# THÈSE DE DOCTORAT

Thèse préparée et soutenue publiquement par

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pour obtenir le grade de Docteur de l'UNIVERSITÉ DE LILLE

En ÉNERGÉTIQUE, THERMIQUE, COMBUSTION

ÉCOLE DOCTORALE

Sciences de la Matière, du Rayonnement et de l'Environnement

Laboratoires d'accueil

IFP Energies nouvelles et Laboratoire de PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A)

# Development of optical and chemical diagnostics to characterize and control particulate and gaseous emissions from combustion systems

Développement de diagnostics optiques et chimiques pour caractériser et contrôler les émissions particulaires et gazeuses des systèmes de combustion

Soutenue le 7 décembre 2022

devant la commission d'examen

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"When you are studying any matter, or considering any philosophy, ask your self only 'What are the facts, and what is the truth that the facts bear out ?' Never let yourself be diverted, either by what you wish to believe, or by what you think could have beneficial social effects, if it were believed. But look only and solely at ' what are the facts ?'"

Bertrand Russell

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# Acknowledgements

I would like to express my deepest gratitude to my supervisors Dr. Pascale DESGROUX, Dr. Philipp SCHIFFMANN, Dr. Alessandro FACCINETTO, Arnaud FROBERT, Dr. Stephane RAUX and Dr. Matthieu LECOMPTE who generously provided knowledge and expertise and without whom this endeavor would not have been possible. The greatest thanks I have to give them is to have trusted me enough to let me explore paths going beyond what was initially planned and to have offered me a freedom that I greatly appreciated. I would like to acknowledge IFP Energies nouvelles for the full funding of this work. I am also extremely grateful for all jury members Prof. Jérôme YON, Dr. Barbara D'ANNA, Dr. Georgios KELESIDIS, Dr. Cornelia IRIMIEA and Prof. Cristian FOCSA who reviewed and examined this thesis.

I would like to express my sincere thanks to Richard TILAGONE, Dr. Christian ANGEL-BERGER, Dr. Benjamin HANOUNE, Prof. Frédéric PAROL, Prof. Jean-Paul CORNARD, Dr. Julian KASHDAN, Dr. Antonio PIRES DA CRUZ, Dr. Michele BARDI, Dr. Mickael LEBLANC and Dr. Mickael MATRAT for their generous support, their fruitful directives, and their constructive encouragement throughout the course of this thesis. Thanks should also go to Jérôme CHEREL, Vincent RICORDEAU, Clement BRAMOULLE, Emmanuel METGE, Mélanie LOOS, Bruno BOURRY and Laurent DAYDE for logistic assistance and the help in building experimental setups. I am also thankful to Michele KUWARTH, Mulero CHANTAL, Hélène ROUMILHAC and Charline BARAT for their administrative assistance throughout the past three years. I also would like to thank Dr. Guillaume LEFEVRE, Dr. Ahmed SHAIK PERVEZ and Dr. Lucia GIARRACCA-MEHL for the constructive discussions I had the pleasure to have with them and for their thoughtful directives. Special thanks to Dr. Eric KOHLER, Dr. Virgile ROU-CHON, Hedwige PONCET and Dr. Maxime MOREAUD for the help with electron microscopy imaging and processing, Dr. Perrine COLOGON and Pascal HAYRAULT for the help with gas chromatography analysis and Nicolas NUNS for the help with time-of-flight secondary ion mass spectrometry. I am extremely grateful for their invaluable patience and feed back. I would like to thank Prof. Christine ROUSSELLE, Prof. Andreas KEMPT and Prof. Luc VERVISCH for their guidance as part of the mid-term evaluation process. I also would like to address my thanks to Dr. Andreas EHINGER and Anne DANRE for all the support and work as part of the doctoral seminars and training provided by IFP School's Doctoral College.

I would like to extend my sincere thanks to IFPEN'S R104 and R107 PhD candidates/graduates Dr. Claudia CANTARELLI, Dr. Erwan RONDEAUX, Daniel CARLOS DA SILVA, Ivano CORNACCHIA, Dr. Andreas KOPT, Kamal SHWAY SHWAY, Dr. Abhijit PADHIARY, Adrian VENEGAS REYNOSO, Jeremy CREUX, Antoine SABRIE, Pakedam LARE, Hadj Ahmed BELG-HAZALI and Adan REYES REYES with whom I shared unforgettable and joyful three years. To my family, words can not express how much I am grateful for your support all along the way. Without you I could not have undertaken this journey. This page is left intentionally blank

This thesis is dedicated to my father May his memory forever be a comfort and a blessing This page is left intentionally blank

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## Abstract

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# Chapter 1

# Introduction

### 1.1 Background

Air pollution caused by particulate matter (PM) emissions [1], raise significant health and environmental concerns. Much of the interest around PM emissions control stems from the adverse effects they can have on human health due to their hazardous composition and small size, hence the use of indicators such as  $PM_{10}$  and  $PM_{2.5}$  for air quality monitoring. These two quantities refer to PM whose aerodynamic diameter is less than or equal to 10 and 2.5 µm, respectively. The inhalation of  $PM_{2.5}$  particles or ultrafine particles (whose diameter is less than 100 nm) can cause serious respiratory and cardiovascular disorders [2, 3]. These PM emissions are also dangerous as they may contain certain organic compounds such as polycyclic aromatic hydrocarbons (PAHs), that are known to be carcinogenic [4–6]. The presence of PM in ambient air has also important drawbacks on environment and on climate as they are considered to be the second most important emissions after  $CO_2$  [7], thus impacting the atmosphere radiative exchange in various ways [8–11].



Figure 1.1. Sectors contributing to NO<sub>2</sub> (in green) and PM<sub>10</sub> (in blue) emissions (percentage in mass) reported by the EU 28 member states, adapted from the  $2018^{\text{th}}$  European Environment Agency (EEA) report [12].

Many human activities have been associated to such emissions. In Europe, the main sector contributing to PM emissions is transport [12]. In 2018, road transport accounted for  $\sim 75$  % of the total inland freight transport in Europe [13], and passenger cars were by far the most predominant mode ( $\sim 83$  % share in passenger-kilometers of inland passenger transport in the European Union (EU) in 2017) for passenger transport in all EU member states [13]. PM emissions also come from power generation plants that use combustion processes based on heavy fuel, coal or biomass. Some PM emissions are released in the ambient air after the

occurrence of domestic/forest fires or come from waste incineration processes for instance. The wear of certain mechanical components such as brakes, landing gears and tires also contribute to PM emissions [14, 15], eventhough they may be different from the combustion-generated ones. Regardless of the emitting source of these PM, they all share the harmful effects on human health, on environment and on climate, hence the need for them to be monitored.

Figure 1.1 shows the sectors contributing to  $PM_{10}$  reported by the EU 28 member states [12] and shows that transport and commercial residential combustion are the main contributors to this kind of emissions. The 2018<sup>th</sup> European Environment Agency (EEA) report concludes that, in general, the road transport sector is the largest contributor to total nitrogen dioxide (NO<sub>2</sub>) emissions in the EU, while fuel combustion in the commercial, institutional and households sector is the largest contributor to overall primary (i.e., those released directly into the atmosphere) PM emissions, particularly in some eastern European countries [12]. In this regard, in 2005 the World Health Organization (WHO) recommended a PM<sub>10</sub> annual exposure threshold of 20 µg/m<sup>3</sup>, and in 2008 the EU recommended to set that threshold at 40 µg/m<sup>3</sup>. Annual exposure limits were also set to 25 µg/m<sup>3</sup> (EU) and 10 µg/m<sup>3</sup> (WHO) for PM<sub>2.5</sub> and to 40 µg/m<sup>3</sup> (EU and WHO) for NO<sub>2</sub>. However, until 2016, in large parts of Europe, the concentration limits in terms of PM (set either by the EU or by the WHO) continued to be exceeded in terms of PM<sub>10</sub>, PM<sub>2.5</sub> (see Figure 1.2) and NO<sub>2</sub> (see Figure 1.3) [12].



**Notes:** Observed concentrations of PM<sub>25</sub> in 2016. The possibility of subtracting contributions to the measured concentrations from natural sources and winter road sanding/salting has not been considered. Dots in the last two colour categories indicate stations reporting concentrations above the EU annual limit value (25 µg/m<sup>3</sup>). Dots in the first colour category indicate stations reporting values below the WHO AQG for PM<sub>25</sub> (10 µg/m<sup>3</sup>). Only stations with more than 75 % of valid data have been included in the map. The French overseas territories' stations are not shown in the map but can be found at https://www.eea.europa.eu/data-and-maps/dashboards/air-quality-statistics

Source: EEA, 2018a.

Figure 1.2. 2016 annual data on the geographic distribution of particulate emissions concentrations  $PM_{2.5}$  in Europe, adapted from [12].

In France, according to a recent report of the French Agency for Environment and Energy Management [16], road traffic is responsible for 30 % of  $PM_{2.5}$  emissions in Ile-de-France region and 58 % of  $PM_{2.5}$  emissions in Paris only. This may lead to an overall deterioration of air quality, the repercussion of which can be quite serious to the point that the 2021 WHO air quality guidelines [17] suggest on recent evidence that adverse effects on human health occur at annual exposure levels of half of  $PM_{2.5}$  and quarter for NO<sub>2</sub> compared to the previously recommended values back in 2005. This new insight and the ever more urgent climate crisis show the importance of minimizing the emissions of gaseous pollutants and PM worldwide.



Notes: Observed concentrations of NO<sub>2</sub> in 2016. Dots in the last two colour categories correspond to values above the EU annual limit value and the WHO AQG (40 μg/m<sup>3</sup>). Only stations with more than 75 % of valid data have been included in the map. The French overseas territories' stations are not shown in the map but can be found at https://www.eea.europa.eu/data-and-maps/dashboards/air-quality-statistics
 Source: EEA. 2018a.

Figure 1.3. 2016 annual data on the geographic distribution of  $NO_2$  emissions in Europe, adapted from [12].

In what follows, focus is brought upon PM and gaseous pollutants emissions originating from combustion-based processes and particularly light-duty vehicles (LDV), addressing some of their reglementary aspects as well as some technical solutions that aim to reduce these emissions.

#### PM and gaseous pollutants originating from engine combustion

PM resulting from engine combustion, containing mostly soot particles, can have different sizes, morphologies, chemical compositions and radiative properties depending on the conditions under which they were formed: fuel type, combustion temperature, pressure, equivalence ratio and so on. Once emitted into the atmosphere, these primary PM can also undergo various interactions such as oxidation, adsorption or condensation of other chemical species which can form a coating around the particles and eventually alter their radiative properties [7, 18]. Until about 20 years ago, diesel engines produced much more soot particles (10 to 100 times more) compared to spark ignition engines [19]. Figure 1.4 shows the typical size 4

distribution of such emissions where the largest mass concentrations are observed for soot with diameters between 100 and 300 nm (accumulation mode), while in the range 5 nm to 50 nm, with less than 20 % mass concentration, the number concentration reaches more than 90 % (nuclei mode).



Figure 1.4. Typical size distribution of diesel engine soot both in mass and number (standardized concentrations), from Kittelson [19].

To limit PM emissions impact on health and environment, internal combustion engine transportation vehicles have been subject to various regulations worldwide (US, EU, China, etc.) for a number of years [20]. This led to the use of exhaust after treatment systems to comply with these regulations that became more restrictive over the years. For instance, EU regulations have evolved within two decades from Euro 3 (2000) [21] to the current Euro 6d-temp (2020) [22] and reduced reglementary emission thresholds from 500 mg/km to 80 mg/km for nitrogen oxides (NO<sub>x</sub>) and from 50 to 4.5 mg/km for solid PM emissions for light duty vehicles. The latter is also regulated in number with a threshold set at 6.0 ×  $10^{11}$  particles/km and uses a more realistic and challenging driving cycle as an intermediary step toward real world driving emission conformity. To take into account the measurement procedures sensitivities and avoid measurement errors, the current standard excludes the smallest particles below 23 nm. An active work is being engaged to reduce this threshold down to 10 nm [23, 24].

To comply with these requirements, many technical solutions have been developed by adopting combustion strategies promoting emissions reduction [25] and using after treatment emission reduction solutions [26] combining a diesel oxidation catalyst (DOC) followed by a diesel particulate filter (DPF) for diesel vehicles for instance. The latter consists of trapping particles suspended in the exhaust, retaining them on porous walls separating adjacent channels in a monolithic substrate. On the one hand, the DOC oxidizes the carbon monoxide as well as the unburned hydrocarbons. However, it also oxidizes NO into  $NO_2$  which assists the oxidation of PM in the DPF [27-31]. Despite the use of particulate filters, it has been observed that the regulatory thresholds in terms of soot number concentration can be exceeded downstream the DPF during certain operating conditions. This is particularly the case for high load engine conditions as well as during DPF regeneration phase [32, 33]. Under such operating conditions, the particle number concentration can reach, respectively, up to 50, and between 2000 and 3000 times compared to normal operating conditions [33]. In an engine exhaust various gaseous pollutants are also present, such as  $NO_x$ , carbon monoxide (CO) and some unburned hydrocarbons (HC). These pollutants, which are harmful both for human health and for environment, are also subject to regulations. For instance, selective catalytic reduction is used for the reduction of  $NO_x$  emissions. On the other hand, the use of those after treatment components can alter the chemical composition of exhaust PM emissions as well [34].

Under current laws and regulations, despite the health hazards PM emissions may cause, worldwide liquid fuels consumption is expected to continue at a constant pace through 2050 [35]. As the world's population grows, and passenger and freight travel expand, the use of petroleum derivatives for gasoline and jet engines is expected to continue to grow fulfilling most demand for transportation energy for the next 30 years [35]. This means that fuel choice is also important to lower pollutant and greenhouse gas emission levels. One possible alternative is the use of other fuels with lower carbon emission potential. This is the case of biofuels blended with fossil gasoline, diesel or synthetic fuels produced from biomass conversion. Using such fuels can be advantageous since they are compatible with today's engine technologies. On the other hand, the use of new fuels might have an impact on combustion and as such on pollutants and soot particles emissions. The new emission factors when using such fuels need to be characterized and closely monitored. Hence the need for adapted PM sources capable of reproducing at laboratory scale combustion exhaust using those fuels.

## 1.2 Research goals

To understand the origin of PM emissions from various combustion sources, laboratory PM sources capable of burning different fuels are needed. Using an engine for such purposes is expensive, complex and does not permit to easily and independently change the emission characteristics because of the three-dimensional turbulent combustion with its inherent stochastic pollutant emission. In this regard, diffusion or premixed flames generated in laboratory environment using well documented reference burners such as the McKenna burner [36-38] or the Santoro burner [39-41] offer an easier control. These burners were, and continue to be, used to study the soot particles formation process and they can be used for the calibration of measurement systems. However, soot generators are preferred since they are much easier to use and operate, making it possible to mimic soot particles that originate from various combustion sources. During the last two decades, the so-called miniCAST soot generators (from Jing Ltd) have been widely used to generate soot aggregates [42-51] to serve as a calibration surrogate, yet they are limited by design to a single gaseous fuel (i.e., propane). A number of other commercial soot generators have been recently under investigation such as the miniature inverted soot generator (from Argonaut Scientific, Corp) [52-54] that allows the use of ethylene, propane, ethane or fuel blends with methane and nitrogen. Another interesting soot generator is the diesel miniCAST (from Jing Ltd) that uses diesel-like fuels [55, 56]. These laboratory tools seem to meet the need for evaluating PM characteristics when alternative fuels are used while offering a flexible use to challenge measurement approaches in respect to variations in PM properties and therefore helping improving measurement procedures to render more accurate result.

There have been important advances in the development of methods and instrumentation used for the characterization and control of PM and gaseous pollutant emissions. These means are usually expensive and typically designed to be stationary, hence the interest to develop more mobile, reliable and low cost measurement devices to monitor emissions ultimately under real driving emissions (RDE) tests, while meeting certain sensitivity criteria. Recently, IFP Energies nouvelles has been working on the development of an optical measurement system, based on optical absorption in the ultraviolet (UV) spectral range and used as a multi-gas analyzer [57, 58]. The device is a portable absorption cell allowing, using a miniature spectrometer, to measure light attenuation through an absorbing medium (containing in this case a gas mixture). This measurement system is to be improved to be able to perform on-board monitoring of both PM and multiple gaseous pollutant emissions during RDE testing. This goal is to be achieved within this PhD topic entitled "**Development of optical and chemical diagnostics to characterize and control particulate and gaseous emissions from combustion systems**". As such, the work carried out in this thesis aims at (i) developing a measurement procedure based on optical extinction to monitor PM and/or some of the major gaseous pollutants (NO, NO<sub>2</sub> and NH<sub>3</sub>) produced by a combustion system, and (ii) shedding light on the links that may exist between PM chemical composition and their measured optical extinction coefficient. To this end, reliable data describing PM physico-chemical properties must be acquired to then focus the efforts on providing a methodology for the analysis of optical extinction coefficient and PM chemical composition. To meet this measurement challenge and avoid the complexity of a real engine configuration, a modular combustion bench was built in which gaseous pollutants and PM can be monitored independently. This experimental setup was equipped with the version of the miniCAST soot generator that has the ability to burn liquid fuels, thus allowing to study the impact of the chemical composition of the fuel on PM physico-chemical properties.

To fulfill these objectives, first it is proposed to characterize the miniCAST over a wide range of operating conditions using two fuels (i.e., diesel B7 and dodecane) and evaluate soot particles morphology, size distribution, mass concentration, and optical extinction coefficient. The purpose of these measurements is to evaluate the soot generator ability to produce stable and repeatable PM emissions and intercompare soot volume fraction determined by three different methods that are granulometry (combining size measurement and morphology), mass, and optical which is necessary for developing a methodology for PM optical control. Second, is it proposed to study the chemical composition of the combustion products that the miniCAST generates focusing on the organic content of both the condensed gas phase and the particulate phase. This is to be carried out by combining gas chromatography (GC), to examine low mass PAHs in the gas phase, and time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis, to characterize the heavy PAHs in both the condensed gas phase and particulate phase. For ToF-SIMS diagnostic, the obtained mass spectra often contain a large quantity of data that needs to be carefully inspected in order to extract meaningful information. Consequently, it is also proposed to improve existing methodology for ToF-SIMS mass spectra post-processing. This investigation aims ultimately to identify the operating points/conditions associated with the highest/lowest presence of organic compounds to elucidate the relationship between PM chemical composition and their optical extinction coefficient. Moreover, the use of an oxidation catalyst (catalytic stripper) on the burner exhaust was used to evaluate the impact of this thermal treatment at 350 °C on the chemical composition of exhaust gases, on the size and morphology of soot aggregates, and consequently on their optical extinction coefficient. Finally, it is proposed to measure the optical extinction coefficient of PM and gaseous pollutants such as NO, NO<sub>2</sub>, and/or NH<sub>3</sub> injected first separately, then simultaneously, with the goal of proposing a procedure for their simultaneous control taking into account possible interference of gaseous pollutants with PM.

#### Structure of the manuscript

This thesis manuscript is structured in eight chapters. The 1<sup>st</sup> one introduces the PhD topic, by presenting both scientific and practical background to this research work, while the 2<sup>nd</sup> one provides a state-of-the-art on soot characterization by addressing its formation process, how soot particles could be chemically, physically, morphologically, and optically described, introducing numerous parameters, concepts, techniques and models used to do so. This is followed by the 3<sup>rd</sup> chapter that details the experimental setup used in this work which involves instrumentation for PM and gaseous pollutants generation under controller environment as well as technical means used for diagnostics purposes. Some of the used diagnostics provide raw data that need specific processing before it can be of use, hence the 4<sup>th</sup> chapter that describes methodologies that were used or even developed in this work to provide meaningful and interpretable information. The methodology developed in this thesis can be transposed for studying other (emerging) fuels like biofuels or synthetic fuels (e-fuels) in the

near future. As for the 5<sup>th</sup>, 6<sup>th</sup>, and 7<sup>th</sup> chapters they are devoted to results and discussion. As such, a mapping of the diesel fueled miniCAST generator is proposed in the 5<sup>th</sup> chapter describing soot aggregates size distributions, morphological key parameters, and optical extinction coefficients, while the 6<sup>th</sup> chapter provide a detailed chemical characterization of the exhaust of the miniCAST burner. As for the 7<sup>th</sup> chapter, it addresses the separate and/or simultaneous monitoring of PM and gaseous pollutants emissions. Finally, the 8<sup>th</sup> chapter is dedicated to summarizing the major finding detailed in the previous chapters and formulates perspectives in the light of what have been previously discussed.

The research work presented here was carried out in the framework of a joined collaboration between the PC2A laboratory (Univ. Lille) and IFP Energies nouvelles (IFPEN) who fully funded this project. The main part of this work was conducted within IFPEN/R10 mobility and systems department laboratories and the PC2A laboratory. Also, part of the experiments were carried out in the Regional Platform of Surface Analysis (Institut Chevreul, Univ. Lille), and IFPEN's R05 physics and analysis department, whose support are greatly appreciated.

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# State-of-the-art on soot characterization

Throughout this manuscript, particulate matter (PM) is considered to be a combustion product where the non-volatile part (nvPM), representing the components of particles that are not volatile above 350 °C, can be distinguished from the volatile part (vPM) that could include water, unburned fuel and PAHs [59]. The nvPM contributions to PM are solid and consist primarily of mature soot particles [59]. Those mature soot particles can vary in size from a few nanometers to a few hundred micrometers [60]. They may also have various chemical compositions and radiative properties. To be able to describe these aspects, this chapter is structured in five sections providing (i) a brief description of soot formation process in agreement with Michelsen *et al.* [59] recent review of terminology, followed by a stateof-the-art on (ii) the methods used for the chemical characterization of soot, (iii) size and morphological characterization of soot and (iv) optical properties of soot. The last section (v) is devoted to describe those aspects for soot aggregates produced by miniCAST soot generators and compare some of them to those of a diesel engine.

## 2.1 Soot formation

Soot formation is a complex process, including several physico-chemical mechanisms [61] that are usually described as a series of simplified stages as shown in Figure 2.1. The first steps in the soot formation process involve the production of gas phase hydrocarbons soot precursors [59] (see Figure 2.1.(a)).



Figure 2.1. Schematic diagram of the major steps in soot formation and the representative species produced as the process proceeds. The relative scale of these images changes between the panels, with the structure ranging from < 1 nm (a) to  $\sim 100 \text{ nm}$  (e), from Michelsen *et al.* [59].

During a combustion process, the fuel undergoes several oxidation reactions and transformations giving rise to a whole range of products. This decomposition leads first to the formation of small radicals and molecules among which acetylene ( $C_2H_2$ ) is produced in significant quantities [62]. Small radicals and molecules recombine to form progressively larger species. Once the aromatic rings form, they can grow fast and generate a vast family of PAHs according to certain mechanisms such as H abstraction,  $C_2H_2$  addition (HACA) [63]. This mechanism consists of a sequence of repetitive reactions, involving acetylene and other species in the gas phase, resulting by molecular growth, in the formation of PAHs. Other reaction paths are proposed in literature for the formation of the first aromatic rings and their growth into PAHs [64–67] and several theoretical and experimental studies [68, 62, 69–73] show that soot precursors are made of PAHs molecules as schematized in Figure 2.1.(a).

These soot precursors are then subject to an inception process, which remain complex and ambiguous [74], leading to the appearance of the first soot nuclei whose estimated size is of the order of 1 to 3 nm [75]. As particles continue to evolve, they collide and grow, thereby adding mass to particles and progressively forming quasi-spherical primary particles. These primary particles coagulate and agglomerate furthermore forming eventually fractallike aggregates called soot aggregates as shown in Figure 2.1.(e). As combustion products are generated, some volatile organic species present in the gas phase, depending on the degree of dilution and cooling, may also adsorb or condense on existing particles or nucleate to form new particles [19]. Consequently, soot particles include incipient soot particles, mature soot particles, and all of the intermediate particulate stages between inception, maturity and complete oxidation to gas phase species [59].

## 2.2 Methods for the chemical characterization of soot

A large part of the information available on soot formation process comes from studies using laboratory premixed and diffusion flames. Many of these studies, relied on studying soot chemical composition at different heights above the burner (HAB) to elucidate the complex soot formation process. However, one of the objectives of the research conducted here is to study the relationship between combustion exhaust (particularly PM) chemical composition and their optical extinction/absorption coefficient. Several experimental studies have shown an amplification of the absorption coefficient for soot particles with an organic coating almost by a factor of 2 compared to soot particles without coating [76–82]. Consequently, this section proposes to focus the attention on chemical diagnostics that allow the characterization of the chemical composition of combustion exhaust when probed far from the flame which is the case for soot generators emissions.

Mature soot particles that are emitted into the atmosphere fall into a category of strongly absorbing atmospheric particles called black carbon (BC) [59]. In climate or environmental studies, this designation refers to particles with high optical absorption capacities in the visible spectral region [18]. When those particles are extremely high in carbon relative to other elements they are described as elemental carbon (EC) [59]. One way to differentiate soot according to their chemical composition, is to describe them according to their organic content. When doing so, one can define total carbon (TC) as the sum of the organic part called organic carbon (OC) and the EC part. Distinguishing OC from EC is defined operationally according to experimental protocols, that may change from one study to another [83]. In general, this type of analysis, called thermogravimetric or thermo-optical analysis, is based on the analysis of mass loss of a PM sample which is introduced into an oven. During the first heating stages, the OC part, made up of volatile and semi-volatile species present on the surface and even within the soot, is desorbed first. The remaining carbon matrix, more resistant to heat, is the EC part. This type of analysis offers the possibility to have a general idea on the organic compounds fraction in a PM sample. More generally, in the context of exploring the relationship between optical extinction coefficient and combustion exhaust (both gas and

particulate phase) chemical composition is important to be characterized quantitatively and qualitatively.

To get a more precise idea on combustion exhaust chemical composition, selective and quantitative techniques such as gas chromatography can be used. This technique consists of probing a PM sample and put it in contact with a solvent to extract the chemical species it contains. The obtained solution is then evaporated and sent through a column allowing to separate the chemical species according to their retention times [84]. To detect these species as they exit the separation column, various detectors can be used. The most often used detection method is flame ionization detection (FID) making this technique (i.e., GC-FID) a reliable and sensitive one for quantitative analysis. GC analysis can also be coupled with a mass spectrometer (MS) allowing the technique (i.e., GC-MS) to provide more definite qualitative information [85]. It should be kept in mind that these techniques have - and continue - to evolve. From a sampling perspective using ex-situ GC-based diagnostics is more pertinent for characterizing gas phase components than characterizing particulate phase components. If applied on particulate phase, using a solvent extraction method, the results won't allow to recognize molecular species that are adsorbed on the surface of PM from those present within the PM itself. On the other hand, GC-FID is advantageous for gas phase analysis since one can apply the diagnostic without a need for a solvent. Details on the GC-FID technique, which will be used in this work, is available in section 3.4.



Figure 2.2. Comparison between L2MS mass spectra for SP1, SP2, SP3, and SP4 samples recorded with  $\lambda_i = 266$  nm for front filters (FF) (lower spectra) and back filters (BF) (upper spectra). Note that four different areas have been averaged to yield each of these spectra. Proposed structural formulae based on molecular formulae obtained from mass spectra are also shown, from Ngo *et al.* [86].

As for particulate phase, several techniques exist for soot surface chemical composition analysis such as two step laser mass spectrometry (L2MS) [87–92]. This technique consists of, first irradiating the surface of a soot sample with a pulsed laser beam of a few nanoseconds. Molecular species are desorbed from the sample as a consequence of the local heating it undergoes. Then, a second pulsed laser beam is directed, after a delay, towards the plume resulting from the first desorption step in order to ionize it. The resulting ions are then analyzed using a mass spectrometer. Figure 2.2 displays mass spectra obtained with such technique, applied on four different soot samples, corresponding to four operating points using a propane fuel miniCAST soot generator. SP1, SP2, SP3, and SP4 corresponds to those operating points and FF (front filter) and BF (back filter) inscriptions refer to samples containing particulate phase and the associated gas phase, respectively. As shown in this Figure, a number of PAHs, identified by their m/z, may or may not be present. This example shows that for SP2 and SP3 operating points, heavier PAHs (m/z > 250) are detected in the samples containing soot (FF) compared to the operating points SP1 and SP4 which seem to be less loaded in PAHs. This can be linked to the operating conditions under which these soot were obtained, which will be discussed furthermore in section 2.5. Figure 2.2 also show that the gas phase (BF) contains mostly low mass molecular species, whose quantitative characterization could have been done GC-FID.

Other techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) are also used for PM chemical characterization [93, 86]. With this technique, an energetic beam of primary ions,  $Bi_3^+$  for instance, is used to bombard the surface of a PM sample. The primary ions bombarding the surface to be analyzed (e.g., PM deposit), produce a variety of ionized "secondary" species which are then extracted and identified using a time-of-flight mass spectrometer. Figure 2.3 shows mass spectra, using such technique, on the same four operating points previously mentioned. Here it can be observed that the mass spectra obtained using ToF-SIMS are rich in peaks compared to those obtained using L2MS. As a matter of fact, during the desorption phase using L2MS technique, a low intensity laser beam is usually used, inducing less fragmentation compared to ToF-SIMS that uses rather energetic ionizing beam. This induces more fragmentation, therefore requiring a suitable post processing in order to identify the molecular species adsorbed on soot surface. Nevertheless, these techniques remain semi-quantitative and the quality of the spectra obtained will also depend on the sampling conditions as well as on the resolving power of the used mass spectrometer. Details on the ToF-SIMS technique, which will be used in this work, are available in section 3.4.



Figure 2.3. ToF-SIMS mass spectra of samples SP1, SP2, SP3 and SP4 obtained in positive polarity for front filters (FF) (lower spectra) and back filters (BF) (upper spectra). For visualization purposes, showing the m/z 150–500 range. Note that for SP2 and SP3 samples front and back filters have different scales, from Ngo *et al.* [86].

## 2.3 Size and morphological characterization of soot

To be able to characterize soot particles, it is necessary to define a number of parameters describing their size, mass and volume. As mentioned previously, soot aggregates have a fractal-like form as illustrated by the diagram in Figure 2.4, where its basic constituent element called primary particle or monomer is characterized by a primary particle diameter  $(D_p)$ . This diameter may have a size dispersion even within a soot aggregate. It has been shown that such dispersion follows a lognormal probability density function (i.e., pdf) (2.1) [94, 95]. It is also possible to consider several equivalent diameters for an aggregate. Here, an aggregate equivalent diameter is defined as being a sphere diameter, which with a given instrument would give the same size measurement as the considered particle. The volume equivalent diameter  $(D_{ve})$  is defined as being the diameter of a sphere having the same volume as the considered soot aggregate [96]. Other diameters are also used to describe soot particle size. Those most often used are, the electrical mobility diameter  $(D_m)$  the aerodynamic diameter  $(D_a)$ , and the gyration diameter  $(D_g)$ . Figure 2.4 recapitulates these different characteristic diameters.



Figure 2.4. Representation of the characteristic diameters of a soot nanoparticle, from Ouf [97].

It has been observed that soot aggregates size distributions, expressed in  $D_a$ , in  $D_g$  or in  $D_m$ , usually follow a lognormal pdf (2.1) [98]. To refer to a characteristic diameter of a size distribution one can use, for instance, the geometric mean diameter  $D_{geo,m} = \exp((\sum_i^k N_i \ln(D_i))/PN)$  (with  $N_i$  and  $D_i$  the number and diameter, of each class of size 'i', respectively, and PN the particle number  $PN = \sum_i^k N_i$ ) sometimes referred to as GMD, and the geometric standard deviation ( $\sigma_{geo,D}$ ) to describe its polydispersion. Figure 2.5 shows an example of such size distribution for diesel engine soot [99] expressed in electrical mobility diameter ( $D_m$ ). When fitted with a lognormal pdf, this distribution returns a  $D_{geo,m}$  of 112 nm and a  $\sigma_{geo,D}$  of 1.56.

$$n(D) = \frac{dN(D)}{dD} = \frac{1}{D\ln(\sigma_{\text{geo},D})\sqrt{2\pi}} e^{-\frac{\left(\ln(D/D_{\text{geo},m})\right)^2}{2\ln(\sigma_{\text{geo},D})^2}}$$
(2.1)

- D<sub>geo,m</sub> : Geometric mean diameter [nm] ;
- $\sigma_{\text{geo},D}$  : Geometric standard deviation ;



Figure 2.5. Example of a diesel engine (4-cylinder, 4-stroke, turbocharged, intercooled, common-rail, 2.0 L Nissan diesel engine, fulfilling Euro 5 standard) soot size distribution (expressed in mobility-equivalent diameter) downstream a DOC and DPF, and its fitting using the lognormal pdf (2.1), adapted from Rodríguez-Fernández *et al.* [99].

For a soot aggregate containing  $\mathrm{N}_\mathrm{p}$  monomers, assumed to be spherical,  $\mathrm{D}_\mathrm{ve}$  is written as:

$$D_{ve} = N_p^{\frac{1}{3}} D_p \tag{2.2}$$

One can deduce the aggregate volume (V<sup>agg</sup>) and mass (m<sup>agg</sup>) expressed as follows:

$$V^{agg} = \frac{\pi}{6} D_{ve}^3 = \frac{\pi}{6} N_p D_p^3$$
(2.3)

$$\mathbf{m}^{\mathrm{agg}} = \rho_{\mathrm{p}} \frac{\pi}{6} \mathbf{D}_{\mathrm{ve}}^3 \tag{2.4}$$

•  $\rho_p$ : Bulk density  $[g/cm^3]$ ;

For a total number of aggregates PN (assumed to be identical), the soot volume fraction  $(f_v)$  is therefore written as:

$$f_v = \frac{\pi}{6} N_p D_p^3 P N \tag{2.5}$$

Another mass equivalent diameter  $(D_{me})$ , can be defined as well. This diameter is very close to  $D_{ve}$ , except that it does not take into account the aggregate internal void. For a particle with no internal void,  $D_{me} = D_{ve}$ . However, for a particle having such voids,  $D_{ve} \ge D_{me}$ . Accordingly, one can define the volume of aggregate material  $(V_m^{agg})$  which is the volume occupied by all solid and liquid material forming the particle. This volume can be expressed as a function of  $D_{me}$  as follows:

$$V_m^{agg} = \frac{\pi}{6} D_{me}^3 \tag{2.6}$$

Particle size measurement instruments often determine particle size based on the ratio of the drag force experienced by the particle to another force applied on it. This drag force varies depending on the flow regime characterized by the dimensionless number of Reynolds (Re) (2.7), and taking into account the continuity aspect of the medium in which the aerosol (e.g., soot particles) is moving, which can be characterized by the dimensionless number of Knudsen (Kn) (2.8). The latter is defined as the ratio of the mean free path (l) of the molecules of the carrier gas (2.9), and a characteristic radius of the particle (r = D/2) [100, 96].

$$Re = \frac{vD}{\nu}$$
(2.7)

$$Kn = \frac{l}{r} = \frac{2l}{D}$$
(2.8)

- v: Carrier gas velocity [m/s];
- $D = 2 \times r$ : Particle characteristic diameter [m];
- v: Carrier gas kinematic viscosity  $[m^2/s]$ ;
- l: Carrier gas mean free path [m];

$$l = l_{R} \left(\frac{P_{0}}{P}\right) \left(\frac{T}{T_{0}}\right) \frac{\left(1 + \frac{S}{T_{0}}\right)}{\left(1 + \frac{S}{T}\right)}$$
(2.9)

- $l_R = 66.5$  [nm]: Mean free path of air at normal temperature and pressure conditions  $(T_0 = 293.15 \text{ [K]} \text{ and } P_0 = 101.3 \text{ [kPa]})$ ;
- P: Pressure [kPa];
- T: Temperature [K] ;
- S = 110.4 [K]: Sutherland constant ;

For an aerosol carried by a gas at low Reynolds (i.e.,  $\text{Re} \ll 1$ ), as it is the case for soot particles, one can distinguish three regimes, as described by [101].

