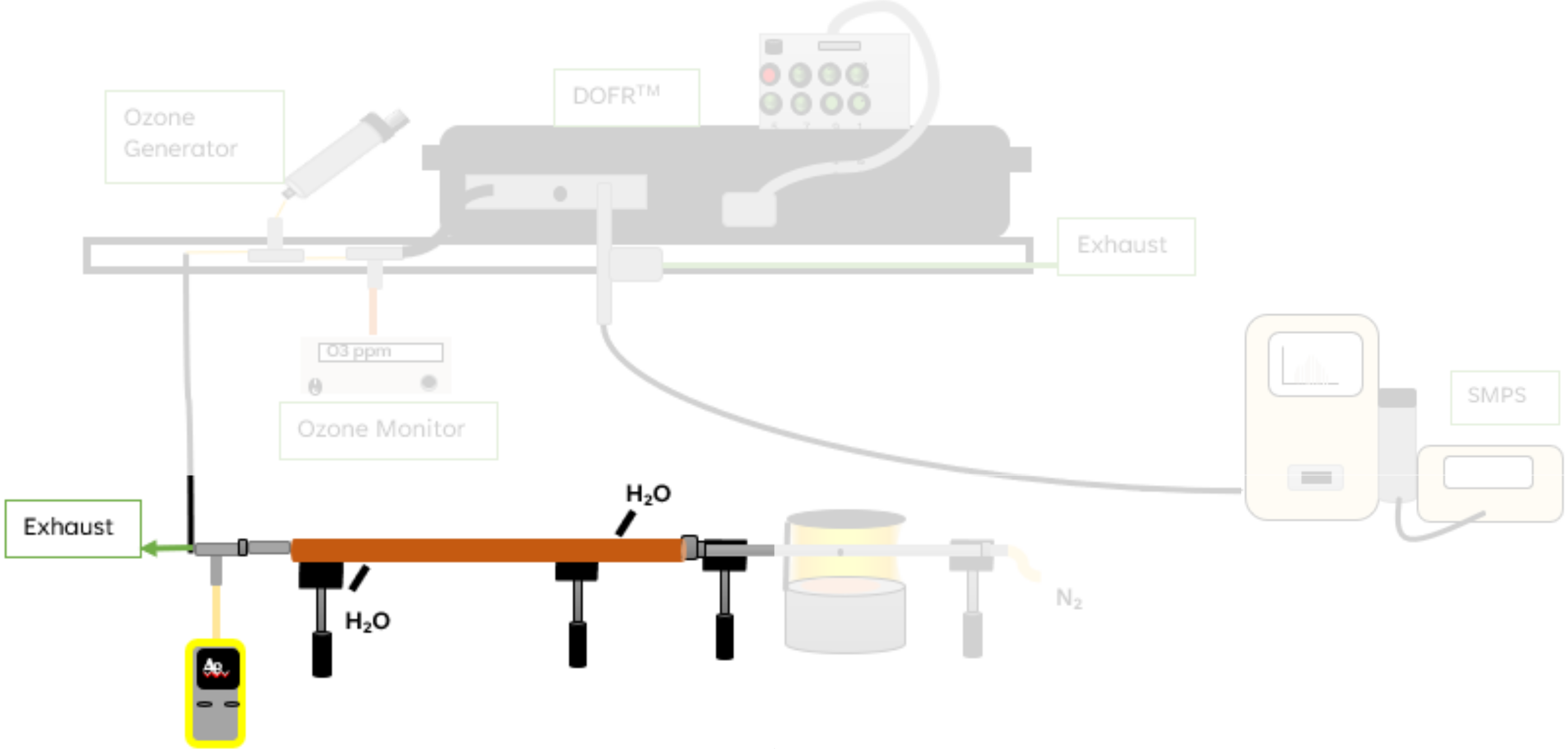


1) McKenna Burner with 6cm Diameter;

2) N_2 Dilution Flow;

3) Metal Probe with 0.2mm Orifice (PSDs) or 0.6mm (Mass Spectra).

EXPERIMENTAL SETUP



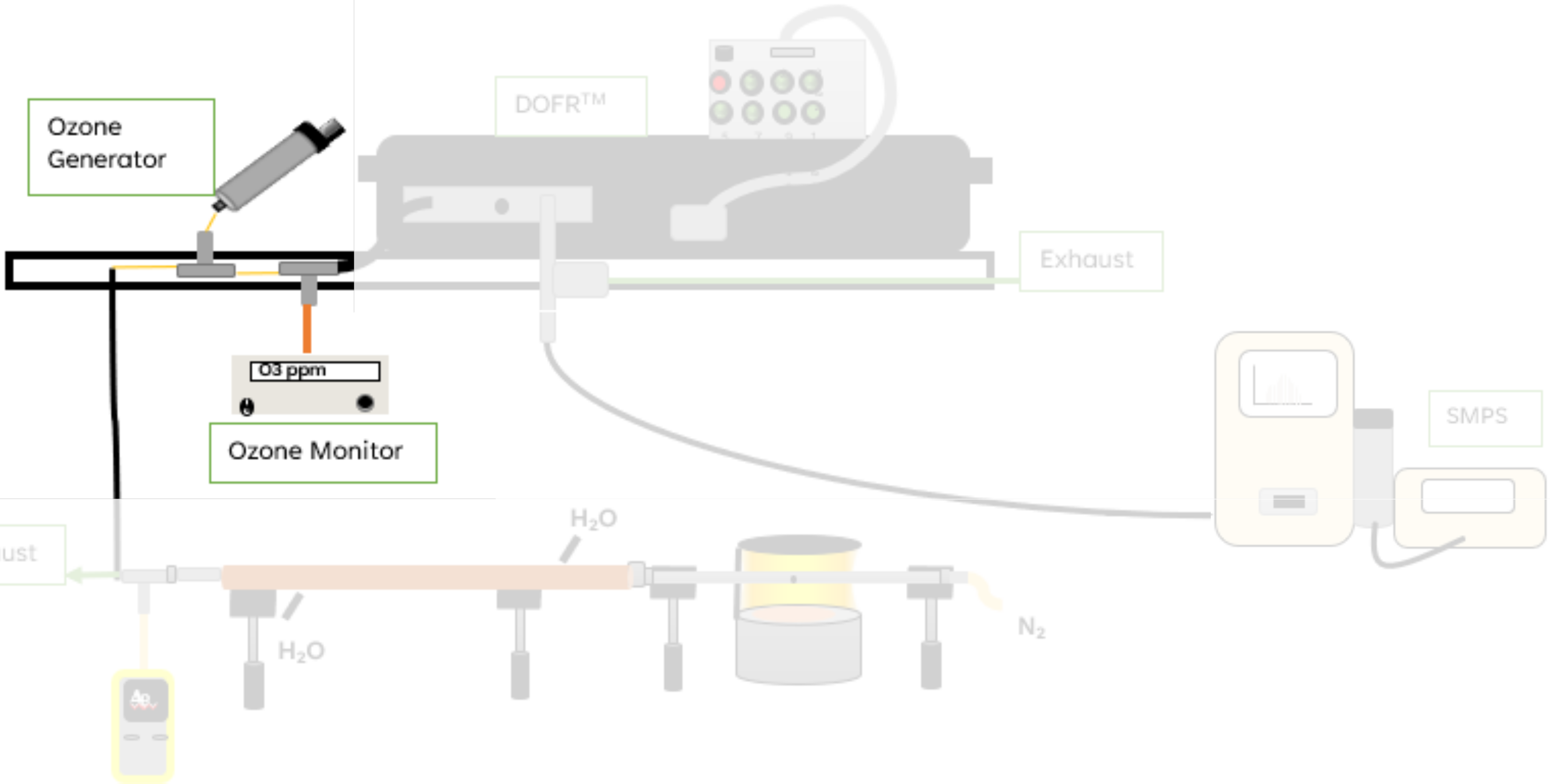
4) Manometer to Control the Pressure

5) Probe Cooling Water

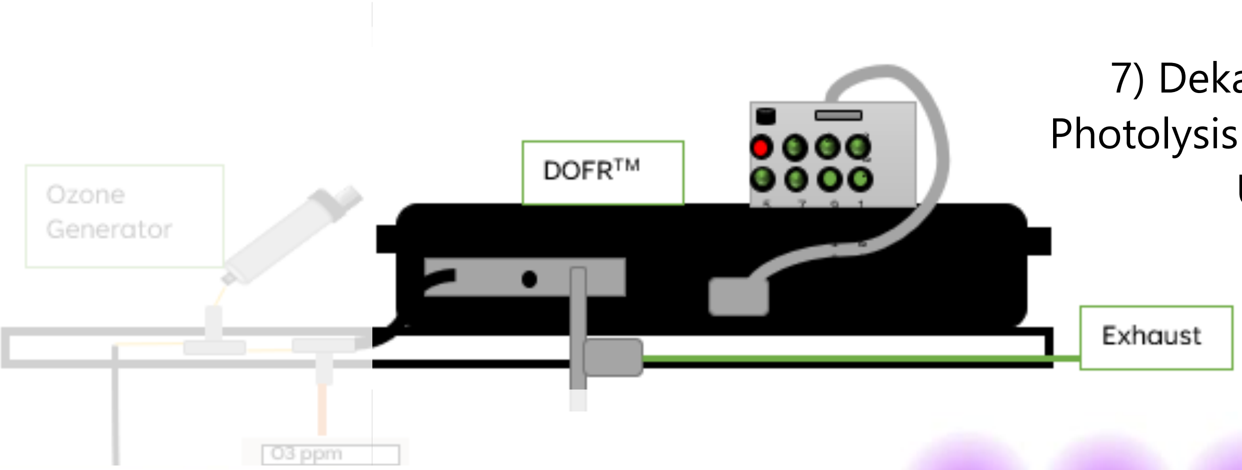
EXPERIMENTAL SETUP

6) Ozone Generator producing O_3 from photolysis by 185 nm UV radiation

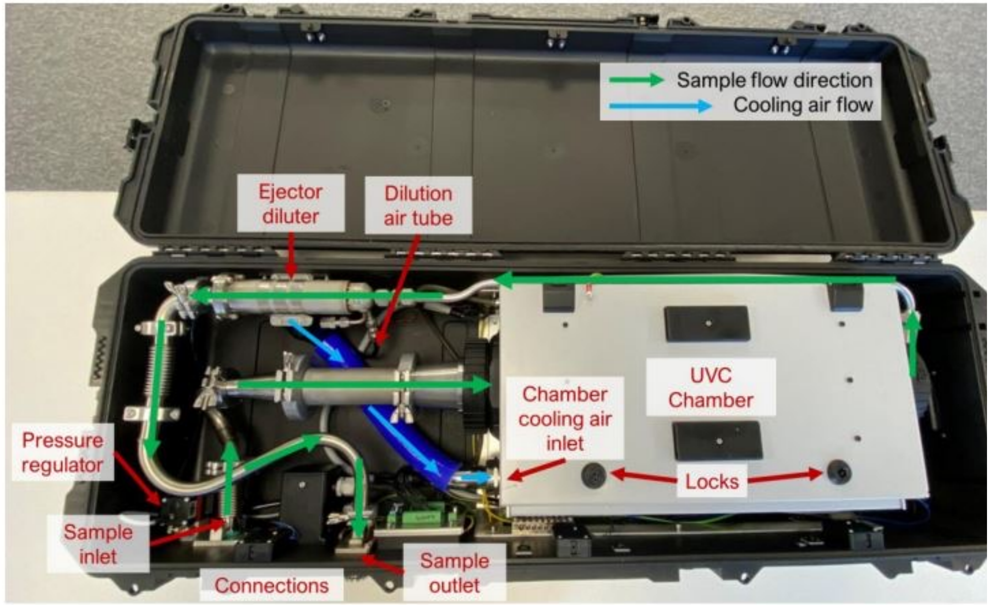
7) Dual Beam Ozone Concentration Monitor

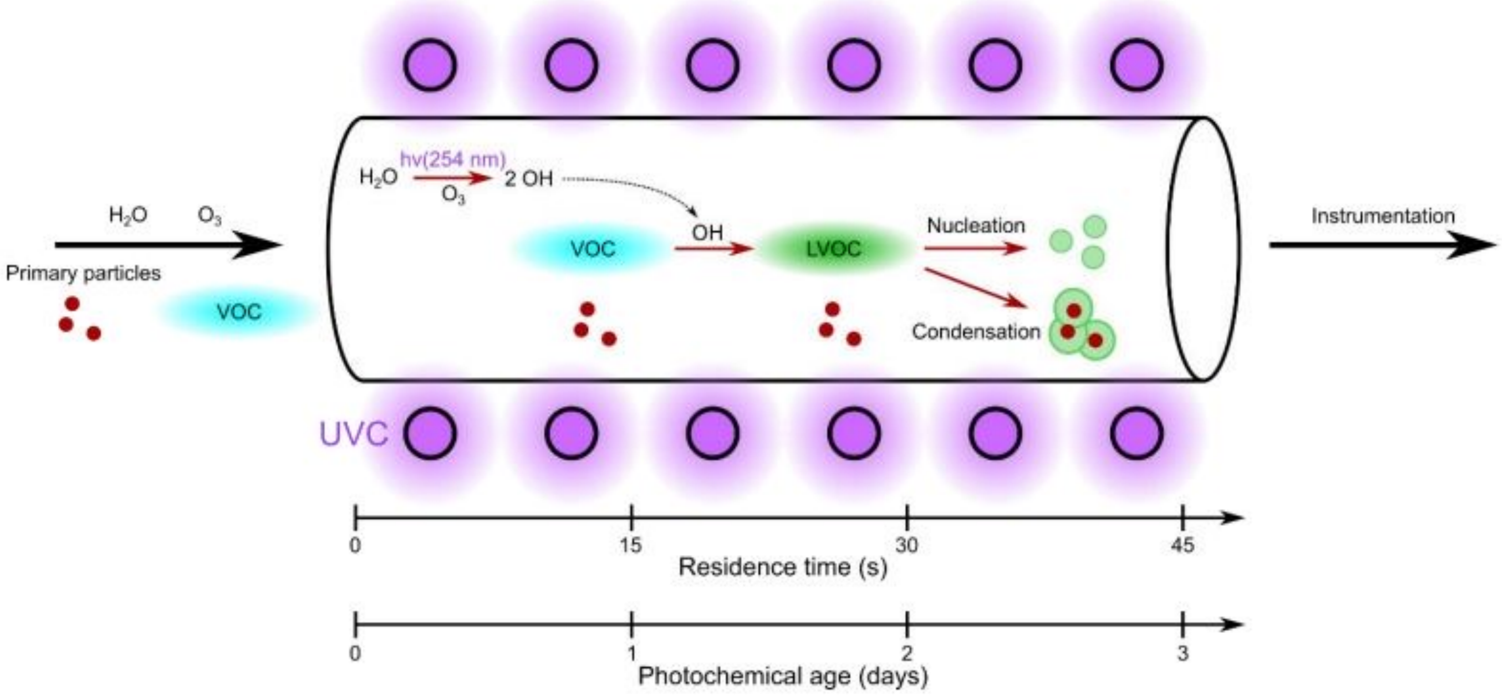


EXPERIMENTAL SETUP



7) Dekati Oxidation Flow Reactor (DOFR™). Photolysis of O_3 is promoted through a 254nm UV radiation generating OH radicals.

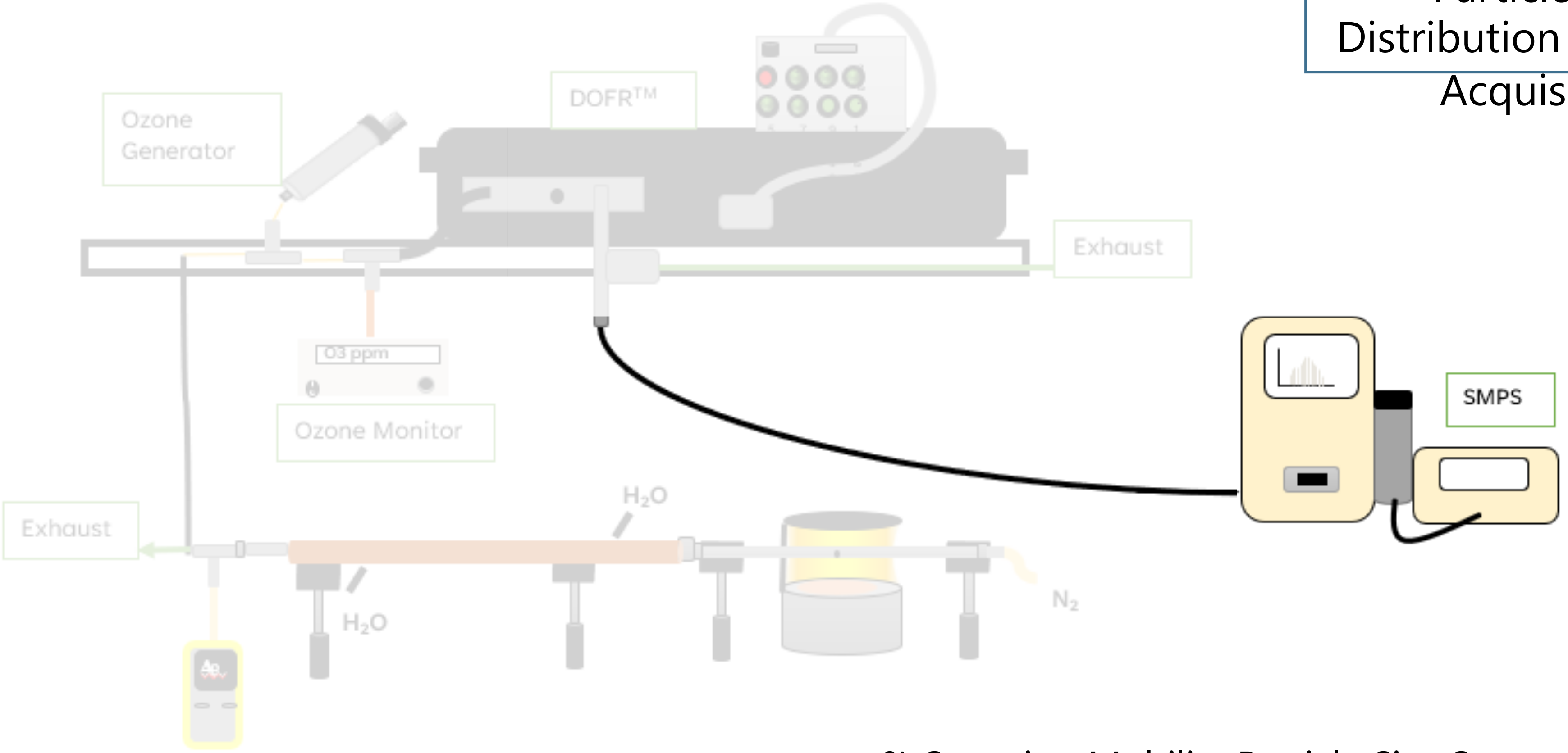




Reference: Dekati Oxidation Flow Reactor Datasheet

EXPERIMENTAL SETUP

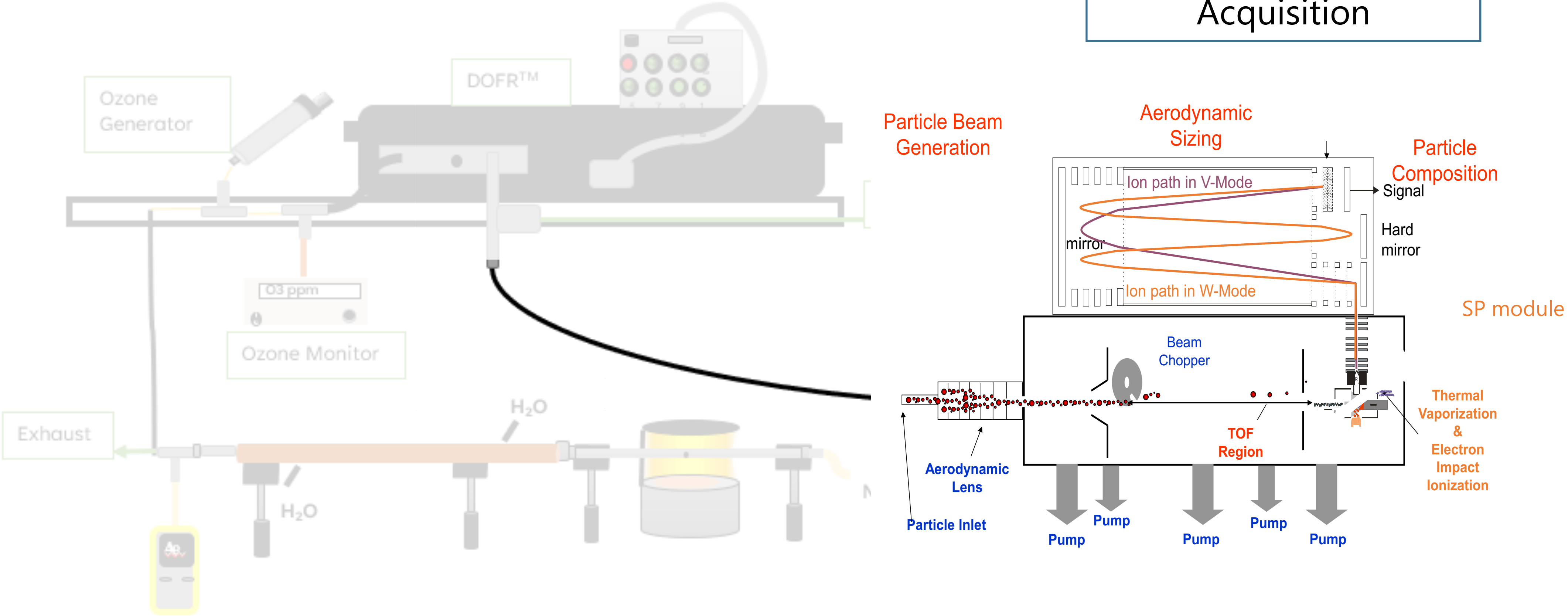
Particle Size Distribution Functions Acquisition



8) Scanning Mobility Particle Size System Consists in:
- Differential Mobility Analyzer (DMA)- Model 3085 TSI;
- Condensation Particles Counter (CPC)- Model 3776 TSI.