• Continuum regime: This is the case where particles have a very large mean diameter compared to the carrier gas mean free path (i.e.,  $\text{Kn} \ll 1$ ). In such conditions, the gas surrounding the particles is considered as a continuum fluid. The drag force follows then Stokes law and is written as:

$$F_{Drag} = 3\pi\mu v_r D \tag{2.10}$$

- $\mu$ : Carrier gas dynamic viscosity [Pa.s];
- $\bullet \ v_r:$  Particle relative velocity [m/s] ;
- Transition regime: which satisfies  $0.1 \le \text{Kn} \le 10$ . It is a transient regime between the continuum regime and the so-called free molecular regime;
- Free molecular regime: This is the case where the particles have a very small mean diameter compared to the carrier gas mean free path (i.e.,  $\text{Kn} \gg 1$ ). In such conditions, the flow can be described as a series of ballistic collisions of gas molecules with the particles. The real drag force is then overestimated using Stokes law, since the particles slide on the molecules in contrast to the continuum regime;

When the carrier gas relative velocity at a particle surface is different from zero, the drag force is reduced [102, 103]. This is significant when the flow around the particle is outside the continuum regime. To take these different regimes into account, [104] proposed a corrective coefficient known as Cunningham ( $C_c$ ) slip correction factor based on Kn and expressed as follows:

$$C_{c}(Kn) = 1 + Kn \left( 1.142 + 0.558e^{-\frac{0.999}{Kn}} \right)$$
 (2.11)

Also, the nonspherical particles undergo more drag than their equivalents in  $D_{ve}$ , since they have more interaction surface area with the carrier gas molecules [103]. Thus, a second correction, taking into account the increase in the drag force exerted on a particle due to its nonsphericity, must be applied. This correction, expressed by the dynamic shape factor  $\chi$ (2.12), introduced by [105], is defined as the ratio of the resistance force (typically the drag force) on the nonspherical particle to the resistance force on its volume equivalent sphere when both move at the same relative velocity with respect to the carrier gas [102]. [103] discuss in detail the effect of the flow regime on this parameter.

$$\chi = \frac{F_{Drag}(D)}{F_{Drag}(D_{ve})}$$
(2.12)

Taking into account these two corrections, (2.10) becomes:

$$F_{\text{Drag}} = \frac{3\pi\mu v_r \chi D_{ve}}{C_c(D_{ve})}$$
(2.13)

Some instruments, such as the scanning mobility particle sizer (SMPS) measure an electrical mobility diameter  $(D_m)$ . This diameter corresponds to a sphere diameter which would have the same electrical mobility  $(Z_e)$  as the considered particle. This electrical mobility is associated with the terminal velocity  $(v_T)$  acquired by a particle in an electric field (E) when the electrostatic force ( $F_E = n_e \ e \ E$ ) balances the drag force (2.13). Thus, for a sphere having an electrical mobility diameter  $(D_m)$ , carrying  $n_e$  elementary charges, and moving in an electric field (E), one can write:

$$Z_e = \frac{v_T}{E} = \frac{n_e e C_c(D_{ve})}{3\pi\mu\chi D_{ve}} = \frac{n_e e C_c(D_m)}{3\pi\mu D_m}$$
(2.14)

- $Z_e$ : Electrical mobility  $[m^2/V.s]$ ;
- $v_T$ : Terminal velocity [m/s];
- E: Electric field [V/m];
- n<sub>e</sub>: Number of elementary charges ;
- e: Elemental charge (e =  $1.6 \times 10^{-19}$  [C]);

Using (2.14) and assuming that the particle of interest and its equivalent in  $D_{ve}$  have the same electric charge, one may deduce the relation linking  $D_m$  to  $D_{ve}$  [102, 103] expressed as follows:

$$D_{\rm m} = D_{\rm ve} \chi \frac{C_{\rm c}(D_{\rm m})}{C_{\rm c}(D_{\rm ve})}$$
(2.15)

Soot particles can also be characterized by their  $D_a$  generally determined using an electrical low pressure impactor (ELPI). It is defined as the diameter of a sphere having a standard density ( $\rho = 1 \text{ g/cm}^3$ ) that settles at the same terminal velocity ( $v_T$ ) as the particle of interest, when the drag force balances the force of gravity ( $F_p = m^{agg}$  g). From (2.13) and (2.4), this terminal velocity can be written as:

$$v_{\rm T} = \frac{C_{\rm c}(D_{\rm ve})\rho_{\rm p}D_{\rm veg}^2}{18\mu\chi} = \frac{C_{\rm c}(D_{\rm a})\rho_{\rm 0}D_{\rm a}^2g}{18\mu}$$
(2.16)

 $D_a$  may then be expressed as a function of  $D_{ve}$  as follows:

$$D_{a} = D_{ve} \sqrt{\frac{1}{\chi} \frac{\rho_{p}}{\rho_{0}} \frac{C_{c}(D_{ve})}{C_{c}(D_{a})}}$$
(2.17)

On the other hand, it is possible to geometrically define the so-called gyration diameter  $(D_g)$  which is the diameter of a sphere having the same moment of inertia as the particle of interest. Considering N<sub>p</sub> primary particles constituting the particle, D<sub>g</sub> is written as:

$$D_{g}^{2} = \frac{3}{5}D_{p}^{2} + \frac{4}{N_{p}}\sum_{i}d_{i}^{2}$$
(2.18)

•  $d_i$ : Distance separating the i<sup>th</sup> monomer from the particle's center of mass ;

It is also of interest to be able to describe soot particles morphology through a law combining the primary particle diameter  $(D_p)$ , and the gyration diameter  $(D_g)$ . Such law is called the fractal law. It describes soot particles morphology by introducing a fractal dimension  $(D_f)$  and a fractal pre-factor  $(k_f)$  coefficients and is written as:

$$N_{p} = k_{f} \left(\frac{D_{g}}{D_{p}}\right)^{D_{f}}$$
(2.19)



Figure 2.6. Example of diesel soot TEM images. (a): linear shaped particle and (b): compact particle, from Li *et al.* [106].

The fractal dimension  $(D_f)$  may vary between 1 and 3. A small fractal dimension (i.e.,  $D_f \sim 1$ ) describes a linear structure as illustrated in Figure 2.6.(a), while a high fractal dimension (i.e.,  $D_f \geq 2$ ) rather describes a compact aggregate as shown in Figure 2.6.(b). For soot aggregates, this fractal dimension often varies, for diesel engines, between 1.5 and 2.3 [107]. The fractal law parameters are often determined by analyzing transmission electron microscopy (TEM) images, either manually or using automated post processing algorithms [108, 95].

Among all these diameters, the most relevant one is  $D_g$  when it comes to light-matter interaction as it will be presented in section 2.4. Yet, size distribution measurement devices often provide particles sizes expressed in  $D_m$  or  $D_a$ . Therefore, converting these diameters into a  $D_g$  by simple conversion laws is of great importance. [109] introduced a simple relation, connecting the gyration diameter and the electrical mobility diameter  $D_m$ , of the form  $\beta = D_g/D_m$ . As one may expect this law depends on the flow regime [110]. In fact, [110] found  $\beta$  = 1.03 in the continuum regime, while in the transition regime this ratio is about  $\beta = 1.33$ . Based on the results of several studies, [111] proposes the following relations connecting D<sub>g</sub> to D<sub>m</sub> as a function of the flow regime and taking into account the number of monomers per particle:

• In the continuum regime  $(D \gg l)$ :

$$egin{array}{lll} {
m D_m} = {
m D_p}{
m N_p^{0.45}} & ; & {
m N_p} < 100 \ {
m D_m} = 0.65{
m N_p^{0.56}} & ; & {
m N_p} > 100 \end{array}$$

• In the free molecular regime  $(D \ll l)$ :

$$D_{\rm m} = D_{\rm p} N_{\rm p}^{0.45}$$
 ;  $\forall N_{\rm p}$  (2.21)

On the other hand, in the transition regime, [112, 113] found that this ratio fall within the range  $1.03 < \beta < 1.35$ . Knowing that soot particles flow often takes place in a transient state, a conversion ratio of  $\beta \sim 1.3$  seems to be reasonable for diesel soot as considered by [37, 114].

Another important soot property is its effective density which is defined as the ratio of the soot mass to its volume evaluated on the basis of the mobility diameter [115–117] (2.22). It is often measured by combining two aerosol measurements, using a differential mobility analyser and a centrifugal particle mass analyser (DMA-CPMA) for instance [118–121, 103].

$$\rho_{\rm eff} = \frac{6}{\pi} \frac{\mathrm{m}^{\mathrm{agg}}}{\mathrm{D}_{\mathrm{m}}^3} \tag{2.22}$$

Combining (2.4) and (2.22),  $\rho_{\text{eff}}$  can also be put in the form:

$$\rho_{eff} = \rho_p \left(\frac{D_{ve}}{D_m}\right)^3 \tag{2.23}$$

Combining (2.2), (2.4), and (2.19), particle mass can be expressed by (2.24). It has been observed, empirically [122], that this mass follows a similar power law, involving the mobility diameter as formulated in (2.25).

$$m^{agg} = \frac{\pi}{6} k_f \rho_p D_p^{3-D_f} D_g^{D_f}$$
(2.24)

$$m^{agg} \propto D_m^{D_{fm}}$$
 (2.25)

One can deduce, from (2.22) and (2.25), that effective density  $(\rho_{eff})$  can be expressed as follows:

$$\rho_{eff} \propto D_m^{D_{fm}-3} \tag{2.26}$$

For a spherical particle,  $\rho_{eff}$  is equivalent to soot bulk density  $\rho_p$  (e.g.,  $D_m = D_{ve}$ ). As their name suggests, fractal aggregates are nonspherical. Consequently,  $\rho_{eff}$  decreases with  $D_m$  due to the growth of the "porosity" of the aggregate. As soot aggregates have complex shapes,  $\rho_{eff}$  reflects, in fact, both the aggregate density and its morphology. This specificity is expressed through the mass-mobility exponent,  $D_{fm}$ , which has so far been interpreted as being the fractal dimension by a number of research group [122, 123]. However, it is observed that this exponent takes often values greater than the actual fractal dimension ( $D_f$ ), introduced by the fractal law. This is mainly explained by the fact that the  $D_m$  that intervenes in  $\rho_{eff}$  definition is different from  $D_g$  that intervenes in the fractal law [124]. Furthermore, high resolution TEM images revealed that at the nanometer scale, soot aggregates can exhibit different arrangements [125]. Figure 2.7 displays a closer look to such arrangements. The amorphous nanostructure has often been identified in soot at their early formation stage (nuclei) and in condensed species [126, 127]. This nanostructure often describes a disordered and isotropic arrangement of crystallites of variable nanometric size. This description is consistent with particles composed of aromatic species or a mixture of aromatic and aliphatic content [59]. In contrast, the nanostructure known as shell-core rather refers to soot whose cores (1 to 2 nm size [128, 129]) are amorphous and to which graphene layers are stacked and aligned relative to one another in an alternating pattern. Soot particles can have different graphitization levels, crystallite length, spacing and size of the graphitic zone [130–132] depending on the fuel type used to generate these particles and the maturity level they reached.



Figure 2.7. Example of closer look into soot nanostructure, for soot resulting from pyrene pyrolysis: (a): amorphous structure, (b): graphitic structure, from Vander Wal *et al.* [125].

## 2.4 Optical properties of soot: Theoretical background

To use optical diagnostics such as optical extinction measurement for soot particulate emission monitoring, a theoretical background on light-matter interaction in the particular case of small particles such as soot is needed. Therefore this section aims to introduce the quantities used to describe light extinction by soot particles. When a set of particles undergo electromagnetic radiation as schematized in Figure 2.8, two phenomena can occur. First, absorption through which these particles will store part of the received energy, and second, scattering through which these particles will spatially redistribute a part of the incident light [133]. The transmitted light intensity (I<sub>t</sub>) can be measured by a detector placed downstream from the particles. When compared to the case where these particles are absent, with a transmitted light intensity (I<sub>0</sub>), information on light attenuation (the presence of these particles cause) is derived. These two intensities, can be measured using an extinction cell, then used to deduce an extinction coefficient (K<sub>ext</sub>) through Beer-Lambert's law (2.27) [134]. This coefficient can then be interpreted within an appropriate theory.



Figure 2.8. Extinction by a collection of particles, adapted from Bohren *et al.* [133].

$$K_{ext} = -\frac{1}{L} ln \left( \frac{I_t(\lambda)}{I_0(\lambda)} \right)$$
(2.27)

- L: Optical path [m];
- $I_t(\lambda)$ : Transmitted light intensity in presence of particles ;
- $I_0(\lambda)$ : Transmitted light intensity in absence of particles ;

The quantification of absorption and scattering phenomena is usually done by determining quantities known as absorption cross-section ( $C_{abs}$ ) and scattering cross-section ( $C_{sca}$ ), the sum of which gives the extinction cross-section ( $C_{ext}$ ).  $C_{abs}$  and  $C_{sca}$  reflect the ratio of the energy absorption rate and of the energy scattering rates by the particles to the incident irradiance [133], respectively. Models that describes these quantities for fractal-like aggregates, are consequently needed as they are linked to  $K_{ext}$  and particle number concentration PN as in (2.28).

$$K_{ext} = \sum_{i} N_i \times C_{ext,i} = \sum_{i} N_i \times C_{abs,i} + N_i \times C_{sca,i}$$
(2.28)

- $N_i$ : Number of particles of type 'i' per unit volume [particle/m<sup>3</sup>];
- +  $C_{abs,i}\!:$  Absorption cross-sections of particles of type 'i'  $[m^2/particle]$  ;
- C<sub>sca.i</sub>: Scattering cross-sections of particles of type 'i' [m<sup>2</sup>/particle] ;

To be able to describe the light-matter interaction for soot particles, it is necessary to introduce the complex refractive index (m) (2.29). This wavelength dependent quantity is often used to describe material optical properties. Here, its imaginary part (k) determines the attenuation of an electromagnetic wave as it propagates through the considered medium, while its real part (n) represents the phase velocity meaning the ratio of the light velocity in vacuum to the light velocity in this medium. Experimental determination of such parameter is by no means trivial in wavelength regions where a solid or liquid is appreciably absorbing [133]. Yet, it is crucial to know the wavelength dependence of such parameter as it intervenes in the models used to interpret  $K_{ext}$  for instance.

$$\mathbf{m} = \mathbf{n} - \mathbf{i}\mathbf{k} \tag{2.29}$$

A first approach is Mie theory, within which the straightforward analytical resolution makes possible the rigorous modeling of absorbed and scattered light cross-sections by spherical particles having a homogeneous composition. This solution takes the form of an mathematical sequence [133] whose terms to the fourth order are expressed as in (2.30) and (2.31) for extinction and total scattering cross-sections, respectively. Absorption cross-section is then deduced applying  $C_{abs} = C_{ext} - C_{sca}$ .

$$\begin{split} C_{ext} &= \pi^2 D_p^2 x_p Im \left( \frac{m^2 - 1}{m^2 + 2} \left[ 1 + \frac{x_p^2}{15} \left( \frac{m^2 - 1}{m^2 + 2} \right) \frac{m^4 + 27m^2 + 38}{2m^2 + 3} \right] \right) \\ &+ \frac{2\pi^2 D_p^2}{3} x_p^4 Re \left( \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 \right) \\ C_{sca} &= \frac{2\pi^2 D_p^2}{3} x_p^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \end{split}$$
(2.30)

- D<sub>p</sub>: Particle diameter ;
- $x_p = \frac{\pi D_p}{\lambda}$ : Shape factor ;

A special case of Mie theory is Rayleigh's approximation valid for spherical particles of very small diameter compared to the wavelength  $D_p \ll \lambda$  (i.e., shape factor  $x_p \ll 1$ ). Within Rayleigh's limit the absorption and total scattering cross-sections of an unpolarized light by a spherical particle are defined, respectively by:

$$C^{p}_{abs} = \frac{4\pi x_{p}^{3}}{k^{2}} E(m)$$

$$(2.32)$$

$$C_{sca}^{p} = \frac{8\pi x_{p}^{6}}{3k^{2}}F(m)$$
 (2.33)

•  $k = \frac{2\pi}{\lambda}$ : Wave vector norm ;

The two functions E(m) (2.34) and F(m) (2.35) are called the absorption and scattering functions, respectively. They are functions of the complex refractive index and are expressed as follows:

$$E(m) = Im\left(\frac{m^2 - 1}{m^2 + 2}\right)$$
 (2.34)

$$F(m) = \left| \frac{m^2 - 1}{m^2 + 2} \right|^2$$
(2.35)

However, Rayleigh's approximation cannot be applied directly to soot aggregates whose size is of the same order of magnitude as the wavelength. Nevertheless, this approximation remains valid for primary particles constituting an aggregate itself. These have a diameter of a few tenths of nanometers, relatively small compared to the wavelength usually used and which is a few hundred nanometers (i.e., 200 nm - 1000 nm). Since an aggregate is made of  $N_p$  monomers (under the assumption of being in point contact) using this approximation one can express the absorption and the total scattering cross-sections of an aggregate as follows:

$$C_{abs}^{agg} = N_p C_{abs}^p \tag{2.36}$$

$$C_{sca}^{agg} = N_p C_{sca}^p \tag{2.37}$$

Nevertheless, this approach does not take into account the complex morphology of the soot aggregates or any interactions between monomers within the same aggregate. Although this approach is enough to describe absorption phenomena, it is however insufficient to describe scattering phenomena. This approximation is therefore extended within Rayleigh Debye Gans (RDG) theory, to take into account the non-sphericity of soot aggregates. This extension consists in considering that a particle with a relatively large diameter can be taken as the sum of a set of smaller elements respecting Rayleigh's approximation. Two hypotheses should therefore be emphasized. First, that the monomers are in contact with only one monomer and that they do not exhibit any size dispersion. Second, that these monomers do not interact with each other, hence the following two criteria proposed by van de Hulst [135] that must be verified :

$$|m-1| \ll 1$$
;  $2x_p|m-1| \ll 1$  (2.38)

Other similar limitations exists as the one proposed by Berry *et al.* [136]. It consists of taking into account the fractal dimension  $(D_f)$ , the number of primary particles per aggregates  $(N_p)$ , and the shape factor  $(x_p)$ . They proposes that the aggregate must satisfy the following two conditions :

$$D_f > 2$$
 ;  $N_p < x_p^{-D_f}$  (2.39)

Later the RDG theory was adopted by Dobbins *et al.* [137] then by Köylü *et al.* [138]. To account for particles fractal aspect, particularly for differential and total scattering cross-sections, these authors introduced a structure factor (g), thus adapting (2.36) onto (2.40), henceforth modeling the total scattering cross-sections in the framework of Rayleigh Debye Gans for Fractal Aggregates (RDG-FA) theory.

$$C_{sca}^{agg} = N_p^2 C_{sca}^p (D_f, D_g, \lambda)$$
(2.40)

This structure factor (g) proposed by Dobbins *et al.* [137] is expressed as follows:

$$g(D_{f}, D_{g}, \lambda) = \left(1 + \frac{1}{3D_{f}} \left(k(\lambda)D_{g}\right)^{2}\right)^{-\frac{D_{f}}{2}}$$
(2.41)

For much more detail concerning this theory the reader is referred to the review of Sorensen [111]. Since then, many works focused on finding the limits of validity of this theory [139, 140]. As explained in section 2.3 soot particles are fractal-like aggregates. Consequently, the RDG-FA theory is used to model soot optical extinction coefficient ( $K_{ext}$ ) which is expressed as follows:

$$K_{ext} = \underbrace{\int N(D_g) N_p C_{abs}^p n(D_g) dD_g}_{Absorption} + \underbrace{\int N(D_g) N_p^2 g(D_f, D_g, \lambda) C_{sca}^p n(D_g) dD_g}_{Scattering}$$
(2.42)

As (2.42) suggests, the extinction coefficient (K<sub>ext</sub>) varies linearly with particle number PN. With respect to N<sub>p</sub>, the number of primary particle per aggregate, the absorption coefficient (K<sub>abs</sub>) varies linearly while the total scattering coefficient (K<sub>sca</sub>) varies quadratically with it. For D<sub>p</sub>, one can see that  $K_{abs} \propto D_p^3$ , while  $K_{sca} \propto D_p^6$ . On the other hand, the dependence of the extinction coefficient is less obvious with respect to D<sub>g</sub>,  $\sigma_{geo}$  and D<sub>f</sub> since they intervene in the size distribution density and in the structure factor (g). (2.42) also suggests that the wavelength decay of the scattering contribution is faster and varies as  $\lambda^{-4}$ , compared to the absorption contribution which varies as  $\lambda^{-1}$ . To shed light on the impact of RDG-FA model parameters, the following paragraph propose a brute-force sensitivity study of modeled optical extinction coefficient.

#### **RDG-FA** modeled optical extinction spectra

For soot aggregates, understanding the impact their size and morphological parameters on the extinction coefficient is essential to identify those who induce the most variation within appropriate range of variation and challenge the RDG-FA ability to accurately model light extinction by soot aggregates. The phenomenological study carried out here, highlights the importance of accounting for soot morphological parameters that are (i) soot primary particle diameter  $(\overline{D}_{p})$ , (ii) fractal dimension  $(D_{f})$  and (iii) fractal pre-factor  $(k_{f})$  besides soot size distribution parameters (assuming a lognormal pdf (2.1)) that are (i) the geometric mean diameter ( $D_{geo,m}$ ), (ii) the geometric standard deviation ( $\sigma_{geo,D_m}$ ) and (iii) particle number (PN). As introduced before, the RDG-FA model uses aggregates gyration diameters  $(D_g)$ . Since soot aggregates electrical mobility diameters  $(D_m)$  were measured in this work, a variation range of mobility-equivalent geometric mean diameter is considered instead, and converted into gyration one using the conversion of the form  $\beta = D_g/D_m \sim 1.3$  as explained in section 2.3. Given the literature data on soot particles presented later in section 2.5, the following variation ranges are considered :  $2.5 \times 10^6 < {\rm PN} ~(\#/{\rm cm}^3) < 2.5 \times 10^7;~40 <$  $D_{geo,m}$  [nm] < 110; 1.5 <  $\sigma_{geo,D_m}$  < 1.9 ; 10 <  $\overline{D_p}$  [nm] < 40; 1.5 <  $D_f$  < 2.3 and 1.94 <  $k_f$ < 2.00. In what follows, RDG-FA was used to simulate K<sub>ext</sub>. In these simulations E(m) and F(m) functions taken from Bescond *et al.* [46] that corresponds to their CAST 1 set point were used.



Figure 2.9. (a) RDG-FA modeled soot extinction coefficient  $K_{ext,soot}$  for a reference aggregate characterized by the following parameters:  $PN = 1.37 \times 10^7 \ \#/cm^3$ ,  $D_{geo,m} = 75 \text{ nm}$ ,  $\sigma_{geo,D_m} = 1.7$ ,  $\overline{D_p} = 25 \text{ nm}$ ,  $D_f = 1.851$ , and  $k_f = 1.970$ , showing both absorption and scattering contributions and (b) the percentage of scattering in extinction.

Accordingly, graphs of Figure 2.10 show the impact of each of those parameters on K<sub>ext</sub> with respect to a reference aggregate characterized by the following parameters: PN = 1.37  $\times 10^7 \ \text{\#/cm}^3$ , D<sub>geo,m</sub> = 75 nm,  $\sigma_{\text{geo,D_m}} = 1.7$ ,  $\overline{\text{D}_p} = 25$  nm, D<sub>f</sub> = 1.851, and k<sub>f</sub> = 1.970. Extinction coefficients of this reference aggregate correspond to the green curves on all Figure 2.10 subplots.

Figure 2.9.(a) shows RDG-FA predicted  $K_{ext}$  for the reference aggregate with both absorption and scattering contributions to the extinction process, both of which evolve differently with respect to the wavelength. The RDG-FA model predicts that the wavelength decay of the scattering contribution that varies as  $\lambda^{-4}$ , occurs rapidly compared to the absorption one which varies as  $\lambda^{-1}$ . Thus, the absorption contribution is the most dominant (> 90 %) for wavelengths  $\lambda > 400$  nm as shown in Figure 2.9.(b). However, over the UV spectral region the contribution of the total scattering, which depends on particles size, reaches up to 15 %, at  $\lambda = 200$  nm, and therefore cannot be neglected. This phenomenological study based on different parameters variations, considered acceptable for diesel-like aggregates, makes it possible to establish important observations. As (2.42) suggests, the particle number concentration (PN) is a multiplying factor having the same amplifying effect on  $K_{ext}$  (see Figure 2.10.(a)). Meanwhile, the increase in  $D_{geo,m}$  or in  $\sigma_{geo,D_m}$  both results in higher  $K_{ext}$  as shown in Figures 2.10.(b-c). This increase is slightly higher in the UV spectral range which may be explained by the fact that when an aerosol is polydispersed, the largest particles of the size distribution strongly impact scattering particularly in the UV spectral region (see Appendix B). Figures 2.10.(b-c) also show that  $K_{ext}$  is more sensitive to the  $D_{geo,m}$  variation rather than aggregates  $\sigma_{geo,D_m}$ , at least within the chosen variation ranges. On the other hand, soot aggregate size intervenes in the absorption term only through the size distribution density while in the scattering term this diameter intervenes both in the size distribution density and in the structure factor (g) (2.41) which is a decreasing function of particles size. Nevertheless, the scattering contribution still increases with the geometric mean diameter because the effect of the size distribution density prevails (see Appendix B).

Moreover,  $\overline{D_p}$  and  $D_f$  have also a significant impact on these spectra.  $\overline{D_p}$  has a greater impact on the scattering term as it evolves as  $\overline{D_p}^6$ , compared to the absorption term that evolves as  $\overline{D_p}^3$ . However, combined with as spectral variation of  $\lambda^{-1}$  and  $\lambda^{-4}$  for absorption and scattering terms, respectively,  $K_{ext}$  gets eventually amplified at  $\lambda = 300$  nm much more compared to  $\lambda = 900$  nm as shown is Figure 2.10.(d). The last significant effect is that of  $D_f$  that contributes to the amplification of the scattering contribution more than it does for the absorption one (see Appendix Figure B.1). Physically, this means that when a soot particle is compact ( $D_f > 2$ ) it scatters significantly more light. Finally, it would seem that the extinction coefficient is less sensitive to  $k_f$  variation at least within the selected range, as shown in Figure 2.10.(f). Therefore, such parameter may be fixed.



Figure 2.10. Extinction coefficient (K<sub>ext</sub>) sensitivity to size distributions - assuming lognormal pdf - parameters (a) PN, (b)  $D_{\text{geo},m}$ , and (c)  $\sigma_{\text{geo},D_m}$ , and to morphological parameters (d)  $\overline{D_p}$ , (e)  $D_f$ , and (f)  $k_f$ . Contributions of absorption and scattering coefficients  $K_{abs}$  and  $K_{sca}$ , respectively in  $K_{ext}$  are available in Appendix B. For each parameter the sensitivity is considered in contrast to a reference aggregate (corresponding to the green curves) that has the following characteristics: PN =  $1.37 \times 10^7 \ \#/\text{cm}^3$ ,  $D_{geo,m} = 75 \text{ nm}$ ,  $\sigma_{geo,D_m} = 1.7$ ,  $\overline{D_p} = 25 \text{ nm}$ ,  $D_f = 1.851$ , and  $k_f = 1.970$ .


Figure 2.10. Continued

# 2.5 Properties of soot particles produced by miniCAST soot generators and comparison with typical engine soot

The Miniature Combustion Aerosol STandard soot generator so-called miniCAST, is a soot particle production device designed by Jing, Ltd [141] and is considered as a reference device in several soot-related studies [42–51]. The most used version of this device, produces soot under controlled combustion conditions thanks to a propane laminar diffusion flame. Figure 2.11 displays a functional schematic of this device version, where the fuel ( $C_3H_8$ ) (possibly assisted by a mixing gas flow, usually  $N_2$ ) and the oxidation air, can be controlled. These are routed coaxially from the bottom to the top of the burner where the combustion takes place. The resulting combustion products are then sent to the miniCAST exhaust thanks to a nitrogen quench flow to prevent further oxidation of soot particles. The resulting flow is then diluted using a dilution air flow to limit aggregate agglomeration in the exhaust. 26



Figure 2.11. Functional schematic of the propane fuel miniCAST soot generator burner, adapter from Jing Ltd [141].

Over the years, several measurement techniques have been used to determine relevant properties of soot particles generated by such a device. One may expect that reported data in literature may depend on the device model, on the measurement techniques, on the analysis methods, and on experimental protocols followed by researchers or even on the overall experimental setup itself. As each research groups generates soot for a given purpose, this is very often the case. Therefore, data inter-comparison may be a complicated task. Accordingly, the aim of this section is to highlight the great variability in this data, while focusing, when possible, on inter-comparisons revealing major soot properties. Table 2.1 recapitulates the main studies that have characterized or used a CAST or a miniCAST burner. This nonexhaustive list provides for each study, the soot generator model, the analysis techniques or measurement equipment used to examine a given number of properties. In what follows, PM chemical composition, morphological, and optical properties are discussed in respect to the miniCAST operating conditions. Moreover, the way these properties evolve with respect to one another is also addressed. This section is structured as follows: first soot chemical composition is presented in terms of organic content that is examined as well as how it varies with soot size, then in terms of much detailed chemical composition. Morphological properties are then reviewed, before addressing literature data on optical properties. Along this discussion, comparison to diesel engine soot will be presented.

For a meaningful comparison, the use of the flame overall equivalence ratio ( $\varphi$ ) (Appendix A shows how it is calculated) is helpful particularly when it comes to compare mini-CAST soot properties. When this parameter is relevant, an operating point is said fuel-rich when  $\varphi \geq 1$  and fuel-lean when  $\varphi \leq 1$ , thus allowing characterizing a given operating point. Other research groups prefer using the overall flame Carbon/Oxygen (C/O) atomic ratio to refer to an operating point. This ratio is expressed in (2.43) for a C<sub>3</sub>H<sub>8</sub>/air laminar diffusion flame [42].

$$C/O = 7.16 \times \frac{Q_{fuel}}{Q_{air}}$$

$$(2.43)$$

- $Q_{fuel}$  : Fuel (propane) volume flow rate ;
- $\bullet~{\rm Q}_{\rm air}$  : Oxidation air volume flow rate ;

Table 2.1. Non-exhaustive list of studies that have characterized and/or used the CAST/mini-CAST burner using propane vs examined properties. <sup>1</sup>: Studies that used an ageing/residence chamber; <sup>2</sup>: Studies that used a thermodenuder, a Catalytic Stripper or an equivalent solution. (Consult the list for acronyms for abbreviations K.1)

Reference	$\mathbf{CAST}/\mathbf{miniCAST}$ model	Analysis technique measurement device and numerical method/approach	Examined properties
Saathoff et al. [142]	$C_3H_8/air$ Diffusion flame: CAST	Thermographic analysis	%  OC/TC
Schnaiter <i>et al.</i> $[42]^1$	$ m C_3H_8/air$ Diffusion flame CAST	SMPS - CPC - TEM Thermographic carbon analysis Extinction cell, Nephelometer Aethalometer	Size distribution PN Morphology % OC/TC Optical properties
Barthazy et al. [143]	$ m C_3H_8/air$ Diffusion flame: CAST	SMPS - CPC Thermographic analysis	Size distribution PN % OC/TC
Marsh <i>et al.</i> $[144]^2$	C <sub>3</sub> H <sub>8</sub> /air Diffusion flame Model: 6201 C	SMPS- CPC Thermographic analysis	Size distribution PN % OC/TC
Crawford <i>et al.</i> $[145]^1$	$C_3H_8/air$ Diffusion flame CAST & miniCAST	SMPS - CPC Thermographic analysis	Size distribution PN % OC/TC
Mamakos et al. $[43]^{1,2}$	$C_3H_8/air$ Diffusion flame Model: 5200	SMPS, CPC Thermo-optical analysis ELPI, TEM	Size distribution PN % OC/TC Effective density Morphology
Moore <i>et al.</i> [44] <sup>2</sup>	C <sub>3</sub> H <sub>8</sub> /air Diffusion flame Model: 4202	SMPS thermal/optical analysis EchoChem (SMPS-AEP) - AFM HR-ToF-AMS	Size distribution PN % OC/TC PAH Concentration Effective density Morphology Chemical composition
Maricq $\begin{bmatrix} 146 \end{bmatrix}^1$	$C_3H_8/air$ Diffusion flame Model: 5201 C	SMPS - TEM Photoacoustic absorption method Thermal analysis	Size distribution Morphology BC
Kim <i>et al.</i> [45] <sup>1</sup>	$C_3H_8/air$ Diffusion flame Model: 6201 C	SMPS - CPC - TEM Absorption Photometer Nephelometer Aethalometer Thermal-optical analysis	Size distribution PN Morphology Optical properties % EC/TC
Yon <i>et al.</i> [147]	$ m C_3H_8/air$ Diffusion flame Model: 5206	DMA - CPC - CPMA TEM Thermo-optical analysis	Effective Density Morphology % OC/TC
Durdina et al. [47] <sup>1</sup>	C <sub>3</sub> H <sub>8</sub> /air Diffusion flame Models: 5201 C & 6203 C	DMA-CPC CPMA, DMS LII, MSS, TEM Thermal-optical analysis	Size distribution Effective density Morphology % OC/TC
Bescond et al. [46]	$C_3H_8/air$ Diffusion flame Model: 5201 C	Experimental m SMPS - TEM - TEOM (DMA-CPMA) Thermo-optical analysis Extinction cell Numerical RDG-FA Lorentz-Drude	neasurements Size distribution Mass concentration Morphology Effective density % EC/TC Optical properties models Optical properties
Grondin <i>et al.</i> $[148]^1$	$C_3H_8/air$ Diffusion flame Model: 4202	EEPS PPS - TEM	Size distribution PN Mass concentration Morphology
Paz et al. [149] <sup>1</sup>	$C_3H_8/Air$ Diffusion flame Model: 5203 C	SMPS - SEM Thermogravimetric analysis	Size distribution PN Morphology % OC/TC

Saffaripour et al. [48]	$C_{3}H_{8}/air$ Diffusion flame TEM Model: 5201 C		Morphology	
Török et al. $[150]^1$	$C_3H_8/air$ Diffusion flame Model: 5201 C	SMPS, SP-AMS Thermo-optical analysis Extinction cell Aethalometer	Size distribution Chemical composition %OC/TC Optical properties	
		leasurements		
Yon <i>et al.</i> $[151]^1$	$ m C_3H_8/air$ Diffusion flame Model: 5206	SMPS, LII SAXS Scattering measurements	Size distribution Volume fraction Primary spheres and aggregates size	
		Numerical models		
		RDG-FA	Inversion process	
		Experimental measurements		
Lefevre <i>et al.</i> [152]		Extinction cell	Optical properties	
Lefevre et al. [153]	$C_3H_8/air$ Diffusion flame Model: 5201 C	SMPS-CPMA Scattering measurements	Size distribution Effective density Optical properties	
		Numerical models		
		RDG-FA	Optical properties	
Marhaba <i>et al.</i> [50]	${ m C_3H_8/air}$ Diffusion flame Model: 5201 C	TEM - XPS NEXAFS - FTIR Thermal-optical analysis	Morphology Nanostructure Chemical composition % OC/TC	
Ess <i>et al.</i> $[154]^1$	C <sub>3</sub> H <sub>8</sub> /air Diffusion flame or partially premixed Model: 5201 BC	SMPS Thermo-optical analysis Aethalometer	Size distribution PN % EC/TC Optical properties	
Malmborg <i>et al.</i> $[49]^1$	$C_3H_8/air$ Diffusion flame Model: 5201 C	SP-AMS, HRTEM	Chemical composition Morphology	
Ngo [56]	$ m C_3H_8/air$ Diffusion flame Model: 5201 C	L2MS, SIMS	Chemical composition	

#### Chemical composition

Figure 2.12 gathers literature data on soot particle organic fractions as a function of  $\varphi$  and C/O atomic ratio. When analyzing soot samples produced by an early CAST burner model for different C/O atomic ratios, Saathoff et al. [142] observed an OC/TC ratio as low as 1.4 % at C/O = 0.29 (slightly fuel-lean condition). It increased up to 80.2 % at C/O = 1 (fuel-rich condition). Proceeding with the same measurement protocol, Schnaiter et al. [42] Barthazy et al. [143] and Paz et al. [149] reported comparable organic fraction levels within similar C/O ratio range as shown in Figure 2.12. In those two studies, OC/TC ratios were often varied by increasing the oxidation air flow rate while keeping a fixed propane flow rate. Thus, the general trend was an organic fraction level reaching  $\sim 80$  % for a C/O ratio close to unity and decreasing to less than 10 % for a C/O  $\sim 0.3$ . Later, Marsh *et al.* [144], Crawford et al. [145], Mamakos et al. [43], Yon et al. [147], Kim et al. [45], Ess et al. [154] and Marhaba et al. [50] observed an OC/TC ratio that reached higher values (up to 80 %) at only C/O ratios between 0.4 and 0.6. Part of this variations may be attributed to different miniCAST models that were used as reported by Durdina et al. [47] when they compared two propane fuel miniCAST models (5201 C and 6203 C) and found different EC fraction at the same  $\varphi$  $\sim$  1. Part of this results disparity, may also be attributed to different experimental protocols used to distinguish OC from EC fractions. Although the majority of the results follow the same trend over the C/O ratio range 0.2 - 0.6, OC/TC ratios under fuel-lean conditions down to C/O  $\sim 0.2$  reported by Moore *et al.* [44] reveal an opposite trend. In their study, soot organic content reached higher values ( $\sim 80 \%$ ) under very fuel-lean conditions. It is worth mentioning that, the C/O (or  $\varphi$ ) ratio does not incorporate the changes in soot characteristics resulting from adding mixing gas  $(N_2)$  with the fuel. According to Moore *et al.* [44], doing so induced both a decrease in soot size distribution mode along with an increase in the OC/TC ratios. This might be explained by the increase in fuel velocity inside the burner pipes, leaving less time for soot to grow in size.



Figure 2.12. Literature data [142, 143, 42, 144, 145, 43–45, 147, 47, 46, 149, 150, 50, 154] on soot particles organic fractions (OC/TC) as a function of the overall flame equivalence ratio ( $\varphi$ ) and C/O atomic ratio, for propane CAST/miniCAST burners. The gray line corresponds to the stoichiometric conditions (C/O = 0.3 or  $\varphi$  = 1).

This dual dependency makes results inter-comparison even more difficult [44]. Accordingly, when analyzing soot organic content results, one must keep in mind to which size they correspond. As for soot aggregates size distributions, the CAST/miniCAST device provides lognormal-like size distribution, where the geometric mean diameter can vary over a wide range. When decreasing the oxidation air flow rate for instance, going from fuel-lean to fuelrich conditions, soot aggregates were observed to grow reaching maximum size under slightly fuel-lean condition before starting to decrease, covering the range 10 - 130 nm in modal size [44]. As for aggregate polydispersion, Saffaripour *et al.* [48] reported a geometric standard deviations varying typically from 1.6 to 1.8. Under slightly fuel-rich conditions ( $1 < \varphi <$ 1.15), soot aggregates, taken from diluted CAST/miniCAST exhaust, bimodal size distributions have also been reported in Schnaiter *et al.* [42] and Moore *et al.* [44] with nucleation modes that were attributed to a strong presence of condensable organic species.

Additionally, Ngo *et al.* [86] used the previously mentioned chemical characterization techniques L2MS and SIMS to chemically discriminate particulate and gas phases miniCAST exhausts using a two-filter collection method. The two filters method was designed in a way to be able to retain the solid particles on a front filter (FF) while allowing the gas phase to cross it to be captured on a back filter (BF). The mass spectra, obtained using these two techniques were shown earlier in section 2.2 and are all dominated by signals attributed to aromatic species, particularly PAHs. As mentioned before, these mass spectra corresponds to four operating points SP1, SP2, SP3 and SP4 obtained by increasing oxidation air flow rate ( $Q_{SP3}^{air} < Q_{SP4}^{air} < Q_{SP1}^{air}$ ). When doing so, a significant variation in the shape of the mass spectra have been observed. According to [86], even though the increase in contribution for each mass spectra is not the same, SP3 set point that has the lower oxidation air flow rate seems to produce more of the heavier PAHs. When these mass spectra were post-processed, the deduced PAH signals corresponding to the particulate phase also seem to decrease as the oxidation air flow rate increased. Figure 2.13 gathers information extracted from both L2MS (a) and SIMS (b) mass spectra performed on these set points.

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Figure 2.13. (a): Variation in total PAH signal detected with L2MS at  $\lambda_i = 266$  nm (All values are normalized to the partial ion cont (PIC) corresponding to the signal of all selected peaks), (b): Total PAH signal detected with SIMS on front (orange) and back (blue) filters plotted as a function of oxidation air flow. PAH contribution is divided into adsorbed species non-volatile ( $m/z \ge 252$ , semi-volatile ( $m/z \ 176-242$ ) and volatile ( $m/z \ 78-166$ ) fractions. OC/TC values reported in the literature are plotted in grey for comparison, from Ngo *et al.* [86]

Both techniques show that PAH content on front filters, containing soot particles (orange bars) follows the same trend as the OC/TC ratios, reported by [46] and [147], and obtained from thermo-optical analysis. It clearly shows that SP3 set point is different from the others. It is worth mentioning that this same set point has been described in literature to have significant small crystallites forming a distinct disordered arrangement as well as exhibiting a distinctive optical extinction behavior as it will be discussed further down. In Figure 2.13.(a), the total PAH signal on back filters (blue bars) also follows the trend observed on front filters for samples SP3, SP2 and SP4, with the exception for SP1 for which the PAHs signal on the back filter increases [86]. These authors attributed this to the nature of its PAH content for SP1 set point, which likely includes more volatile and semi-volatile aromatic species. It is worth mentioning that the dominant class of chemical compounds in L2MS or SIMS mass spectra (Figure 2.13 (a) vs. (b)) is linked to the ionization process ( $\lambda_i = 266 \text{ nm vs. } Bi_3^+$ ion beam). Semi-volatile compounds  $(m/z \ 178 \ - \ 228)$  dominate in spectra generated with the 266 nm ionization wavelength, whereas high-mass aromatic compounds  $(m/z \ 250 \ - \ 550)$ dominate SIMS mass spectra. This suggests that miniCAST samples contain PAHs with high stability in the high-mass range, which are eventually less prone to fragmentation in SIMS with respect to other semi-volatile compounds. Consequently, a smaller relative fraction of molecules is fragmented in L2MS, which leads to a more reliable PAH content determination in the semi-volatile mass range from their L2MS mass spectra compared to SIMS.

#### Morphological properties

Over the years, many techniques have been used to measure relevant soot morphological parameters  $D_p$  and  $D_f$ . Schnaiter *et al.* [42] reported one of the first morphological observations of soot aggregates produced by a CAST burner. Through TEM visualization they observed that these aggregates consisted of small individual particles with a diameter around 30 nm under fuel-rich conditions (C/O = 0.45), although they also observed some isolated particles with ~ 120 nm diameter under the same conditions. Others such as Mamakos *et al.* [43] used coupled DMA-ELPI measurements, to estimate primary particle diameter,  $D_p$ , and found, assuming a given soot density, that  $D_p$  increased from 9 nm (C/O = 0.23) up to 34 nm (C/O = 0.42). Assuming a different soot density, Durdina *et al.* [47] reported  $D_p$  varying from 15 nm (C/O = 0.15) to 45 nm (C/O = 0.30) which were confirmed later by TEM observations. Using atomic force microscopy imaging, [44] found that the primary particle diameters can vary between 20 and 30 nm. Other authors such as Chen *et al.* [155], have estimated the average size of primary particles based on specific surface area measurements and report  $D_p$  values varying in the range 15 to 47 nm. Through TEM observations and

under fuel-lean conditions (C/O = 0.22), Kim et al. [45] observed soot particle with a fractal dimension of  $D_{\rm f} = 1.74 \pm 0.08$  and a  $D_{\rm p}$  between 10 and 12 nm. In contrast to methods based on simply observing TEM images or those requiring a soot density assumption, automated post processing methods are advantageous as they provide more statistically reliable data. The euclidean distance mapping-based scale analysis (EDM-SBS) algorithm proposed by Bescond et al. [95], is one of the available algorithms allowing such processing. Using such approach on TEM images of miniCAST soot, Bescond *et al.* [95] found a  $D_p$  varying between 18.3 and 24.4 nm. Despite the different analysis methods and image processing procedures used to extract soot morphological parameters, it would seem that the general trend is that under fuel-lean conditions, soot aggregates, produced using a propane fuel miniCAST, consist of primary particles with a diameter  $D_p \sim 10$  nm and which increases up to  $\sim 40$  nm under fuel-rich conditions. Table 2.2 gathers some morphological parameters reported in literature for diesel engines soot. Given this data, diesel engine soot may have primary particle diameter varying in the range 10 - 40 nm with a fractal dimension varying between 1.5 and 2.3 [107]. Consequently, soot aggregates generated by a miniCAST using propane can be considered similar to diesel engine ones from a morphological perspective.

Reference	Source	Fuel	$\overline{\mathrm{D}_\mathrm{p}}$ [nm]	$\mathbf{D}_{\mathrm{f}}$
Lee <i>et al.</i> [156]	2.4 L, single cylinder	Diesel	28.5 - 34.4	1.80 - 1.88
Lapuerta et al. [157]	2.2 L, 4-cylinder	Diesel	$\approx 25$	1.42 - 2.73
Li et al. [106]	5.79 L, 6-cylinder	Diesel	18 - 29	1.2 - 1.74
Agudelo et al. [158]	2-cylinder	Diesel	$\approx 30 \pm 8$	2.01
Ye et al. [159]	6.4 L, 8-cylinder	Diesel	17 - 33	1.4 - 2.2
Soriano et al. [160]	2.2 L, 4-cylinder	Diesel	24.32	2.5
Cadrazco et al. [161]	2.5 L, 4-cylinder	Diesel	22.74 - 41.74	1.63 - 2.27

 Table 2.2. Inter-comparison of morphological key parameters of soot aggregates of diesel engine exhaust reported in literature.

In addition, soot particles generated by such device (i.e., miniCAST) exhibited different nanostructure as one can observe from high resolution TEM images displayed in Figure 2.14. Here, it seems that under slightly fuel-lean condition (a) a graphitic appearance is observed, in comparison to rather amorphous one for soot produced under a fuel-rich condition (b). Recently, Lapuerta *et al.* [107] reviewed several aspects regarding soot particle generated from diesel engines and concluded that with an increasing engine load, soot aggregates nanostructure became more and more ordered. The review also highlights the effect induced by the change of fuel. It would seem that soot particles generated using bio-diesel have also more ordered nanostructure and smaller primary particle diameters than those obtained with diesel.



Figure 2.14. TEM Images of propane fuel miniCAST soot: (a) fuel-lean condition ( $\varphi = 0.943$ ) (b): fuel-rich condition ( $\varphi = 1.053$ ), from Malmborg *et al.* [49].

#### **Optical properties**

Regarding the optical properties of miniCAST soot particle, many research groups have been interested in the wavelength dependence of their absorption and/or scattering crosssections and how they are affected by soot aggregate size, morphology and chemical composition. Some have been particularly interested in the Ångström absorption exponent ( $\alpha$ ), also referred to as AAE, that describes the absorption spectral decay in the visible spectral range. As discussed in section 2.4, the scattering contribution decrease faster with the wavelength compared to the absorption one. So, at higher wavelengths ( $\lambda \geq 700$  nm), the scattering can be neglected and the absorption coefficient can be then described using a power law [162–164] of the form:

$$K_{ext} \approx K_{abs} \propto \lambda^{-\alpha}$$
 (2.44)

•  $\alpha$ : Ångström absorption exponent, also referred to as AAE coefficient ;

Figure 2.15 gathers  $\alpha$  values as a function of the overall equivalence ratio ( $\phi$ ) and C/O atomic ratio. The data indicates that this exponent increases from  $\sim 1$  up to values between 2.2 and 4, when moving from fuel-lean to fuel-rich conditions. When doing so, according to what it was previously shown in Figure 2.12, the OC/TC ratio increased from < 10 % up to OC/TC > 80 %.



Figure 2.15. Literature data [42, 45, 46, 150, 152, 154] on the Ångström ( $\alpha$ ) absorption exponent as a function of overall flame equivalence ratio ( $\varphi$ ), and C/O atomic ratio, for soot aggregates produced by CAST/miniCAST burners using propane. The gray line corresponds to the stoichiometric conditions (C/O = 0.3 or  $\varphi = 1$ ).

This correlation has been confirmed later on by Ess *et al.* [154] as shown in Figure 2.16.(d). In their study, soot aggregates generated over the C/O atomic ratio range  $\sim 0.2$  - 0.54 have been characterized in size as shown in Figure 2.16.(a). Their respective Ångström absorption exponent and EC/TC ratio have been measured and plotted as a function of their

geometric mean diameters (GMD) as summarized in Figures 2.16.(b) and 2.16.(c). This data shows that under fuel-rich conditions, particles of smaller size exhibiting very low EC contents have fairly high  $\alpha$ . On the other hand, for aggregates obtained under fuel-lean conditions which they managed to obtain with relatively small sizes (~ 50 nm), this exponent (i.e.,  $\alpha$ ) remains low around ~ 1.2. It seems that, the more soot aggregate contain organic compounds, the more  $\alpha$  is important, reflecting a strong wavelength dependence.



Figure 2.16. (a) Geometric mean diameter (GMD) (and associated uncertainties) of particle size distribution as a function of overall C/O ratio, with the gray dashed line at C/O = 0.3 marking overall stoichiometric conditions, correlation of (b) AAE, (c) EC/TC ratio with GMD of the number size, and (d) correlation of AAE with EC/TC ratio for particles generated with a diffusion flame distribution, from Ess *et al.* [154].

Other experimental studies have been interested in measuring the wavelength dependence of soot particles complex refractive index. As previously mentioned in section 2.4, such material-dependent parameters intervenes in the absorption and scattering function, E(m)and F(m). Knowledge of their wavelength variation allows accurate modeling of soot extinction coefficient. In literature, Dalzell *et al.* [165], Lee *et al.* [166], Habib *et al.* [167] and Chang *et al.* [168] have been the first to carry on such work providing wavelength variations of the complex refractive index, and from that of E(m) and F(m) over a wide spectral range (UV-VIS-NIR) as shown in Figure 2.17. Even though, these optical properties were determined for soot aggregates under different flame conditions and fuels (using mainly premixed flame), they still exhibit similarities particularly for the absorption function E(m).



Figure 2.17. Literature data on (a) absorption and (b) scattering functions as a function of the wavelength for soot particles emitted by miniCAST using propane, adapted from Yon *et al.* [37].

Later Yon *et al.* [37] compared the absorption and scattering functions obtained for a diesel flame soot particles with those of previously cited authors and observed a similar behavior as shown in Figure 2.17. Although these studies provide results which may be different, due to the different approaches and/or the different operating conditions, generally, it seems that the absorption function E(m), reaches a maximum around  $\lambda = 250$  nm and evolves towards an almost constant behavior -  $0.2 \leq E(m) \leq 0.4$  - for wavelengths between 600 and 1000 nm. Over this wavelength range, the scattering function F(m) also reaches a constant value around  $\sim 0.3$  but exhibit a greater spectral variation in the UV spectral range.



Figure 2.18. (a) Absorption and (b) scattering functions as a function of wavelength. Results are based on RDG-FA model, adapted from Bescond *et al.* [46].

In contrast, Bescond *et al.* [46] have been the first to report wavelength dependence of absorption and scattering functions for soot aggregates produced by miniCAST soot generator using propane. They observed, for instance, that these two functions have higher values for aggregates having a high organic fraction level, particularly in the UV spectral range as shown in Figure 2.18. On the other hand, for soot aggregates with a low organic fraction level a less notable wavelength dependence is observed. Moreover, over the near infrared spectral range, this trend is reversed. It would appear that soot with a high OC content has lower E(m)

#### In conclusion:

The extensive literature review presented in this section, shows that laboratory soot generators such as the miniCAST offer an outstanding advantage of generating, in a laboratory scale, soot aggregates in many aspects similar to those emitted by diesel engines. The use of those soot generators also offers the possibility of understanding how aggregate size, morphology, organic fraction and optical properties evolve and eventually depends from each other. Until now, only soot aggregates produced by miniCAST using propane have been extensively studied on those aspects. While this soot generator version is able to provide engine-like soot aggregates, it does not meet the need for evaluating PM characteristics when other fuels are used, particularly diesel or kerosene or even biofuels. So far, few studies have explored this area [55, 56, 169, 170]. For instance, in Mueller et al. [55] they focused the impact of the chemical composition of fuel additives on soot aggregates, while Ngo [56] and Berthier [169] PhD work focused mainly on studying the chemical composition of soot aggregates using Jet A-1 fuels. Overall, there seems to be a significant lack of information for soot aggregates characteristics using liquid fuels in such soot generators. Therefore, efforts must be made to provide a ground floor for the use of soot generators with liquid fuels such as diesel and Kerosene. The use of such experimental tools may also be expanded to the study of biofuels and investigate their impact on the generated PM in the future.

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# Chapter 3

# Experimental setup

Combustion exhaust emissions which contain PM and gaseous pollutants depend on various parameters inherent to combustion systems (internal combustion engine, gas turbine, etc): operating conditions, fuel properties and so on, which can be challenging to control and most of the times don't allow to modify systematically one pollutant at a time. If optical extinction coefficients are measured directly on a complex mixture containing particulate matter (PM) and other gaseous pollutants, elucidating the impact of exhaust physico-chemical properties on measured optical extinction coefficients will be difficult. This is why possessing appropriate tools to control each pollutant, with the possibility of varying PM characteristics, in a complex mixture is crucial to avoid such complexity. This is also important to produce repeatable exhaust characteristics for a consistent calibration, while avoiding associated costs of a real powertrain setup. Consequently, in this thesis a modular combustion bench schematized in Figure 3.1 is used as a source for synthetic exhaust gas mixture where gaseous pollutants concentrations and PM emissions can be controlled independently.



Figure 3.1. Schematic of the experimental exhaust bench and aerosol characterization setup.

This experimental setup allows studying gaseous pollutants and PM at desired mixing ratio and dilution rate. PM are generated by means of a miniCAST soot generator by burning a liquid fuel, while up to 6 different gas molecules can be injected using a sonimix gas calibrator. The  $\sim 30$  L/min exhaust flow exiting the soot generator is further diluted by an external high flow rate dilution system ( $\dot{m}_{air, max} = 160$  kg/h), while the exhaust vein is maintained at atmospheric pressure (1013 hPa) thanks to an open collector design. Gas and particulate phase produced by the soot generator are monitored online using a pegasor particle sensor, type-M (PPS-M, Pegasor, Oy) for aggregate number concentration monitoring, and a graphite 52M, model D (Envea) analyzer for total hydrocarbon content (THC) measurement. The exhaust is then sampled at 1.5 L/min and routed through a pre-treatment loop, where it can be filtered using a DIF.5K micro-fibers particle filter (Classic Filters) whose efficiency was evaluated at 99.994 % in the size range of 6 - 225 nm. The exhaust can also be thermally treated at 350 °C using a catalytic stripper, model CS-015 (Catalytic Instruments, GmbH) to separate only solid particles or sampled as it is (raw).

The resulting exhaust is then subject to several diagnostics to characterize some of its physico-chemical properties. This involves mass concentration measurement using a micro tunnel sampler, size distribution measurement using a scanning mobility particle sizer (SMPS) and morphology evaluation using electron microscopy imaging of collected aggregates. Furthermore, ex-situ gas chromatography - flame ionization detection (GC-FID) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are also performed to provide information on gas and particulate phase chemical composition. Finally, exhaust gases containing PM (raw, filtered or thermally treated) combined (or not) with gaseous pollutants (NO, NO<sub>2</sub> and NH<sub>3</sub>) are injected into an optical extinction cell to measure optical extinction coefficients.

The following sections detail the physical working principles of each of the sample pretreatment and analyzer equipment used. The procedures and setting choices are also laid out to achieve the best quality raw data.

### 3.1 Exhaust generation

#### Soot generator

In this work, a miniCAST, model 5102 D soot generator from Jing Ltd [141] that uses liquid fuels is used as a source to generate PM. Figure 3.2 illustrates the dual burner design where liquid fuel is preheated by a lower non-sooting  $C_3H_8/air$  heating flame (1) and burns in a diffusion type sooting flame (2) in the upper part of the burner.



Figure 3.2. Descriptive schematic of miniCAST, model 5102 D, burner for liquid fuels. The indicated parameters are key parameters to change aerosol properties.

The upper flame is fueled by two coaxially arranged vertical tubes carrying in the center a  $C_3H_8/air$  mixture and in the peripheral tube the liquid fuel. The lower flame (1) is fueled by a homogeneous mixture of 30 mL/min of  $C_3H_8$  and 300 mL/min of air and is used for preheating the liquid fuel routed through the annular space. The central tube is used to deliver a  $C_3H_8/air$  mixture (10 mL/min of  $C_3H_8$  with 20 mL/min of mixing air) to sustain the idle flame on the burner's top, which is the ignition source for the sooting flame that consumes the liquid fuel as shown in Figure 3.2. Upon each use, 30 minutes warm-up period is needed during which the burner runs under idle condition. During that time oxidation air flow rate is by default set to 3 L/min. Consequently, oxidation air provides enough oxygen for complete combustion of the heating flame. Once ready, mixing air and oxidation air flow rates can be tuned over 10 - 250 mL/min and 1 - 3 L/min ranges, respectively. By adding the desired liquid fuel flow rate, the idle flame on the top burner is replaced by a bright yellow sooting flame (2). Soot aggregates are then formed in the sooting flame (2) which is quenched using 7.5 L/min of N<sub>2</sub>, thus sending formed aggregates to the burner outlet. A subsequent dilution by 20 L/min of filtered air avoids excessive coagulation. The factory mass flow controller (e.g., mini-CORI-FLOW) for liquid fuel is limited to 70  $\mu$ L/min and was found to be a major source for flame instability. To improve test-to-test repeatability it was replaced with a Pharmacia syringe pump, model P-500, to deliver precise and constant liquid fuel flow allowing both a wider and stable operating range between 0 and 250  $\mu$ L/min.

It is worth mentioning that working with this miniCAST version required additional attention to achieve repeatable results. The burner needs to be disassembled and cleaned regularly to avoid long term soot production drifts. As a matter of fact, possible deposits of organic matter may occur in the annular space where liquid fuel is heated resulting in clogging/coking the liquid fuel pipe. Under such high temperature conditions, the liquid fuel is suspected to undergo pyrolysis before reaching the burner top. An electronic heating system might have eventually been a better choice for precise liquid fuel preheating and temperature regulation. On a practical note, it is recommended to drain the remaining liquid fuel inside the burner after each use and continuously monitor soot production in respect to a reference operating point. When a significant drift in soot production is observed a complete disassembly, cleaning and ultrasound bath of the burner's pipes are recommended.

#### Gas mixer

In order to accurately mimic vehicle exhaust, gaseous pollutants are injected using a sonimix gas mixer from LNI (Suissgas), model 7100 multi-gaz 6L. NO, NO<sub>2</sub> and NH<sub>3</sub> are added to create a complex and much realistic exhaust. The gas mixer shown in Figure 3.3 allows to prepare standard gas mixtures to calibrate gas monitors for instance. Thanks to multiple mass flow controllers, this apparatus provides a high flexibility allowing to combine up to 6 different gases within large flow rate ranges. The sonimix provides from 0.5 to 5 L/min of gas mixture at ambient temperature and pressure. For optimum accuracy, 30 minutes stabilization period is needed.



Figure 3.3. Sonimix gas mixer from LNI (Suissgas), model 7100 multi-gaz 6L.

In this work, a 900 and 4500 ppm NO, a 2000 ppm NO<sub>2</sub> and a 5000 ppm NH<sub>3</sub> gas cylinders were used to supply the 500 mL/min, 5 L/min, 5L/min and 50 mL/min mixer channels, respectively. The 900 and 4500 ppm NO gas cylinders contain in fact 40.6 ppm (i.e., 4.3 %) and 219 ppm (i.e., 4.7 %) of residual NO<sub>2</sub>, respectively. The gas mixer was operated at fixed flow mode using N<sub>2</sub> as a carrier gas and delivering 2 L/min of gas mixture. For experiments involving these gaseous pollutants or their mixtures only 0.5 L/min (out of the 2 L/min delivered) was added to 1 L/min combustion exhaust that could contain

PM produced by the soot generator or only air in case the later was under idle condition. Consequently, gaseous pollutants and combustion exhaust gases were additionally diluted by a factor of 3 and 1.5, respectively. As a results, NO, NO<sub>2</sub> and NH<sub>3</sub> were varied in the range 9 - 1113 ppm (with a residual NO<sub>2</sub> between 0 and 54 ppm), 7 - 482 ppm and 6 - 42 ppm, respectively. Finally, a 2.5 minutes injection period was respected when NO and/or NO<sub>2</sub> mixtures were injected (5 minutes if NH<sub>3</sub> was injected alone or with other pollutants) before acquiring optical extinction coefficients to ensure stabilized flow rates that were injected at 25 °C.

### 3.2 Exhaust pretreatment

For most experiments conducted in this work, as combustion exhaust left the burner, ~ 554 L/min (~ 19:1 dilution ratio) of dry filtered air at ambient temperature was added in the first external dilution stage as shown in Figure 3.1. The exhaust main vein is a 5 cm diameter pipe, therefore flow is turbulent ( $\text{Re} \approx 1.6 \times 10^4$ ). Consequently, turbulent mixing is the main mixing mechanism while effects of molecular diffusion play merely a secondary role [171]. So, prior to any sampling an entry length of  $L_{h,turbulent} = 1.359$  D Re<sup>1/4</sup> [172, 173] (with D the pipe's diameter) that is 0.8 m was respected to ensure homogeneous mixing. Exhaust was then sampled either as it is (untreated/raw), filtered to remove particles and allow to study combustion gas phase independently, or thermally treated using a catalytic stripper as shown in Figure 3.1. From now on, raw and thermally treated exhaust will be referred to as untreated and CS-treated, respectively.

#### Catalytic stripper

There are two main reasons behind the use of the catalytic stripper (CS) in this work. The first reason is to understand the impact of oxidizing vPM on the physico-chemical properties of combustion exhaust and how all of those affect optical extinction coefficient. The second reason is that emission thresholds set by the current regulations discussed in Chapter 1 concern only non-volatile PM (nvPM), and the use of the CS on miniCAST exhaust shall allow to access the ability of this burner to produce nvPM for calibration purposes.

In this work, a catalytic stripper, model CS-015 (Catalytic Instruments, GmbH) was used. When the exhaust passes through the CS, volatile and semi-volatile species are oxidized. In contrast to other heating treatment instruments such as thermodenuder, the CS offers the advantage of being maintenance-free and not requiring frequent replacement of the adsorbing substrate, hence facilitating the study of numerous operating conditions. To enable the oxidation process within the CS, a minimum of 5 % vol. oxygen is required. Given the high dilution ratios used in this work, this requirement is always met. Before exiting the CS, the exhaust is cooled to ambient temperature (25 °C) by an integrated heat exchanger. For efficient oxidation of vPM, the CS-015 model is designed for a nominal flow rate of 1.5 L/min, which corresponds to a residence time of ~ 0.2 s to 0.4 s [174]. Under such conditions, the device offers an oxidation efficiency > 99 % of both propane, and > 99.0 % of 30 nm tetracontane (CH<sub>3</sub>(CH<sub>2</sub>)<sub>38</sub>CH<sub>3</sub>) particles with an inlet concentration of  $1.0 \times 10^4 \text{ }\#/\text{cm}^3$  [175]. On the other hand, the major drawback of CS is particles loss within the device which is size dependent. In fact, the amount of particle that are able to cross the CS is impacted by the diffusion and thermophortic losses within it as shown in Figure 3.4.



Figure 3.4. Modeled solid particle penetration. In blue, losses due to diffusion only [176]. In red, losses including thermophoretic effects [177, 178]. Measurement data corresponds to a catalytic stripper, model CS-015, from Catalytic Instruments GmbH & Co.KG [175] application note CI-0009.

This Figure shows the solid particle penetration variation as a function of the mobility diameter (provided by the manufacturer) and indicates that at 100 nm only ~ 70 % (in number) of solid particles get to cross the CS. That is ~ 30 % of particle losses to be expected around 100 nm and decreases to 60 % particles losses at 10 nm. This solid particle penetration (P) is modeled by (3.1) (provided by the manufacturer [175]) as a function of the particle diameter (D<sub>p</sub>) where  $x_i$  are fitting parameters ( $x_1 = 0.19$ ,  $x_2 = 499$ ,  $x_3 = 0.925$ ,  $x_4 = 36.0$ , and  $x_5 = 0.670$ ).

$$P = \left(x_1 e^{-\frac{x_2}{D_p^2}} + x_3 e^{-\frac{x_4}{D_p^2}}\right) x_5$$
(3.1)

These solid particle penetrations were obtained for silver spherical particles [175]. As a result, these percentages might be expected to vary for soot aggregates due to there complex shape. Particles losses in the CS for soot aggregates generated with the miniCAST will be discussed in Chapter 5.

## 3.3 Mass, size and morphology diagnostics

Particulate matter (PM) mass and size are still today key characteristics to define the possible drawbacks on human health. PM mass measurement has long been a standard measurement for regulatory purposes as well as particulate number measurement. Carrying out such measurement for a laboratory-grade diesel exhaust aerosol, as it is attended for the mini-CAST soot generator used in this work, is valuable to identify the generator production range in respect to current regulatory thresholds and access its ability to be used as a calibration source. Accordingly, this section details the instrumentation used to evaluate mass concentrations, mobility-equivalent size distribution, and soot aggregate morphological properties. Exemplary results and post-processing of the data provided by these techniques are presented later in section 4.1 for several operating points.

#### Mass measurement

For PM mass measurement, PM deposit on borosilicate microfibers filters (Pallflex, Emfab) are carried out using an automated antistatic micro tunnel sampler. Before using the filters, they were first heated for 4 hours at 180 °C and left to cool over night at room temperature in a particle-free environment. Exhaust was then sampled at Q = 1.5 L/min over  $\Delta t = 10$  minutes period. Using a XP6 microbalance (Mettler Toledo,  $\pm 0.0004$  mg

repeatability) filters weights were measured prior to sampling and after 4 hours resting period during which they were stored in a particle-free environment at ambient temperature. Soot deposit mass  $\Delta m$  was then measured, and soot mass concentration  $C_s = \frac{\Delta m}{\Delta t \times Q}$  calculated. Figure 3.5 shows an example of such particulate matter deposit. Consequently,  $C_s$  is the total mass concentration containing both non-volatile PM (nvPM) and volatile PM (vPM).



Figure 3.5. Example of particulate matter deposit on borosilicate microfibers filters.

#### Scanning mobility particle sizer (SMPS)

A scanning mobility particle sizer (SMPS, TSI, Inc) was used that allows measuring submicron aerosol size distribution based on particles electrical mobility (see section 2.3). The apparatus model used here, combines an electrostatic classifier, model 3080, a long-differential mobility analyzer (L-DMA) column, model 3081, along with a X-ray neutralizer, model 3088, all shown in Figure 3.6 and a condensation particle counter (CPC), model 3775, displayed in Figure 3.8. Measuring an aerosol size distribution is a multi-stage process consisting of (i) particles preparation by limiting maximum particle size entering the device using an impactor, then give the sampled particles a known charge distribution using a neutralizer; (ii) particles classification: to classify particles based on their electrical mobility using the L-DMA column, and (iii) counting the particles number for each class using the CPC, thus deducing a size distribution.



Figure 3.6. Schematic of (a) the electrostatic classifier, model 3080 and (b) the impactor and showing (c) the X-ray neutralizer, model 3088, and (d) the long differential mobility analyzer (L-DMA) column, model 3081 from TSI Inc [179, 180].

At the electrostatic classifier's inlet, an impactor (Figure 3.6.(a)) is used to stop largest particles carrying multiple charges from being sampled. Particles with enough inertia are unable to follow flow streamlines within the impactor, therefore unable to cross it, while smallest particles following the streamlines pass through. A cut-point diameter,  $D_{50}$ , corresponding to the aerodynamic diameter starting from which 50 % of particles are impacted, can then be calculated as a function of aerosol flow rate and impactor nozzle size as follows:

$$D_{50} = \sqrt{\frac{9\pi Stk\mu W^3}{4\rho_p C_c Q}}$$
(3.2)

Where:

- D<sub>50</sub> : Particle cut-point diameter (cm, 50 % cut efficiency) ;
- Stk : Stokes number = 0.23;
- $\mu$  : Carrier gas dynamic viscosity [g/(cm.s)];
- W : Nozzle diameter [cm] ;
- $\rho_p$  : Particle density  $[g/cm^3]$ ;
- C<sub>c</sub>: Cunningham Slip Correction (see equation 2.11);
- Q : Aerosol flow rate  $[cm^3/s]$ ;

To chose an appropriate particle size range, three nozzle sizes are available, to which a flow rate range is recommended to be used, as shown in Table 3.1. In this work, the 0.071 cm nozzle size is used while operating at 1.5 L/min sampling flow rate. Under such conditions  $D_{50}$  is set to ~ 536 nm which means that only aggregates with an aerodynamic diameter below 536 will be possible to measure.

Table 3.1. Flow range for each impactor nozzle and their corresponding  $D_{50}$  cut-point diameter.

Flow Range $[L/min]$	Nozzle Size [cm]	$D_{50}$ [nm]
0.2 - 0.8	0.0457	850 - 320
0.3 - 1.0	0.0508	812 - 413
0.6 - 2.1	0.071	979 - 491

To have an accurate size measurement, particles charge distribution must be known. Within the L-DMA column, particles are separated according to their electrical mobility  $(Z_e)$ which is proportional to the number of charges on the particles and inversely proportional to particle's electrical mobility diameter  $(D_m)$  (see equation 2.14). This means that the charge distribution of the sampled particles has to be known to calculate the mobility from the electric field. To give the sampled particles a known charge distribution a X-ray neutralizer, model 3088, based on a low-energy (< 9.5 keV) soft X-ray source is used to generate high concentrations of ions with positive and negative polarity to ionize air molecules, creating nearly equal numbers of positive and negative charges. When the aerosol enters the neutralizer, air ions are attached to oppositely charged particles. Ions quickly interact with particles and "neutralize" excess charges. For a sample flow rate between 0.3 and 5 L/min, the neutralizer offers enough residence time to effectively induce a known charge distribution. Figure 3.7 displays such charge distributions as a function of the particles size, and show that the majority of the aerosol in charge equilibrium exists as singly charged particles. Yet, a fraction of the particles still exist with multiple charges. Using the device software, this charge distribution is eventually taken into account when returning a size distribution.



Figure 3.7. Fraction of total particle concentration that carries -6 to +6 elementary charges as a function of mobility diameter in nm, adapted from TSI Inc [179] (Table B-1).

The next step is separating particle that have the same  $Z_e$  using the L-DMA column. The column consists of two coaxial electrodes insulated from each another. The outer one is electrically grounded, while the inner one, called collector rod, is modulated at a negative electric potential of -10 kV to 0 kV to create an electrical field in the annular space between the two electrodes of variable strength. The polydisperse flow enters the L-DMA column from the top and flows in an axial direction as indicated in Figure 3.6. Meanwhile, a particlefree air flow, called sheath-air-flow, enters the L-DMA column as well, passes to an annular chamber, then through a fine mesh to generate a constant velocity laminar flow field all the way down through the classifier. The annular flow, containing the aerosol, is introduced into the classifier region and smoothly merged with sheath-air-flow as shown in Figure 3.6. Through the classifier region, particles are selected by a modulated equilibrium of electrostatic and aerodynamic forces. As introduced in sub-section 2.3, tuning the electric field (E) particles can be selected according to their Z<sub>e</sub>. The electric field causes positively charged particles to be attracted through the sheath air to the negatively charged collector rod. When deflected, particles end-up on the collector rod at a location that depends on particle's Z<sub>e</sub>, classifier flow rates, and classifier geometry. Particles with high electrical mobility (e.g. small mobility diameter experiencing lower aerodynamic force) are quickly deflected to the collector rod and precipitate at its upper portion, while particles with low electrical mobility (e.g. big mobility diameter experiencing higher aerodynamic force) are collected on the lower part of the collector rod. Consequently, only particles within a narrow range of electrical mobility are able to reach a small orifice located at the end of the column, therefore providing a near monodisperse aerosol. It is recommended to maintain a ratio of 10 between the sheath-air-flow and the polydispersed flow within the L-DMA column.

At the L-DMA column outlet, a quasi-monodisperse aerosol is then recovered and fed to the CPC shown in Figure 3.8 to measure the particle number/concentration for each class. The counting is based on the measurement of particles scattered light. The particles pass through a butanol saturator, heated at 39 °C, then cooled to 14 °C using a condenser therefore increasing particles size until they reach a detectable size hence provides sufficient scattering signal for the counting of each particle passing the optical sensor. The CPC, model 3775, used here is sensitive to particles in a size range of 4 nm to < 3  $\mu$ m and can measure a number concentration between 0 and 10<sup>7</sup> particle/cm<sup>3</sup>.



Figure 3.8. Condensation particle counter (CPC), model 3775 (TSI, Inc), from TSI Inc [181].

When the SMPS system is assembled a 1.5 L/min inlet flow rate, a 15 L/min sheath-airflow rate, and a 0.071 cm impactor nozzle diameter, are chosen respectively, resulting in aerosol size distribution in the range of 6 to 225 nm. The size scan time of the system is 120 s and requires stable aerosol generation over this period to produce smooth size distribution curves. The sampling flow rate is also compatible with the CS nominal 1.5 L/min flow rate. For all experiments, three consecutive soot particles size distribution measurements were systematically performed, providing statistics on soot particulate number (PN), mobility-equivalent geometric mean diameter  $D_{geo,m} = \exp((\sum_{i}^{k} N_{i} \ln(D_{m,i}))/PN)$  (with N<sub>i</sub> and  $D_{m,i}$  the number concentration and mobility diameter, respectively, of each class of size 'i'), and geometric standard deviation ( $\sigma_{geo,D_m}$ ) rendered by the device software. For all these experiments multicharged effects were corrected. Finally, soot particles mobility-equivalent size distribution measurements using SMPS system are visualized in "normalized" concentrations dN/dlogD<sub>m</sub>. This is done to be able to compare size distribution measurements with the ones reported in literature that might be measured using models with different size distribution resolutions resulting from a varying number of channels.

#### Pegasor Particle Sensor - type M (PPS-M)

The Pegasor particle sensor, type M (PPS-M, Pegasor, Oy) is one of the reference devices used in the automotive sector to monitor exhaust particulate number and/or mass concentration. This device offers a rapid (i.e., 1 Hz) measurement, making it a valuable tool to validate soot production stability throughout all experiments. This sensor operates by electrostatically charging particles passing through it. As charged particles leave the sensor a current is produced. Using this diffusion charging principle, the latter current, called escaping current, is measured by an electrometer then used to deduce particulate number and/or mass concentration [182, 183]. Figure 3.9 describes the PPS-M working principle. 12 L/min of clean compressed air are used to pump 6 L/min of sample gas into the sensor using Venturi effect. At the beginning of this process, compressed air flow is ionized using a corona discharge generated around a sharp tip at high voltage. Exhaust gas sample is then mixed with the ionized air where ions are transferred to particles through a random collisions process. Then, an ion trap, operated at 400 V, is used to remove the free ions left, while only the charged particles manage to exit the Farady cage (indicated in red dashed line in Figure 3.9). The escaping current  $I_n = I_{out}$  -  $I_{in}$  shown in Figure 3.9 generated by the flow of the charges carried by particles exiting the ion trap, is then measured.



Figure 3.9. Pegasor particle sensor, type M (PPS-M, Pegasor, Oy), adapter from Ntziachristos *et al.* [182].

To measure particulate number and/or mass concentrations, the sensor is pre-calibrated with respect to a diesel engine exhaust providing equation 3.3 and 3.4 to deduce these concentrations [183]. When the sensor is operated at high inlet flow rate -  $Q_{in} = 6 \text{ L/min}$  - and knowing that the PPS-M background signal is ~ 100 fA and its maximum range is  $6.82 \times 10^6$  fA, the sensor is able to measure particulate number and/or mass concentrations in the ranges  $5 \times 10^3$  to  $3.5 \times 10^8 \text{ \#/cm}^3$  and  $1 \text{ µg/m}^3$  to  $80 \text{ mg/m}^3$ , respectively.

Number 
$$[\#/cm^3] = I_n \frac{288}{Q_{in}(L/min)}$$
 (3.3)

Mass 
$$[mg/m^3] = I_n \frac{6.3 \times 10^{-5}}{Q_{in}(L/min)}$$
 (3.4)

During all experiments raw exhaust was routed to the PPS-M inlet by means of an antistatic heated sample line maintained at 180 °C, the sensor body was maintained at 250 °C, and the ion trap voltage was kept at 400 V same as in [183]. In this work, this sensor is used primarily to monitor soot particles production stability hence being installed after the first dilution stage and before sampling exhaust gases for other diagnostics as shown in Figure 3.1.