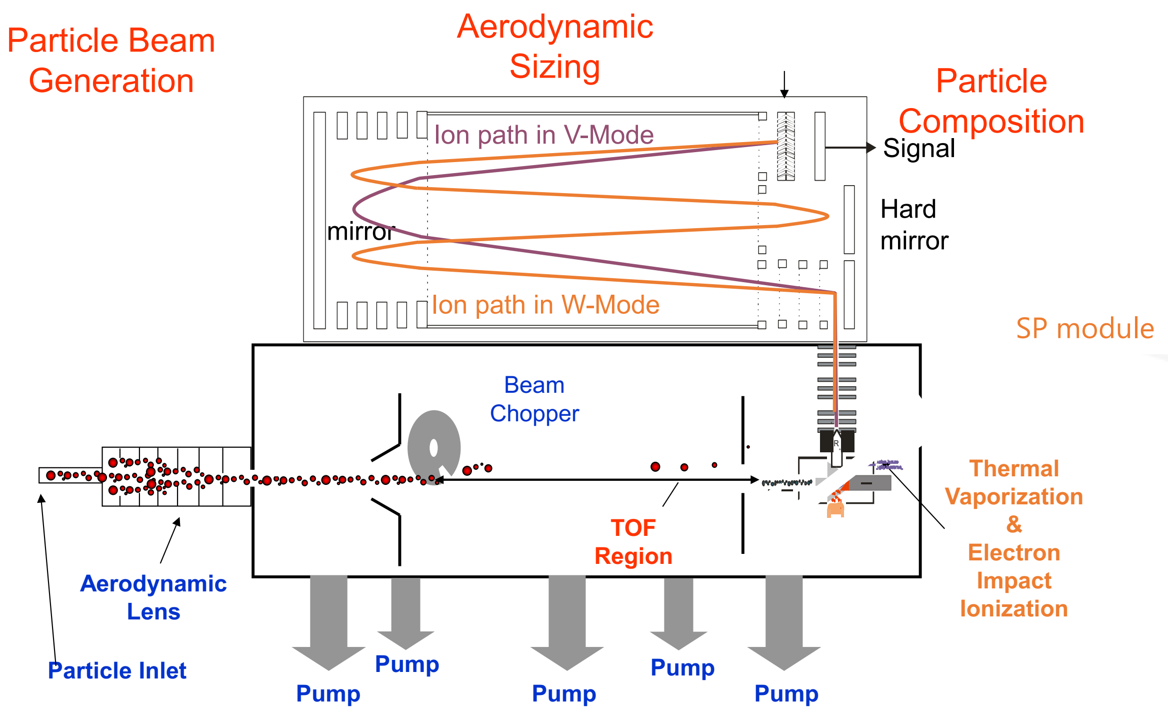
EXPERIMENTAL SETUP

Mass Spectra Acquisition

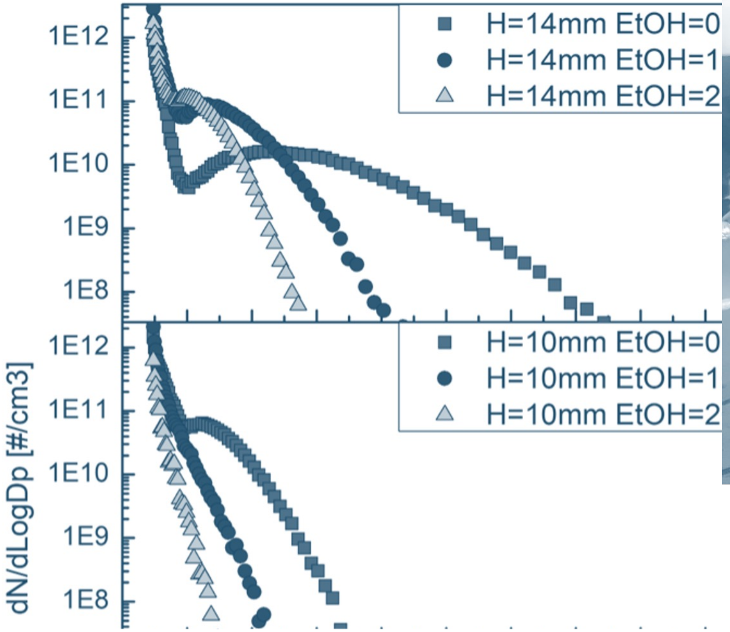


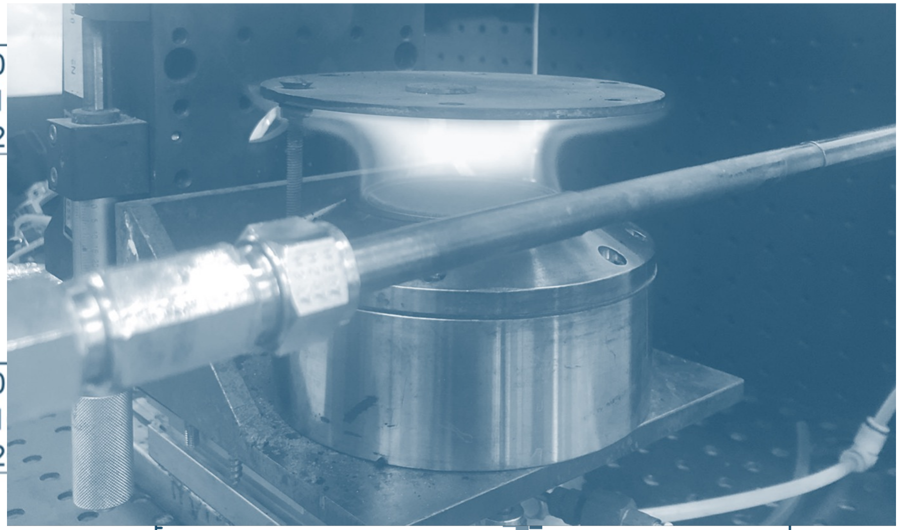
Aerodyne HR-TOF-AMS

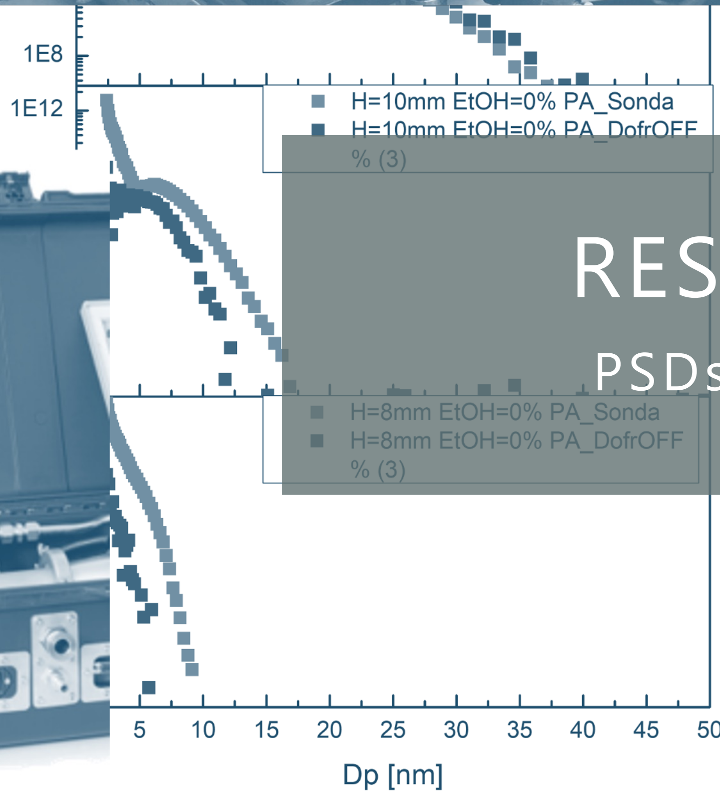
EXPERIMENTAL SETUP
Mass Spectrometry



- The Aerodyne HR-TOF-AMS performs quantitative measurements of size resolved chemistry of submicron non-refractory and BC-refractory (SP- Module) aerosol particles.
- Aerodynamic lens (PM 2.5) allow measurements in a range of (70-3500 nm).
- Ionization by electron impact (70 eV).





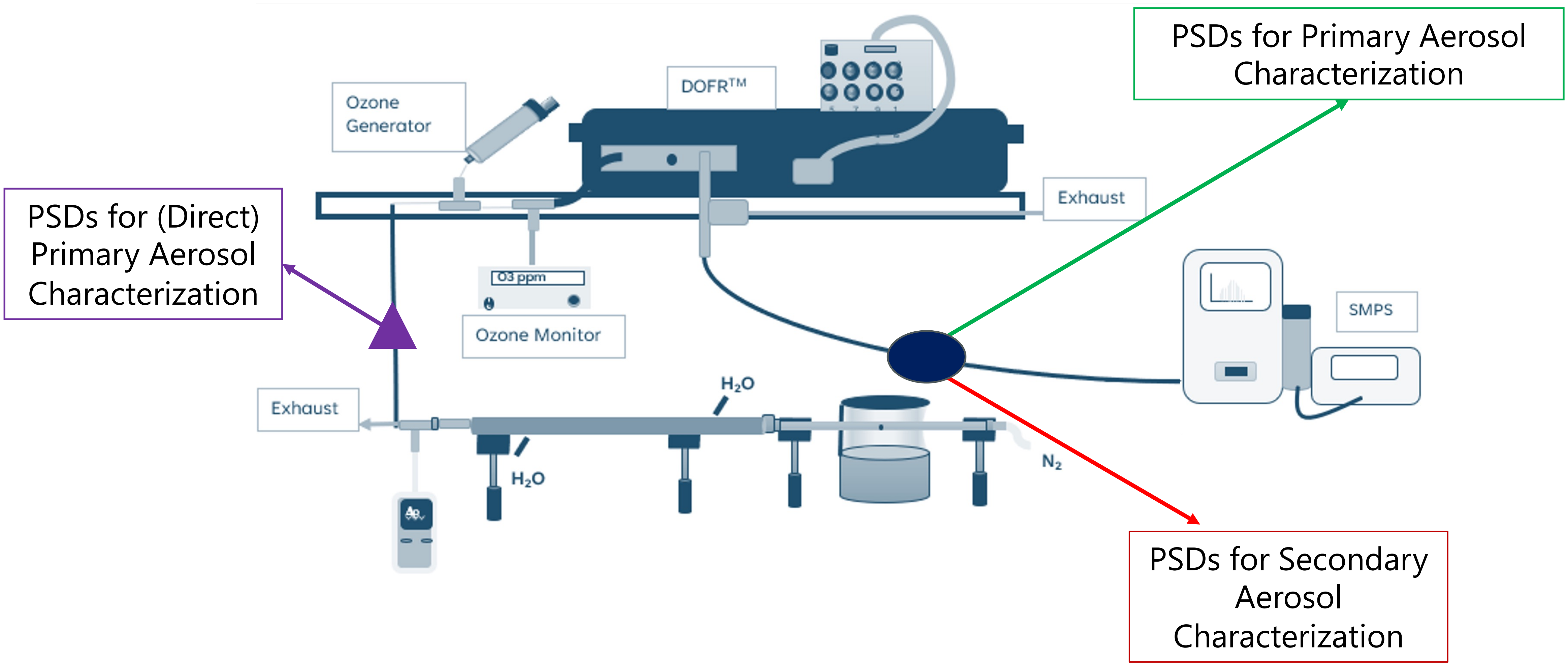


RESULTS DISCUSSION

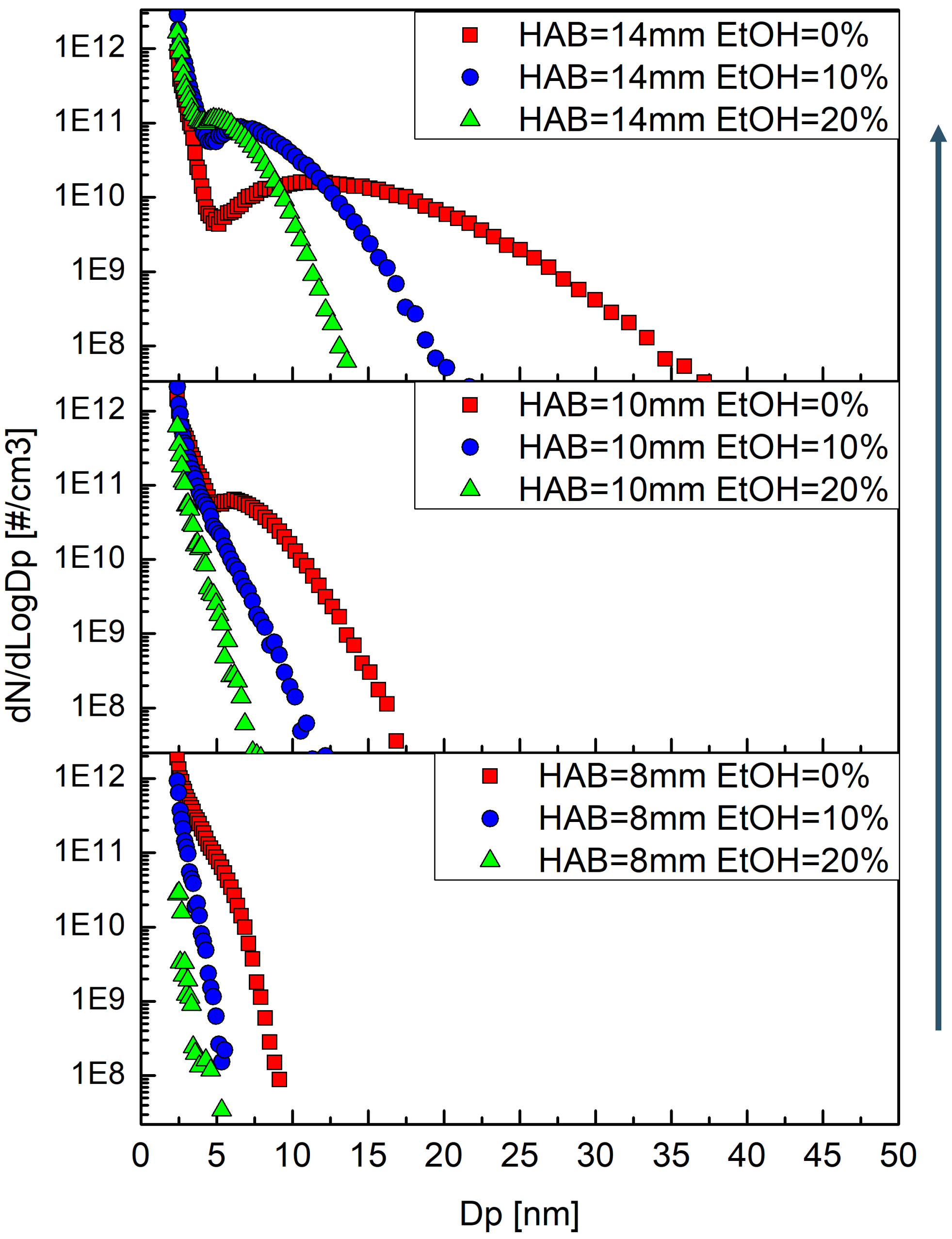
PSDs and Mass Spectra Analysis

EXPERIMENTAL SETUP

Two Collecting Points for the PSDs functions were used:

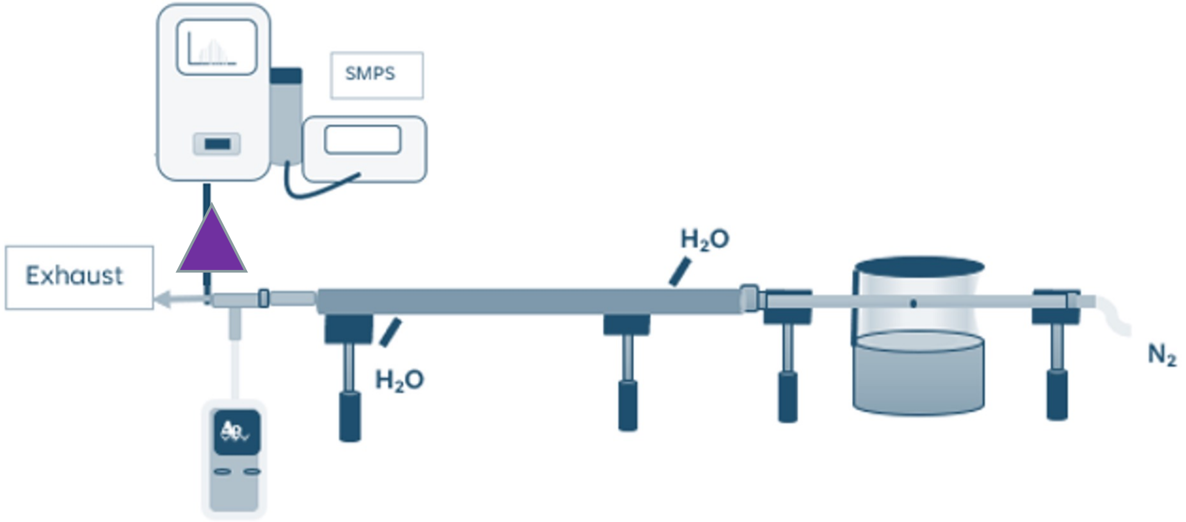


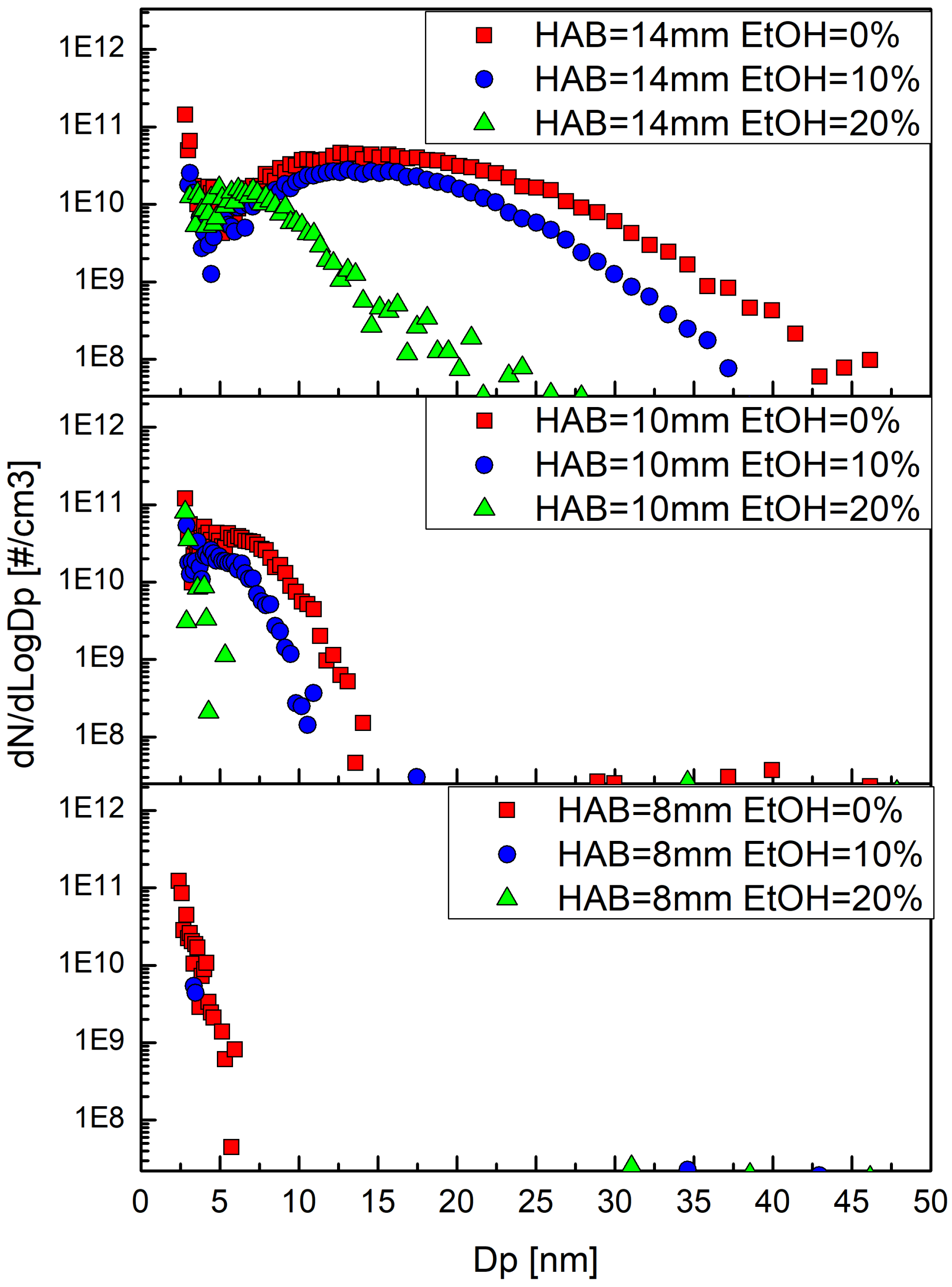
PRIMARY AEROSOL



By Increasing the height, the signals of the PSDs become more intense and the **bimodality** is more marked.

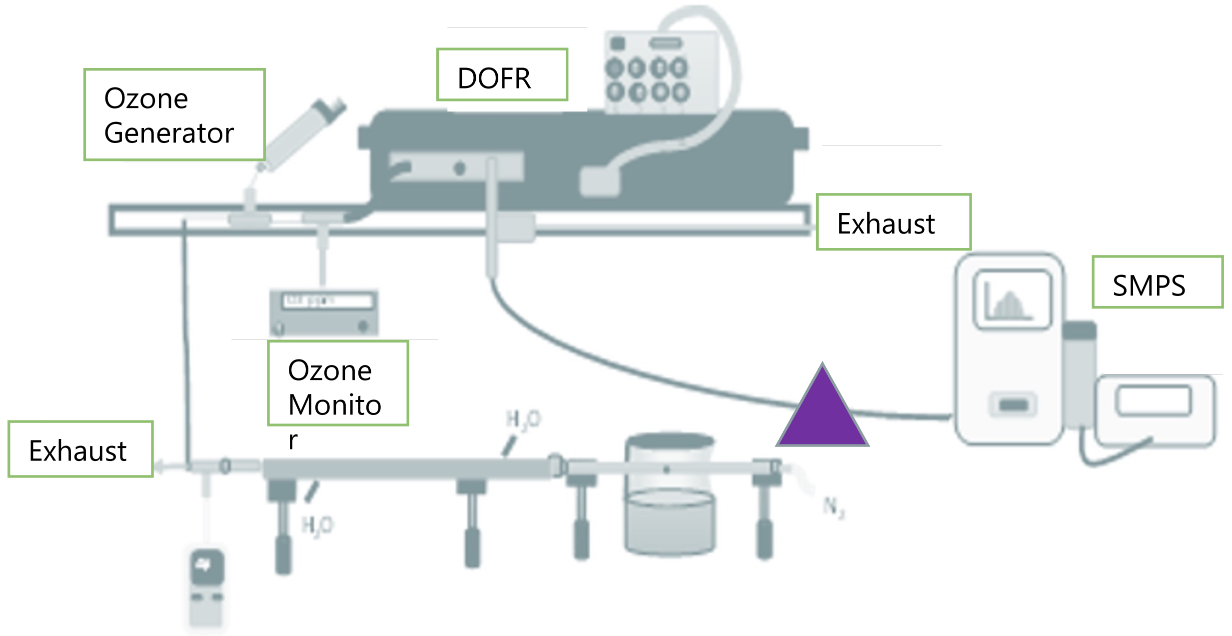
Ethanol addition seems delaying the particle formation and at the same HAB, the EtOH addition moves the PSDs function to lower Particle Diameter (Dp)



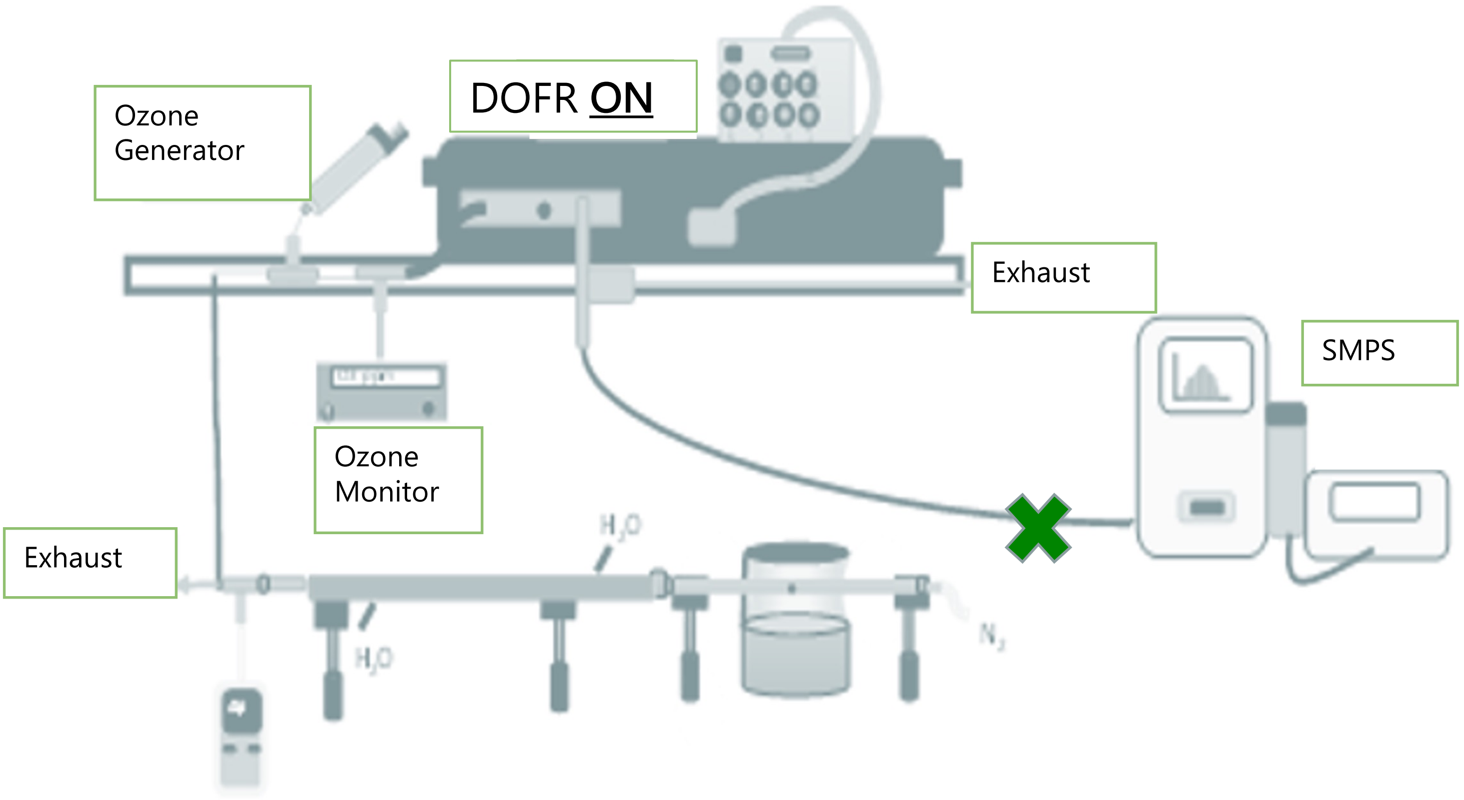


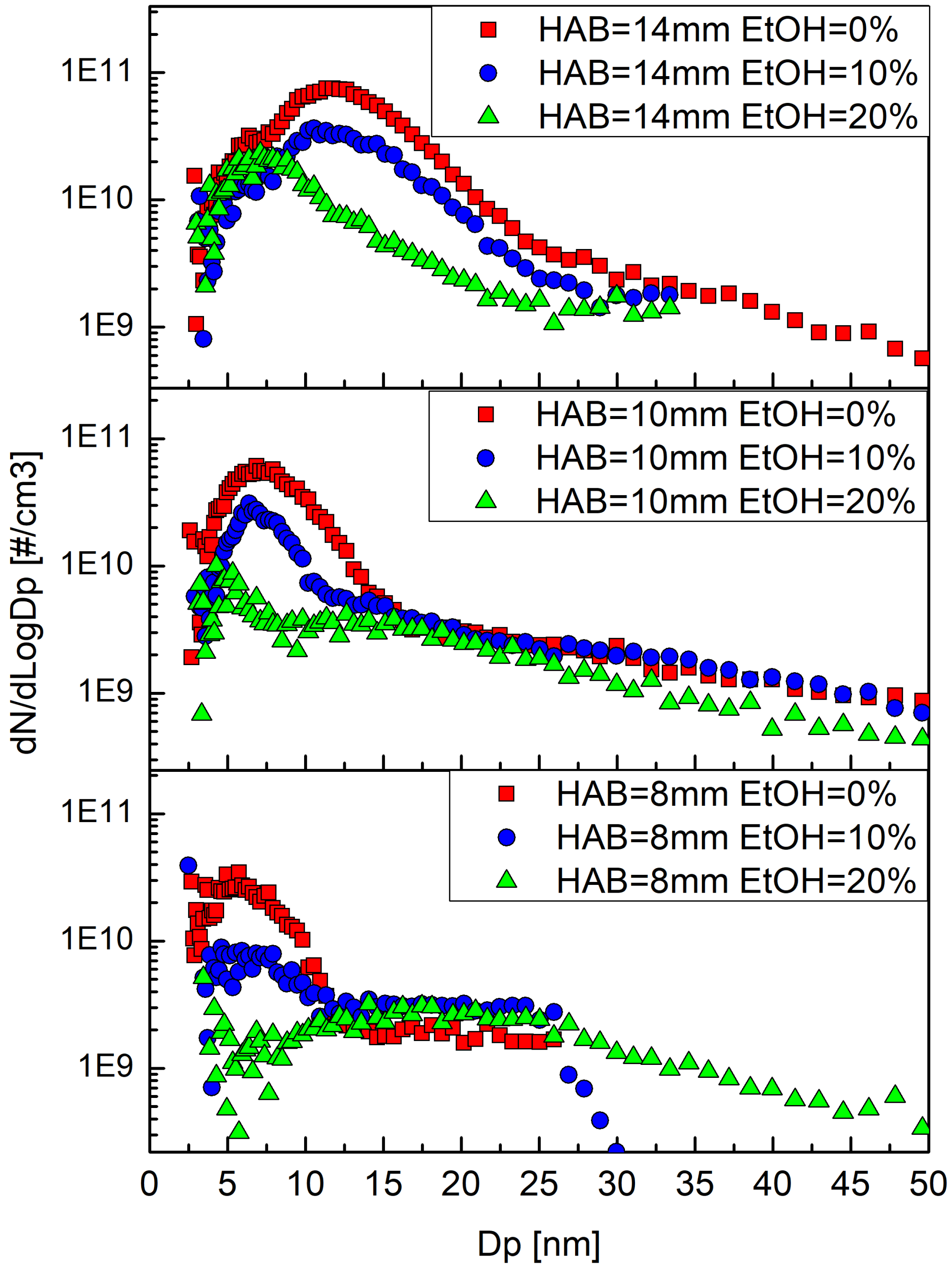
PRIMARY AEROSOL

Also , ethanol addition affects particle formation processes.