#### Electron microscopy imaging

Describing soot aggregates as spherical particles does not reflect their actual geometry. Such aggregates are in fact made of spheres that can be arranged in complex structures. One of the possible ways to acquire more information on how these particles are arranged is to observe them using electron microscopy. For these experiments, a second dilution stage (resulting in  $\sim 220:1$  total dilution ratio) located further down the line was deemed necessary to lower soot particles PN levels to avoid overloading the sampling media. This second dilution was done using an ejector diluter (Dekati, Ltd), operated using N<sub>2</sub> as a dilution gas, to sample 1.5 L/min from the exhaust to be compatible with both CS and SMPS nominal flow rate. Once the exhaust is diluted, soot particles were probed, downstream the second dilution stage, using a mini particle sampler (MPS, Ecomesure) as they cross a perforated Au holey carbon film, 400 mesh (Agar Scientific, Ltd), TEM grid located halfway the MPS tube as shown in Figure 3.10. This sampling was operated at 20 mL/min using a Gilian, GilAir Plus (Sensidyne, LP) pump positioned downstream the MPS tube while varying sampling duration time between 10 and 40 s.



Figure 3.10. Mini particle sampler (MPS, Ecomesure).

TEM grids were then analyzed, within 2 weeks' after their preparation, to acquire scanning transmission electron microscopy (STEM). This was done using a Nova Nano SEM 450 microscope operated with 30 kV acceleration voltage and using STEM II detector with bright field detection under immersion mode and 6  $\mu$ s scanning time. On average 20 STEM images (see Figure 3.11.(a)), each having a size of 1536  $\times$  1024 pixels, were acquired at fixed magnification ( $\times$  60.000), making the optical resolution of  $\sim$  1.378 nm/Pixel. These images were then processed to evaluate soot particles morphological key parameters following a methodology detailed in section 4.2.



Figure 3.11. Example of (a) STEM,(b) TEM and (c) HRTEM microscopy images of soot aggregates.

For a much more detailed characterization, both TEM (see Figure 3.11.(b)) and highresolution TEM (see Figure 3.11.(c)) images were acquired allowing the assessment of soot internal structure at a single monomer scale. This was done using JEM, either 2100F or F200, JEOL Ltd, microscopes operated with an acceleration voltage of either 200 or 80 kV, respectively. A lower acceleration voltage was deemed necessary, particularly for fuel-rich operating points, to help stabilize the specimen during the image acquisition process. The post processing of microscopy images is discussed later in section 4.2. Microscopy image acquisition were done with the help of Dr. Eric KOHLER (R05/IFPEN), Dr. Virgile ROUCHON (R05/IFPEN) and Hedwige PONCET (R10/IFPEN) to whom I am very grateful.

### 3.4 Chemical diagnostics

Combustion exhaust produced by the miniCAST burner consist of both gas and particulate phase. The goal here is to describe their chemical composition qualitatively and quantitatively as accurately as possible. Unfortunately, there is no single analysis technique able to draw the complete picture of exhaust chemical composition both qualitatively and quantitatively over the entire mass range. This means that one has to compose with analysis techniques limitations, and use their complementarity. As discussed in section 2.2, flame ionization detection (FID) is reliable for quantitative measurement of carbon containing species, reproducible and covers a wide mass range which makes it, in this case, suitable for the continuously monitoring of the gas phase organic content. That is why choice was made to use the FID-based graphite 52M, model D (Envea), analyzer for total hydrocarbon content (THC) monitoring. This is complemented by the use of ex-situ gas chromatography - FID (GC-FID) to help quantitatively identify gas phase species more likely to contain low-mass (i.e., m/z < 150) species. As for high-mass range (i.e.,  $m/z \ge 150$ ) choice was made to use ex-situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) to qualitatively describe both gas and particulate phases organic content. Accordingly, this section details the here mentioned instrumentation used to characterize PM chemical composition.

#### Flame ionization detection (FID)

To monitor combustion exhaust gas phase production, a graphite 52M, model D (Envea), analyzer was used. A portion of 7 L/min of exhaust gases sampled after the first dilution stage - placed next to the PPS-M sampling point - are routed to the analyzer over an entirely heated sampling system. The dual flame ionization detector (FID) system is shown in Figure 3.12. The analyzer is composed of a dual burner supplied with a  $H_2/He$  (35 mL/min) mixture and air (800 mL/min). The decomposition of hydrocarbons at high temperature in the cone of the burner's flame provides an ionizing current whose intensity is directly proportional to the number of carbon atoms of the analyzed sample. This signal is then processed and converted to a total hydrocarbons (THC) content. The analyzer model used here is equipped with two FIDs (i.e., channels) as shown in Figure 3.12. The first one is equipped with a non-Methane Hydrocarbons converter and measures CH<sub>4</sub> content only, while the second one measures all THC content. Consequently, one can deduce the non-Methane Hydrocarbons (n-MHC) part by subtraction (THC -  $CH_4$ ). The analyzer was set to a sensitivity to measure hydrocarbon content over the range of 0 - 1000 ppmC range. Here, ppmC refers to units of parts per million carbon, which means that 1 ppm of methane is equivalent to 1 ppmC, while 1 ppm propane corresponds to 3 ppmC.



Figure 3.12. Schematic of graphite 52M, model D (Envea), showing a sample pathway towards two FID analyzers (one for a  $CH_4$  channel and the other one for THC channel), adapter from Envea [184].

#### Gas chromatography - Flame ionization detection (GC-FID)

Under fuel rich conditions, exhaust gases are expected to contain a significant amount of gas phase containing some light absorbing molecular species that may affect the optical extinction diagnostic. Consequently to shed the light on this matter and evaluate the catalytic stripper ability to oxidize exhaust gas phase, a heated pump (to avoid condensation inside the pump circuit) was used to inflate a 3 L Tedlar bags (at a flow rate of 1.5 L/min) with exhaust gas phase after being filtered. Samples were then analyzed ex-situ few minutes after sampling by gas chromatography - flame ionization detection (GC-FID). Three analytical lines, distributed on two chromatographs, model Varian 450-GC, were used to characterize gas phase organic content, particularly low-mass PAHs. The first line was dedicated to methane measurement, while the other two were used to detect other gaseous species in the range  $C_2$ - $C_6$  and  $C_6$ - $C_{12}$ , respectively, as schematized in Figure 3.13.



Figure 3.13. Schematics of GC-FID setup combining two GCs, model Varian 450-GC.

Portions of gas phase samples were taken and sent simultaneously to the different analytical lines. Helium was used as carrier gas, the pressure at the head of the columns was kept constant throughout the analysis, and detection was performed using FIDs (using a  $H_2/air$ flame using 30 mL/min of  $H_2$  and 300 mL/min of air). For the methane line, 2 mL gas sample passed through a  $CH_4$  sampling loop before going through a Porapak Q column (2)  $m \times 1/8$ ). As for the two other analytical lines, analysis was performed on 180 mL of gas phase samples, first trapped in a sample preconcentration trap (SPT) injector, which is a liquid nitrogen cooled trap, then thermodesorbed at 175 °C and sent in a Al203 column (50  $m \times 0.53 \text{ mm}$ , film thickness 5  $\mu$ m) for C<sub>2</sub>-C<sub>6</sub> range and in a DB1 column (60 m  $\times 0.53 \text{ mm}$ , film thickness  $1.5 \ \mu\text{m}$ ) for C<sub>6</sub>-C<sub>12</sub> range. Analysis was done through a temperature gradient sequence programmed, for the  $C_2$ - $C_6$  line, from - 15 °C to 10 °C at a 2 °C/min rate then from 10 °C to 40 °C at a 5 °C/min rate then up to 200 °C at a 10 °C/min rate. As for the  $C_{6}$ - $C_{12}$  analytical line, temperature was set for 10 minutes at 10 °C then was set to reach 200 °C with a 10 °C/min rate. Detected peaks in each chromatograph (Example shown in Figure 3.14), were related to a proper compound through response factors determined via a calibration procedure operated beforehand. Gas chromatography analysis was done with the help of Pascal HAYRALT and Dr. Perrine COLOGON (R05/IFPEN) to whom I am very grateful.



Figure 3.14. Example of gas chromatograms showing detected species peaks (Response of an FID) as a function retention time using (a) the  $CH_4$  column, (b) the  $C_2$ - $C_6$  column, and the  $C_6$ - $C_{12}$  column. Closer look into the red rectangle areas are given in the right of each chromatograph.

#### Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

The previous diagnostic focuses on characterizing exhaust gas phase. Yet, it is limited to identify molecular species containing 12 carbon atoms at the uppermost which corresponds typically to a low mass range (i.e., m/z < 150). To identify high mass absorbing molecular species in both gas and particulate phase, ex-situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) was also performed. This diagnostic was used to characterize the exhaust organic content, particularly high-mass (i.e., m/z > 150) PAHs adsorbed on soot's surface. Using this technique, the composition at the surface of a solid sample is analyzed by sputtering it with a focused primary ions beam as schematized in Figure 3.15. The sputtering produces a variety of "secondary" species which are then extracted and identified using time-of-flight mass spectrometer (ToF-MS). When a cluster of primary ions bombards a selected region of interest (ROI) at the sample surface, the resulting energy transfer induces a collision cascade among the solid top layer's atoms. Atoms and molecules are then sputtered, a small percentage of which exits in ionized state forming a "secondary ion" plume. The resulting ions from the sputtered region are then extracted by electrical lenses and sent into a ToF-MS in order to be identified. Primary  $Bi_3^+$  ions, generated using a liquid metal ion gun (LMIG), were used since they proved to be efficient for organic compounds, as harsh fragmentation of molecules is avoided using these clusters as primary ions [93].



Figure 3.15. Schematic diagram of the SIMS working principle, from Irimiea [93].

PM deposit samples were prepared using an impactor system made, as shown in Figure 3.16.(a), of a metallic tube placed vertically and whose outlet faces a single side polished (with an average of all surface peaks and valleys Ra of  $\approx 0.2$  to 0.5 µm) Ti 10 × 10 mm<sup>2</sup> (1 mm thickness) wafer (Figure 3.16.(b)). Using a vacuum pump, soot particles are sucked through the sampling line, go through the impactor tube, and impact the wafer placed on the center of a metallic mesh. Consequently, soot particles impact and stick on the wafer's surface while the rest of the flow is redirected to the exhaust through the metallic mesh. Ideally, if PM is uniformly deposited on the wafer surface, ions having the same mass will have approximately the same time-of-flight. However, in presence of a rough surface, ions that have the same mass coming from the sputtered region may have to travel slightly different trajectories, and therefore will have slightly different times of flight which may result in loss of mass accuracy and mass resolution. To keep the impact of the sample topography to a minimum, sampling time was varied between 20 and 120 minutes as a function of the burner's soot production and the global dilution ratio to ensure that only the necessary amount of PM deposit is extracted on the polished Ti wafer surface.

The vacuum pump flow rate was set to 1.5 L/min to be compatible with the CS nominal flow rate when dealing with CS-treated samples. To avoid any possible contamination organic, Ti wafers were heated for 2 hours at 450 °C then etched with a phosphoric

acid solution prior to sampling and stored in glass petri dishes (see Figure 3.16.(c)). Once the deposit is done, wafers were put back in their storage boxes and analyzed in the week following their preparation. Care was taken to limit contamination that might originates from the sampling line itself. As a matter of fact, preliminary test revealed a significant contamination from fluorinated organic compounds. As it turned out, this contamination originated from the piezo igniter used to ignite the miniCAST's burner and whose insulation cable was located near the flame. Once the cable was denuded and the sampling line was cleaned with ethanol, the contamination disappeared almost entirely.



Figure 3.16. Sampling system for ToF-SIMS analysis showing the impactor system (a), a Ti wafer after being sampled (b) then stored (c).

The ToF-SIMS 5 (ION-TOF, GmbH) instrument of the Regional Platform of Surface Analysis (Institut Chevreul, Univ. Lille), was used to acquire mass spectra. Prepared samples were inserted on a sample's holder (see Figure 3.17.(a)) and put inside the instrument's loading chamber (see Figure 3.17.(f)). Once closed and put under  $\sim 10^{-7}$  mbar residual pressure, a valve separating the latter chamber and an analysis chamber (see Figure 3.17.(c)) is opened to insert the sample's holder on a mobile stage (see Figure 3.17.(b)) using a magnetic cane. The mobile stage offers five degrees of freedom allowing to analyze a variety of samples, including those having a rough surface. To avoid sample-to-sample contamination, samples were analyzed separately, even though the sample's holder allows analyzing several samples at once. The analysis chamber is also designed to avoid any interaction between primary and/or secondary ion beams with the gas present in the analysis chamber or any deposition from the sputtered layer over the sample surface.



Figure 3.17. ToF-SIMS 5 instrument, ION-TOF GmbH, at the Regional Platform of Surface Analysis (Institut Chevreul, Univ. Lille) showing (a) sample holder, (b) mobile stage, (c) analysis chamber, (d) primary ion source, (e) ToF analyzer and (f) loading chamber.

Within an analysis area of 500  $\mu$ m × 500  $\mu$ m, primary Bi<sub>3</sub><sup>+</sup> ions beam at 25 keV was used targeting various locations of samples deposit. The instrument was operated under static mode (estimated ion dose of ~ 10<sup>11</sup> ions/cm<sup>2</sup>) to analyze only the deposit's upper layers of matter (1-2 nm). Under such conditions ToF-SIMS mass spectra similar to the one shown in Figure 3.18.(a) were acquired. Figure 3.18.(b) show a closer look of a mass spectrum where each peak corresponds to an ionized species.



Figure 3.18. (a) Example of a ToF-SIMS mass spectrum and (b) a closer look into the red rectangle area showing some peaks.

The way particulate matter is deposited might provide information on the gas phase and soot particles. In fact, previous studies used a similar sampling system, and suggest that the central deposit include both condensable gas phase and soot particles while its peripheral area, that sometimes form a hallow includes only condensable gas phase [185]. Accordingly, for each sample, 6 ROIs were acquired, 3 targeting the central deposit (i.e., on spot) as shown in Figure 3.16 and 3 others targeting the peripheral area around it (i.e., off spot) as shown in Figure 3.16. ToF-SIMS mas spectra acquisition was done with the help of Nicolas NUNS (Univ-Lille) to whom I am very grateful. The post processing of SIMS spectra is discussed later in section 4.4.

## 3.5 Light extinction measurement

Optical extinction coefficients are measured over the 202 - 1026 nm optical range with a 1.5 nm resolution. This was done using a continuous deuterium-halogen light source, model DH 2000 (Ocean Optics, Inc) that emits, in the UV-VIS-NIR range, a spectrum on one side of the tube while the transmitted spectrum was analyzed on the opposite end with a Q-mini, Wide UV (Broadcom, Inc) spectrometer as shown in Figure 3.19.



Figure 3.19. Schematic of the optical extinction cell.

The spectrometer has a 20  $\mu$ m entrance slit, 300 lines/mm transmission grating, 50 mm focal length and uses a 2500-pixel linear CCD sensor. The single pass extinction cell is built of stainless-steel tube (L = 1 m long, 4 mm inner diameter) while 1.5 L/min of exhaust gases passed through it. Optical connection on both ends were done using a 10 mm focal length collimating lens, model 74-UV (Ocean optics, Inc), and a QP-450-0.25-XSR optical fiber (Ocean Optics, Inc) whose relative transmission are both shown in Figure 3.20 and Figure 3.21, respectively.



Figure 3.20. Relative transmission of collimating lens 74-UV (Ocean optics, Inc).



Figure 3.21. Relative transmission of QP-450-0.25-XSR optical fiber (Ocean Optics, Inc).

The intensity of transmitted light crossing exhaust  $(I_t(\lambda))$  (see Figure 3.22) was recorded with 40 ms exposure time and was performed simultaneously with SMPS size distribution measurements. The choice of 40 ms exposure time lays within the linear behavior of the spectrometers as shown in Figure 3.22.(a). During post-processing, the spectra were averaged over ~ 400 s which is the time needed to acquire 3 consecutive size distribution measurements. A reference baseline  $(I_0(\lambda))$  was measured on a reference air flow (see Figure 3.22.(b)), before and after each recording at the sample outlet end. The optical extinction coefficient was calculated using Beer-Lambert law [134] (3.5).

$$K_{ext} = -\frac{1}{L} ln \left( \frac{I_t(\lambda)}{I_0(\lambda)} \right)$$
(3.5)



Figure 3.22. Qmini Wide UV spectrometer count as a function of exposure time at variable wavelengths.



Figure 3.23. (a) example of a reference baseline  $(I_0(\lambda))$  and the intensity of transmitted light crossing exhaust  $(I_t(\lambda))$  and (b) the corresponding extinction curve.

Figure 3.23.(a) also shows that boundary effect at the lowest (200 nm) and the highest (1000 nm) wavelength might occur, thus interpreting measured optical spectra at those wavelength should be done carefully. On the other hand, care was taken to first avoid contamination from one operating condition to another by cleaning the optical cell upon running each operating point and second avoid lens fouling issues by regularly cleaning the optical cell.

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# Chapter 4

# Methodologies

The research work conducted in this thesis aims at (i) developing a measurement procedure based on optical extinction to monitor PM produced by a combustion system and (ii) shedding light on the links that may exist between PM chemical composition and its measured optical extinction coefficient. To meet this challenge, the choice was made to work with a miniCAST burner that uses liquid fuels to generate PM. So, first it is required to identify stable and reproducible operating conditions representative of various combustion conditions that could be encountered for other similar combustion systems. Second, the generated PM need to be described from different facets such as size distribution, morphology and mass concentration to document the miniCAST soot generator capabilities. Some of this data, such as aggregates size distributions and mass concentrations do not need much post-processing before it can be interpreted. However, soot aggregates morphological key parameters are not directly measured. They are deduced from the analysis of electron microscopy images. This is also the case for ToF-SIMS mass spectra that holds part of the information on PM chemical composition. Consequently for electron microscopy images and ToF-SIMS mass spectra one need to follow specific methodologies to retrieve meaningful information.

Accordingly, this chapter is structured in four parts. The first part introduces the burner's operating conditions. This involves the burner settings, the investigated liquid fuels and sampling conditions. At this point, soot production stability and repeatability are discussed. The second part of this chapter addresses the sampling protocol and methodology in acquiring and post-processing electron microscopy images to evaluate soot aggregates morphology. The third part proposes to challenge the RDG-FA model to reproduce measured extinction coefficients over the visible and near infrared range by addressing the impact of accounting for (or not) total scattering contribution and variations in soot optical properties. On that basis, a methodology for soot volume fraction retrieval from measured extinction coefficients is introduced where soot optical properties variations with the wavelength and from one operating point to another is accounted for. Finally, the fourth part of this chapter describes the methodology developed during this work for an efficient ToF-SIMS mass spectra post-processing.

# 4.1 Operating conditions, soot production stability and repeatability

#### 4.1.1 MiniCAST burner settings

The miniCAST used in this work allows the adjustment of three parameters which are the liquid fuel flow rate (from 0 to 250  $\mu$ L/min), the oxidation air flow rate (from 1 to 3 L/min) and the mixing air flow rate (from 10 to 250 mL/min). Consequently, a map of 34 operating points summarized in Table 4.1 was designed to cover, in terms of flame overall equivalence ratio, a wide operating range (i.e., 0.104 - 1.673) ( $\phi$ ) (Appendix A shows how it is calculated). Here, the inscription 'OP' is used to refer to a burner operating point. Experiments were conducted using two fuels with different compositions. As a reference,

diesel B7 (which is a standard fuel for light duty vehicles) is used for most experiments and dodecane is used to provide the scientific community with experimental data for the purpose of numerical simulations. When using dodecane, only six OPs (OP2, OP9, OP17, OP27, OP32 and OP34 as highlighted in Table 4.1) were studied. Although only some of the diagnostics described in Chapter 3 were performed on all 34 OPs, focus is brought upon only these six strategically chosen OPs to run all diagnostics when using diesel B7, as they are quasi-evenly spaced within the explored operating range.

Table 4.1. Liquid fuel miniCAST burner operation point settings and resulting flame overall equivalence ratio ( $\varphi$ ). OPs in bold are those for which all diagnostics presented in Chapter 3 were performed.

Operating point (OP)	Liquid fuel flow rate	Mixing air flow rate	Oxidation air flow rate	Internal dilution air flow rate	Flame overall equivalence ratio
point (OI)	$[\mu L/min]$	$[\mathrm{mL}/\mathrm{min}]$	[L/min]	[L/min]	φ
	Diesel B7				
OP1	16.67	10	2	20	0.104
OP2	50	100	3	<b>20</b>	0.187
OP3	50	50	3	20	0.192
OP4	50	100	2.8	20	0.202
OP5	50	100	2.6	20	0.220
OP6	50	100	2.4	20	0.241
OP7	50	100	2.2	20	0.268
OP8	50	150	2	20	0.294
OP9	50	100	<b>2</b>	<b>20</b>	0.300
OP10	50	10	2	20	0.313
OP11	50	100	1.8	20	0.342
OP12	50	10	1.6	20	0.418
OP13	100	100	3	20	0.373
OP14	100	150	2	20	0.588
OP15	100	100	2	20	0.601
OP16	150	100	3	20	0.560
OP17	100	10	<b>2</b>	20	0.626
OP18	200	150	3	20	0.735
OP19	200	100	3	20	0.747
OP20	200	10	3	20	0.768
OP21	200	100	2.8	20	0.808
OP22	150	150	2	20	0.881
OP23	150	100	2	20	0.901
OP24	200	100	2.6	20	0.880
OP25	150	10	2	20	0.939
OP26	200	100	2.4	20	0.966
<b>OP27</b>	<b>250</b>	100	3	<b>20</b>	0.933
OP28	200	100	2.2	20	1.071
OP29	200	150	2	20	1.175
OP30	200	100	2	20	1.201
OP31	200	10	2	20	1.251
<b>OP32</b>	<b>250</b>	100	2	<b>20</b>	1.502
OP33	200	10	1.6	20	1.673
OP34	<b>250</b>	10	<b>2</b>	<b>20</b>	1.564
	Dodecane				
OP2	50	100	3	20	0.172
OP9	50	100	2	20	0.277
OP17	100	10	2	20	0.578
OP27	250	100	3	20	0.862
OP32	250	100	2	20	1.387
<b>OP34</b>	250	10	2	20	1.445

### 4.1.2 Sampling conditions

As explained in Chapter 3, miniCAST's exhaust was diluted using either one external dilution stage or two external dilutions stages, the use of which may alter soot aggregates size distribution properties through coagulation and agglomeration processes within the sampling line. Exhaust dilution is mainly performed to lower soot aggregates concentrations so it does not saturate measuring instruments such as SMPS and PPS-M. Figure 4.1 describes soot aggregates size distribution parameters (PN, D<sub>geo,m</sub> and  $\sigma_{geo,D_m}$ ) measured by the SMPS for an untreated exhaust obtained under OP9 as a function of the global dilution ratio (volumetric ratio). Each sub-figure shows, two data sets. The first data set with global dilution ratios < 30 corresponds to the case where only the first external dilution stage was varied, while the rest of the data points corresponds to the case where both the first and second external dilutions stages were used. It is worth reminding that the second external dilution stage imposes a fixed dilution ratio (~ 11: 1) and that for both data sets variation in the global dilution ratio was obtained by varying the amount of added air using the first external dilution stage.



Figure 4.1. Impact of dilution over soot aggregates (a) number (PN), (b) mobility – equivalent geometric mean diameter (D<sub>geo,m</sub>) and (c) geometric standard deviation for untreated exhaust obtained under OP9 using diesel B7.

Looking at Figure 4.1.(a), one can see that PN decreased almost proportionally to the imposed global dilution ratio, using either the first external dilution stage or both the first and second external dilutions stages. Figure 4.1.(b) shows that increasing the global dilution ratio by a factor of ~ 10 resulted in shifting OP9's  $D_{geo,m}$  towards the lower size by ~ 9.4 nm (-12 %) while its  $\sigma_{geo,D_m}$  increased by 0.04 (+ ~ 3 %) as shown in Figure 4.1.(c). Looking at Figure 4.2 it can be observed that the dilution process did not significantly change the shape of OP9's aggregate size distribution. As a result, the choice was made to carry out all experiments at the same global dilution ratio of ~ 19 :1. If soot aggregates coagulation along the sampling line occurs, this is not a problem as long as all diagnostics are performed at approximately the same location downstream the sampling line.



Figure 4.2. Aggregate size distributions for variable dilution ratio under OP9 for untreated (raw) exhaust using diesel B7. The dashed curve correspond to the dilution ratio of  $\sim 19:1$ .

#### 4.1.3 MiniCAST stability over time

Conducting experiments on a soot containing exhaust requires that properties of soot aggregates size distribution (PN,  $D_{\text{geo},m}$  and  $\sigma_{\text{geo},D_m}$ ) generated under a given condition remain stable for extended time periods. This is very important if such soot generator has to be used as reference for calibrating other instruments. After integrating the soot generator into the experimental setup, improving the control of mass flow controllers and the burner stability, the miniCAST was operated over 6 months (April 2021 - September (2021) for both short (< 20 minutes) and long (up to 90 minutes) periods of time. Soot production stability was monitored using the PPS-M which was installed after the first external dilution stage and before preparing exhaust for diagnostics as shown previously in Figure 3.1. Soot PN was found to be rather stable within 10 % coefficient of variation (i.e., coefficient of variation (x) = mean(x)/std(x)) of soot PN for most experiments and across the tested OPs, except OP2 where this coefficient was found to be close to 20 %as shown in Figure 4.3. Soot PN was slightly less stable (coefficient of variation increased to  $\sim 20$  %) in June 2021 when the soot generator showed signs of clogging issues. After being cleaned (as explained in section 3.1) soot production stability returned to the level described before.


Figure 4.3. Coefficient of variation of soot PN (coefficient of variation (x) = mean(x)/std(x)). PN was estimated using PPS-M.

# 4.1.4 Soot production repeatability

The measurement of soot aggregates size distributions (for OP2, OP9, OP17, OP27, OP32 and OP34) over 6 months testing period (April 2021- September 2021) showed that soot production remained stable. To minimize possible variations, the choice was made to consider the fuel-lean operating point OP9 as a reference condition to be tested each time the burner was used and any significant drift form OP9's D<sub>geo,m</sub> triggered a cleaning procedure of the burner. As a result, soot aggregates PN, D<sub>geo,m</sub> and  $\sigma_{\text{geo,D_m}}$  varied at worse of 30 % (e.g., OP2), 17 % (e.g., OP2) and 5 % (e.g., OP2) and at best of 4 % (e.g., OP27), 7 % (e.g., OP34) and 0.5 % (e.g., OP34), respectively as shown in Figure 4.4. Moreover, these same levels of repeatability were observed even when a catalytic stripper (CS) was used to thermally treat the exhaust (see Appendix Figure C.1). Overall, these variations are satisfying in respect to what have being reported for the miniCAST using propane where PN varied by a factor of 2 over a similar evaluation period according to Moore *et al.* [44]. Indeed, several factors can contribute to such variations such as soot accumulation in the sampling lines or valves or clogging/coking issues in the burner particularly when liquid fuels are used.

# In conclusion :

▶ Using the miniCAST soot generator, supplied with diesel B7, stable and reproductible soot production over a wide range of operating conditions has been demonstrated to be possible.



Figure 4.4. (a, b, c): SMPS measured aggregates number (PN), mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ) and geometric standard deviation ( $\sigma_{geo,D_m}$ ) as function of flame overall equivalence ratio ( $\varphi$ ) for OP2, OP9, OP17, OP27, OP32 and OP34 operating points over time for untreated (raw) exhaust. (d, e, f) Their respective deviations to the mean curve accounts for repeatability over 5 months. Uncertainties account for 3 size distributions measured consecutively. Data not corrected for dilution (~ 19:1).

# 4.2 Soot morphological analysis

Quantifying soot morphological parameters is valuable for many reasons, first of which is understanding how varying combustion conditions affect these parameters for a laboratory soot generator that uses liquid fuels and whether it can be considered as a reliable source to mimic engine-like soot aggregates from a morphological point of view. Beyond that, those parameters can be used, in addition to aggregate size distribution, to interpret measured optical extinction coefficients as discussed later in subsection 5.1.3 and evaluate soot volume fraction as discussed later in subsection 5.2.1. Acquiring such data can also give some insights upon how fuel composition may or may not impact soot aggregate morphology. One may also wonder how does the catalytic stripper affects aggregates morphology and nanostructure. Such study comes both with experimental and numerical challenges. Consequently, this section details the methodology followed to evaluate soot aggregate morphological parameters based on electron microscopy imaging techniques. Accordingly, a preliminary investigation was carried out to determine optimal sampling conditions for a selection of operating conditions. Then electron microscopy images were acquired as explained in section 3.3 gathering scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HRTEM) images. Finally, STEM images are post processed to determine morphological parameters (i.e., mean primary particle diameter  $(\overline{D_p})$ , fractal dimension  $(D_f)$ , fractal pre-factor  $(k_f)$  and primary particles geometric standard deviation  $(\sigma_{\text{geo},D_p})$ ).

#### 4.2.1 Sampling conditions

Probing soot aggregates for electron microscopy imaging can be challenging because one must determine optimal sampling conditions to accommodate with soot PN variability. Conducting these experiments was done using a second dilution stage that allowed lowering soot PN therefore avoiding TEM grids overload. To help decide on sampling times, a preliminary investigation was conducted where soot aggregates produced under OP9 and OP27 - since they almost cover the lower and upper bounds of PN variation range - were probed under variable sampling times (10, 30 and 60 seconds) as summarized in Table 4.2. Untreated exhaust diluted at  $\sim 220:1$  were sampled at 20 mL/min using a Gilian, GilAir Plus (Sensidyne, LP) pump positioned downstream the MPS tube.

Operating point (OP)	Condition	$\begin{array}{l} \textbf{Sampling flow} \\ \textbf{rate} \; [mL/min] \end{array}$	Sampling time [s]	Global dilution ratio
Diesel B7				
OP9	Untreated	20	10	220:1
OP9	Untreated	20	30	220:1
OP9	Untreated	20	60	220:1
OP27	Untreated	20	10	220:1
OP27	Untreated	20	30	220:1
OP27	Untreated	20	60	220:1
Blank (under idle)	Untreated	20	60	220:1

Table 4.2. Soot aggregates sampling conditions for the preliminary investigation. Soot deposits weredone on Au holey carbon film (300 mesh) TEM grids.



Figure 4.5. Scanning electron microscopy (SEM) images of representative miniCAST soot aggregates deposited on Au holey carbon film (300 mesh) TEM grids, using diesel B7 for untreated exhaust under (a, b, c) OP9 and (d, e, f) OP27 for (a, d) 10-seconds, (b, e) 30-seconds and (c, f) 60-seconds.

64

OP9

OP27

Scanning electron microscopy (SEM) observations shown in Figure 4.5 were acquired using a SEM Crossbeam 350 (Zeiss, GmbH) microscope, operated with an acceleration voltage of either 15, 25, or 30 kV with bright field detection using an aSTEM detector. These observations show that soot deposits were homogeneous within each sample and that no significant overload was observed. SEM observations also indicate that as sampling time increased, more particles are captured by TEM grids and that more particles are captured under OP27 compared to OP9 for similar sampling times which is coherent with the fact that under OP27 - at constant dilution ratio - more particles are generated compared to OP9 (see Figure 4.5.(a)). Additionally, a blank sample was prepared last as shown in Figure 4.6. The corresponding TEM grid seemed clean compared to loaded ones although some particles are still observed in few regions of the grid. However their distribution is absolutely not homogeneous which leads to believe that such contamination is minor. As for optimal sampling times, it seemed that a proper amount of aggregate deposits was obtained at 30seconds and 10-seconds for OP9 and OP27, respectively. Combustion exhaust being sampled well after being produced in the burner's flame and under high dilution, it is assumed that aggregate morphological parameters are invariant in respect to the dilution process as as suggested by Ouf et al. [186].



Figure 4.6. Scanning electron microscopy (SEM) image of the blank sample sampled for 60 seconds.

Consequently, sampling times summarized in Table 4.3 were determined considering soot PN for each of the selected operating points/conditions. This testing matrix has been chosen in order to evaluate the impact over soot morphology and internal structure, first of miniCAST's operating points (i.e., combustion conditions), second that of using a catalytic stripper and third that of fuel composition variation. According to the experimental protocol detailed in section 3.3, STEM, TEM and HRTEM images were acquired. The following subsections will focus on using STEM images to extract soot morphological parameters.

Operating point (OP)	Condition	$\begin{array}{l} \mathbf{Sampling \ flow} \\ \mathbf{rate} \ [\mathrm{mL/min}] \end{array}$	Sampling time [s]	Global dilution ratio
Diesel B7				
OP2	Untreated	20	40	220:1
OP9	Untreated	20	30	220:1
OP17	Untreated	20	15	220:1
OP27	Untreated	20	10	220:1
OP32	Untreated	20	10	220:1
OP27	Untreated	20	10	220:1
OP9	CS-treated	20	40	220:1
OP27	CS-treated	20	20	220:1
OP34	CS-treated	20	15	220:1
Dodecane				
OP9	Untreated	20	30	220:1
OP27	Untreated	20	10	220:1
OP27	Untreated	20	10	220:1

 Table 4.3.
 miniCAST setting and exhaust sampling conditions for STEM, TEM and HRTEM electron microscopy imaging diagnostics.

# 4.2.2 STEM images analysis

Retrieving aggregate morphological parameters from electron microscopy images is a challenging task for many reasons, first of which is the sampling media made of a carbon film that makes it difficult to get aggregates with enough contrast with the background and second, resulting from the sampling protocol itself that uses MPS tube (see section 3.4), where perforated TEM grids are needed, in contrast to thermophoretic sampling that are usually used [36, 37, 187, 188] to probe soot aggregates in a flame using filled TEM grids instead. Consequently, this making it even more difficult as the background is not restricted to the carbon film itself, but could also be void as shown in Figure 4.7. The main goal of this subsection is to retrieve aggregate morphological parameters from STEM microscopy images. This was achieved following four major post processing steps as summarized in Figure 4.7.



Figure 4.7. STEM images post processing steps.

This post processing begins, by segmenting raw STEM images into single binary aggregates. To overcome background-related issues, the choice was made to use a semi-automated method (i.e., SLIDER method [189]) allowing the user to intervene, when necessary, to help indicate an aggregate border. Then, a second post processing (i.e., EDM-SBS [95]) was performed on each single aggregate providing information (i.e., S(D) functions so-called EDM-SBS functions) encompassing scales encountered in each single aggregate. That same information was then interpreted to evaluate soot aggregates mean primary particle diameters  $(\overline{D_p})$  and geometric standard deviation  $(\sigma_{\text{geo},D_p})$  following an approach proposed by Bescond *et al.* [95]. Finally, a fractal analysis was conducted in order to evaluate both fractal dimension  $(D_f)$  and fractal prefactor  $(k_f)$ . The following paragraphs will therefore detail each of these steps, explaining the hypotheses that were made and discussing related uncertainties.

#### 4.2.2.1 Segmentation process

Considering the nature of STEM images acquired in this work, automated segmentation methods proved to be inefficient due to difficulties in distinguishing aggregates from the background. Consequently, segmentation was done using a largely-manual method, wherein the threshold is adjusted with a SLIDER in a Graphical User Interface (GUI) [189]. This method offered the possibility of adjusting a threshold on small regions in each image. The segmentation process is illustrated on an example in Figure 4.8, where the SLIDER method is applied on raw STEM images of aggregates obtained under OP9 and OP34 for an untreated exhaust using diesel B7 (see Figures 4.8.(a)), thus indicating each aggregate contour (see Figures 4.8.(b)) after SLIDER method was applied. All truncated aggregates were systematically discarded. Rendered binary images resulting from the determined contours of each single aggregate were then generated (see Figures 4.8.(c)), where aggregates are shown in white. Then, each aggregate was identified, isolated and inverted (see Figures 4.8.(d)). The uncertainty of determining an aggregate projected surface was calculated based on the edge pixels [189]. Accordingly, if one considers an average error of 2 pixels on the border, which is equivalent to adding or subtracting twice the perimeter from the overall area, then the percent error in the area would be 1-(A  $\pm$  2P)/A where P is the number of perimeter pixels and A the total number of pixels considered in each aggregate [189]. Consequently, when the image quality allowed it, care was taken to keep that uncertainty as low as possible. An overview of segmentation process for all studied conditions is given in Appendix D.



Figure 4.8. Segmentation process showing examples of (a) raw STEM images; (b) aggregates contours obtained using SLIDER method [189]; (c) the corresponding binary images; and (d) isolated aggregates after being inverted.

On average 20 STEM images were processed per configuration. As each image contained more than 5 aggregates, on average more than 150 single aggregate per configuration were successfully retrieved with a satisfying error on aggregate area of at best ~ 7 % and at worse ~ 11 %, except for OP34 for which that error was evaluated to ~ 16 % as summarized in Table 4.4. In respect to similar studies from literature [95, 189], this was considered to be sufficient enough for a statistically representative result. However, not all studied configurations were conclusive. This is particularly the case of OP9 and OP27 operating points in the case of using dodecane for an untreated exhaust, for which STEM images quality was judged insufficient to retrieve isolated aggregates with reasonable error (< 16 %).

Fuel					Diesel E	87				Dodecane
Condition			Unt	reated			0	CS-treat	ed	Untreated
Operating point (OP)	OP2	OP9	OP17	OP27	OP32	OP34	OP9	OP27	OP34	OP34
Number of extracted aggregates	139	198	156	179	138	164	141	229	164	145
Error on aggregate area [%]	$\pm 10$	$\pm 11$	$\pm 7$	$\pm 8$	$\pm 8$	$\pm 7$	$\pm 9$	$\pm 8$	$\pm 9$	$\pm 16$

 Table 4.4. Number of considered aggregates for each of the studied configurations and error estimation on aggregates area determination using the SLIDER semi-automated method [189]

# 4.2.2.2 EDM-SBS process

The following processing step consist of applying Euclidian Distance Mapping-Surface Based Scale (EDM-SBS) method proposed by Bescond *et al.* [95]. This approach consists of applying series of image transformations, where each single aggregate area (S) is progressively eroded. Consequently, eroded surface areas may be computed as a function of the erosion level (k). The EDM-SBS then consists of studying the dependence of the eroded surface area to erosion magnitude. Figure 4.9 shows a summary of these image transformations applied on the blue and red aggregates in Figures 4.8.(d).



Figure 4.9. EDM-SBS protocol [95] applied on two aggregates corresponding to studied configurations indicated left of each row. The protocol consists of taking a binary image of an isolated aggregate (a), whose area is  $S_{k=0}$ , inverting it (b) and getting its corresponding Euclidean distance map (EDM) (c). The process continues through a loop over 'k' gray levels of the EDM image and applying a threshold at level 'k' to get an eroded surface hence image (d), inverting it to get image (e) reapplying an EDM calculation to get image (f) and reapplying a threshold at level 'k' - this is equivalent to a dilatation of the previous eroded surface - hence getting image (g), whose area is  $S_k$ . Images (d), (e), (f) and (g) show the example of level k = 10.

During this process, each single aggregate binary image goes through multiple transformations beginning with computing its initial surface area  $S_{k=0}$  corresponding to the black area of Figures 4.9.(a). This image is first inverted as shown in Figures 4.9.(b), therefore allowing to render its corresponding distance map as shown in Figures 4.9.(c). The latter is a level of gray image representing the smallest distance to the border within the aggregate. The protocols continue through a loop over 'k' gray levels, where each time a threshold at that 'k' level is applied on its corresponding distance map image. This results in an eroded surface, for instance at k = 10 as shown in Figures 4.9.(d). The resulting images is then inverted before reapplying the same process (i.e., EDM calculation and thresholding at same 'k' level) once more. Comparing Figures 4.9.(g), corresponding to an "opening" operation at k = 10 and Figures 4.9.(a) for both aggregates, one can clearly see that at k = 10 the first aggregate obtained surface is more altered, indicating that for the first aggregate most of the image structure have smaller scales compared to the second aggregate. This shall be verified considering all aggregates for each of the studied conditions. As mentioned before, EDM-SBS approach consists of studying the dependence of  $S_k$  as a function of the scale 2k+1 [95]. Knowing that the image resolution is ~ 0.725 pixels/nm, it is then possible to deduce a surface S(D) at each scale diameter (D) using the following conversions :

$$D = \frac{(2k+1)}{\text{Resolution}} \quad ; \quad S = \frac{N_{\text{pixel}}}{\text{Resolution}^2} \tag{4.1}$$

Figure 4.10.(a) displays S(D) function obtained when EDM-SBS protocol was applied on the second aggregate of Figure 4.9 (under OP34). As the same process was applied on all 164 aggregates obtained under the same condition, one can deduce a normalized mean EDM-SBS function (S(D)/S(0)) at each scale diameter (D) as shown in Figure 4.10.(b).



Figure 4.10. Representation of (a) EDM-SBS function considering one aggregate and (b) the normalized mean EDM-SBS function over N = 164 aggregates, for OP34 operating point in the case of using diesel B7 for untreated exhaust.

The EDM-SBS process described before was then applied to the rest of the investigated configurations resulting in normalized mean EDM-SBS function (S(D)/S(0)) similar to the one displayed in Figure 4.10.(b). The following subsection will focus on using these curves to define a geometric mean primary particle diameter and a standard geometric deviation describing primary particles size distributions.

#### 4.2.2.3 Normalized mean EDM-SBS function interpretation

Normalized mean EDM-SBS functions were obtained for all studied conditions, it is now proposed to focus on studying the dependence of these functions in respect to the scale diameter (D). In their work, [95] proposed three approaches. The first one considers that aggregates are made up of polydisperse spheres with no overlapping. In this case, an analytical expression can be obtained allowing to express the mean EDM-SBS function as follows:

$$\frac{S(D)}{S(0)} = 1 - \frac{\int_{-\infty}^{D} D^2 f(D) dD}{\int_{-\infty}^{+\infty} D^2 f(D) dD}$$

$$f(D) = D \times e^{-\frac{1}{2} \left(\frac{\ln(D) - \ln(Dgeo, p)}{\ln(\sigma_{geo}, D_p)}\right)^2}$$
(4.2)

However, as highlighted by Bescond *et al.* [95] soot aggregates may have different shapes, potentially with a significant amount of overlapping/necking between individual monomers.

Unfortunately, there is no model describing S(D)/S(0) decrease while accounting for these variations. Hence approaches consisting in calibrating S(D)/S(0) functions against controlled soot. To do so, Bescond *et al.* [95] proposed first a virtual aggregate based calibration considering first aggregates with spheres in point contact. Considering the case of a lognormal size distribution, obtained S(D)/S(0) were observed to behave similarly (i.e., curves superimposed when S(D)/S(0) > 0.2) when plotted against  $X = (\ln(D)-\ln(D_{geo,D}))/\ln(\sigma_{geo,D_p})$ . This led the authors to propose the following analytical law:

$$\frac{S(D)}{S(0)} = \frac{1}{2} \left[ 1 + \operatorname{erf}\left(\frac{\frac{\ln(D) - \ln(D_{\text{geo}, p})}{\ln(\sigma_{\text{geo}, D_p})} - a}{\sqrt{2}b}\right) \right]; \quad a = 1.3887; \quad b = -1.0277 \quad (4.3)$$

Nevertheless, when overlapping/necking effects were taken into account, S(D)/S(0) functions were no longer superimposed and were observed to decrease both quickly and at much higher scale diameter. Therefore, interpreting S(D)/S(0) curves with the model of (4.3) will probably overestimate the modal diameter and the standard deviation of the agglomerates [95]. Consequently, interpreting S(D)/S(0) would be more consistent considering a calibration against realistic soot. Hence the third approach, consisting of manually determining primary particles size distributions on the basis of which the following sigmoid law model was proposed:

$$\frac{\mathrm{S(D)}}{\mathrm{S(0)}} = \left(1 + \exp\left(\frac{\frac{\mathrm{ln(D)} - \mathrm{ln(D_{geo, p})}}{\mathrm{ln}(\sigma_{geo, D_{p}})} - \beta}{\Omega}\right)\right)^{-1}$$

$$\Omega = 0.80 \pm 0.03$$

$$\beta = 1.90 \pm 0.03$$
(4.4)

The calibration process proposed by Bescond *et al.* [95] consisted of finding  $\beta$  and  $\Omega$  coefficients of (4.4) knowing  $D_{\text{geo},p}$  and  $\sigma_{\text{geo},D_p}$  determined manually. Then,  $\beta$  and  $\Omega$  obtained values allow to evaluate  $D_{\text{geo},p}$  and  $\sigma_{\text{geo},D_p}$  for a giving S(D)/S(0) curve. In Bescond *et al.* [95], using TEM observations, 2496 and 441 primary particles were extracted manually for aeronautics and ethylene soot aggregates, respectively, using Image J software and used to build primary particles size distribution histograms. These histograms were then fitted with a lognormal pdf to find  $D_{\text{geo},p}$  and  $\sigma_{\text{geo},D_p}$  that were used to fit their corresponding S(D)/S(0) curve and eventually evaluated  $\beta$  and  $\Omega$  at 1.90  $\pm$  0.03 and 0.80  $\pm$  0.03, respectively.



Figure 4.11. Sigmoid law variation in respect to (a)  $\beta$  and (b)  $\Omega$  variations.

Being aware that the resulting histograms depend on the number of circles considered and on the operator, we will proceed in a similar manner. However, before proceeding with this approach one may wonder how does  $\beta$  and  $\Omega$  coefficients impact the sigmoid law and what physical parameters they are impacting? Figure 4.11.(a) and Figure 4.11.(b) highlight that impact.

For a given  $D_{\text{geo,p}}$  and  $\sigma_{\text{geo,Dp}}$ , one can see that as  $\beta$  increases, S(D)/S(0) decrease occurs at a higher scale diameter. This means that a lower  $\beta$  will underestimate  $D_{\text{geo,p}}$ . On the other hand (always for a given  $D_{\text{geo,p}}$  and  $\sigma_{\text{geo,Dp}}$ ) increasing  $\Omega$  results in less pronounced slope of S(D)/S(0), therefore impacting the estimation of  $\sigma_{\text{geo,Dp}}$ . To find accurate  $\beta$  and  $\Omega$ coefficients, a calibration procedure was conducted considering the case of OP34 operating point using diesel B7 for an untreated exhaust since it presented the lowest error on aggregate area. For this condition, 506 primary particles were determined manually from STEM images - using Image J software - allowing to build the primary particles size distribution of Figure 4.12.(a). Fitting this size distribution with a lognormal pdf rendered  $D_{\text{geo,p}} = 39.97$  nm and  $\sigma_{\text{geo,Dp}} = 1.38$ . Fitting its corresponding S(D)/S(0) curve with a sigmoid law (4.4) assuming  $\Omega = 0.80$  and  $\beta = 1.90$  as proposed by Bescond *et al.* [95] rendered the blue curve in Figure 4.12.(b),  $D_{\text{geo,p}} = 48.38 \pm 0.26$  nm and  $\sigma_{\text{geo,Dp}} = 1.295 \pm 0.004$ . Besides the fact that this fit is not optimal,  $D_{\text{geo,p}}$  was found to be overestimated in respect to STEM analysis data but also in respect to TEM observations (presented later in section 5.1.2).



Figure 4.12. (a) Manual determination of primary size distribution considering 506 primary particles for OP34 operating point in the case of using diesel B7 for untreated exhaust; (b) normalized mean EDM-SBS function fit.

As discussed before,  $D_{\text{geo},p}$  overestimation is probably due to a lower value of  $\beta$ . Consequently, both  $\beta$  and  $\Omega$  coefficients were reevaluated considering the manually determined size distribution shown in Figure 4.12.(a). This resulted in  $\Omega = 0.6699 \pm 0.009$  and  $\beta = 2.1636 \pm 0.012$ . All given uncertainties correspond to a 95 % confidence interval of the fitting sigmoid function. Fitting S(D)/S(0) curve once again with these reevaluated coefficients resulted in a more accurate fit as shows the green curve in Figure 4.12.(b) with evaluated  $D_{\text{geo},p} = 39.18 \pm 0.19$  nm and  $\sigma_{\text{geo},D_p} = 1.394 \pm 0.003$ . As such, results of the calibration conducted herein were used for the rest of the studied conditions summarized in Table 4.5.

Fuel	Condition	Operating point (OP)	D <sub>geo,p</sub> [nm]	$\sigma_{geo,D_p}$
Diesel B7	Untreated	OP2	$22.29\pm0.37$	$1.518 \pm 0.012$
Diesel B7	Untreated	OP9	$17.99\pm0.37$	$1.580 \pm 0.015$
Diesel B7	Untreated	OP17	$34.38\pm0.31$	$1.497\pm0.007$
Diesel B7	Untreated	OP27	$35.19\pm0.21$	$1.431\pm0.004$
Diesel B7	Untreated	OP32	$34.42\pm0.35$	$1.425\pm0.007$
Diesel B7	Untreated	OP34	$39.18 \pm 0.19$	$1.394 \pm 0.003$
Diesel B7	CS-treated	OP9	$19.70\pm0.34$	$1.567 \pm 0.013$
Diesel B7	CS-treated	OP27	$34.47 \pm 0.27$	$1.377 \pm 0.005$
Diesel B7	CS-treated	OP34	$35.20\pm0.26$	$1.394 \pm 0.005$
Dodecane	Untreated	OP34	$25.26\pm0.53$	$1.521 \pm 0.016$

**Table 4.5.** Soot mean primary particle diameters,  $D_{\text{geo},p}$  and geometric standard deviation  $\sigma_{\text{geo},D_p}$  extracted from STEM images. All uncertainties correspond to 95 % confidence interval of the fitting procedure using the sigmoid law.

Corresponding normalized mean EDM-SBS curves are shown in Figure 4.13.(a). Here, data corresponding to STEM images analysis are shown in symbols while the sigmoid law fit is plotted in straight lines. This Figure show that studied conditions exhibit different mean primary diameters as the decrease of S(D)/S(0) functions occurs much latter for fuel-rich (i.e., OP32 and OP34) operating points compared to fuel-lean ones (i.e., OP2, OP9, OP17 and OP27) considering raw (i.e., untreated) exhaust using diesel B7 data set. Consequently,  $D_{\text{geo},p}$  was observed to increase from 17.99 nm up to 39.18 nm when the miniCAST was tuned from fuel-lean to fuel-rich conditions. On the other hand,  $\sigma_{\text{geo},D_p}$ , was observed to decrease from fuel-lean to fuel-rich conditions - except for OP2 - thus varying from 1.580 down to 1.394.



Figure 4.13. Normalized mean EDM-SBS functions for all studied configurations, (a) against scale diameter D and (b) against  $X = (\ln(D) - \ln(D_{geo, D_{D}}))/\ln(\sigma_{geo, D_{D}})$ .

As for Figure 4.13.(b), displaying normalized mean EDM-SBS functions against  $X = (\ln(D) - \ln(D_{geo,p}))/\ln(\sigma_{geo,D_p})$ , it shows that whatever the studied configuration, all curves are superimposed, leading to believe, as suggested by Bescond *et al.* [95], that after size normalization, these soot are morphologically similar, in terms of their fractal dimension  $(D_f)$  and fractal prefactor  $(k_f)$ , despite their different aggregate size distributions. This assumption will be investigated in the next paragraph.

#### 4.2.2.4 Fractal analysis

After determining the diameters of soot primary particles, it is proposed in this subsection to evaluate the remaining parameters describing soot aggregates morphology which are the fractal dimension  $(D_f)$  and the fractal prefactor  $(k_f)$ . In order to evaluate these two parameters, two laws are used. The first one is the fractal law (4.5) expressing the number of primary particles per aggregate  $(N_p)$  as a function of the aggregate gyration diameter  $(D_g)$  and the diameter of soot primary particles  $(D_p)$ .

$$N_{p} = k_{f} \left(\frac{D_{g}}{D_{p}}\right)^{D_{f}}$$

$$(4.5)$$

In the previous subsection, primary particles were considered polydisperse. For the sake of simplicity, primary particles are from now on considered monodisperse with a mean primary particle diameter  $\overline{D_p} \approx D_{\text{geo},p}$ . On the other hand, evaluating  $D_f$  and  $k_f$  requires another equation. In previous works Samson *et al.* [190] and Köylü *et al.* [191] suggested to link the number of primary particles per aggregate (N<sub>p</sub>) to aggregates projected area. As such, the following expression was proposed:

$$N_{p} = k_{a} \left(\frac{A_{a}}{A_{p}}\right)^{\alpha}$$
(4.6)

- k<sub>a</sub>: Prefactor projected area ;
- A<sub>a</sub>: Aggregate projected area ;
- A<sub>p</sub>: Primary particle projected area  $(\pi D_p^2/4)$ ;
- α: Projected area exponent ;

Following Bescond *et al.* [95] approach, using (4.6) by (i) assuming  $k_a = 1.155$  and  $\alpha = 1.095$  as suggested by Köylü *et al.* [191] and Sorensen *et al.* [192], (ii) computing gyration diameter (D<sub>g</sub>) using L/D<sub>g</sub> = 1.49 correlation as proposed by Köylü *et al.* [191] (L being the projected maximum length of an aggregate) which is very close to the values of 1.48 used by Yon *et al.* [37] and of 1.50 used by Brasil *et al.* [193] and (iii) constraining the problem with  $k_f \propto ((D_f + 2)/D_f)^{D_f/2}$  as suggested by Sorensen *et al.* [192], both D<sub>f</sub> and  $k_f$  were evaluated by means of a least-square minimization algorithm.



Figure 4.14. Evolution of number of primary particles per aggregate (N<sub>p</sub>) as a function of D<sub>g</sub>/D<sub>p</sub> ratio based on EDM-SBS analysis for (a) OP9 and (b) OP34 cases using diesel B7 for untreated exhaust.

Accordingly, Figure 4.14 above shows fractal analysis results for (a) OP9 and (b) OP34 operating points using diesel B7 for an untreated exhaust. As this Figure shows, care was taken to consider a wide range of aggregate sizes for each case and the fitting procedure was applied accounting only for data points with  $N_p > 5$ . With such log-log representation  $D_f$  and  $k_f$  can easily be linked to the slope and intercept of each of the cloud points. Table 4.6 recapitulates evaluated  $D_f$  and  $k_f$  values for all studied configurations. The rest of fractal law fitting data is made available in Appendix E.

**Table 4.6.** Fractal dimension  $(D_f)$  and fractal prefactor  $(k_f)$  evaluation combing fractal law analysis<br/>and STEM images data.

Fuel				-	Diesel E	37			Dodecane	
Condition			Unt	reated			0	CS-treat	ed	Untreated
Operating point (OP)	OP2	OP9	OP17	OP27	OP32	OP34	OP9	OP27	OP34	OP34
D <sub>f</sub> k <sub>f</sub>	$1.839 \\ 1.967$	$1.805 \\ 1.960$	1.941 1.988	$1.831 \\ 1.966$	$1.862 \\ 1.972$	$1.844 \\ 1.968$	$1.849 \\ 1.970$	$1.790 \\ 1.957$	$1.834 \\ 1.966$	$1.920 \\ 1.984$

# In conclusion :

- ► Key parameters (D<sub>geo,p</sub>, σ<sub>geo,D<sub>p</sub></sub>, D<sub>f</sub> and k<sub>f</sub>) describing soot aggregates morphology were evaluated under various operating conditions.
- ▶ This challenging task was accomplished through a careful selection of sampling conditions avoiding TEM grids overload and by combining methodologies for microscopy images post processing (e.g., segmentation [189] and EDM-SBS [95] processes).
- ▶ This allowed to overcome images background related issues and provides enough aggregates (> 150 per configuration) and accurately retrieve those key parameters via a real-soot calibration approach.

# 4.3 Evaluating soot volume fraction from optical extinction coefficient

One of the goals of this thesis is to propose a procedure to evaluate soot volume fraction  $(f_v)$  from measured optical extinction coefficient  $(K_{ext})$  for a combustion exhaust. This can be challenging since  $K_{ext}$  may hold information on other compounds (other than soot) that might affect the light attenuation process. Also, soot aggregates not only absorb light but also scatter it. Soot optical properties also play a significant role in the way how soot aggregate absorb and scatter light. So, any proposed procedure should account for these aspects and/or find the circumstances under which their impact is either insignificant or constant. Therefore, this section is structured in three parts where (i) absorbing gas phase (if found) contribution to  $K_{ext}$  is examined (ii) optical extinction coefficients are modeled in the framework of the RDG-FA theory to finally assess the impact of accounting for (or not) total scattering contribution to  $K_{ext}$  and (iii) variations in soot optical properties are taken into account. On that basis, a wavelength range is identified within which  $f_v$  can be estimated relying on  $K_{ext}$  measurement while using an empirical model that accounts for soot optical properties wavelength variation.

In this work, optical extinction coefficients ( $K_{ext}$ ) are measured over a wavelength range between 200 nm and 1000 nm using a one-meter long optical cell. In a light extinction cell through which combustion exhaust circulates, light attenuation can occur either due to absorbed light from absorbing molecular species and/or small particles (soot in this instance) that might also scattered light or a combination of these phenomena occurring all at once. Thus,  $K_{ext}$  (4.7) is written as the contribution of soot aggregates extinction coefficient ( $K_{ext, soot}$ ), which is the sum of soot aggregates absorption coefficient ( $K_{abs, soot}$ ) and total scattering coefficient ( $K_{sca, soot}$ ) plus the sum of absorption coefficients of all absorbing molecular species ( $K_{abs,i}$ ) that the exhaust might contain.

$$K_{ext} = \underbrace{K_{abs,soot} + K_{sca,soot}}_{K_{ext,soot}} + \sum_{i} K_{abs,i}$$
(4.7)

# 4.3.1 Absorbing gas phase contribution

When measuring light attenuation in-situ across a flame, absorption from PAHs and condensed species are expected to be responsible for a significant part in the extinction coefficient, particularly at small wavelengths [194, 195]. Above 532 nm it is suggested that PAHs are less likely to absorb light [196–198]. Even though light extinction measurements carried out in this work were performed far from the flame, such an impact can still be expected since these measurements are performed between 200 nm and 1000 nm. Figure 4.15 displays examples of measured K<sub>ext</sub> for an untreated exhaust obtained under (a) OP9 and (b) OP27 while using diesel B7. Here, one can see that in both cases  $K_{ext}$  exhibit some absorption peaks over the UV range (wavelength below 400 nm) suggesting that the exhaust contains absorbing species other than soot aggregates. In this case, those absorbing species are either part of soot aggregates or exist in the gas phase.



Figure 4.15. Optical extinction coefficients (K<sub>ext</sub>) for an untreated (raw) exhaust obtained under (a) OP9 and (b) OP27 while using diesel B7.

To evaluate how much light attenuation is due to absorbing species in the gas phase, a high efficiency particle filter was used and  $\sum_{i} K_{abs,i}$  were measured as shown in Figure 4.16. These measurements show that miniCAST's exhaust does contain a light absorbing gas phase that survived all along the sampling line at ambient temperature. Also,  $\sum_{i} K_{abs,i}$ is more significant under OP27 than OP9, one can expect that this gas phase contains a higher concentration of light absorbing species under OP27 compared to OP9. It can also be observed that the noticeable absorption peaks seen in Figure 4.15 most probably come from this gas phase, but what these measurements most importantly demonstrate is that this gas phase only absorbs UV light and that  $K_{ext}$  above 400 nm is, in this case, solely due to soot aggregates and to what they might be deposited on their surface externally. Consequently, one can deduce  $K_{ext}$ , soot =  $K_{ext} - \sum_{i} K_{abs,i}$ . In this work,  $\sum_{i} K_{abs,i}$  measurements were done only for a selection of operating conditions (e.g., untreated exhaust obtained under OP2, OP9, OP17, OP27, OP32 and OP34 using either diesel B7 or dodecane). Until mentioned otherwise, the gas phase contribution ( $\sum_{i} K_{abs,i}$ ) to  $K_{ext}$  is systematically removed for those operating conditions. For the rest of investigated OPs, it is assumed that above 400 nm  $K_{ext} \approx K_{ext,soot}$ . Since the impact of absorbing gas phase has been identified it is proposed to focus the attention on optical extinction coefficients measured between 400 nm and 1000 nm and use the RDG-FA model to examine the impact of total scattering and soot optical properties on  $K_{ext,soot}$ .



Figure 4.16. Optical absorption coefficients of all absorbing molecular species  $(\sum_i K_{abs,i})$  measured using a particle filter for untreated (raw) exhaust obtained under (a) OP9 and (b) OP27 while using diesel B7.

# 4.3.2 Total scattering contribution

K<sub>ext,soot</sub> is the sum of soot absorption coefficient (K<sub>abs,soot</sub>) and total scattering coefficient (K<sub>sca,soot</sub>) (4.8). Since the goal is to evaluate soot volume fraction (f<sub>v</sub>) which is proportional to K<sub>abs,soot</sub>, the question is under what circumstances K<sub>sca,soot</sub> can be neglected and if not how much it contributes to K<sub>ext,soot</sub>. With  $\overline{D_p} \sim 17$  nm Yon *et al.* [37] reported a contribution of total scattering in extinction of ~ 7 % at  $\lambda = 370$  nm. Similarly, Migliorini *et al.* [36] estimated that the maximum contribution for total scattering can reach up to 8 % at  $\lambda = 450$  nm and drops for higher wavelengths. As  $\overline{D_p}$  increases this contribution is expected to increase furthermore.

$$\begin{split} \mathrm{K}_{ext,soot} &= \mathrm{K}_{abs,soot} &+ \mathrm{K}_{sca,soot} \\ &= \frac{\pi^2 \overline{\mathrm{D}_p}^3 \mathrm{PN}}{\lambda} \mathrm{E}(\mathrm{m}) \int_0^\infty \mathrm{N}_p \mathrm{n}(\mathrm{D}) \mathrm{d}\mathrm{D} + \frac{2\pi^5 \overline{\mathrm{D}_p}^6 \mathrm{PN}}{3\lambda^4} \mathrm{F}(\mathrm{m}) \int_0^\infty \mathrm{N}_p^2 \mathrm{g}(\mathrm{D},\lambda,\mathrm{D}_f) \mathrm{n}(\mathrm{D}) \mathrm{d}\mathrm{D} \\ &= \underbrace{\frac{6\pi \mathrm{E}(\mathrm{m})}{\lambda} \mathrm{f}_v}_{absorption} + \underbrace{\frac{2\pi^5 \overline{\mathrm{D}_p}^6 \mathrm{PN}}{3\lambda^4} \mathrm{F}(\mathrm{m}) \int_0^\infty \mathrm{N}_p^2 \mathrm{g}(\mathrm{D},\lambda,\mathrm{D}_f) \mathrm{n}(\mathrm{D}) \mathrm{d}\mathrm{D} \\ \end{split}$$
(4.8)

According to the RDG-FA model (4.8), it is expected for  $K_{sca,soot}$  to vary as  $\lambda^{-4}$  thus decreasing much faster with the wavelength compared to  $K_{abs,soot}$ . So, if  $K_{sca,soot}$  is insignificant, then  $K_{ext,soot} \approx K_{abs,soot}$  and would vary as  $\lambda^{-1}$  with E(m) constant. This is valid as long as soot aggregates verify the Rayleigh approximation [137] :  $x_p = \pi \overline{D_p} / \lambda \ll 1$ . Under OP9 and OP27,  $\overline{D_p}$  were evaluated to ~ 18 nm and ~ 35 nm, respectively which means that at

400 nm,  $x_p = 0.14$  and 0.27 for OP9 and OP27, respectively. Under such conditions, neglecting total scattering contribution might be judged inconsistent. Moreover, Figures 4.17.(a,b) show measured K<sub>ext,soot</sub> under OP9 and OP27 and their fit with a power law of the form  $\lambda^{-\alpha}$ . Both extinction coefficients are found to deviate from  $\lambda^{-1}$ . As a matter of fact, OP9's and OP27's K<sub>ext,soot</sub> are found to behave as  $\lambda^{-1.56}$  and  $\lambda^{-1.46}$ , respectively. This means that K<sub>ext,soot</sub> deviation from  $\lambda^{-1}$  may be due to either (i) a wavelength variation of the absorption function E(m), (ii) the total scattering contribution, or both as suggested by Yon *et al.* [37] and Simonsson *et al.* [199]. So, it is proposed to examine these two assumptions.



Figure 4.17. Optical extinction coefficient (K<sub>ext,soot</sub>) obtained for an untreated (raw) exhaust under (a) OP9 and (b) OP27 using diesel B7 and  $\lambda^{-\alpha}$  fitting, for 400 <  $\lambda$  [nm] < 1000, resulting in (a)  $\alpha = 1.56$  and (b)  $\alpha = 1.64$ .

Examining the second assumption means that one is able to distinguish  $K_{sca,soot}$  from K<sub>abs,soot</sub> which is not feasible relying solely on light extinction measurement. Even if aggregates number, size and morphology are unequivocally determined, the absorption and scattering functions E(m) and F(m) remain unknown functions. This shortfall can be compensated using models such as Lorentz-Drudes [133] that uses dispersion relations for optical refractive index of soot. Combined with the previous mentioned aggregates descriptors and a measurement of K<sub>ext,soot</sub>, E(m) and F(m) functions can be estimated. Proceeding accordingly, for soot aggregates generated by a McKenna hybrid burner using a diesel fuel, Yon et al. [37] found that F(m) depended much less on the wavelength in the range  $380 < \lambda$  [nm] < 1000 recommending a value of F(m) = 0.31  $\pm$  0.08. Later, Bescond et al. [46] applied a similar approach while additionally accounting for the effect of internal multiple scattering in evaluating E(m) and F(m). In their study that concerned soot aggregates generated by a miniCAST burner using propane, F(m) was found to vary, across the operating conditions, between 0.42 and 0.16 for  $380 < \lambda$  [nm] < 1000 and with a less noticeable variation when approaching higher wavelengths (i.e.,  $F(m) = 0.23 \pm 0.06$  at 700 nm). The objective here is not to evaluate the wavelength variations of E(m) and F(m) functions for soot aggregates generated by a miniCAST burner using diesel or any other fuel. Instead, it is proposed to use Yon et al. [37] F(m) recommended value for  $400 < \lambda$  [nm] < 1000 and the RDG-FA model (4.8) to estimate how much total scattering contribute to extinction. Having measured aggregates size distribution and morphological key parameters, K<sub>sca,soot</sub> is estimated for OP9 and OP27. In this regard, an additional assumption is made to convert mobility diameters (measured in this work) to gyration diameters (needed for the RDG-FA model) using  $\beta = D_g/D_m =$ 1.3 for the reasons discussed previously in section 2.3. Consequently, Figure 4.18 shows the estimated percentages of  $K_{sca,soot}$  in  $K_{ext,soot}$ . With  $D_p \sim 18$  nm, the contribution of total scattering in extinction under OP9 remains below 10 % in agreement with Yon *et al.* [37] and Migliorini *et al.* [36]. However looking at OP27's case, these calculations show that indeed for aggregates with higher  $\overline{D_p}$  (~ 35 nm in this case) total scattering cannot necessarily be neglected as it reaches on average ~ 12 % at 400 nm. Therefore, assigning the extinction to be equal to the absorption has to be judged from case-to-case.



Figure 4.18. Estimated percentages of total scattering in soot extinction coefficients for soot aggregates obtained under OP9 and OP27 (for an untreated (raw) exhaust while using diesel B7), using RDG-FA model incorporating aggregate size distribution and morphological parameters and assuming a constant scattering function F(m) = 0.31 for  $400 < \lambda$  [nm] < 1000. Shadow areas corresponds to uncertainties accounting for K<sub>ext.soot</sub> measurement standard deviation and  $\Delta$  F(m) = 0.08.

Now that  $K_{sca,soot}$  can be reasonably estimated, one can examine the second assumption regarding E(m) wavelength variation. Accordingly, using calculated  $K_{sca,soot}$  and measured  $K_{ext,soot}$ ,  $K_{abs,soot}$  shown in Figures 4.19.(a,b) were obtained for both OP9 and OP27 cases. These Figures also show the power law fit of  $K_{abs,soot}$ , only this time  $\alpha$  values were found to be slightly different than those previously evaluated from  $K_{ext,soot}$ . Nevertheless,  $K_{abs,soot}$ still deviate from the expected  $\lambda^{-1}$  to  $\lambda^{-1.49}$  and  $\lambda^{-1.51}$  for OP9 and OP27, respectively. This means that this wavelength dependency must be due to E(m) wavelength variation.



Figure 4.19. Optical absorption coefficients (K<sub>abs,soot</sub>) obtained under (a) OP9 and (b) OP27 (for an untreated (raw) exhaust while using diesel B7 and  $\lambda^{-\alpha}$  fitting, for 400 <  $\lambda$  [nm] < 1000, resulting in (a)  $\alpha = 1.49$  and (b)  $\alpha = 1.51$ .

Considering the classic RDG-FA model (4.8) accounting for total scattering and assuming that F(m) = 0.31 [37] and E(m) = 0.35 [199] for  $400 < \lambda$  [nm] < 1000, modeled Kext.soot were obtained. Figure 4.20 displays measured and modeled K<sub>ext,soot</sub> and shows that fixing E(m) value for all wavelength, a perfect match between measured and modeled Kext.soot is only found for some wavelengths, that are different as demonstrates OP9's and OP27's examples. Moreover, this result shows that accounting for the total scattering contribution (with constant F(m)) is not enough to explain the wavelength decrease (e.g., second assumption). Furthermore, since absorption is the dominant phenomena in extinction then E(m)must be wavelength dependent (e.g., first assumption). Going back to the initial objective of soot volume fraction  $(f_v)$  estimation, it seems cautious to exploit K<sub>ext</sub> above 700 nm since the Rayleigh approximation would remain acceptable even for aggregates with  $\overline{D_p}$  as high as OP27's. However, since  $f_v$  is constant during the measurement, an assumption on E(m)value highly conditions the estimation of  $f_v$ . By the way, using here E(m) = 0.35 used by Simonsson *et al.* [199] seems to be accurate as shown in Figure 4.20 above 700 nm. Yet, it does not guaranties that it will work for other operating conditions. Similar calculations were made for a selection of operating points and conditions for which size distributions, morphological key parameters,  $K_{ext}$  and  $\sum_i K_{abs,i}$  were measured. This concerns soot aggregates of (i) untreated exhaust obtained under OP2, OP17, OP32 and OP34 using diesel B7, (ii) CS-treated exhaust obtained under OP9, OP27 and OP34 using diesel B7 and (iii) untreated exhaust obtained under OP34 using dodecane. The result of these calculations and are made available in Appendix Figure F.1.



Figure 4.20. Optical extinction coefficient ( $K_{ext,soot}$ ) obtained under (a) OP9 and (b) OP27 (for an untreated (raw) exhaust while using diesel B7 and RDG-FA modeled  $K_{ext,soot}$ ) using (4.8) assuming E(m) = 0.35 and F(m) = 0.31, for  $400 < \lambda$  [nm] < 1000.

On the other hand, Yon *et al.* [200] reported, on the basis of simulations, that total scattering and absorption are enhanced for small aggregates, particularly for longer wavelengths due to multiple scattering that enhances interactions among primary spheres. Accordingly correction factors h and A for absorption and total scattering, respectively were introduced and were both found to increase with the wavelength. In a similar work Kelesidis *et al.* [201, 41], considering aggregates with D<sub>m</sub> between 7 and 300 nm with  $\overline{D_p}$  between 7 and 15 nm found that at  $\lambda = 1064$  nm, h coefficient varied as  $h = 1.24 - 0.77 \times D_m^{-0.7}$ , where D<sub>m</sub> is expressed in nm. This means that for D<sub>m</sub> > 50 nm, this enhancement factor reaches asymptotically ~ 1.22 which is not negligible. Moreover, the RDG-FA model is used under the assumption that soot primary particles are in point contact within an aggregates. However, using simulated aggregates, overlapping and necking in soot primary particles were found to affect significantly the absorption and scattering properties of soot aggregates, particularly in the near UV range due to the enhanced multiple scattering effects within an aggregate [147]. The point that these studies make is that even at higher wavelength where one can safely assume that Rayleigh approximation is valid the RDG-FA classic theory may still underestimate absorption by soot aggregates. Yet, even if h correction is used, an *a priori* knowledge on aggregate size is needed to incorporate such correction, making the practical use of this approach difficult especially that E(m) still needs to be known. Hence, the interest of focusing the attention on finding a way to reasonably predict E(m).

#### 4.3.3 Spectral dependence correction

In the previous section, it was concluded that if the classic RDG-FA model accurately fits measured  $K_{ext,soot}$ , then E(m) must necessarily be wavelength dependent. To account for the non- $\lambda^{-1}$  deviation within Rayleigh approximation, López-Yglesias *et al.* [202] and Simonsson *et al.* [199] suggested an empirical correction of E(m) as in (4.9). Here, C<sub>E</sub> (referred to as E(m)<sub>ref</sub> by Simonsson *et al.* [199]) refers to a fitting constant and  $\alpha$  is the Ångström absorption exponent [162]. As such, E(m) becomes a wavelength-dependent function.

$$\mathbf{E}(\mathbf{m}) = \frac{\mathbf{C}_{\mathbf{E}}}{\lambda^{\alpha - 1}} \tag{4.9}$$

Similarly as before, it is proposed to model  $K_{ext,soot}$  using the classic RDG-FA model (4.8) accounting for total scattering and assuming F(m) = 0.31 [37] for  $400 < \lambda$  [nm] < 1000 and instead of fixing a value for E(m), (4.9) is used with  $\alpha$  (evaluated from  $K_{abs,soot}$  fit) to find  $C_E$  values that allow to fit modeled  $K_{ext,soot}$  to measured  $K_{ext,soot}$ . The fit is performed using a least-square minimization algorithm with  $C_E$  as an adjusting parameter. Accordingly, Figure 4.21 displays the result of this fit and shows the good agreement between measured and modeled  $K_{ext,soot}$  using this approach.



Figure 4.21. Optical extinction coefficient obtained for an untreated exhaust under (a) OP9 and (b) OP27 and RDG-FA fitting using (4.8) assuming F(m) = 0.31 and incorporating the spectral correction of (4.9) for  $400 < \lambda$  [nm] < 1000.

Yet, what Figure 4.21 does not show is the disparity in  $C_E$  values and therefore in E(m). For instance, at 700 nm, E(m) was found to take  $0.32 \pm 0.05$  for OP9 while it took  $0.38 \pm 0.04$  for OP27. Table 4.7 gathers  $\alpha$ ,  $C_E$  and E(m) at  $\lambda = 700$  nm found for other operating points and conditions for which the same calculations were performed and Figure 4.22 shows obtained E(m) function for these operating points as a function of the wavelength between 400 nm and 1000 nm.

**Table 4.7.** Obtained values for Ångström absorption exponent ( $\alpha$ ), C<sub>E</sub> fitting constants and absorption function E(m) at 700 nm after subtracting the contribution of total scattering.