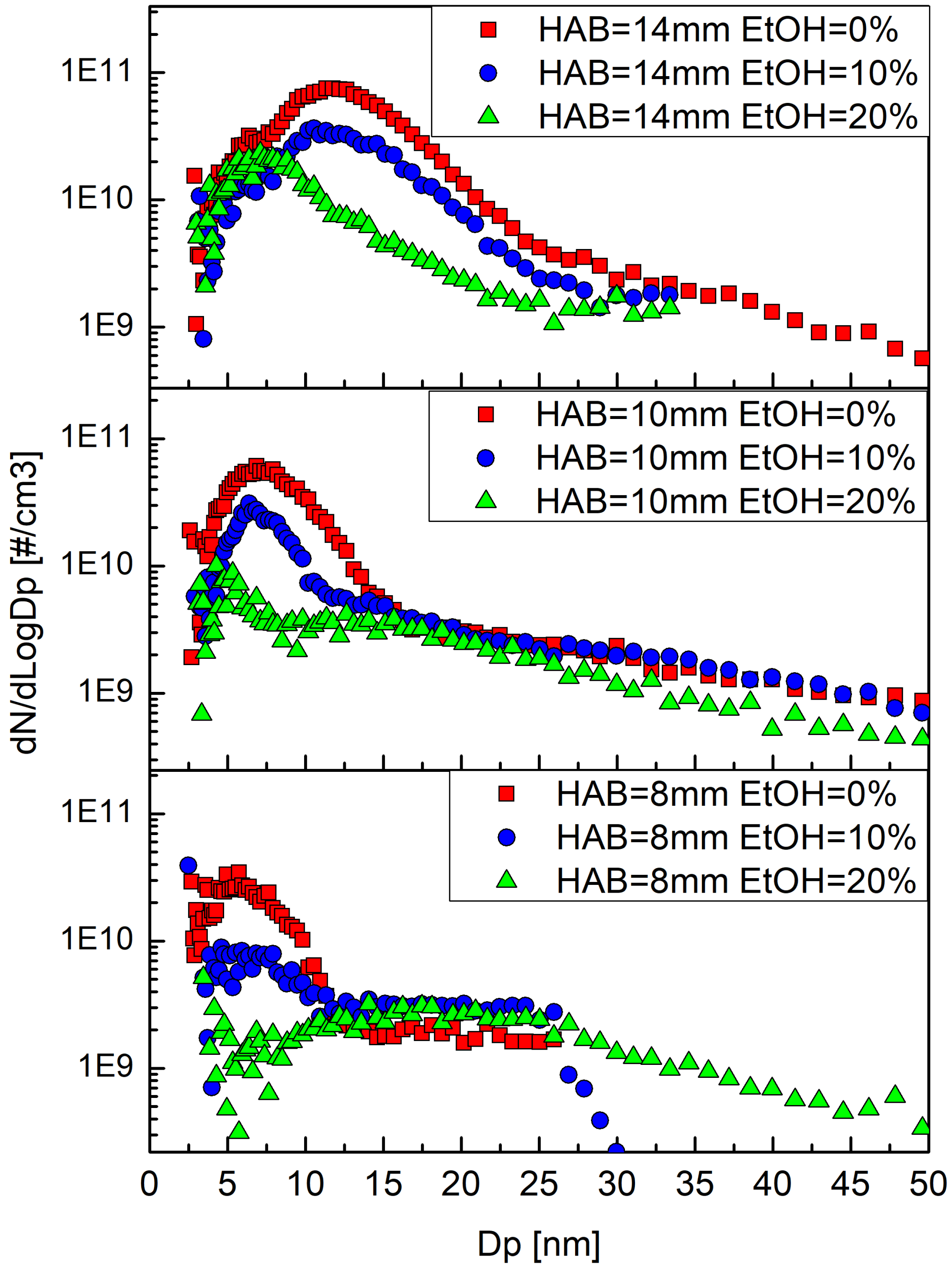
SECONDARY AEROSOL





SECONDARY AEROSOL

Same HABs	EtOH increase, shifts the PSD peak at lower diameters
Same EtOH	Higher signals at higher HAB

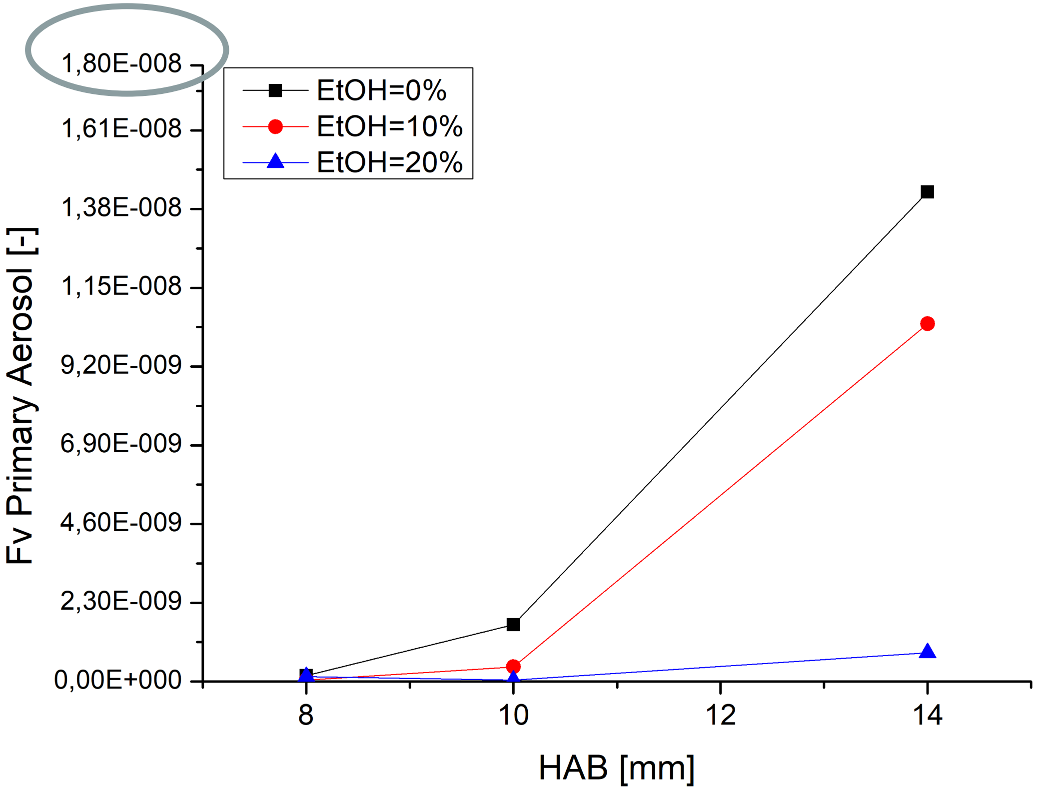


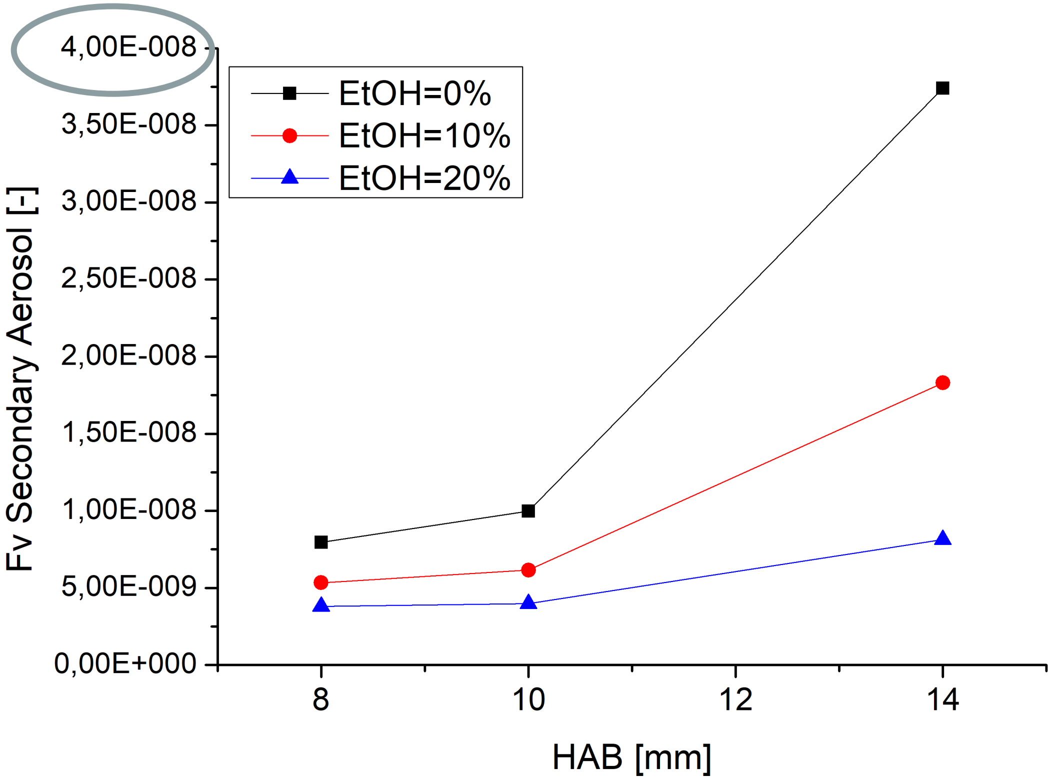
FV CALCULATION

To evaluate the soot formation processes, an ulterior variable has been considered: **Soot Volume Fraction**

$$f_v = \sum_{i=1}^{k} f_{v,i} = \sum_{i=1}^{k} v_i \cdot N_i$$

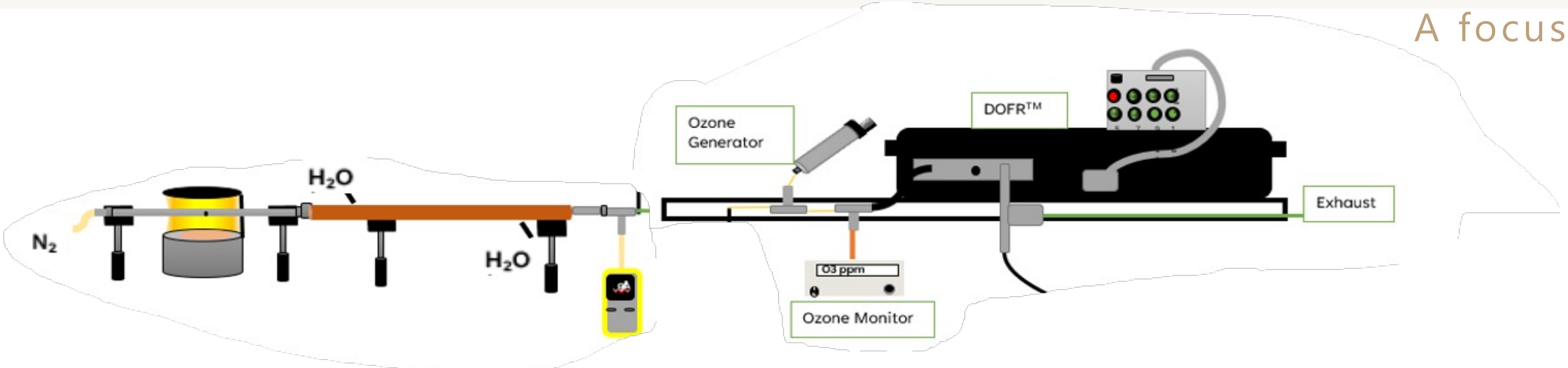
This calculation was done assuming spherical shape of particles.