Fuel				]	Diesel B	7				Dodecane
Condition			Untr	eated			0	S-treate	d	Untreated
Operating point (OP)	OP2	OP9	OP17	OP27	OP32	OP34	OP9	OP27	OP34	OP34
α	1.38	1.49	1.34	1.51	2.04	2.13	1.41	1.27	1.66	1.55
$C_E \text{ [nm}^{\alpha-1}\text{]}$	$\begin{array}{c} 3.96 \\ \times \ 10^{-4} \end{array}$	$\begin{array}{c} 3.01 \\ \times \ 10^{-4} \end{array}$	$\begin{array}{c} 2.99 \\ \times \ 10^{-3} \end{array}$	$\begin{array}{c} 2.63 \\ \times \ 10^{-4} \end{array}$	$\begin{array}{c} 6.97 \\ \times \ 10^{-8} \end{array}$	$\begin{array}{c} 5.48 \\ \times \ 10^{-8} \end{array}$	$\begin{array}{c} 6.88 \\ \times \ 10^{-4} \end{array}$	$\begin{array}{c} 8.48 \\ \times \ 10^{-3} \end{array}$	$\begin{array}{c} 1.18 \\ \times \ 10^{-5} \end{array}$	$\begin{array}{c} 7.66 \\ \times \ 10^{-5} \end{array}$
$\frac{E(m)}{\text{at }\lambda=700 \text{ nm}}$	0.10	$\begin{array}{c} 0.32 \\ \pm \ 0.05 \end{array}$	$\begin{array}{c} 0.38 \\ \pm \ 0.02 \end{array}$	$\begin{array}{c} 0.38 \\ \pm \ 0.04 \end{array}$	$\begin{array}{c} 0.18 \\ \pm \ 0.03 \end{array}$	$\begin{array}{c} 0.50 \\ \pm \ 0.10 \end{array}$	$0.22 \\ \pm 0.10$	$\begin{array}{c} 0.39 \\ \pm \ 0.07 \end{array}$	$\begin{array}{c} 0.15 \\ \pm \ 0.06 \end{array}$	$\begin{array}{c} 0.17 \\ \pm \ 0.04 \end{array}$



Figure 4.22. Soot absorption function E(m) obtained by fitting modeled  $K_{ext,soot}$  to measured  $K_{ext,soot}$  accounting for total scattering and assuming F(m) = 0.31 for  $400 < \lambda$  [nm] < 1000 and using (4.9) to account for E(m) wavelength variation.

Figure 4.21 shows that the classic RDG-FA model can accurately model  $K_{ext,soot}$  (while accounting for total scattering assuming constant F(m) = 0.31) only if E(m) (see Figure 4.22) is both wavelength dependent and variable from one operating point to another. To reasonably predict E(m) value independently from the wavelength and the operating condition it is proposed to exploit  $C_E$  fitting constant which until now has not been exploited. Here (4.9) use is advantageous since E(m) wavelength dependency is solved using  $\alpha$ , but it only pushes the problem of finding its absolute value to the fitting constant  $C_E$ . On the other hand,  $C_E$  is by definition invariant with the wavelength making it dependent on the operating condition only. Meanwhile, the only information one can extract from a wavelength-resolved absorption coefficient, without any prior knowledge is  $\alpha$ , hence the idea to explore the possible correlation between  $C_E$  and  $\alpha$ . As it turned out, these two parameters were found to linearly correlate, following (4.10), in a semi-log scale as shown in Figure 4.23.

$$\ln(C_{\rm E}) = -a \times \alpha + b$$
;  $a = 13.98 \pm 0.66$ ;  $b = 12.47 \pm 1.06$  (4.10)



Figure 4.23.  $C_E$  fitting constant as a function of the Ångström absorption exponent ( $\alpha$ ) obtained in this work and those obtained from fitting E(m) literature [165–168, 37, 46] data using (4.9) between 700 nm and 1000 nm.

Besides the empirical correlation observed between  $C_E$  and  $\alpha$  in Figure 4.23, one can see that whatever the studied condition (e.g., OPs, untreated vs. CS-treated and fuel type),  $C_{\rm E}(\alpha)$  appears to follow (4.10). However, because of the semi-log scale in Figure 4.23, any small change in  $\alpha$  would result in a non-negligible variation of C<sub>E</sub> and thus of E(m). Therefore, even though Figure 4.23 shows an unquestionable correlation between  $C_E$  and  $\alpha$ , the quantitative exploitation of (4.9) should be used with caution. Also, if  $\alpha = 1$  then E(m) = 0.22. Using (4.9) also implies than E(m) varies monotonically with the wavelength between 400 nm and 1000 nm. In this regard, many studies [165–168, 37, 46] have provided evaluations of E(m) wavelength variation as discussed in section 2.5. It should be clarified that E(m) values reported in literature concern a variety of experimental conditions (laboratory flames, miniCAST generator etc) and have been deduced using different approaches. Also, it was observed that not all of the reported E(m) wavelength variations are monotonic between 400 nm and 1000 nm (see Figure 2.17 and Figure 2.18). So, we took the liberty of fitting E(m)literature data between 700 nm and 1000 nm (where they are strictly monotone) using (4.9)to deduce their corresponding  $\alpha$  and C<sub>E</sub> that are reported in Figure 4.23. Also, (4.9) remains valid whether  $\alpha$  is evaluated by fitting K<sub>abs,soot</sub> between 400-1000 nm or between 700-1000 nm. Here,  $\alpha$  and C<sub>E</sub> seems to corroborate the correlation observed in this work but still need further investigation to check the validity of this correlation in respect to literature data.

From a practical point of view, when measuring  $K_{ext}$  for a given exhaust that contains soot aggregates one can easily deduce  $K_{ext}$  spectral decay with the wavelength using a power law of the form  $\lambda^{-\alpha}$  providing a monotonic behavior. Only that evaluated  $\alpha$  can be slightly different from the actual Ångström absorption exponent due to total scattering contribution as shown in the previous section. On the other hand, if  $K_{ext}$  is measured between 700 nm and 1000 nm, one can make the argument that Rayleigh approximation is acceptable thus neglecting total scattering contribution and therefore evaluate  $\alpha$  which can be, in this case, assimilated to an Ångström absorption exponent. Consequently, under the Rayleigh regime retrieving  $f_v$  using  $K_{ext} \approx K_{abs,soot} = 6\pi E(m) f_v / \lambda$ , becomes possible using (4.9) and (4.10) independently from both the wavelength and the operating condition. This methodology is yet to be confronted with literature data and tested for other operating conditions different from those used to deduce (4.10). In this work,  $K_{ext}$  measurement was performed on a total of 34 operating points for both untreated and CS-treated exhaust. Therefore, it is proposed to test this methodology on this set of data in Chapter 7.

#### In conclusion :

- ▶ In addition to PM, the miniCAST generates a gas phase that contains species that absorb UV light (< 400 nm).
- ▶ The total scattering contribution to the extinction coefficient can not be necessarily neglected even at large wavelengths.
- ▶ An empirical model for the variation of soot absorption function (E(m)) is proposed accounting for wavelength variation (between 400 nm and 1000 nm) and operating conditions variability.

# 4.4 Mass spectra post processing: methodology for ToF-SIMS mass spectra

In this work, the choice was made to deploy (in addition to other diagnostics presented in Chapter 3) ex-situ time of flight-secondary ion mass spectrometry (ToF-SIMS) to acquire mass spectra to extract information on PM chemical composition. With this diagnostic, the goal is to describe the gas phase and particulate phase organic content produced by the miniCAST burner. The analysis of ToF-SIMS data is challenging due to the large amount of information they contain. Since the goal of using this diagnostic is also to characterize PM chemical composition under various operating conditions, the task of analyzing ToF-SIMS mass spectra can get laborious. In this work, a total of 126 mass spectra were acquired (all studied configurations combined with repeats). This section details the post processing approach used to extract, as accurately as possible, chemical information from the mass spectra.

This section is structured in three parts. First, from existing methodologies, a post processing approach is built. To that end, some existing concepts and numerical tools were used and adapted for the specific case of ToF-SIMS mass spectra. This concerns mass spectra alignment, mass calibration and peak picking which will be discussed in the second part. Finally, the proposed approach also introduces a new method for an automatic construction of a unique peak list which will be described in the third part.

#### 4.4.1 Post processing approach

In the framework of mass spectra post processing, possessing robust numerical tools is of great importance. Mass spectra consist of large amounts of data that need to be carefully inspected to extract both high quality and meaningful information. The ultimate goal of such post processing, schematized in Figure 4.24, is, roughly, transforming raw mass spectra (i.e., input) into a data set (i.e., output), in which a number of detected peaks (i.e., ions) are assigned to their corresponding chemical species, while keeping track of relevant information such as peak intensities, integrated areas and widths. This data is then fed to a multivariate analysis tool to classify the samples and obtain chemical information. Facilitating this process requires knowledge how data was acquired (e.g., continuous measurement vs. single mass spectra), what physical quantity is being measured, the instrument's performance, etc. This is crucial to be able to choose and adapt accordingly the different post processing steps.



Figure 4.24. General description of mass spectra post processing steps.

Such multi-step process usually begins by preconditioning raw data. This can vary from basic data rearrangement to averaging time series data or aligning spectra. Then, two major steps are usually performed. The first one is data calibration where data is transformed from a measured physical quantity (e.g., strength of a magnetic field [203], electrical potential [204, 205], time-of-flight [206]) into another quantity used to identify chemical species. For this purpose, typically m/z is used which is a dimensionless quantity obtained by dividing the mass number of an ion by its charge number [207]. The second step is peak identification which involves peaks picking, fitting and assignment. The individual peaks are then built into a peak list, that eventually is recovered to proceed with multivariate analysis.

Before choosing an adequate approach for ToF-SIMS mass spectra post processing, it is proposed to examine some of the literature dealing with different instrumentation used to acquire mass spectra as shown in Table 4.8. In the last two decades, many mass spectra post processing methodologies have been developed, particularly for atmospheric aerosols studies [208–213]. Although most of these methodologies are developed for specific instruments (see the second column in Table 4.8), they still share some major features (see the sixth column in Table 4.8). For instance, some instruments are employed for real time characterization of the chemical composition of aerosols [208-210]. In this case, usually a high mass resolution is traded for a fast acquisition of a large number of mass spectra, which is needed in atmospheric aerosols studies for time-resolved analyses. In other cases, high mass resolution is not necessarily required because the analysis has to be cost-effective. As a result, many of these instruments have limited resolving power. In contrast to these continuous measurement instruments, for other applications [214, 215] the precise identification of chemical species is required with high resolving power instruments. In those cases, usually less mass spectra are acquired per specimen but they contain a larger amount of data. Regardless of the used instruments, acquired mass spectra have to be eventually processed to maximize the amount of chemical information one can extract from them.

Table 4.8. Exam: Proton TransferResolution Time-of	ples (non-exhaustive) Reaction Time-of-Fligt Flight - Chemical Ion	from literature of m tt; <sup>3</sup> : Atmospheric ization Mass Spectr	press spectra post prepressure interface 1 ometer; <sup>5</sup> : Time-of spec	ocessing routines. <sup>1</sup> Fime-of-Flight Mass FFlight Aerosol Chei trometry	: High-Resolution Time-c Spectrometer; <sup>4</sup> : Micro-C mical Speciation Monitor;	of-Flight Aerosol Maa Drifice Volatility Imp <sup>5</sup> : Time-of-Flight So	ss Spectrometer; <sup>2</sup> actor Inlet - High- scondary Ion Mass
Reference	Instrument	Diagnostic type	Software	Calibration	Main features	$\begin{array}{c} {\rm Mass} \\ {\rm resolution} \ ({\rm m}/\Delta{\rm m}) \end{array}$	Mass accuracy [ppm]
DeCarlo <i>et al.</i> [208]	HR-ToF-AMS <sup>1</sup>	in-situ (time-series)	Igor Pro, Version 5	$m/z = \left(rac{ ext{tot-c}}{a} ight)^{1/ ext{b}}$ (Background-based)	Automatic averaging Mass calibration Peak-fitting routine Signal integration	up to $\sim 4300$ at $m/z$ 200	$\pm$ 7 (up to $m/z$ 200)
Müller <i>et al.</i> [209]	$\rm PTR-ToF^2$	in-situ (time series)	PTR-ToF data analyzer	$m/z = \left(rac{ ext{tof-}eta}{lpha} ight)^2$ (Background-based)	Automated averaging Dead time correction Baseline correction Mass calibration Peak detection (peakdet) Mass peak fitting	4800	10
Junninen <i>et al.</i> [210]	$APi-ToF^3$	in-situ (time-series)	tofTools under MATLAB	$m/z = \left(rac{ ext{tot}- ext{b}}{ ext{a}} ight)^2$	Automatic averaging Mass calibration Baseline detection peak deconvolution Peak identification Peak fitting	3000	$20 \; ({ m at} \; m/z \; 100)$
Stark et al. [211]	MOVI-HRToF-CIMS <sup>4</sup>	in-situ (time series)	Igor Pro, Versions 6.2-6.3 + tofware (Costum)	$ ext{tof} =  ext{p}_1 \left( m/z  ight)^{ ext{p}_2} +  ext{p}_3$	Baseline subtraction Multi-peak fitting Formula generator Free peak list Iterative peak assignment	4000 (above $m/z$ 200)	3.8 (average)
Timonen <i>et al.</i> [212]	${f ToF-ACSM^5}$	in-situ (time series)	Igor Pro $+$ toftware (Verion 2.5.3)	$ ext{tof} = \mathrm{a} + \mathrm{b}\sqrt{(m/z)}$	Baseline subtraction Peak-fitting mass calibration	$500  ext{ at } m/z  ext{ } 50)$	ı
Madiona et al. [213]	ToF-SIMS <sup>6</sup>	ex-situ (single mass spectra)	SurfaceLab 6 + MATLAB	ı	Mass calibration Normalization Peak list creation (up-binning) PCA & Neural networks	4000 - 12 000	·

In this work, mass spectra were acquired using a ToF-SIMS 5 (ION-TOF, GmbH) instrument having maximum nominal resolving power ~ 10 000 (see Chapter 3), thus the data post processing must be adapted accordingly. Also, this post processing can get difficult and time-consuming as one deals with a large set ( > 100) of mass spectra coming from different samples. To deal with the specific case of ToF-SIMS mass spectra, the post processing approach, schematized in Figure 4.25, is proposed. The process starts by considering raw mass spectra (i.e., input) that undergo a preconditioning step (1) where data is rearranged. The choice was made to proceed with spectra alignment (2) followed by the peak picking process (3) allowing to detect peaks in each mass spectrum before continuing with the mass calibration process (4).



Figure 4.25. Proposed methodology for ToF-SIMS mass spectra post processing.

At the end of the mass calibration process (4), two separate steps are then proposed where calibrated data go through a process of constructing a unique peak (5) in a completely automated process. This peak list goes then through a peak assignment process which is userassisted and can only be partially automated if one has previous knowledge on the chemical composition of the samples. For example, if one already knows that the samples are mainly composed of H/C/O, one can easily rule out *a priori* many combinations of elements. In this case, one can check and complete the generated peak list. By the end of this process, data is structured to proceed with adequate chemometrics.

Compared to the general description of mass spectra post processing shown in Figure 4.24, the major improvement proposed in this work is the introduction of the automated peak list construction process (5) to this methodology. This is accomplished by isolating clusters of peaks using as a criterion the probability that they describe the same chemical species based on a mass-defect analysis as it will be detailed in section 4.4.3. As a result, the whole process becomes quicker than before. It should be clarified that part of the implemented algorithms used in this work, particularly in steps (3), (4) and (6) were adapted from Junninen *et al.* [210], while the rest of the algorithms are specific to this work, particularly step (5) highlighted in blue in Figure 4.25. It should also be clarified that each step of this methodology contains a number of adjustable parameters (detection threshold, detection range, peak shoulders detection, etc). This methodology can be described as a semi-automated process, where some processes are automated while others are user-assisted as indicated in Figure 4.25. Finally, the adapted and developed routines are made available under MATLAB.

In mass spectrometry, mass defect analysis is a powerful tool since it allows to graphically access the content of a given mass spectrum and therefore facilitates the identification of unknown species. To understand this tool, some definitions need to be laid out first. In this work, the choice was made to work with unified atomic mass unit (u) in agreement with Murray *et al.* [216] with the following definitions :

- Accurate mass (m/z): It corresponds to the experimentally determined mass of an ion of known charge [216];
- Exact mass (M): It corresponds to the calculated mass of an ion or molecule with specified isotopic composition [216]. The exact mass can be used to evaluate the accuracy of the assignment of an ion species as it will be discussed later in section 4.4.3. M is also used to refer to the monoisotopic mass which is the exact mass of an ion or molecule calculated using the mass of the most abundant isotope of each element [216];
- Nominal mass (m): It corresponds to the mass of a molecular ion or molecule calculated using the isotope mass of the most abundant constituent element isotope of each element rounded to the nearest integer value and multiplied by the number of atoms of each element [216];
- mass defect (Δm): It corresponds to the difference between the nominal mass and the monoisotopic mass of an atom, molecule or ion [216]. The concept of a mass defect relies on the fact that each isotope has a different nuclear binding energy. Therefore, molecules having unique isotopic composition have unique exact mass even if they share the same number of protons and neutrons. Consequently, the difference between the exact mass of a molecule with a given isotopic composition and the nominal mass that is the total number of protons and neutrons that molecules contains, is unique for each isotopic composition;
- Isobaric ions : Ions with the same nominal mass but different exact masses [216];

# 4.4.2 Mass spectra preconditioning, alignment, calibration and peak picking

In this section, four steps of the proposed methodology shown in Figure 4.25 are described. This concerns data preconditioning (1), spectra alignment (2) peak picking (3) and mass calibration (4).

#### Data preconditioning

To apply any kind of automated or semi-automated post processing, at least for some of the post processing steps previously mentioned, data should be structured in the same manner. In this work, ToF-SIMS mass spectra are exported into ASCII format using the proprietary ION-TOF SURFACELAB 7 data acquisition software. As such, data is structured in three-column tables that are (i) channel from which time-of-flight (tof) is deduced (Channel  $= 10 \times \text{tof}$ ), (ii) a pre-calibrated accurate mass (m/z) obtained with a rough mass calibration operated at the moment of data acquisition and (iii) ion count (IC). In this work, a typical ToF-SIMS mass spectrum (with an upper m/z limit set up to ~ 1200) contains ~ 300 000 bins with 0.4 ns bin width (recorded using a binning of 4). In this case, as schematized in Table 4.9, data preconditioning simply means that data tables are resized to have the same length. When dealing with a large data set, mass spectra tables do not necessarily have the same length. This could be due to many reasons, the most common one is dead-time correction being activated at the moment of data acquisition. Therefore, channel (or tof) columns are completed to the same length as the longest available table which is used as reference. In this process, the original data binning is preserved and the parity of the first cell value accounted for as shown in the example of Table 4.9. The same procedure is applied for pre-calibrated m/z column and for each added row IC is simply filled with zeros.

	Raw data		Preconditioned data					
Channel	m/z	IC	Channel	m/z	IC			
			0	0	0			
			1	$4.52 \times 10^{-7}$	0			
			5	$2.28\times10^{-6}$	0			
			:	÷	÷			
23123	0.5001	0	23123	0.5001	0			
23127	0.5003	0	23127	0.5003	0			
÷	÷	÷	:	÷	÷			
1144499	1199.9	0	1144499	1199.9	0			
1144502	1200.0	0	1144502	1200.0000	0			
			1144507	1200.0085	0			
			:	:	÷			
			1148038	1207.4249	0			

Table 4.9. Example of raw and preconditioned mass spectrum data table.

#### Alignment

Due to electrical/electronic jitter, small day-to-day temperature and/or pressure fluctuations inherent to the ToF-SIMS instrument itself and in addition to ionization efficiencies that may vary (for the same species) from one sample to another, the same chemical species may appear at slightly different tof as illustrated in Figure 4.26.(a). To correct this artifacts, the mass spectra need to be re-aligned so that peaks describing the same chemical species have the same tof or m/z coordinates across all samples. This can be done using a matrix of calibration constants (quadratic transformations as it will be explained later), which aligns and calibrates all mass spectra at the same time. Nevertheless, here the choice was made to first align the spectra in the tof scale and then proceed with the mass calibration process. Aligning the mass spectra first in the tof scale using a matrix of linear transformations is in fact advantageous because only one set of calibration constants for all mass spectra need to be determined. Furthermore, it is a simpler process more fulfilling from a mathematical point of view. As it will be discussed later, the calibration process is often an iterative process, which means that if global calibration constants are used, one has to go back to adjust a number of constants equal to three times the number of mass spectra. On the other hand, if alignment and calibration are treated independently, the alignment constants are fixed and no longer need to be evaluated while only the three global calibration constants have to be adjusted.



Figure 4.26. Example of (a) raw time of flight spectra and (b) aligned time of flight spectra.

Aligning similar spectra against each other is usually done by means of cross correlation algorithms by applying an overall offset considering the whole detection range. This approach was deemed insufficient and was observed to result in rather good alignment over limited regions of the mass spectra, but also in misalignment on other regions of the mass spectra. Consequently, it is proposed to proceed with a piece-wise cross correlation hence deducing a lag per interrogation window. This lag was observed to increase with tof suggesting that the mass spectra were stretched along the tof axis. The origin of the stretching has not yet been determined. At this stage of data post processing, applying such a process in an unsupervised way did not render the expected results. Consequently, this process was made user-assisted where the user has the choice of selecting a number of interrogation windows encompassing preferably symmetrical, isolated and well-spaced peaks. For each pre-set interrogation window, the algorithm evaluates the tof lag for each peak (belonging to each mass spectrum) considering an arbitrarily chosen reference spectrum as shown in Figure 4.26.(a). This data is then used to correct the tof axis by applying the linear correction (4.11) thus correcting the observed stretching. Evaluating (4.11) coefficients 'a' and 'b', for each mass spectrum, is then done by a linear regression. Applying such procedure results in aligned spectra as shown in Figure 4.26.(b).

$$tof_{aligned} = a \times tof_{raw} + b$$
 (4.11)

# Peak picking

This step consists of running a parametric peak picking algorithm to locate the peaks in each mass spectrum. In the next step it will be shown that the calibration process is based on a mass defect analysis that requires prior knowledge on peaks locations hence the order of steps (3) and (4) in Figure 4.25. Many peak picking algorithms are available in the literature, some of which are specifically developed for mass spectra analysis. This is the case in Junninen *et al.* [210] who developed a MATLAB algorithm where peaks picking is based on detecting variation in signal derivative and amplitude. This feature is also able to deal, to some extent, with peak overlapping often encountered in such data. Accordingly, the choice was made to use this feature for peak detection, in which peaks are detected at the sign inversion of the second derivative of the mass spectrum, but there are still many factors that impact the number of detected peaks in a mass spectrum.



Figure 4.27. (a) The probability density function of the  $|1^{st}$  derivative | calculated over a 0.2 m/z width window (between 18.00 m/z and 18.20 m/z) and (b) a portion of a mass spectrum showing the impact of the threshold choice (Median, Mean and 10 × Median of the  $|1^{st}$  derivative |).

In a mass spectrum that contains ~ 300 000 bins, peak signals are rare events, the rest of the data is just noise. Müller *et al.* [209] and Junninen *et al.* [210] used a dynamic threshold to separate the peaks from the background noise. In Junninen *et al.* [210], this threshold is based on the absolute value of the 1<sup>st</sup> derivative of a spectrum calculated over a sliding window. When the width of this sliding window is properly chosen, where only few peaks exist per sliding window, the probability density function (pdf) of  $|1^{st}$  derivative | is higher when there is only noise in the sliding window, and lower at the occurrence of peaks. Figure 4.27.(a) illustrates the shape of the  $|1^{st}$  derivative | pdf considering a 0.2 m/z width sliding window encompassing the peaks shown in Figure 4.27.(b).

Given the shape of the  $|1^{st}$  derivative | pdf, the signal threshold can be correlated to a statistical descriptor of that pdf. As shown in Figure 4.27.(a), using the mean of the distribution presents the risk of missing information, while choosing the median of the distribution results in the detection of unnecessary noise. Therefore, a compromise was found at 10 times the median as shown in Figure 4.27.(a) with a 0.2 m/z width sliding window. Figure 4.27.(b) displays a portion of a mass spectrum and the detection thresholds corresponding to these choices and shows that the choice of  $10 \times \text{Median}$  (|  $1^{st}$  derivative |) is satisfying in this case. On average, applying the peak picking process resulted in 550 detected peaks per mass spectrum. Figure 4.28.(a) shows an example of all detected peaks in a mass spectrum over the chosen detection range (0 - 600 m/z). Figure 4.28.(b) shows a closer look indicating local variations of the threshold (in black solid line) and detected peaks (in red circles).



Figure 4.28. Peak picking process result applied on a mass spectrum showing (a) all detected peaks over the entire detection range (0- 600 m/z) and (b) a closer look on some detected peaks.

The peak picking routine, adapted from Junninen *et al.* [210], also performs gaussian fits for all detected peaks. When overlapping peaks are detected, the fit might return slightly shifted peak positions. Junninen *et al.* [210] used this fit to flag peak shoulders considered as such if their fit peak location is more than a threshold value called Dif<sub>Lim</sub> away from the initial detected peak. For low mass resolution mass spectra, peak shoulders can be difficult to assign even by peak fitting. Consequently, it is up to the user to decide whether to account for peak shoulders in the analysis. For instance, Junninen *et al.* [210] used the Dif<sub>Lim</sub> criteria to discard peak shoulders from the analysis. In this regard, Figure 4.29.(a) shows the number of detected peak shoulders across the 126 mass spectra considering a constraining criterion  $\text{Dif}_{\text{Lim}} = 0.01 \ m/z$  and a loose criterion  $\text{Dif}_{\text{Lim}} = 0.1 \ m/z$ . This Figure shows that even with a constraining  $\text{Dif}_{\text{Lim}} = 0.01 \ m/z$ , only 6 shoulders. Finally, Figure 4.29.(b) shows the number of detected peak for all 126 mass spectra, considering both of those criteria and demonstrates that using  $\text{Dif}_{\text{Lim}} = 0.01 \ m/z$  (kept for the rest of the analysis) instead of  $\text{Dif}_{\text{Lim}} = 0.1 \ m/z$  had no effect on the number of detected peaks.



Figure 4.29. (a) The number of detected peak shoulders across the 126 mass spectra considering  $\text{Dif}_{\text{Lim}} = 0.01 \ m/z$  and  $\text{Dif}_{\text{Lim}} = 0.1 \ m/z$  criteria and (b) the number of detected peaks considering those two criteria.

#### Mass calibration

The mass defect analysis is a powerful tool to identify unknown species. On a mass defect plot ( $\Delta m vs. m$ ), since the mass defect of <sup>12</sup>C and <sup>1</sup>H is respectively  $\Delta m_C = 0$  u (by definition) and  $\Delta m_H = + 0.007825$  u, for a given number of carbon atoms, any additional hydrogen atom adds  $m_H = 1$  u to the nominal mass and  $\Delta m_H = + 0.007825$  u to the mass defect. That is why,  $C_i H_j^+$  ions can be found aligned on the bundle of parallel lines having slope equal to  $\Delta m_H$  and intercept equal to 'i' number of carbon atoms. Using pre-calibrated mass spectra, m and  $\Delta m$  are calculated for all detected peaks for each mass spectrum.



Figure 4.30. (a) Mass defect plot showing species used for a first calibration iteration where detected clusters are shown in black dots and the position of some expected ions indicated in red circles; (b) Calibration curve showing, in blue, pre-calibrated data, species used for the last calibration iteration in yellow stars, the resulting calibration law in red line and its extension to the rest of the detection range.

As an example, Figure 4.30.(a) shows some ions following the former described pattern. In principle, this observation can be extended to any isotope, cluster or even molecule once their mass defect is known. So far, in this work, the mass spectra were kept in tof scale. From the operating theory of time-of-flight mass spectrometers [206], a tof-energy quadratic

relationship can be derived, that in turn results in the generic mass calibration (4.12) quadratic law. The determination of the coefficients A, B and C is known as mass calibration.

$$m/z = A + B \times tof + C \times tof^2$$

$$(4.12)$$

The coefficients are determined empirically from the tof and exact mass of known ions. This process is performed iteratively, considering first easily identified ions such as  $C^+$ ,  $CH^+$ ,  $CH_2^+$  and  $CH_3^+$  as shown in Figure 4.30.(a). The mass calibration is then improved by progressively selecting heavier ions, that appear as isolated clusters on the mass defect plot. As soot deposit are performed on Ti wafers, Ti peaks were also added to the set of used species. As such, the calibration curve shown in Figure 4.30.(b) shows the pre-calibrated data (blue-squares), the ions used for the last mass calibration iteration up to 300 u (yellow stars), the best-fit calibration curve (red solid line) and its extension to the full mass range (red dashed line). Finally, all relevant data resulting from the peak picking process are updated with the last-iteration calibration coefficients.

#### Mass resolving power

Accordingly, Figure 4.31.(a) shows examples of detected peaks along with their gaussian fits after the mass calibration. Using the fits of all detected peaks, one can calculate the mass resolution using (4.13).

$$\text{Resolution} = \frac{\text{m}}{\Delta \text{m}_{(\text{FWHM})}} \tag{4.13}$$

The calculated resolution over the entire detection range  $(0 - 600 \ m/z)$  was observed to evolve on average around 10 000 as shown in Figure 4.31.(b) that is in excellent agreement with the value given by the manufacturer. This means that the ToF-SIMS 5 (ION-TOF, GmbH) instrument used in this work allows to resolve ions as close as 0.01 u at 100 m/z.



Figure 4.31. (a) portion of a calibrated mass spectrum showing some detected peaks and their gaussian fits and (b) estimated mass spectrum resolution over the entire detection range (0 - 600 m/z).

# 4.4.3 Peak list construction and assignment

At this point, one can imagine that individual peak lists are obtained as schematized in Figure 4.32. This Figure shows an example of a portion of an i<sup>th</sup> and a k<sup>th</sup> mass spectrum where one can easily notice that individual peak lists contain unstructured data in the sense that the ions highlighted in the blue and the gray rows in each of those tables correspond to probably the same species but are located in different lines (i.e., IDs). A straightforward,

although time consuming, solution would be to assign a molecular formula to each peak within each peak list. Since on average 550 peaks per mass spectrum were detected, manually assigning these species is obviously a laborious task. To ease this process, it is proposed to automatically merge all individual peak lists into one main peak list using the peak list construction routine, thus assigning species afterword once of all. However, this comes with a number of numerical challenges.



Individual mass spectra peak lists

т	i <sup>t</sup>	<sup>h</sup> mas	ss spectr	um			k <sup>th</sup> mass spectrum					
ID	m/z	m	$\Delta m$	tof	IC	ID	m/z	m	$\Delta m$	tof	IC	
:	:	:	:	:	:	:	:	:	:	:	:	
286	112.1186	112	0.1186	$3.50 \times 10^{4}$	$2.69 \times 10^2$	286	110.9412	111	-0.0588	$3.48 \times 10^{4}$	$5.27 \times 10^{2}$	
287	112.9096	113	-0.0904	$3.51 \times 10^{4}$	$1.40 \times 10^{2}$	287	111.0228	111	0.0228	$3.48 \times 10^{4}$	$2.54 \times 10^{3}$	
288	112.9533	113	-0.0467	$3.51 \times 10^{4}$	$1.73 \times 10^{2}$	288	111.0993	111	0.0993	$3.48 \times 10^{4}$	$4.31 \times 10^{1}$	
289	113.0099	113	0.0099	$3.51 \times 10^{4}$	$4.22 \times 10^{2}$	289	111.9149	112	-0.0851	$3.49 \times 10^{4}$	$1.74 \times 10^{2}$	
	113.0408					290	112.0302	112	0.0302	$3.50 \times 10^{4}$	$4.88 \times 10^{2}$	
291	114.0495	114	0.0495	$3.53 \times 10^{4}$	$1.33 \times 10^{3}$	291	112.1173	112	0.1173	$3.50 \times 10^{4}$	$3.91 \times 10^1$	
292	115.0574	115	0.0574	$3.54 \times 10^{4}$	$2.09 \times 10^{4}$	292	112.9083	113	-0.0917	$3.51 \times 10^{4}$	$1.46 \times 10^{2}$	
293	116.0646	116	0.0646	$3.56 \times 10^{4}$	$4.34 \times 10^{3}$	293	112.9520	113	-0.0480	$3.51 \times 10^{4}$	$1.76 \times 10^{2}$	
294	117.0735	117	0.0735	$3.57 \times 10^{4}$	$3.60 \times 10^{3}$	294	113.0086	113	0.0086	$3.51 \times 10^{4}$	$4.48 \times 10^{2}$	
295	118.0447	118	0.0447	$3.59 \times 10^{4}$	$6.81 \times 10^{2}$	295	113.0395	113	0.0395	$3.51 \times 10^{4}$	$1.62 \times 10^{3}$	
:	:	÷	:	:	:	:	:	:	:	:	:	

Figure 4.32. Portion of an i<sup>th</sup> and a k<sup>th</sup> mass spectra individual peak list, showing positions of detected peaks. Rows in blue and gray indicates probably the same species but appearing at different IDs in each individual peaks list.

#### Peak list construction

Considering all the 126 peak list tables, a mass defect plot of all detected peaks is deduced as shown in Figure 4.33.(a) where ion peaks are naturally ordered exhibiting certain patterns as shown closely in Figure 4.33.(b). This advantageous graphical representation of ion peaks is what motivated the automatic peak list construction process described in this section. In Figure 4.33.(b) one can easily notice that at a given nominal mass (e.g., 60 u) many clusters (i.e., isobaric ions) with different mass defect may be found. One of the tasks the peak list construction routine should be able to perform is (i) detect and distinguish how many clusters exist at each nominal mass (m) and (ii) associate peaks belonging to the concerned mass spectra to that identified cluster.

If an ion is detected in all mass spectra, theoretically their corresponding peaks should have the same exact coordinates on a mass defect plot. Yet, within each cluster a dispersion along the mass defect axis is inevitable. Many factors can contribute to this dispersion such as the limited resolving power inherent to the instrument itself, the topography of sample surface or ionization efficiencies that may vary from one sample to another and whose impact is reflected by a slightly different tof, thus of m/z, even after being aligned and calibrated. To meet the challenge of distinguishing how many clusters exist in the entire mass defect plot, the peak list construction routine was programmed to scan the mass defect plot along the nominal mass axis with dynamic search windows. During the scan, the routine performer an iterative hierarchical clustering that determines how many clusters exist at each nominal mass. At the beginning, the algorithm needs to be initialized with the minimum  $\Delta m$  distance beyond which two clusters can be considered distinct as indicated with a red arrow in Figure 4.33.(b). Obviously, this separation distance depends on m and  $\Delta m$  at which the scanning is being performed.



Figure 4.33. (a) Mass defect plot showing all detected ion peaks across the 126 mass spectra over the entire mass detection range (0 - 600 m/z) and (b) a closer look (zoom area) showing examples of search windows (blue rectangles) encompassing data clusters (black dots) being identified as describing probably the same ion at 60 u.

In the previous post processing steps, all detected peaks have been fitted with a gaussian fit. Figure 4.34.(a) shows that the evaluated full width at half maximum (FWHM) of peaks evolve linearly with m/z up to ~ 150 m/z. This is consistent with DeCarlo *et al.* [208] who observed that peaks below 100 m/z had gaussian widths that varied linearly with their m/zand also with Junninen et al. [210] who reported that above 180 m/z, the unconstrained peak fitting deviated from a linear behavior. In Figure 4.34.(a) the average value of all peaks FWHM at a given m is fitted with a 2<sup>nd</sup> order polynomial function (chosen arbitrarily), here referred to as the initialization threshold. In this work, the choice was made to initialize the separation distances in the iterative hierarchical clustering with the initialization threshold at each scanned m. As a result, at each m the peak list construction routine calculates all the distances between adjacent points (i.e., peaks) and each time this distance is superior than the initialization threshold, a new cluster is added. This hierarchical clustering also provides clusters locations and dispersion along the  $\Delta m$  axis. Consequently, search windows encompassing each single cluster shown in blue in Figure 4.33.(b) are determined. Then, a search is performed within each search window to identify the mass spectra whose peaks are found inside that window and associate them using their IDs in each individual peak list. However, an issue one may face during that process is when two peaks belonging to the same mass spectra are detected inside the same search window. This is due to the initialization threshold used to separate clusters being too big and to the presence of two data clusters too close to each other. In this case, the peak list construction routine was programmed to vary iteratively the initialization threshold until two or more clusters are unidentified. Otherwise, if the issue persists, the choice was made to keep only the most intense peak identified in the mass spectra that prevents that separation. In this work, among the 1560 clusters the mass defect contained this scenario only occurred 3 times (for clusters that were identified later as background) which means that this proposed methodology efficiently constructs a unique peaks list even for poorly resolved data sets such as the one dealt with here. The peak list construction routine was also programmed to flag all detected clusters that contained less than 'n' number of peaks. In this work, the choice was made to consider all clusters containing less than 3 peaks as not reproductible (as a reminder, 3 mass spectra were acquired on 3 different ROIs in the same experimental conditions for reproducibility). Moreover, during the scanning process, once a cluster is detected, one can access the distribution of peaks of that cluster across all mass spectra data set as shown in 4.34.(b). The example shown in this Figure corresponds to the cluster with a black search window in Figure 4.33.(b).



Figure 4.34. (a) Peaks full width at half maximum (FWHM) fitted with a 2<sup>nd</sup> order polynomial function used as an initialization threshold for the iterative hierarchical clustering process and (b) the distribution of peaks of a cluster identified as  $C_5H_2^+$  by the peak list construction process.