SECONDARY AEROSOL

A focus



In order to isolate the effects of ethanol addition on the secondary aerosol formation an additional PSDs comparison was added.

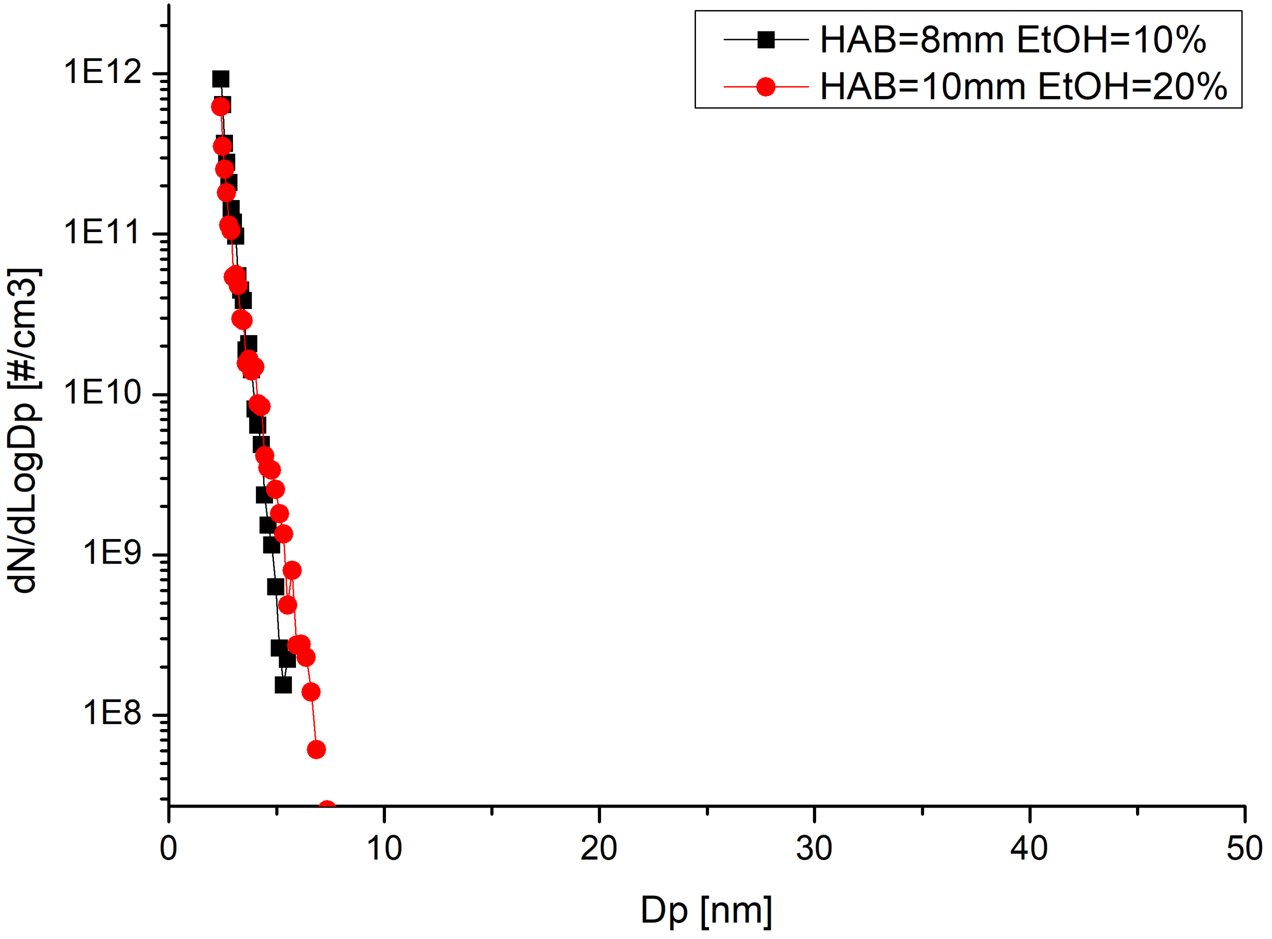
Two conditions:

- HAB=8mm with Ethanol Ratio= 10%;
- HAB= 10mm with Ethanol Ratio=20%;

Have the same PSD function relatively to the Primary Aerosol.

Hence a comparison between the Fv of these two functions was performed in order to focus on the differences in secondary aerosol formation at different EtOH ratios.

SECONDARY AEROSOL

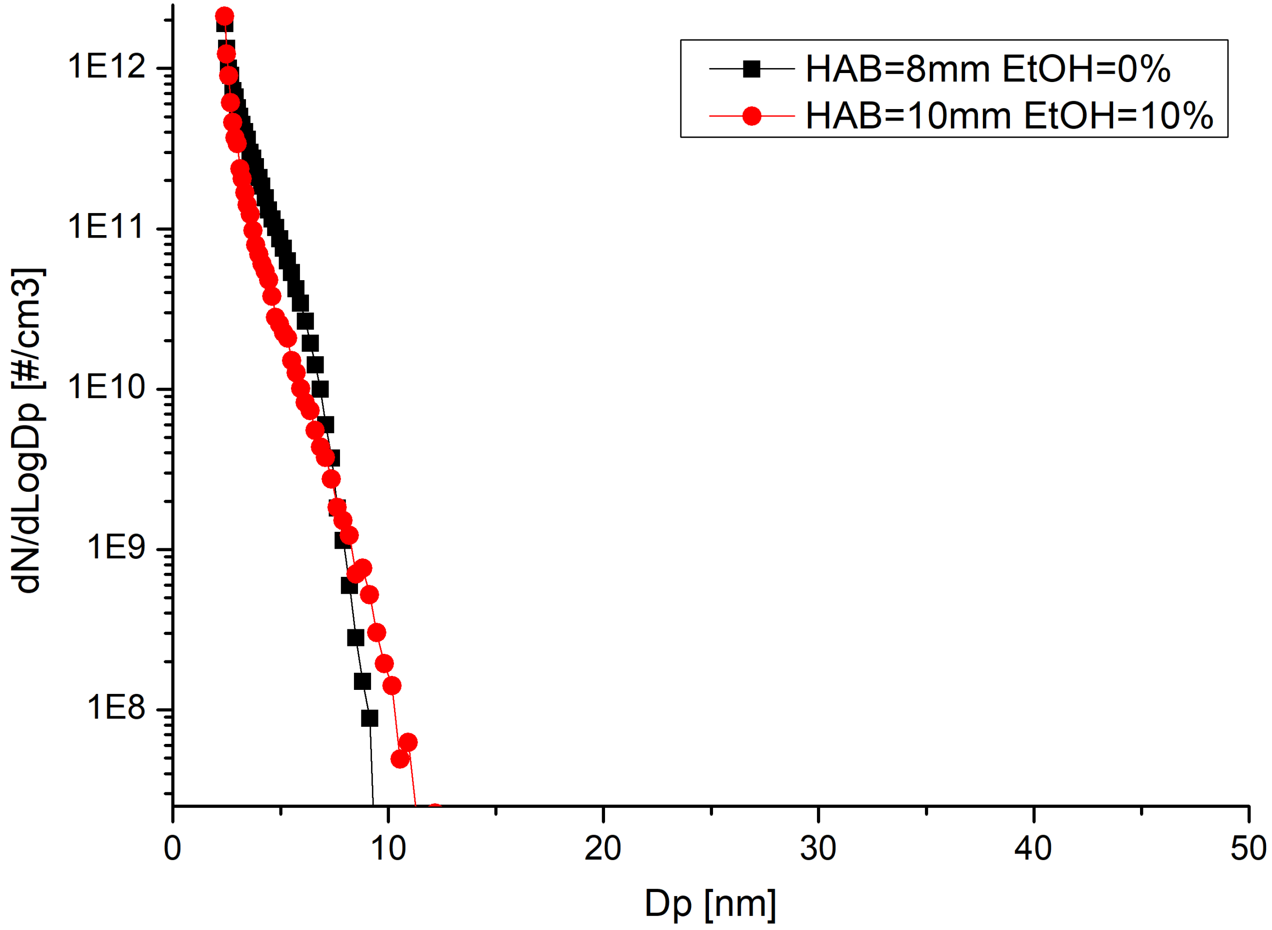


Secondary Aerosol Fv	H=8mm	H=10mm	H=14mm
0%	7.95E-09	9.99E-09	3.74E-08
10%	5.34E-09	6.15E-09	1.83E-08
20%	3.80E-09	3.99E-09	8.13E-09

Also in this case, the Fv of Secondary Aerosol is reduced.
The reduction is equal to **-25,28%**

The same Variation on the Fv of the Primary Aerosol gives **-29,7%**

SECONDARY AEROSOL



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20%	3.80E-09	3.99E-09	8.13E-09

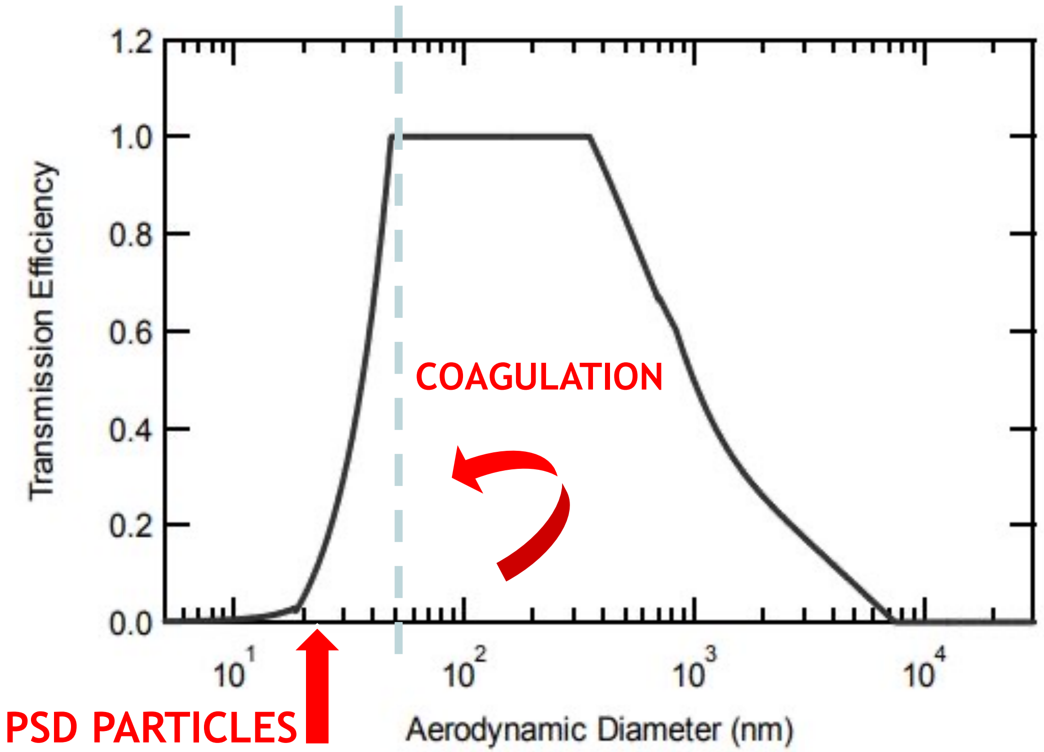
Also in this case, the Fv of Secondary Aerosol is reduced.
The reduction is equal to **-22,64%**

The same Variation on the Fv of the Primary Aerosol gives **-47.77%**

MASS SPECTRA

For the mass spectra collecting the probe used had an **orifice of 0.6 mm**.