At this stage of the post processing, this distribution is very important because it offers the possibility of suggesting an assignment especially if some preliminary information on the chemical composition of the samples is available. In this regard, the peak list construction routine also performs a gaussian fit of that distribution (see Figure 4.34.(b)) and calculates a  $\Delta m$  width window equal to  $\pm 3$  times the gaussian standard deviation to constrain the preliminary assignment as indicated by red dashed lines in Figure 4.34.(b). In this work, most of the expected information from the samples comes from H/C/O ions and since the subtract was made of Ti, a brute force data base was built containing  $C_xH_y^+$  and  $C_xH_yO^+$  (with either  $^{12}C$  or  $^{13}C$ ),  $Ti_xO_y^+$  and  $Ti_xO_yH_z^+$  (with  $^{46}Ti$ ,  $^{47}Ti$ ,  $^{49}Ti$  or  $^{50}Ti$ ) ions. This custom data base was then interrogated to find a match for each cluster. As a result, the cluster in Figure 4.34.(b) was assigned to  $C_5H_2^+$ . This preliminary assignment is more challenging at higher m/z because (i) the number of possible elements combinations increases and (ii) clusters have higher dispersion along the  $\Delta m$  axis. For those reasons, as m/z increases composition assignments become more difficult and often require a user intervention.

The output of the peak list construction routine is shown in Table 4.10. This table shows a portion of the same i<sup>th</sup> and k<sup>th</sup> mass spectra where the peak lists are structured and the previous blue and gray rows are now at the same location (i.e., ID). Also in Table 4.10, some species are detected in only some of the mass spectra and not others. This is the example of the green row where only the i<sup>th</sup> mass spectrum contains the suggested ion while the k<sup>th</sup> do not. Meanwhile, the i<sup>th</sup> and the k<sup>th</sup> mass spectra do not contain the suggested species in the red row (filled with zeros) which is found in other mass spectra. From a practical point of view, merging all individual unstructured peak list tables shown in Figure 4.32 in the form of Table 4.10 is advantageous since it summarizes all the data the user needs in a unique peak list with no repetition. Also, one gets only to inspect and correct the suggested ion species column which is also a significant gain of time. Finally, following this methodology it is worth mentioning that the post processing of all 126 mass spectra from step (1) until step (5) took less than 1 hour.

Species	ID		i <sup>th</sup> mass spectrum				k	$^{ m th}$ ma	ss spectr	rum	]
			$\mid m/z$	m	$\Delta m$	IC	$\mid m/z$	m	$\Delta m$	IC	
:		:	:	÷	:	:	:	÷	:	:	
$C_7H_{10}O^+$	604		0	0	0	0	0	0	0	0	
$[^{13}C]C_7H_{13}^+$	605		110.1026	110	0.1026	$7.46 \times 10^{2}$	110.1012	110	0.1012	$1.65 \times 10^{2}$	
${ m TiPO}_2^+$	606		110.9145	111	-0.0855	$1.42 \times 10^{3}$	110.9131	111	-0.0869	$1.58 \times 10^{3}$	
$ m ^{47}TiO_4^+$	607		110.9425	111	-0.0575	$4.71 \times 10^{2}$	110.9412	111	-0.0588	$5.27 \times 10^{2}$	
	608		0	0	0	0	0	0	0	0	
$C_9H_3^+$	609		111.0242	111	0.0242	$1.29 \times 10^{3}$	111.0228	111	0.0228	$2.54 \times 10^{3}$	
-	610		0	0	0	0	0	0	0	0	
$[^{13}C]C_7H_{13}^+$	611		111.1007	111	0.1007	$1.53 \times 10^{2}$	111.0993	111	0.0993	$4.31 \times 10^{1}$	
$Ti_2O^+$	612		0	0	0	0	0	0	0	0	
$^{49}\text{TiPO}_2^+$	613		111.9188	112	-0.0812	$1.89 \times 10^{2}$	111.9149	112	-0.0851	$1.74 \times 10^{2}$	
${ m TiO}_4^+$	614		0	0	0	0	0	0	0	0	
	615		0	0	0	0	0	0	0	0	
$C_9H_4^+$	616		112.0315	112	0.0315	$2.87 \times 10^{2}$	112.0302	112	0.0302	$4.88 \times 10^{2}$	
	617		0	0	0	0	0	0	0	0	
$C_7H_{12}O^+$	618		112.0827	112	0.0827	$1.91 \times 10^2$	0	0	0	0	
$[^{13}C]C_7H^+_{15}$	619		112.1186	112	0.1186	$2.69 \times 10^2$	112.1173	112	0.1173	$3.91 \times 10^{1}$	
$[^{4'}\mathrm{Ti}]\mathrm{TiH_2O^+}$	620		112.9096	113	-0.0904	$1.40 \times 10^2$	112.9083	113	-0.0917	$1.46 \times 10^2$	
	621		112.9533	113	-0.0467	$1.73 \times 10^{2}$	112.9520	113	-0.0480	$1.76 \times 10^{2}$	
	622		0	0	0	0	0	0	0	0	
	623		0	0	0	0	0	0	0	0	
$C_8HO^+$	624		113.0099	113	0.0099	$4.22 \times 10^{2}$	113.0086	113	0.0086	$4.48 \times 10^{2}$	
$C_9H_5$	625		113.0408	113	0.0408	$1.31 \times 10^{3}$	113.0395	113	0.0395	$1.62 \times 10^{3}$	
ан o+	626		0	0	0	0	0	0	0	0	
C7H13O	627			0	U	0		0	U	0	• • •
149m:1m:110±	628			0	U	0		0	U	0	
50m:o+	629			0	0	0	0	0	0	0	
$^{00}TiO_4^+$	630		0	0	0	0	0	0	0	0	
:			:	÷	÷	:	:	÷	÷	:	

**Table 4.10.** Merged peak lists showing a portion of the i<sup>th</sup> and the k<sup>th</sup> mass spectra accurate mass (m/z), nominal mass (m), mass defect  $(\Delta m)$ , ion count (IC) and suggested species after being structured using the peak list construction routine.

# Peak assignment

Once the peak list construction process is performed and the unique peak list is generated, the last step is to inspect it for possible errors and confirm/correct the suggested assignments or add more assignments. Figure 4.35.(a) shows a closer look into a mass defect plot showing in black dots clusters, in red inscriptions the suggested ions based on the dynamic search windows shown in colored rectangles. To inspect the suggested assignments, one can proceed manually on the generated peak list. Yet, to make this process much easier the developed package proposes a user friendly interface that assists this inspection process. For that end, an interface (not shown here) proposes a live update of the unique peak list while a mass defect plot similar to the one in Figure 4.35.(a) is simultaneously displayed. Figure 4.35.(b) shows the same closer look into the mass defect plot of Figure 4.35.(a) after the verification process. Overall, one can see that most of the preliminary assignments were found accurate which is in itself proof that the peak list construction routine not only helps facilitating the automatic construction of a unique peak list but also partially facilitates the peak assignment process.


Figure 4.35. (a) A portion of the mass defect plot showing the peak list construction process result, indicating search windows (colored rectangles) encompassing clusters (black dots) being identified as describing the same ion with their preliminary assignment (if found) and (b) the same mass defect plot showing confirmed, corrected, and added ion assignment.

Applying the methodology presented here on the total of 126 mass spectra resulted in the detection of 1560 clusters among which 517 (e.g., 33 %) were related to the background while 339 (e.g., 22 %) were not assigned (i.e., unidentified) and 704 (e.g., 45 %) were assigned (i.e., identified) to ions having unique isotopic composition as shown in Figure 4.36.



Figure 4.36. Number of detected clusters classified as background, unidentified and identified ions.

At the end of the assignment process, one can evaluate the accuracy of the assigned formulas for each cluster. This accuracy is evaluated using equation (4.14) that compares the relative error between the m/z (experimentally measured) and M calculated from the assigned formulas. Figure 4.37.(a) shows this accuracy as a function of m/z. At low m/zthe accuracy is poor because m/z appears at the denominator in (4.14). Above m/z 150, the assignments accuracy lays within  $\pm$  25 ppm. This is satisfying considering the fact that all mass spectra analyzed in this work contains mostly organic compounds for which 15-20 ppm accuracy (using a 10 000 resolving power) is considered acceptable [73]. Furthermore, Figure 4.37.(b) shows the assignments accuracy as a function of the cumulative number of assigned clusters and it is found that 341 clusters (all having m/z > 150) have assignments with accuracy lower than 20 ppm.



Accuracy  $[\text{ppm}] = \frac{m/z - M}{m/z} \times 10^6$  (4.14)

Figure 4.37. Assignment accuracy (a) as a function of accurate mass (m/z) and (b) as a function of cumulative number of assigned clusters.

#### In conclusion :

- ▶ Many users have developed custom codes and methodologies for their individual needs. Here, a methodology was presented to efficiently prepare ToF-SIMS mass spectra for multivariate analysis.
- ▶ Building this methodology was inspired from existing methodologies for mass spectra post-processing some of which were used and adapted to the specific case of ToF-SIMS mass spectra.
- ▶ This methodology introduces a new mass defect-based method (i.e., peak list construction routine) for an automatic construction of unique peak list which meets the need for post processing low resolving power data sets while offering a significant gain of time compared to a manual method.

# Characterization of PM emissions produced by a liquid miniCAST burner

The main goal of the results presented in this chapter is to document the capabilities of the liquid fueled miniCAST to generate soot aggregates with controlled size distributions and morphology as well as their corresponding optical extinction coefficients when studied under various operating conditions. The second goal is to use this data to evaluate, as accurately as possible, the soot volume fraction. To achieve this objective, three methods based on aggregate size (combining size distributions and morphologies), mass and optical extinction are compared.

# 5.1 Characterization of soot aggregates

As discussed in Chapter 2, soot aggregates can be described in many ways. Here, it is proposed to focus the attention first on soot aggregates number, size and polydispersion for all 34 operating points (OPs) (introduced in Chapter 4) for untreated (raw) exhaust, based on SMPS statistical analysis. Then, it is proposed to describe soot nanostructure for OP2, OP9, OP17, OP27, OP32 and OP34 and evaluate their morphological descriptors as well as their optical extinction coefficients. All along this description, the impact of using a catalytic stripper (CS) and changing the liquid fuel composition (diesel B7 vs. dodecane) are examined on each of those aspects.

# 5.1.1 Size distributions

In this section it is proposed to examine how the size distributions of soot aggregates is affected (i) when the miniCAST flow rates are adjusted while using the same liquid fuel (e.g., diesel B7), (ii) when diesel B7 is changed to dodecane and (iii) when a CS is used to thermally treat the exhaust at 350 °C.

#### Impact of adjusting miniCAST flow rates while using diesel B7

Focusing first on untreated exhaust, a parametric study was carried out to evaluate the liquid miniCAST burner abilities in terms of soot aggregates size distribution parameters: aggregates number (PN), mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ) and geometric standard deviation ( $\sigma_{geo,D_m}$ ). This study showed that, at fixed oxidation air flow rate (2 L/min), soot PN increased with the liquid fuel flow rate (in this case with  $\varphi$ ) (see Figure 5.1.(a)) while  $D_{geo,m}$  decreased from ~ 90 nm to ~ 55 nm (see Figure 5.1.(b)). For  $\sigma_{geo,D_m}$ , no obvious trend was observed (see Figure 5.1.(c)). These observations remained valid regardless of mixing air flow rate choice, suggesting that the latter has no significant impact over aggregates number, size or polydispersion. In a second parametric study, the mixing air flow rate was kept constant (0.1 L/min) and decreasing the oxidation air flow rate, going from fuel-lean to fuel-rich conditions, made soot PN increase (see Figure 5.1.(d)).



Figure 5.1. SMPS measured aggregate number (PN), mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ) and geometric standard deviation ( $\sigma_{geo,D_m}$ ) as function of flame overall equivalence ratio ( $\varphi$ ) for 34 OPs for untreated (raw) exhaust using diesel B7. OP2, OP9, OP17, OP27, OP32 and OP34 are indicated in colors. (**a**, **b**, **c**) oxidation air = 2 L/min and (**d**, **e**, **f**) mixing air = 0.1 L/min. Uncertainties account for 3 size distributions measured consecutively (May 2021). Data not corrected for dilution (~ 19:1).

Meanwhile, soot aggregates were observed to grow in size from ~ 45 nm and reach a maximum of ~ 105 nm around  $\varphi \sim 0.4$  before decreasing (see Figure 5.1.(e)) down to ~ 60 nm for  $\varphi > 1$ . Using a miniCAST supplied with propane, Moore *et al.* [44] observed a similar trend regarding the evolution of aggregates sizes with the exception of reaching a maximum size under slightly fuel-lean conditions before starting decreasing under fuel-rich conditions, therefore covering the range 10 – 130 nm in modal diameters [44]. We attribute this difference to the difference in the initial hydrocarbon used (propane vs. diesel B7) and to the burner's geometry.

When decreasing the oxidation air flow rate in the miniCAST using diesel B7,  $\sigma_{\text{geo},D_m}$  exhibited two distinct behaviors: at a lower liquid fuel flow rate (50 µL/min),  $\sigma_{\text{geo},D_m}$  decreased rapidly (see Figure 5.1.(f)) and at a higher liquid fuel flow rate (200 µL/min),  $\sigma_{\text{geo},D_m}$  remained quasi-constant at ~ 1.7. Overall,  $\sigma_{\text{geo},D_m}$  was found to vary between 1.516 and 1.818. This behavior is similar to what was observed for soot aggregates generated by a miniCAST using propane where aggregates  $\sigma_{\text{geo},D_m}$  were reported to vary from 1.6 to 1.8 [48]. All these observations demonstrate the usefulness of the miniCAST burner investigated in this work in producing soot aggregates at variable sizes and concentrations by controlling only three flow rates (oxidation air, mixing air and liquid fuel flow rates) hence offering the user a panel of choices.

#### Impact of the fuel composition (diesel B7 vs. dodecane)

Figure 5.2 shows mobility-equivalent size distributions averaged over 3 consecutively measured size distributions representing OP2, OP9, OP17, OP27, OP32 and OP34 operating points. Figure 5.2.(a) shows these size distributions when diesel B7 was used, while Figure 5.2.(b) shows those obtained under the same OPs when using dodecane. Although all of these size distributions exhibit a monomodal shape (which was by the way observed for all 34 OPs), the major difference one can point out here is that using dodecane smaller aggregates are obtained. For instance, using dodecane instead of diesel B7, OP9's D<sub>geo,m</sub> shifts from ~ 79 nm to ~ 37 nm. Also, the smallest D<sub>geo,m</sub> = 28.5 nm was obtained using dodecane under OP32. Finally, at fixed OP, using dodecane was found to produce less PN compared to diesel B7 (statistical descriptors of size distributions reported in Figure 5.2 are made available in Appendix Table G.1).



Figure 5.2. Soot aggregates mobility-equivalent size distributions obtained under OP2, OP9, OP17, OP27, OP32 and OP34 for untreated (raw) exhaust using (a) diesel B7 and (b) dodecane. Each size distribution is the average of 3 consecutive size distributions (July 2021). Data not corrected for dilution ( $\sim$  19:1). Statistical descriptors of these size distributions are made available in Appendix Table G.1.

In this work, SMPS size measurements were limited to  $D_{max} = 224.7$  nm. As a result, for some OPs the size distributions upper tail can be truncated as shown in Figure 5.2.(a). This means that if the soot volume fraction ( $f_v$ ) is evaluated considering solely the measured size distribution,  $f_v$  will be underestimated because of the missing large diameter values. To overcome this lack, the choice was made to extrapolate the measured sized distributions up to 400 nm. Consequently, a pdf that accurately fits the measured part should be first found. Usually, aerosol size distributions tend to be described using a lognormal pdf (5.1).

$$\mathbf{n}(\mathbf{D}) = \frac{\mathrm{dN}}{\mathrm{dD}_{\mathrm{m}}} = \frac{1}{\mathrm{D}\ln\left(\sigma_{\mathrm{geo},\mathrm{D}_{\mathrm{m}}}\right)\sqrt{2\pi}} \mathrm{e}^{-\frac{\left(\ln\left(\mathrm{D}/\mathrm{D}_{\mathrm{geo},\mathrm{m}}\right)\right)^{2}}{2\ln\left(\sigma_{\mathrm{geo},\mathrm{D}_{\mathrm{m}}}\right)^{2}}}$$
(5.1)

This observation is merely empirical but has the benefit of summarizing a resolved size distribution using only three parameters (PN,  $D_{\text{geo},m}$  and  $\sigma_{\text{geo},D_m}$ ). However, for spherical particles assuming a size distribution behaves according to a lognormal pdf may yield erroneous values particularly for distribution moments higher than the second order [111] such as  $f_v$  which is a 3<sup>rd</sup> order moment [217]. Figure 5.3.(a) shows a size distribution example where a monomodal lognormal pdf is not indeed accurate ( $R^2 = 0.87$ ) (black bold dotted line). In this case, a bi-modal lognormal pdf was found to render a better fit ( $R^2 = 0.99$ ) (green solid line). In other words, a bimodal lognormal pdf is mathematically accurate, but it does not necessarily has a physical reality. On the other hand, Figure 5.3.(b) shows an example where a monomodal lognormal pdf is accurate enough ( $R^2 = 0.99$ ) (black bold dotted line). Either way, for each size distribution the density function (monomodal or bimodal lognormal) that renders the best fit is considered to extrapolate the size distribution tail as shown in Figure 5.3. The impact of such extrapolation over  $f_v$  is discussed later in section 5.2.1.



Figure 5.3. Fitting of measured soot aggregates mobility-equivalent size distributions obtained under (a) OP27 and (b) OP34 for untreated (raw) exhaust using diesel B7, with either monomodal or bimodal lognormal pdfs and extrapolating truncated data from 224.7 nm to 400 nm. Data not corrected for dilution ( $\sim 19:1$ ).

#### Impact of the catalytic stripper

It is worth reminding that emission thresholds set by current emission regulations such as Euro 6d-temp (2020) [13] discussed in Chapter 1 concerns only non-volatile PM (nvPM) above 23 nm that survive oxidation at 350 °C. In this regard, the catalytic stripper (CS) set to 350 °C allows to examine the size distributions of nvPM produced by the liquid miniCAST which can be used for calibration purposes. Accordingly, Figure 5.4 shows mobility-equivalent size distributions averaged over 3 consecutively measurements representing OP2, OP9, OP17, OP27, OP32 and OP34 operating points only this time for a CS-treated exhaust. Figure 5.4.(a) shows these size distributions when diesel B7 was used, while Figure 5.4.(b) shows those obtained under the same OPs using dodecane. Compared to Figure 5.2 (corresponding to an untreated exhaust), one can observe that regardless of the operating point and the used liquid fuel, using the CS affects the shape of the size distributions that looks more flattened. To examine in detail how the CS affects the soot aggregates size distribution descriptors (PN,  $D_{\text{geo},\text{m}}$  and  $\sigma_{\text{geo},\text{D}_{\text{m}}}$ ), the same parametric study discussed in the beginning of this section was conducted on all 34 OPs while using diesel B7. The results of this study are shown in Appendix Figure H.1.



Figure 5.4. Soot aggregates mobility-equivalent size distributions obtained under OP2, OP9, OP17, OP27, OP32 and OP34 for a thermally treated (CS-treated) exhaust using (a) diesel B7 and (b) dodecane. Each size distribution is the average of 3 consecutive size distributions (July 2021). Data not corrected for dilution ( $\sim$  19:1). Statistical descriptors of these size distribution are available in Appendix Table G.1.

Overall, almost all variations in PN,  $D_{\text{geo},m}$  and  $\sigma_{\text{geo},D_m}$  previously reported for the untreated exhaust remain valid for the CS-treated one. The only exception concerns  $\sigma_{\text{geo},D_m}$  at fixed mixing air at 0.1 L/min at a higher liquid fuel flow rate (200 µL/min) for which  $\sigma_{\text{geo},D_m}$  was observed to increase from 1.7 to 1.8 instead of remaining quasi-constant at ~ 1.7 for the untreated condition. Using measured PN,  $D_{\text{geo},m}$  and  $\sigma_{\text{geo},D_m}$  for all 34 OPs for both untreated and CS-treated exhaust, the variation from untreated to CS-treated condition is calculated for each of those parameters.

Accordingly, Figure 5.5 displays those evolutions and shows some interesting observations. It should be clarified that in this work, for each OP the CS was used on the entire aggregates size classes without any prior size selection. In Figure 5.5.(b), at fixed oxidation air (2 L/min), one can see that PM crossing the CS saw their D<sub>geo,m</sub> shift (by up to 20 %) toward lower sizes as  $\varphi$  increased. While, at fixed mixing air (0.1 L/min) under fuel-lean conditions (see Figure 5.5.(e)) D<sub>geo,m</sub> was not much affected. Furthermore,  $\sigma_{\text{geo,D_m}}$  (see Figures 5.5.(c,f)) was observed to overall increase with  $\varphi$ . This suggests that as PM crosses the CS, its size distribution gets more flattened for fuel-rich than fuel-lean conditions.

On top of these observations, the impact of CS on PN is maybe the most important one. In fact, as PM crosses the CS a significant loss in aggregates PN (see Figures 5.5.(a,d)) was observed which can be explained by diffusion and thermophoretic losses within the CS. These PN losses were observed to vary on average between 25 % and 30 %. As introduced in Chapter 3, PN losses within the CS are expected to be size dependent.



Figure 5.5. Variations (due to the CS use) in soot aggregates number ( $\Delta$  PN), mobility-equivalent geometric mean diameter ( $\Delta$  D<sub>geo,m</sub>) and geometric standard deviation ( $\Delta$   $\sigma_{geo,D_m}$ ) as function of flame overall equivalence ratio ( $\varphi$ ) for 34 OPs using Diesel B7. OP2, OP9, OP17, OP27, OP32 and OP34 are indicated in colors. These variations are calculated using data reported in Figure 5.1 and Figure H.1. (**a**, **b**, **c**) oxidation air = 2 L/min and (**d**, **e**, **f**) mixing air = 0.1 L/min.

In this regard, it is proposed to confront the particle penetration function measured in this work and those expected accounting for diffusion and thermophoretic losses as proposed by Catalytic Instruments GmbH & Co.KG [175]. Contrarily to PN losses, the particle penetration refers to the amount of PN able to cross the CS compared to the case where the CS is bypassed. Accordingly, Figure 5.6 shows the particle penetration as a function of aggregates  $D_{geo,m}$ . Again, since for each OP the CS was used on the entire aggregates size classes without any prior size selection, the choice was made to plot particle penetration as a function of  $D_{geo,m}$  measured when the CS was bypassed ( $D_{geo,m_{(Untreated)}}$ ). It is worth reminding that the solid particle penetration (red curve) given by Catalytic Instruments GmbH & Co.KG [175] was obtained for size selected silver spherical particles. Overall, Figure 5.6 shows that particle penetration of soot aggregates fluctuates between 60-80 %.



#### Fixed mixing air = 0.1 L/min



Figure 5.6. Particle penetrations as function of  $D_{\text{geo},m}$  measured when the CS was bypassed  $(D_{\text{geo},m_{(\text{Untreated})}})$  for 34 OPs. Particle penetrations were calculated from  $\Delta$  PN variations (due to the CS use) using data reported in Figure 5.5. OP2, OP9, OP17, OP27, OP32 and OP34 are indicated in colors. (a) oxidation air = 2 L/min and (b) mixing air = 0.1 L/min.

#### 5.1.2 Morphology and nanostructure

Similarly to the previous section, it is proposed to examine how soot aggregates nanostructure and morphology are affected (i) when the miniCAST flow rates are adjusted while using the same liquid fuel (e.g., diesel B7), (ii) when diesel B7 is changed to dodecane and (iii) when the CS is used to thermally treat the exhaust at 350 °C.

### Impact of adjusting miniCAST flow rates while using diesel B7

With the help of electron microscopy diagnostic, STEM, TEM and high-resolution TEM images of soot aggregates, shown in Figure 5.7, were taken for the 6 investigated OPs (OP2, OP9, OP17, OP27, OP32 and OP34) and reveal morphological and nano-structural change between fuel-lean and fuel-rich conditions. Although all are forming fractal-like agglomerates, TEM observations show that under fuel-lean conditions (OP2, OP9, OP17 and OP27), primary particles have more perceptible edges than under fuel-rich conditions (OP32 and OP34), for which primary particles exhibit more overlap and a smoother aggregate external surface.

Meanwhile, at a primary particle scale, high-resolution TEM images show a progressive transition from highly graphitized structures (i.e., OP2 and OP9) to less structurally organized (i.e., OP17 and OP27) towards a total amorphous texture (i.e., OP32 and OP34). When exploring the nanostructure of soot aggregates generated by miniCAST using propane under a narrow  $\varphi$  range (0.97-1.02), Grondin *et al.* [148] reported no significant change in primary particles internal organization which remained graphitic overall. However, when exploring a wider  $\varphi$  range (0.49-1.01 by Durdina *et al.* [47], 0.74-1.33 by Saffaripour *et al.* [48], 0.97-1.46 by Marhaba *et al.* [50] and 0.94-1.24 by Ess *et al.* [51]), many studies seem to agree on primary particles nanostructure evolution with respect to  $\varphi$  as previously described.

When dealing with soot aggregates, soot morphology is usually incorporated using the so-called fractal law linking the number of primary particles per aggregate  $(N_p)$  to primary particle diameter  $(D_p)$  and particle gyration diameter  $(D_g)$ . This power law (5.2) describes soot aggregates morphology by introducing a fractal prefactor  $(k_f)$  and a fractal dimension  $(D_f)$ .

$$N_{p} = k_{f} \left(\frac{D_{g}}{D_{p}}\right)^{D_{f}}$$
(5.2)

Therefore, the second part of this analysis focuses on morphological parameters assessment that was performed *a posteriori*, by analyzing STEM images following the methodology detailed in section 4.2. This methodology consists of segmenting raw STEM images into single binary aggregates which was done using a semi-automated method [189, 218] to overcome background-related issues as it allows the user to intervene when necessary to help define an aggregate border. On average, more than 150 single aggregates per sample were successfully retrieved. Compared to similar studies [218, 50, 46, 43, 186] this is considered statistically sufficient. Euclidian Distance Mapping – Surface Based Scale (EDM-SBS) [95] protocol was then applied on each single aggregate to provide information encompassing scales encountered in each single aggregate. That same information was then interpreted to evaluate soot aggregates geometric mean primary particle diameter (D<sub>geo,p</sub>) and its geometric standard deviation ( $\sigma_{geo,D_p}$ ) following a real soot-based calibration approach as proposed by Bescond *et al.* [95]. Finally, with the help of correlations expressing N<sub>p</sub> as a function of aggregate and primary particles projected areas proposed by Sorensen *et al.* [192] and Köylü *et al.* [191], a fractal analysis was conducted to evaluate both D<sub>f</sub> and k<sub>f</sub>.

Table 5.1. Morphological properties of soot aggregates obtained under OP2, OP9, OP17, OP27,
OP32 and OP34 operating points for untreated (raw) and CS-treated exhaust using diesel B7 and
dodecane, resulting from STEM images (shown in Figure 5.7) analysis. Dgeo,p uncertainties correspond
to 95 $\%$ confidence interval of the sigmoid law (4.4) fit.

Operating point (OP)	Fuel	Condition	Number of extracted aggregates	D <sub>geo,p</sub> [nm]	$\sigma_{geo,D_p}$	$D_{f}$	k <sub>f</sub>
OP2	Diesel B7	Untreated	139	$22.3\pm0.4$	$1.518 \pm 0.012$	1.839	1.967
OP9	Diesel B7	Untreated	198	$18.0\pm0.4$	$1.580\pm0.015$	1.805	1.906
OP17	Diesel B7	Untreated	156	$34.4\pm0.3$	$1.497\pm0.007$	1.941	1.988
OP27	Diesel B7	Untreated	179	$35.2\pm0.2$	$1.431\pm0.004$	1.831	1.966
OP32	Diesel B7	Untreated	138	$34.4\pm0.4$	$1.425 \pm 0.007$	1.862	1.972
OP34	Diesel B7	Untreated	164	$39.2\pm0.2$	$1.394 \pm 0.003$	1.844	1.968
OP9	Diesel B7	CS-treated	141	$19.7\pm0.3$	$1.567 \pm 0.013$	1.849	1.970
OP27	Diesel B7	CS-treated	229	$34.5\pm0.3$	$1.377 \pm 0.005$	1.790	1.957
OP34	Diesel B7	CS-treated	164	$35.2\pm0.3$	$1.394\pm0.005$	1.834	1.966
OP34	Dodecane	Untreated	145	$25.3 \pm 0.5$	$1.521 \pm 0.016$	1.920	1.984



Figure 5.7. Scanning transmission electron microscopy (STEM) (top row), transmission electron microscopy (TEM) (middle row) and high-resolution transmission electron microscopy (HRTEM) (bottom row) images of representative miniCAST soot aggregates, using diesel B7 for untreated exhaust: (a) OP2, (b) OP9, (c) OP17, (d) OP27, (e) OP32 and (f) OP34.

The analysis results, summarized in Table 5.1 show that overall, soot  $D_{\text{geo},p}$  increased from ~ 18.0 nm up to ~ 39.2 nm when the burner was switched from fuel-lean to fuel-rich conditions, while its  $\sigma_{\text{geo},D_p}$  was observed to slightly decrease, thus varying from 1.580 down to 1.394. However, evaluated  $D_f$  and  $k_f$  showed no obvious trend and were observed to vary in the ranges 1.805 - 1.941 and 1.960 - 1.988, respectively. These values are also similar to the ones reported for soot aggregates produced by miniCAST using propane [46]. Here primary particles were considered polydisperse. For the sake of simplicity, primary particles are from now on considered monodisperse with a mean primary particle diameter  $\overline{D_p} \approx D_{\text{geo},p}$ . These results are also in agreement with diesel engine aggregates whose  $\overline{D_p}$  and  $D_f$  are generally found to vary between 10 nm and 40 nm and between 1.5 and 2.2, respectively [107, 157, 106, 158–161].

#### Impact of the catalytic stripper

When the CS was used, evaluated  $D_{\text{geo},p}$  and  $\sigma_{\text{geo},D_p}$  were found similar to those obtained for the untreated aggregates (see Table 5.1). This suggests that the CS thermal treatment has a major impact neither on the size of the monomers nor on their polydispersion, at least not that could be seen with such diagnostics.



Figure 5.8. Scanning transmission electron microscopy (STEM) (top row), transmission electron microscopy (TEM) (middle row) and high-resolution transmission electron microscopy (HRTEM) (bottom row) images of representative miniCAST soot aggregates, using diesel B7 for CS-treated exhaust obtained under (a) OP9, (b) OP27 and (c) OP34.

On the other hand, the CS was found to turn structured into amorphous nanostructure regardless of the miniCAST OP. Figure 5.8 underlines such an impact, particularly for fuellean condition OP9, where essentially all graphene-like layers disappeared once the heating treatment was applied, while under OP34 (fuel-rich condition), primary particles nanostructure remained amorphous for both untreated and CS-treated conditions. Such observations were confirmed for several other HRTEM images taken from separate locations on TEM grids. According to Haller *et al.* [219] heating soot aggregates produced by a miniCAST supplied with propane up to 870 °C following a thermo-desorption protocol resulted in rather reordering graphene layers under fuel-rich condition. When applying a similar process, using a CS operated at 12 L/min and 350 °C Durdina *et al.* [47] concluded that soot internal structure became more ordered. Since neither of the two latter operating conditions are replicated in this work, the impact of the CS on soot particle's internal structure under the conditions studied here will need further detailed investigation involving a large number of HRTEM images and more adapted diagnostic tools. On the other hand, it was observed that the primary particles boundaries became slightly more noticeable under CS-treated fuel-rich condition OP34 compared to their respective untreated ones, while remaining fairly similar under OP9 and OP27 (see Figure 5.8). This might suggest that a significant amount of condensed semi-volatile organic compounds might be overlayed all over the aggregate surface and that was partially removed once heated at 350 °C. This is still to be confirmed using adequate tools describing accurately soot surface chemical composition.

#### Impact of the fuel composition (diesel B7 vs. dodecane)

Finally, Figure 5.9 shows STEM, TEM and HRTEM representative soot aggregates using dodecane for untreated exhaust. Unfortunately, STEM images analysis of samples obtained under OP9 and OP27 were inconclusive because of difficulties in isolating enough aggregates. However, under OP34 the analysis was conclusive and showed that soot aggregates using dodecane exhibit smaller (by  $\sim 14$  nm) monomer size compared to its equivalent OP34 using diesel B7 (for untreated exhaust). On the other hand, while using dodecane, HRTEM showed no internal arrangement for both OP27 and OP34. As HRTEM was inconclusive for OP9 using dodecane, the same trend previously observed using diesel B7 could not be extended to dodecane.



Figure 5.9. Scanning transmission electron microscopy (STEM) (top row), transmission electron microscopy (TEM) (middle row) and high-resolution transmission electron microscopy (HRTEM) (bottom row) images of representative miniCAST soot aggregates, using dodecane for untreated exhaust: (a) OP9, (b) OP27 and (c) OP34.

#### 5.1.3 Optical extinction coefficients

In this section, it is proposed to examine the optical extinction coefficients  $(K_{ext})$  measured for the miniCAST exhaust under various operation points. Starting with the untreated (raw) exhaust and while using diesel B7, Figure 5.10.(a) shows K<sub>ext</sub> measured over the 200 - 1000 nm wavelength range for OP2, OP9, OP17, OP27, OP32 and OP34. Under the fuel-lean condition OP2, K<sub>ext</sub> exhibits a typical soot response in the sense that the spectrum has a maximum between 225 nm and 250 nm as previously observed by Schnaiter et al. [220] and Bescond et al. [46]. This is followed by a spectral decrease as a function of the wavelength over the VIS-NIR range (wavelength > 400 nm) as already seen in numerous studies [46, 37, 220, 221]. Compared to OP2, under OP9 K<sub>ext</sub> is higher since a higher number of aggregates with larger sizes are being produced. Looking into OP17 and above, an additional absorption signal with noticeable broad peaks were observed over the UV range (wavelength < 400 nm), indicating the presence of other absorbing species, most likely polycyclic aromatic hydrocarbons (PAHs) in the gas phase. This means that  $K_{ext}$  is resulting from 2 contributions: soot aggregates extinction (K<sub>ext,soot</sub>), that accounts itself for both soot aggregates absorption (K<sub>abs,soot</sub>) and soot aggregates scattering  $(K_{sca,soot})$  and the sum of all gas species absorption coefficients  $(\sum_{i} K_{abs,i})$  (5.3).

$$K_{ext} = \underbrace{K_{abs,soot} + K_{sca,soot}}_{K_{ext,soot}} + \sum_{i} K_{abs,i}$$
(5.3)

Using a particle filter,  $\sum_{i} K_{abs,i}$  were acquired for each OP as shown in Figure 5.10.(b). This Figure shows that gas species absorption coefficients increased with  $\varphi$ . It also clearly demonstrates that the gas phase absorbs only UV light and that  $K_{ext}$  above 400 nm is solely due to soot aggregates and to what they might be deposited on their surface externally. Furthermore, once the CS was used,  $K_{ext}$  displayed in Figure 5.10.(c) show that part of the produced absorbing gas phase was oxidized bringing the extinction coefficients to the same shape (particularly in the UV) as OP2's or OP9's under untreated conditions. All of these observations remained valid when using dodecane (see Figures 5.10.(d-f)) instead of diesel B7, although while using dodecane the light extinction measurements suffered from some noise. As previously described in section 5.1.1, soot aggregates produced while using dodecane had lower D<sub>geo,m</sub> and PN compared to the case where diesel B7 was used. Consequently, noisy  $K_{ext}$  particularly under OP9 and OP32 (see Figures 5.10.(d,f)) are explained by the limited optical path (1 m in this case) that does not detect enough light attenuation under these conditions.

Overall, what all measured  $K_{ext}$  share is their wavelength monotonic decrease over the VIS-NIR range which can be modeled with a power law relation  $\lambda^{-\alpha}$  with  $\alpha$  the Ångström absorption exponent. As discussed in Chapter 4,  $\alpha$  needs to be evaluated from  $K_{abs,soot}$  instead of  $K_{ext,soot}$  due to the total scattering contribution that can not be necessarily neglected. Therefore, is it proposed to account for the total scattering contribution as explained in Chapter 4 and evaluate  $\alpha$  by fitting  $K_{abs,soot}$  with a power law of the form  $\lambda^{-\alpha}$ . In order to account for the total scattering contribution, one needs information on both aggregates size distribution and morphology. Due to time and resource constraints, morphological parameters were evaluated only for 10 operating conditions that cover the burner's operating range as shown in Table 5.1. Consequently,  $\overline{D_p}$  for the remaining OPs are interpolated in respect to  $\varphi$  as shown in Figure 5.11. For ease of use,  $\overline{D_p}$  interpolation was done using a second order polynomial function. This choice was completely arbitrary and is not related to any particular phenomenon. Meanwhile,  $D_f$  and  $k_f$  were fixed at 1.851 and 1.970, respectively. These values correspond to the mean values of the  $D_f$  and  $k_f$  in Table 5.1 (all cases combined). Consequently,  $K_{abs,soot} = K_{ext,soot} - K_{sca,soot}$  were obtained as explain in Chapter 4.





Raw

Dodecane



Filtered

Figure 5.10. Optical extinction coefficients (Kext) measured under OP2, OP9, OP17, OP27, OP32 and OP34 for (a,d) untreated (raw) exhaust, (b,e) a filtered exhaust and (c,f) for a thermally treated (CS-treated) exhaust using (a, b, c) diesel B7 and (d, e, f) dodecane.

5.1.