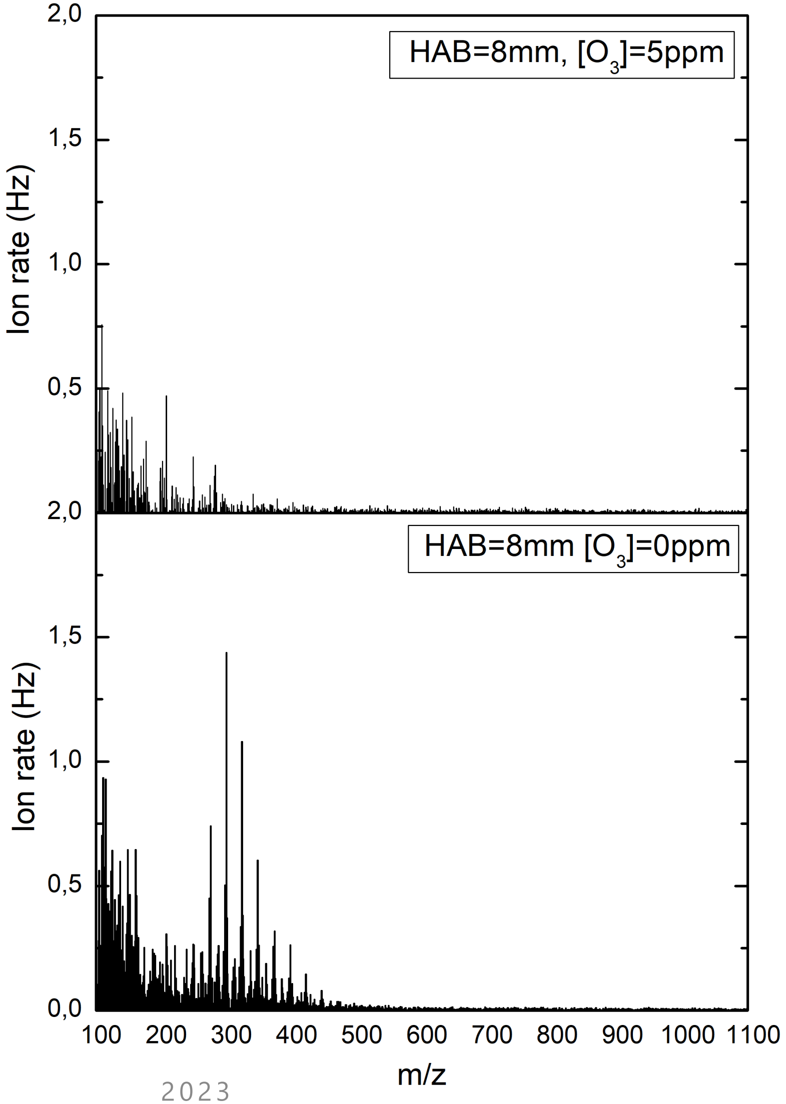
The reason was driven by the will of sampling flame **particles which were already coagulated** according to the lens transmission efficiency.

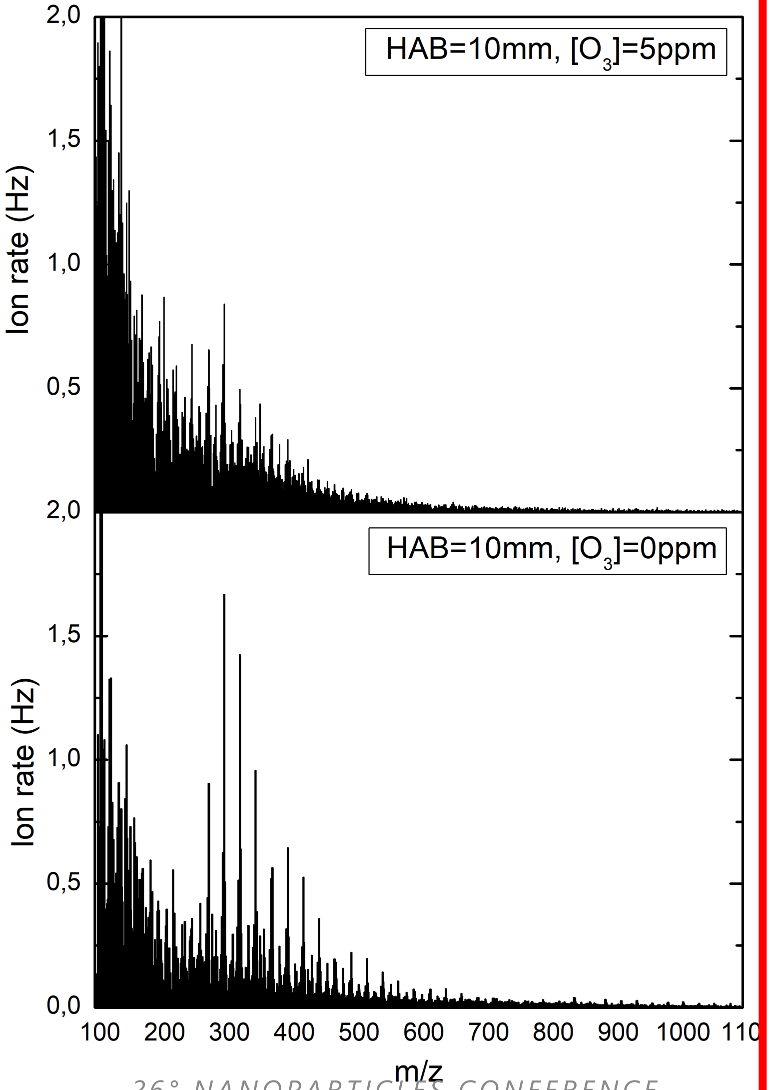


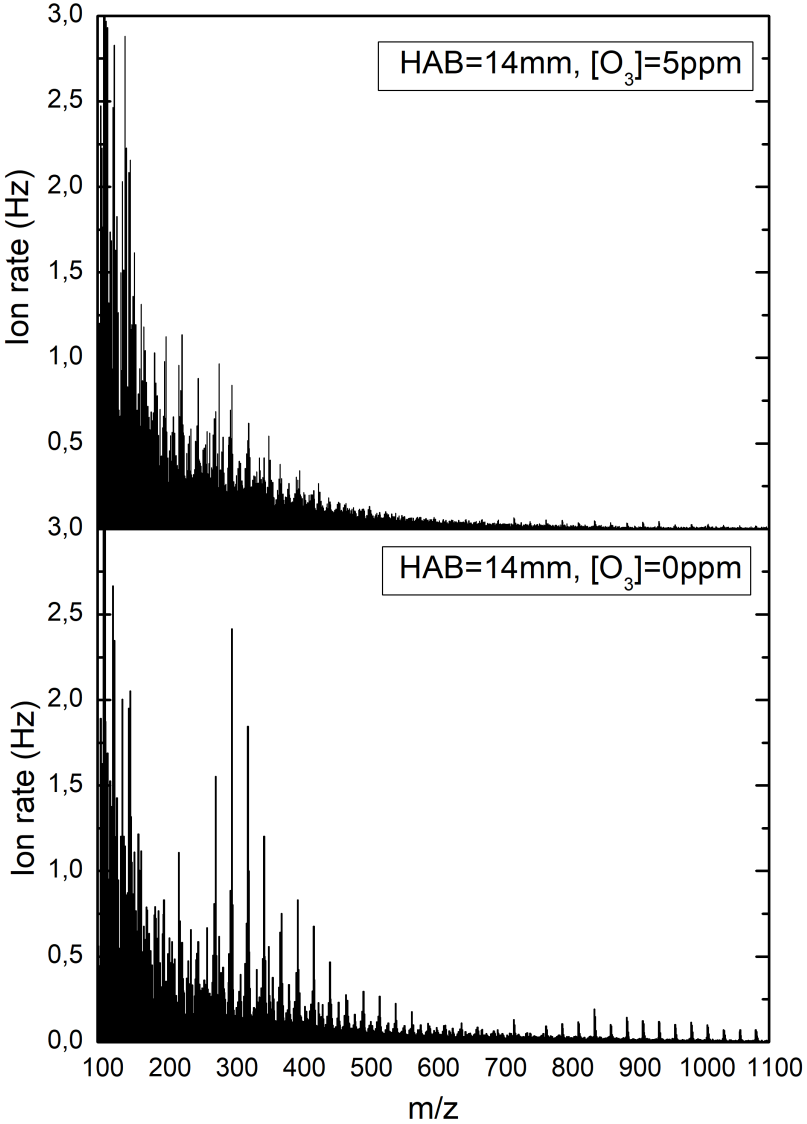
TRANSMISSION EFFICIENCY LIMIT

50 nm

MASS SPECTRA
A FOCUS ON UN-DOPED FLAME

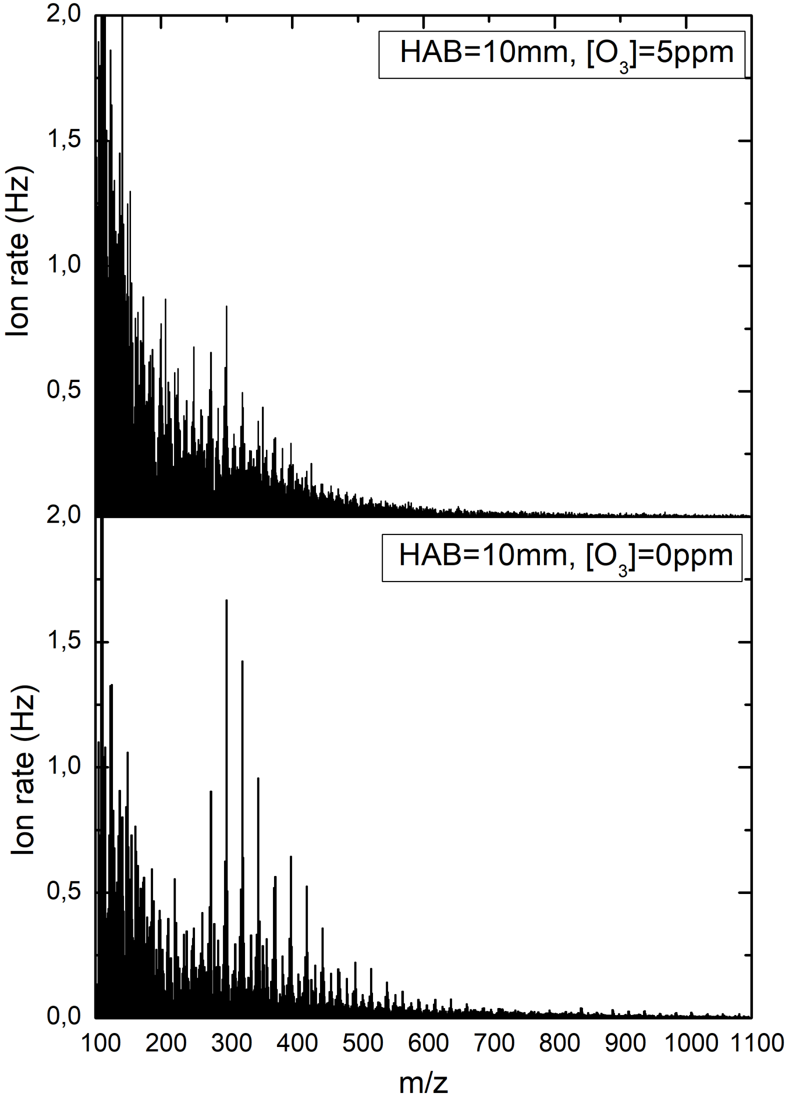


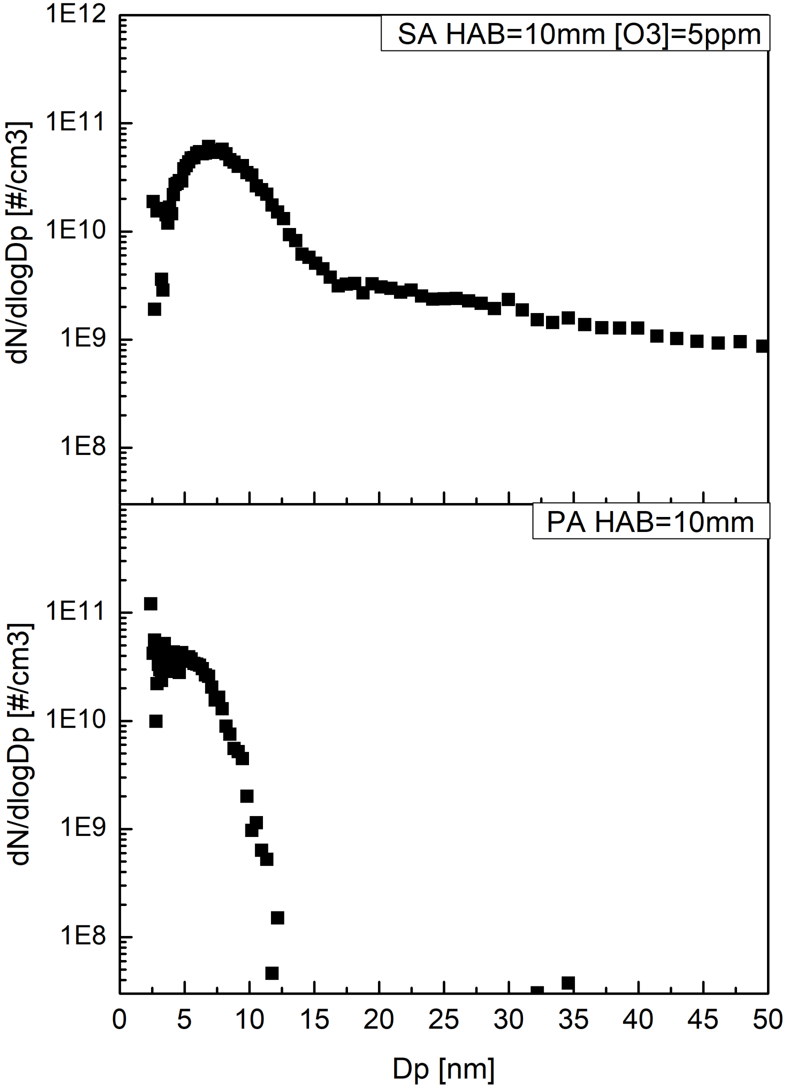




MASS SPECTRA

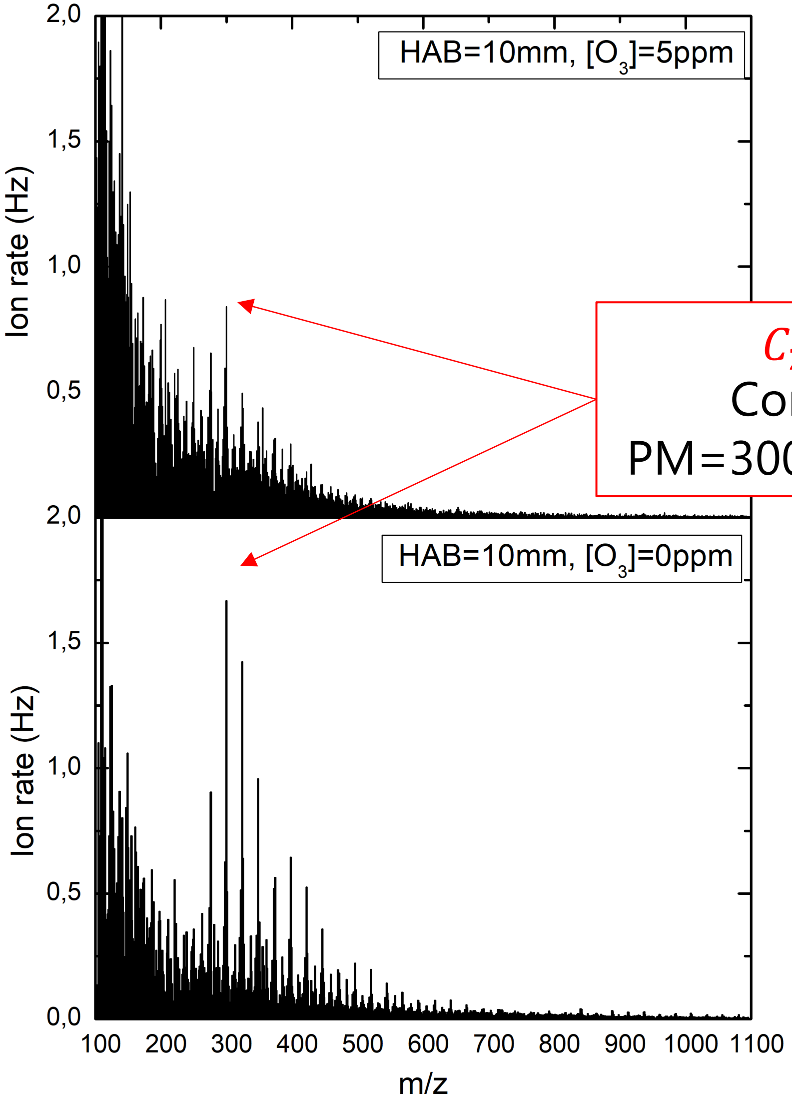
A FOCUS ON UN-DOPED FLAME

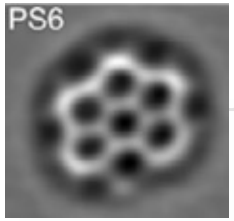


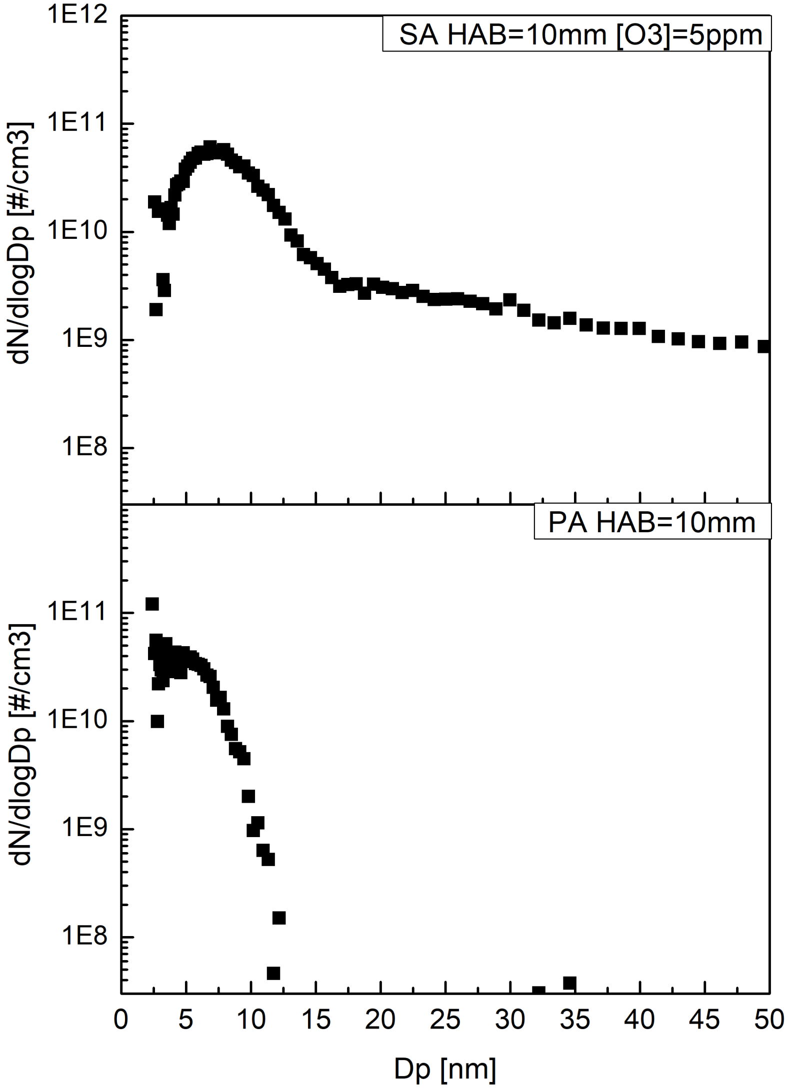


MASS SPECTRA
A FOCUS ON UN-DOPED FLAME

Reference: *Portraits of soot molecules reveal pathways to large aromatics, five-/seven-membered rings, and inception through π-radical localization,* Lieske et al., 2023







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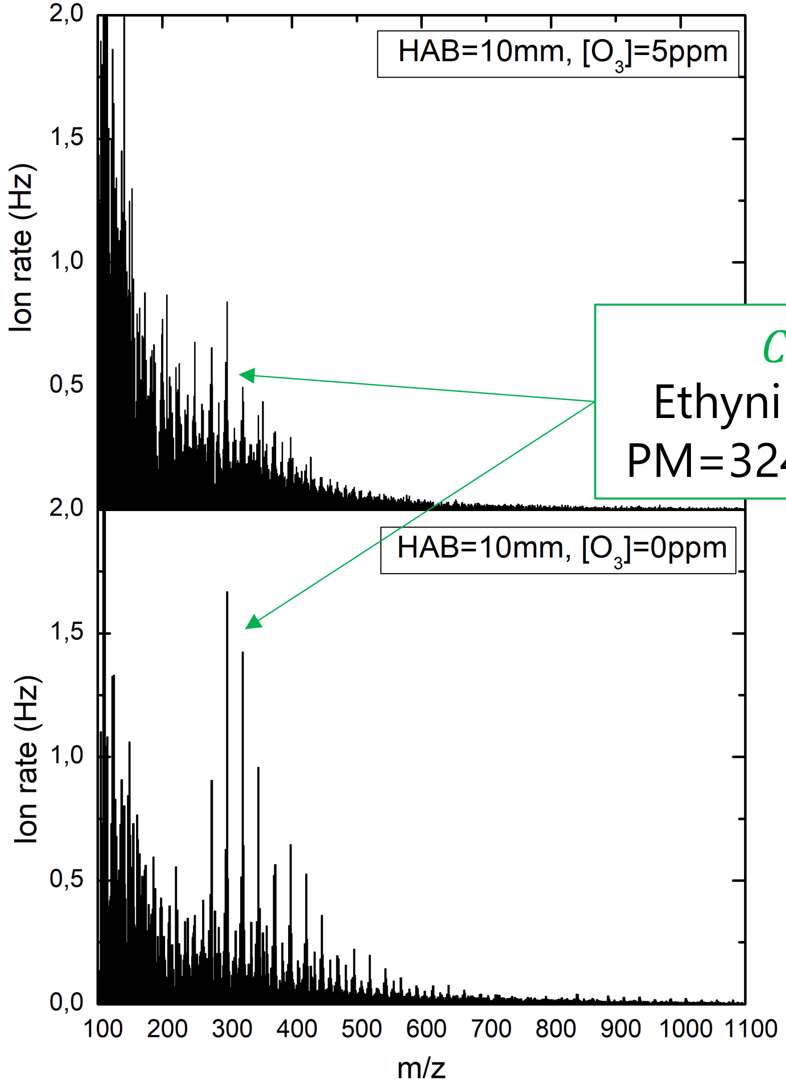
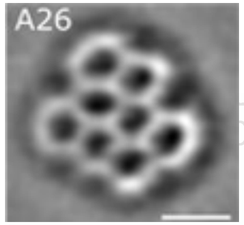
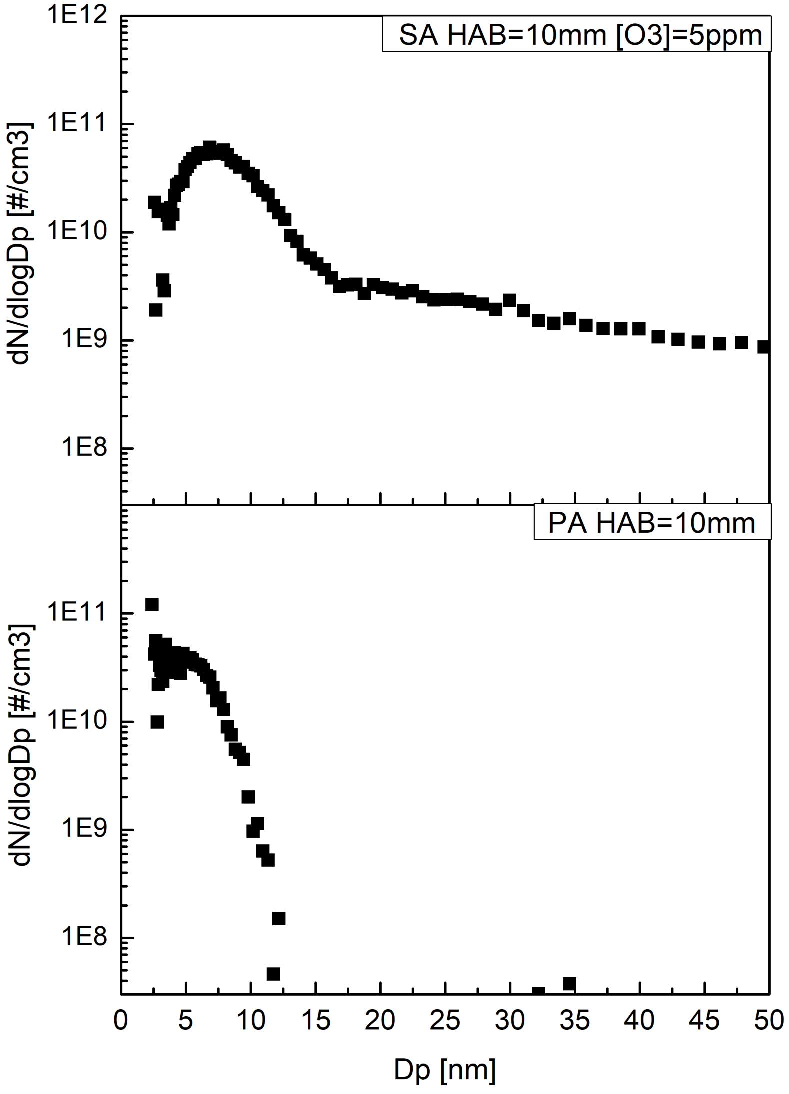


$C_{26}H_{12}$
Ethynil-coronene
PM=324.35 [g/mol]





CONCLUSIONS

PRIMARY AEROSOL

PA production seems to be affected by Ethanol addition

SECONDARY AEROSOL

The EtOH doping ratio affects also the SA produced after 2 aging days

ENVIRONMENTAL IMPACT

EtOH decreases the size of the produced particles

HEALTH IMPACT

The increased production of smaller particles can represent a drawback in terms of health impact

FURTHER STEPS

Additional investigations are required in order to have a complete picture of the EtOH effects in combustion

FURTHER INVESTIGATIONS

- Mass spectra of the doped-flame have to be completed;

- Additional steps need to be performed by coupling the analysis with optical filter investigations and toxicological analysis.

THANK YOU FOR THE ATTENTION

Alessia Pignatelli

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