Characterization of soot aggregates



Figure 5.11. Evaluated mean primary particles diameter  $(\overline{D_p})$  reported in Table 5.1 as a function of flame overall equivalence ratio ( $\varphi$ ). The straight line indicates interpolated  $\overline{D_p}$  for the 34 other OPs as a function of  $\varphi$ .

Regardless of the exhaust condition (untreated vs. CS-treated) using either diesel B7 or dodecane, fitting  $K_{abs,soot}$  with  $\lambda^{-\alpha}$  law between 400 nm and 1000 nm resulted in  $\alpha > 1$  as summarized in Table 5.2. These values also account for day-to-day variations. Considering only diesel B7 untreated conditions,  $\alpha$  was found to vary from  $1.32 \pm 0.09$  (under OP9) up to  $2.06 \pm 0.12$  (under OP32).

Operating	Fuol	α		
point (OP)	ruer	Untreated	CS-treated	
OP2		$1.42\pm0.04$	-	
OP9	37	$1.32\pm0.09$	$1.26\pm0.15$	
OP17	el I	$1.72\pm0.20$	$1.44\pm0.03$	
OP27	iese	$1.68\pm0.03$	$1.22\pm0.05$	
OP32	D	$2.06\pm0.12$	$1.27\pm0.10$	
OP34		$2.01\pm0.17$	$1.45\pm0.21$	
OP9	0)	_	-	
OP17	ane	2.25	1.48	
OP27	dec	1.42	1.27	
OP32	)0(	-	-	
OP34		1.55	1.66	

**Table 5.2.** Ångström absorption exponent ( $\alpha$ ) evaluated by fitting K<sub>abs,soot</sub> using a power law of the form  $\lambda^{-\alpha}$  between 400 nm and 1000 nm. Uncertainties correspond to day-to-day variations.

Furthermore, the Ångström absorption exponent ( $\alpha$ ) was evaluated from the fitting of K<sub>abs,soot</sub> between 400 nm and 1000 nm of all 34 OPs while using diesel B7, or using dodecane only under OP17, OP27 and OP34. Obtained  $\alpha$  is shown in Figure 5.12. On average, in this study  $\alpha$  was observed to slightly increase with  $\varphi$  hence varying from 1.05 (under OP11) to 2.25 (under OP33). Figure 5.12 also gathers  $\alpha$  evaluated for soot aggregates generated by miniCAST using propane [42, 45, 150, 152, 154]. Compared to this work, much significant increase of  $\alpha$  with  $\varphi$  have been reported particularly by Kim *et al.* [45] and Ess *et al.* [154]. This dispersion may be due to differences in experimental conditions under which soot aggregates were obtained as much as it can be explained by how the power law fitting is performed and whether total scattering has been accounted for or not. Despite all of that,  $\alpha$  values obtained in this work are very well embedded in the domain covered by those previously reported in literature. Moreover, for soot aggregates generated by miniCAST using propane in a diffusion type flame Ess *et al.* [154] have reported that  $\alpha$  increased with the organic content of the aggregates as discussed in Chapter 2. Similar observations have also been reported by both Schnaiter *et al.* [42] and Lefevre *et al.* [152].

The point that these studies made is that, the more soot aggregates contain organic compounds, the more  $\alpha$  is higher thus reflecting a strong wavelength decrease. In this regard, when the CS was used in the present study,  $\alpha$  was observed to decrease for both fuel-lean and fuel-rich conditions hence varying between 1.10 and 1.66 as shown in Figure 5.12. These findings suggest that PM obtained under these OPs exhibit different chemical compositions, responsible for such wavelength decrease. Investigating this aspect will be the main goal of Chapter 6. Finally, for the untreated conditions, using either diesel B7 or dodecane, an overview of soot aggregates characteristics are summarized in Table 5.3.



Figure 5.12. Ångström absorption exponent ( $\alpha$ ) as a function of overall flame equivalence ratio ( $\varphi$ ), and C/O ratio, for all 34 miniCAST OP using diesel B7 for both untreated (raw) and thermally treated (CS-treated) exhaust vs. literature [42, 45, 150, 152, 154] for CAST/miniCAST burner using propane. The gray line corresponds to the stoichiometric conditions (C/O = 0.3 or  $\varphi$  = 1).

**Table 5.3.** Overview of soot aggregates characteristics (PN corrected for dilution,  $D_{\text{geom},D_m}$ ,  $\overline{D_p}$ ,  $D_f$  and  $\alpha^*$ ) of soot aggregates generated by a miniCAST burner using diesel B7 or dodecane for untreated (raw) exhaust. \* Evaluated by fitting  $K_{\text{abs,soot}}$  by a power law ( $\lambda^{-\alpha}$ ) between 400 nm and 1000 nm accounting for total scattering.  $\overline{D_p}$  values in gray are interpolated according to Figure 5.11 while  $D_f$  is kept constant at 1.851.

Operating point (OP)	$\rm PN~[\#/cm^3]$	$D_{geo,m}$ [nm]	$\sigma_{geom,D_m}$	$\overline{\mathrm{D}_{\mathrm{p}}} \; [\mathrm{nm}]$	$D_{f}$	α*
Diesel B7						
OP1	$7.1 \pm 0.1 \times 10^{7}$	$87.8 \pm 1.0$	$1.671 \pm 0.010$	15.5	1.851	1.37
OP2	$6.1 \pm 0.7 \times 10^{7}$	$45.0 \pm 2.9$	$1.818 \pm 0.013$	$22.3\pm0.4$	1.839	$1.42\pm0.04$
OP3	$1.2 \pm 0.0 \times 10^{8}$	$94.1\pm0.6$	$1.597 \pm 0.006$	18.6	1.851	1.26
OP4	$8.1 \pm 0.2 \times 10^{7}$	$49.8\pm0.5$	$1.749 \pm 0.008$	18.9	1.851	-
OP5	$1.1\pm0.0\times10^8$	$60.5\pm0.6$	$1.678 \pm 0.012$	19.5	1.851	-
OP6	$1.3 \pm 0.0 \times 10^{8}$	$67.2\pm1.6$	$1.631 \pm 0.005$	20.2	1.851	1.12
OP7	$1.4 \pm 0.0 \times 10^{8}$	$72.4\pm0.2$	$1.623\pm0.011$	21.1	1.851	1.14
OP8	$8.3 \pm 0.2 \times 10^{7}$	$53.4 \pm 0.8$	$1.719\pm0.011$	22.0	1.851	-
OP9	$1.4 \pm 0.0 \times 10^{8}$	$81.2\pm1.6$	$1.590 \pm 0.003$	$18.0\pm0.4$	1.805	$1.32\pm0.09$
OP10	$1.8 \pm 0.1 \times 10^8$	$80.4\pm1.7$	$1.784\pm0.004$	22.5	1.851	1.52
OP11	$1.8 \pm 0.0 \times 10^8$	$77.8\pm0.6$	$1.571 \pm 0.006$	23.4	1.851	1.05
OP12	$2.3 \pm 0.1 \times 10^8$	$67.7\pm0.2$	$1.736 \pm 0.011$	25.5	1.851	1.77
OP13	$2.5 \pm 0.0 \times 10^8$	$104.7\pm0.1$	$1.516 \pm 0.000$	24.3	1.851	1.21
OP14	$2.7 \pm 0.0 \times 10^8$	$79.3\pm0.1$	$1.597 \pm 0.002$	29.7	1.851	1.57
OP15	$2.8 \pm 0.0 \times 10^8$	$83.8\pm0.5$	$1.616 \pm 0.002$	30.0	1.851	1.68
OP16	$3.2 \pm 0.1 \times 10^8$	$88.6\pm4.7$	$1.618 \pm 0.026$	29.1	1.851	1.51
OP17	$2.7 \pm 0.1 \times 10^{8}$	$67.0\pm2.7$	$1.700 \pm 0.015$	$34.4\pm0.3$	1.941	$1.72\pm0.20$
OP18	$3.1 \pm 0.0 \times 10^8$	$89.1\pm0.2$	$1.673 \pm 0.001$	32.6	1.851	1.45
OP19	$3.3 \pm 0.0 \times 10^{8}$	$78.8\pm0.2$	$1.715 \pm 0.002$	32.8	1.851	1.56
OP20	$3.1 \pm 0.0 \times 10^8$	$91.2\pm0.4$	$1.708 \pm 0.007$	33.1	1.851	1.35
OP21	$3.4 \pm 0.1 \times 10^8$	$85.6\pm0.3$	$1.710 \pm 0.009$	33.7	1.851	1.57
OP22	$3.2 \pm 0.1 \times 10^{8}$	$57.5\pm0.2$	$1.630 \pm 0.014$	34.7	1.851	2.19
OP23	$3.5 \pm 0.0 \times 10^{8}$	$64.5\pm0.3$	$1.590 \pm 0.003$	35.0	1.851	2.12
OP24	$3.3 \pm 0.0 \times 10^{8}$	$81.6 \pm 1.3$	$1.713 \pm 0.003$	34.7	1.851	1.66
OP25	$3.1 \pm 0.0 \times 10^{8}$	$67.4 \pm 0.3$	$1.648 \pm 0.008$	35.4	1.851	1.70
OP26	$3.4 \pm 0.0 \times 10^{8}$	$80.8\pm0.5$	$1.709 \pm 0.007$	35.7	1.851	1.65
OP27	$3.7 \pm 0.1 \times 10^{8}$	$70.3\pm1.8$	$1.685 \pm 0.011$	$35.2\pm0.2$	1.831	$1.68 \pm 0.03$
OP28	$3.3 \pm 0.0 \times 10^{8}$	$75.6\pm0.0$	$1.711 \pm 0.005$	36.6	1.851	1.75
OP29	$3.0 \pm 0.0 \times 10^{8}$	$57.7\pm0.7$	$1.709 \pm 0.020$	37.1	1.851	1.94
OP30	$3.4 \pm 0.0 \times 10^{8}$	$60.1 \pm 0.4$	$1.615 \pm 0.005$	37.2	1.851	1.99
OP31	$3.3 \pm 0.0 \times 10^{8}$	$68.4 \pm 0.1$	$1.630 \pm 0.001$	37.3	1.851	1.83
OP32	$3.5 \pm 0.0 \times 10^{8}$	$59.7\pm0.2$	$1.620 \pm 0.006$	$34.4 \pm 0.4$	1.862	$2.06 \pm 0.12$
OP33	$3.7 \pm 0.0 \times 10^{8}$	$60.9 \pm 0.1$	$1.552 \pm 0.003$	35.1	1.851	2.25
OP34	$3.4 \pm 0.0 \times 10^8$	$69.5 \pm 0.2$	$1.623 \pm 0.003$	$39.2 \pm 0.2$	1.844	$2.01 \pm 0.17$
Dodecane						
OP9	$1.7\pm0.0\times10^8$	$36.6\pm0.2$	$1.666\pm0.005$	11.5	1.851	-
OP17	$2.7\pm0.0\times10^8$	$47.5\pm0.2$	$1.660 \pm 0.003$	18.5	1.851	2.25
OP27	$2.7\pm0.0\times10^8$	$40.9\pm0.1$	$1.737\pm0.003$	24.7	1.851	1.42
OP32	$2.4\pm0.0\times10^8$	$28.5\pm0.0$	$1.607\pm0.001$	28.7	1.851	-
OP34	$2.9\pm0.0\times10^8$	$47.2 \pm 0.1$	$1.702 \pm 0.003$	$25.3\pm0.5$	1.920	1.55

#### In conclusion :

In this first part of this chapter, the exhaust of the miniCAST burner was characterized over a wide range of operating conditions covering overall flame equivalence ratios from 0.104 to 1.674 using diesel B7 and from 0.172 to 1.445 using dodecane. PM exhausts were analyzed to describe their mobility-equivalent size distribution, morphology, mass concentration and optical extinction coefficient.

While using diesel B7, the impact of adjusting miniCAST flow rates demonstrated the ability of this burner to produce soot aggregates of variable size distribution and number concentration offering a panel of choice. The burner was found to generate soot aggregates with geometric mean diameters (mobility diameters) in the range 45 - 105 nm with a geometric standard deviation between 1.6 and 1.8. On average, using dodecane instead of diesel B7 resulted in smaller aggregates as low as to 28.5 nm. Thanks to electron microscopy, key parameters describing the aggregates morphology were evaluated. While using diesel B7, the diameter ( $\overline{D_p}$ ) of primary particles was found to vary from ~ 18 nm under fuel-lean conditions up to ~ 39 nm under fuel-rich conditions. Meanwhile, the particles nanostructure was observed to evolve from highly graphitized structures to amorphous texture. Using dodecane instead of diesel B7 resulted also in smaller  $\overline{D_p}$  compared to diesel B7. On the other hand, the use of a catalytic stripper (CS) at 350 °C was found to alter soot aggregates size distributions that became more flattened. Soot aggregates PN losses within the CS were also evaluated and were found in good agreement with modeled losses accounting for diffusion and thermophoresis. However, the CS was not found to significantly alter soot aggregates morphologies.

Regardless of the choice of the liquid fuel, miniCAST exhaust consisted not only of a particulate phase but also of a light absorbing gas phase whose contribution was significant to  $K_{ext}$  over the UV range (< 400 nm) and that increased from fuel-lean to fuel-rich conditions. Second, the Ångström absorption exponent ( $\alpha$ ) retrieved from optical extinction coefficients while accounting for total scattering contribution between 400 nm and 1000 nm was found to increase from 1.05 under fuel-lean conditions up to 2.25 under fuel-rich conditions. Finally, once the exhaust was treated thermally, the contributions to  $K_{ext}$  of absorbing species in the gas phase disappeared and the wavelength decrease in the visible near-IR range became less pronounced with  $\alpha$  varying between 1.11 and 1.66. These observations suggest that the chemical composition of the exhaust, most probably its organic content play a significant role both on the shape and amplitude of  $K_{ext}$ . Therefore, Chapter 6 proposed to study the chemical composition of the combustion products that the miniCAST generates focusing on the organic content of both the gas and the particulate phase.

# 5.2 Comparative methods for soot volume fraction determination

Over the years, many approaches have been reported to evaluate soot volume fraction  $(f_v)$ . These approaches are based either on a single analyzer or on a combination of measurement methods and serve here as a metric of comparison between different assumptions in aggregate modeling and means to compare different diagnostics. First, on the bases of mobility size measurements,  $f_v$  is calculated comparing the spherical particles assumption with the one accounting for aggregates morphology. Then,  $f_v$  evaluated either from mass concentration measurements or optical extinction coefficients are compared to the fractal aggregate approach using standard literature values for soot bulk density and optical properties.

#### 5.2.1 Aggregate soot volume fraction vs. spherical model

In the most simplified approach, soot volume fraction  $(f_v)$  can be evaluated considering soot particles as polydisperse spheres. In this case,  $f_v$  is expressed as the sum over each class of size 'i' of soot aggregate volume having a mobility-equivalent diameter  $D_{m,i}$  and  $N_i$  number of aggregates per unit volume of aerosol (5.4), therefore requiring only mobility-equivalent size distributions as provided by the SMPS measurements. This approach is referred to as "**spherical approach**" (or SMPS). This approach is valid when soot aggregates are spherical but, in our case, oversimplifies the geometry of soot aggregates and thus is expected to overestimate soot volume fraction.

$$f_{v_{(SMPS)}} = \sum_{i}^{k} N_{i} \frac{\pi}{6} D_{m,i}^{3}$$
(5.4)

#### Influence of soot morphology

This second approach assumes that soot particles can be considered as fractal-like aggregates which is supported by the observations done in section 5.1.2. This so-called "fractal-like aggregate approach" (or SMPS + STEM) accounts for morphological aspects by using the soot effective density ( $\rho_{eff,i}$ ) which is size-dependent [147] and defined as the ratio of an aggregate mass and its volume based on its mobility-equivalent diameter [118]. The aggregate mass may be written as a function of  $\overline{D_p}$ ,  $N_p$  and soot bulk density ( $\rho_p$ ), thus one may deduce the ratio (5.5) of  $\rho_{eff,i}$  and  $\rho_p$  which is used to correct the first approach (5.4). In this case, soot particles are treated as polydisperse fractal-like aggregates (assuming monodisperse  $D_{p,i} = \overline{D_p}$  and spherical primary particles size distribution). So, if an aggregate is a sphere, then  $N_p = 1$  and  $D_{m,i} = \overline{D_p}$ .

$$\frac{\rho_{eff,i}}{\rho_p} = N_p \frac{\overline{D_p}^3}{D_{m,i}^3}$$
(5.5)

Using the fractal law (5.2) describing aggregates morphology, the previous ratio can be then expressed as function of measured quantities ( $\overline{D_p}$ ,  $D_f$ ,  $k_f$  and  $D_{m,i}$ ). However, this requires converting the gyration diameter into a mobility-equivalent diameter. A simple conversion law, connecting the gyration diameter ( $D_g$ ) and the electrical mobility diameter ( $D_m$ ), of the form  $\beta = D_g/D_m$  can be used [109]. In fact, the coefficient  $\beta$  depends on the flow regime [110], which is characterized by Knudsen number (Kn). As introduced in section 2.3, in the transient regime (i.e.,  $0.1 \leq Kn \leq 10$ ) which is the case here,  $\beta$  was found to fall in the range  $1.03 < \beta < 1.35$ . Consequently, a conversion ratio of  $\beta \sim 1.3$  is assumed, similarly to Yon *et al.* [37] and Caumont-Prim *et al.* [114]. Combining (5.2) and (5.4), corrected with the density ratio (5.5), soot  $f_v$  can be formulated as in (5.6) while considering aggregates with  $D_{m,i}$  smaller than  $\overline{D_p}$  to be spherical, similarly to the approach proposed by Kelesidis *et al.* [222].

$$f_{v_{(SMPS + STEM)}} = \begin{cases} \sum_{i}^{k} N_{i} \frac{\pi}{6} \beta^{D_{f}} k_{f} \overline{D_{p}}^{3-D_{f}} D_{m,i}^{D_{f}} &; D_{m,i} > \overline{D_{p}} \\ \sum_{i}^{k} N_{i} \frac{\pi}{6} D_{m,i}^{3} &; D_{m,i} \le \overline{D_{p}} \end{cases}$$
(5.6)

#### Influence of size distribution extrapolation

As previously discussed in section 5.1.1, some mobility-equivalent size distributions tails are truncated. As both the fractal aggregate and spherical approaches use the same size distributions, they are most likely to underestimate  $f_v$  when compared with other techniques (optical for instance) where this constrain is lifted. Size distributions extrapolated, as discussed in section 5.1.1, are used to estimate the percentage of  $f_v$  to be added to  $f_{V(SMPS)}$ (see Figure 5.13.(a)) and  $f_{V(SMPS + STEM)}$  (see Figure 5.13.(b)) to overcome this lack. Even though the size distribution extrapolation only adds few percentages in PN (< 2 %), the  $f_v$ correction is more important since this missing information lays in the upper bound of the size distribution with higher sizes. Under the spherical approach, this correction accounted on average for  $15 \pm 5$  % (all 34 OPs considered), while under the fractal aggregate approach it was limited to  $7 \pm 5$  % as shown in Figure 5.13.



Figure 5.13. Percentage of added soot volume fraction to (a)  $f_{v_{(SMPS)}}$  (spherical approach) and (b)  $f_{v_{(SMPS+STEM)}}$  (fractal aggregate approach), resulting from size distributions tail extrapolation for diesel B7.

Figure 5.14 compares the  $f_v$  calculated using the spherical and the fractal aggregate approach. It is found that assuming all particles to be spherical overestimates on average by ~70 % the  $f_v$  compared to taking fractal aggregates into consideration. This is true for 9 data points (6 OPs of untreated and 3 of CS-treated exhaust) for which all parameters in (5.4) and (5.6) were measured except the hypothesis on  $\beta$ . Adding the rest of the 34 OPs to the analysis (for both untreated and CS-treated exhaust), with assumed particles morphology, seems to corroborate the previous statement. Figure 5.14 also shows that this overestimation can reach up to 3 time if an aggregate gyration and mobility-equivalent diameters were considered equivalent (i.e.,  $\beta = 1.0$ ). In a recent work, Kelesidis *et al.* [222] showed that  $f_v$  derived from mobility data (neglecting aggregates fractal aspect) overestimated up to four times the  $f_v$  derived from mass-mobility measurements and that once the fractal-like morphology was accounted for this deviation decreased down to 6 %. In the light of this, we will consider that  $f_{v(SMPS+STEM)}$  computed considering both mobility and morphological data as reference.



Figure 5.14.  $f_{v_{(SMPS)}}$  evaluated assuming polydisperse spherical particles vs.  $f_{v_{(SMPS+STEM)}}$  calculated assuming polydisperse fractal-like aggregates. Data not corrected for dilution (~ 19:1).

#### 5.2.2 Mass based vs. fractal aggregate volume fraction

In this section, a mass-based method to calculate  $f_v$  is used. Using mass filter deposition (see Figure 5.15) mass concentrations were measured as detailed in section 3.3. Table 5.4 summarizes the measured particulate mass concentrations  $C_s$  for both untreated and thermally treated exhaust. The soot volume fraction is obtained from (5.7) by assuming  $\rho_p$ :





Figure 5.15. Soot aggregate samples deposited on borosilicate microfibers filters (Pallflex, Emfab) generated under OP2, OP9, OP17, OP27, OP32 and OP34 operating points grouped by fuel, either diesel B7 or dodecane, for both untreated (raw) and CS-treated exhaust.

Liquid	OP	$C_s [mg/m]$	m <sup>3</sup> ]
fuel	01	Untreated (raw)	CS-treated
	OP2	0.80	0.73
37	OP9	4.00	2.73
el I	OP17	9.53	6.20
ies	OP27	18.07	11.67
D	OP32	7.67	3.00
	OP34	15.27	4.07
	OP9	0.73	0.67
ne	OP17	2.33	1.00
odeca	OP27	0.80	0.47
	OP32	0.73	0.07
D	OP34	2.80	1.07

Table 5.4. Soot mass concentrations for miniCAST operating points for both untreated (raw) and thermally treated (CS-treated) exhaust. Data not corrected for dilution ( $\sim 19:1$ ).

Figure 5.16 shows the initial estimation of  $f_{v_{(Mass)}}$  assuming a value of  $\rho_p$  commonly found in the literature for mature soot  $\rho_p = 1800 \text{ kg/m}^3$  [196], which exhibits a roughly linear correlation with  $f_{v_{(SMPS+STEM)}}$ . On average, using this approach seems to underestimate by 28 %  $f_{v_{(SMPS+STEM)}}$ , except for untreated OP34 whose  $f_{v_{(Mass)}}$  is overestimated. For CS-treated conditions, this trend remained valid, only this time  $f_{v_{(Mass)}}$  value for CS-treated OP34 is more coherent with its corresponding  $f_{v_{(SMPS+STEM)}}$  which suggests that generated aggregates under this operating point consists probably of less dense material whose volatile fraction is oxidized. Modifying the bulk density assumption to  $\rho_p = 1296 \text{ kg/m}^3$  yields a slope of 1:1. This parameter tuning is in the range of previously reported  $\rho_p$  values for soot aggregates produced by miniCAST using propane that varied between 1227 kg/m<sup>3</sup> and 1543 kg/m<sup>3</sup> according to Yon *et al.* [147]. However, in another study, Yon *et al.* [37] used a similar approach and evaluated  $f_v$  on the basis of SMPS size distributions, morphology (assuming  $\beta = 1.3$  for  $D_m - D_g$  conversion) and assuming  $\rho_p = 1740 \text{ kg/m}^3$ , and found that the SMPS-morphology based  $f_v$  is underestimated by a relative factor up to 81 % compared to  $f_v$  deduced from mass measurements. The reasons for this lack of agreement are yet to be determined.



Figure 5.16.  $f_{v_{(Mass)}}$  evaluated from soot deposits assuming a constant soot bulk density ( $\rho_p = 1800 \text{ kg/m}^3$ ) vs.  $f_{v_{(SMPS + STEM)}}$  assuming polydisperse fractal-like aggregates. Data not corrected for dilution (~ 19:1).

#### 5.2.3 Volume fraction derived from extinction measurement

The last approach of  $f_v$  calculation is optical based, where an extinction measurement is used to evaluate  $f_{v(Optical)}$ . In this work, optical extinction coefficients (K<sub>ext</sub>) were measured between 200 nm and 1000 nm. It has been shown in section 5.1.3 that gas phase absorption contribution to K<sub>ext</sub> is limited to below 400 nm. On the other hand, diameter of the primary particles ( $\overline{D_p}$ ) were found to vary between ~ 18 nm and ~ 39 nm (see section 5.1.2). This means that the Rayleigh approximation ( $x_p = \pi \overline{D_p}/\lambda \ll 1$ ) is valid at 700 nm and therefore soot scattering can be neglected (K<sub>ext</sub>  $\approx K_{abs,soot}$ ). In this case, f<sub>v</sub> can be evaluated using (5.8) if the soot absorption function E(m) is known. As a first approach, it is proposed to use a constant value of E(m,  $\lambda = 700$  nm) = 0.35 as considered by Simonsson *et al.* [199].

$$f_{v_{(Optical)}} = \frac{\lambda K_{abs,soot}}{6\pi E(m,\lambda)}$$
(5.8)

Accordingly, Figure 5.17 shows  $f_{V(Optical)}$  evaluated for all investigated cases plotted against  $f_{V(SMPS\,+\,STEM)}$  and against  $f_{V(Mass)}$  (see Figure 5.17.(b)). Overall,  $f_{V(Optical)}$  shows a good agreement with  $f_{V(SMPS\,+\,STEM)}$  although it underestimated it by  $\sim 13$ %.  $f_{V(Optical)}$  also agreed with  $f_{V(Mass)}$  although it overestimated it by  $\sim 25$ %.

What this study most importantly demonstrates, is that despite the uncertainties inherent to each experimental method, the soot volume fraction evaluated with these three methods are in reasonable agreement. Finally, for the untreated conditions, using either diesel B7 or dodecane, soot volume fraction that the liquid miniCAST is able to provide (corrected for dilution) evaluated with these three methods are available in Table 5.5.



Figure 5.17.  $f_{v_{(Optical)}}$  calculated assuming a constant absorption function (E(m) = 0.35) at 700 nm vs. (a)  $f_{v_{(SMPS + STEM)}}$  and (b)  $f_{v_{(Mass)}}$  calculated assuming a constant soot bulk density ( $\rho_p = 1800 \text{ kg/m}^3$ ). Data not corrected for dilution (~ 19:1).

**Table 5.5.** Soot volume fraction  $(f_v)$  evaluated using three methods: granulometric (combining mobility size and morphology)  $f_{V(SMPS + STEM)}$ , mass  $f_{V(Mass)}$  and optical  $f_{V(Optical)}$  for soot aggregates generated by a miniCAST burner using diesel B7 or dodecane for untreated (raw) exhaust. All this data is corrected for dilution (~ 19:1).

Operating point (OP)	$f_{v_{\rm (SMPS+STEM)}} \ [\rm ppb]$	$f_{v_{(Mass)}}$ [ppb]	$f_{V_{(Optical)}}$ [ppb]
Diesel B7			
OP1	$21.0\pm0.4$	-	$26.6 \pm 4.3$
OP2	$14.1 \pm 3.4$	8.4	$3.8 \pm 4.7$
OP3	$39.1\pm0.6$	-	$42.7\pm6.3$
OP4	$8.6\pm0.3$	-	-
OP5	$16.5\pm0.4$	-	-
OP6	$41.0 \pm 2.3$	-	$7.5 \pm 4.1$
OP7	$32.0\pm0.8$	-	$9.6 \pm 4.1$
OP8	$11.8\pm0.5$	-	-
OP9	$42.9\pm0.4$	42.2	$38.8\pm5.9$
OP10	$63.0 \pm 1.4$	-	$86.1\pm7.0$
OP11	$49.7\pm1.0$	-	$23.4 \pm 4.1$
OP12	$62.8 \pm 1.8$	-	$46.2 \pm 5.8$
OP13	$125.4 \pm 1.8$	-	$104.8\pm6.5$
OP14	$101.3\pm0.2$	-	$43.5 \pm 5.4$
OP15	$123.2 \pm 0.8$	-	$74.6 \pm 5.6$
OP16	$152.2 \pm 7.1$	-	$139.2 \pm 9.0$
OP17	$209.4 \pm 0.6$	100.6	$225.7\pm9.3$
OP18	$181.8 \pm 2.5$	-	$142.1 \pm 14.1$
OP19	$210.9 \pm 2.5$	-	$160.9 \pm 17.0$
OP20	$203.9 \pm 2.2$	-	$353.5 \pm 30.0$
OP21	$192.9 \pm 3.2$	-	$164.4 \pm 14.7$
OP22	$82.1 \pm 1.2$	-	$32.0 \pm 5.7$
OP23	$107.2 \pm 1.5$	-	$56.2 \pm 7.1$
OP24	$176.6 \pm 5.2$	-	$138.8 \pm 29.0$
OP25	$117.4 \pm 2.5$	-	$125.2 \pm 25.1$
OP26	$182.9 \pm 1.1$	-	$141.6 \pm 13.7$
OP27	$238.1 \pm 6.1$	190.7	$246.9 \pm 325.4$
OP28	$165.6 \pm 2.0$	-	$109.3 \pm 11.2$
OP29	$91.9 \pm 1.4$	-	$43.0 \pm 11.7$
OP30	$100.4 \pm 1.5$	-	$56.6 \pm 10.6$
OP31	$134.6 \pm 0.5$	-	$120.7 \pm 16.4$
OP32	$144.4 \pm 1.0$	81.0	$85.1 \pm 12.7$
OP33	$99.2 \pm 1.0$	-	$53.8 \pm 10.1$
OP34	$100.1 \pm 2.9$	161.2	$142.8 \pm 27.1$
Dodecane			
OP9	$5.3 \pm 0.2$	7.7	-
OP17	$24.7\pm0.4$	24.6	$14.6 \pm 4.4$
OP27	$27.4\pm0.2$	8.4	$11.8 \pm 4.3$
OP32	$11.6\pm0.0$	7.7	-
OP34	$48.3\pm0.6$	29.6	$17.1 \pm 4.5$

#### In conclusion :

In the second part of this chapter, the soot volume fraction ( $f_v$ ) was evaluated comparing methods based on the measurement of the aggregate size (combining size distribution and morphology), deposited mass and optical extinction. The main conclusions of this study are (i) that  $f_v$  evaluated on the basis of size mobility data alone overestimate by ~ 70 % the one accounting for morphological aspects (fractal aggregate approach), (ii) that  $f_v$  evaluated optically reasonably agreed with both  $f_v$  measured adopting the fractal aggregate approach (within 13 %) and  $f_v$  evaluated from mass concentration measurements (within 25 %) assuming a soot bulk density of 1800 kg/m<sup>3</sup>.

Overall, there are many reasons that make convenient the measurement of  $f_{\rm v}$  using optical methods. First, acquiring optical extinction coefficients over a wide wavelength range (i.e., 200 nm - 1000 nm in this case) offered a considerable advantage that is the freedom to choose the measurement wavelength. The choice of exploiting  $K_{ext}$  measurement at 700 nm was motivated in this case by the absence of gas phase absorption and the negligible contribution of total scattering. Yet, to deduce  $f_v$ , the absorption function E(m) = 0.35 at 700 nm had to be approximated as constant while in reality it may differ from one condition to another and from one wavelength to another. So far, exhaust generated by the miniCAST using liquid fuels contained only PM and its associated gas phase. As introduced in Chapter 1, one of the goals of this work is to exploit the  $K_{ext}$  measurement to simultaneously measure soot  $f_{\rm v}$  and the concentration of other gaseous pollutants such as NO, NO\_2 and NH\_3 a combustion exhaust could contain. This means that interference of gaseous pollutants absorption with PM is possible. So, if  $f_v$  has to be estimated at another wavelength, more information on the spectral dependence of E(m) is required. Hence the usefulness of the methodology presented in Chapter 4 in estimating E(m) independently from both the wavelength (between 400 nm and 1000 nm) and the operating conditions to hopefully reduce the uncertainty in evaluating soot volume fraction using optical-based methods. This topic will be addressed later in Chapter 7.

# Chapter 6

# Characterization of the chemical composition of the exhaust of the miniCAST burner

The results presented in this chapter describe the chemical composition of the exhaust produced by the miniCAST burner under various operating conditions focusing on its organic content. There is no single diagnostic able to draw the complete picture of the chemical composition of the exhaust both qualitatively and quantitatively. Thanks to the reliability and wide mass detection range that flame ionization detectors (FIDs) offer for quantitative measurement of carbon containing species, the choice was made to use a FID-based analyzer for monitoring the total hydrocarbon content (THC). This was complemented by the use of ex-situ gas chromatography - FID (GC-FID) to quantify the low mass species (m/z < 150) in the gas phase. As for the high mass species ( $m/z \ge 150$ ), the choice was made to use ex-situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) to qualitatively describe the organic content of the condensable gas phase and the PM.

Accordingly, this chapter is structured in three parts. The first part is dedicated to describe the chemical composition of the gas phase of the miniCAST exhaust (i) globally through a continuous monitoring of the THC over the entire operating range and (ii) in detail and identify species by GC-FID that contribute to the THC measurement. The second part proposes a complementary description of the condensable gas phase using ToF-SIMS and additionally provides new information on the surface chemical composition of the PM. All along these descriptions, multiple operating conditions are investigated and used to examine the relationship between the chemical composition and the optical absorption coefficient of the exhaust which will be discussed in the third part.

# 6.1 Chemical composition of the gas phase

The chemical composition of the gas phase of the miniCAST exhaust was investigated, first by describing its total hydrocarbon content (THC) while using diesel B7 over the entire operating range (i.e., all 34 OPs) or dodecane on a selection of operating points (i.e., OP9, OP17, OP27, OP32 and OP34). Then, a selection of operating conditions were considered to carry out GC-FID analysis to quantitatively and qualitatively describe (i) the species the gas phase contains and how they evolve from one operating point to another while using diesel B7, (ii) the impact of changing the fuel compositing from diesel B7 to dodecane and (iii) the impact of the thermal treatment using a catalytic stripper (CS).

#### 6.1.1 FID detection

In this work, the total hydrocarbon content (THC) of the gas phase produced by the mini-CAST was continuously monitored using a graphite 52M-D FID-based analyzer (see section 3.4). Accordingly, Figure 6.1 shows the evolution of the THC produced as a function of the global flame equivalence ratio ( $\varphi$ ). This Figure clearly shows that while using diesel B7, the THC produced by the miniCAST increased with  $\varphi$ . Under very fuel-lean conditions ( $\varphi < 0.3$ ), the THC of the miniCAST gas phase is below the FID detection limit and only starts to monotonically increase from  $\varphi \sim 0.6$  to reach  $\sim 300$  ppmC around  $\varphi \sim 1.5$ . Also, switching from diesel B7 to dodecane do not seem to impact the THC which is found to follow the same trend as before (while using diesel B7). The operating points OP9, OP17, OP27, OP32 and OP34 shown in colors describe this trend very well, hence their selection for GC-FID analysis to identify the species in the gas phase. It is worth mentioning that, under the applied dilution ratios (i.e.,  $\sim 19:1$ ), the THC in the gas phase of the miniCAST exhaust using diesel B7 is similar to the peak concentration during cold start and regeneration events for light-and heavy-duty diesel engines which varies between 200 ppmC and 350 ppmC as reported by Giechaskiel *et al.* [174].



Figure 6.1. Total hydrocarbon content (THC) as a function of the global flame equivalence ratio  $(\varphi)$  for 34 OPs for untreated and filtered (using a high efficiency particle filter) exhaust while using diesel B7 and dodecane (OP2, OP9, OP17, OP27, OP32 and OP34 are shown with colors). Black squares correspond to the other OPs. Uncertainties account for 8 minutes of continuous analysis using the graphite 52M-D FID-based analyzer (see section 3.4) (May - July 2021). Data not corrected for dilution (~ 19:1).

# 6.1.2 GC-FID low mass analysis

Due to time and resources constraints, only some operating conditions, summarized in Table 6.1, were selected to carry out the GC-FID analysis following the experimental protocol described in section 3.4. The goal of this analysis is to describe (i) the species the gas phase contains and how they evolve from one operating point to another while using diesel B7, (ii) the impact of changing the fuel compositing from diesel B7 to dodecane and (iii) the impact of the thermal treatment using a catalytic stripper (CS) operated at 350°C. Before analyzing the content of the gas phase under a given operating condition, two blank samples were extracted while the miniCAST was running under idle condition, with and without CS. The analysis of the blanks is available in Appendix Figure I.1 and notably showed the absence of contamination from the sampling line while passing thought the CS or while bypassing it.

Operating point (OP)	Flame overall equivalence ratio φ	Condition	Global dilution ratio
Blank sample		Untreated + Filtered	19:1
Blank sample		CS-treated + Filtered	19:1
	Diesel B7		
OP9	0.300	Untreated + Filtered	19:1
OP17	0.626	Untreated + Filtered	19:1
OP27	0.933	Untreated + Filtered	19:1
OP32	1.502	Untreated + Filtered	19:1
OP34	1.564	Untreated + Filtered	19:1
OP27	0.933	CS-treated + Filtered	19:1
OP34	1.564	CS-treated + Filtered	19:1
	Dodecane		
OP27	0.862	Untreated + Filtered	19:1
OP34	1.445	Untreated + Filtered	19:1

 Table 6.1. Overview of the operating conditions selected for GC-FID analysis of the gas phase of the miniCAST exhaust.

Figure 6.2 displays part of the results of the GC-FID analysis showing the concentration (in ppmC) of identified species (shown in each row). This Figure highlights the impact of changing the miniCAST OP while using diesel B7 for the untreated exhaust. Most of the generated gas phase contains methane, ethylene, acetylene, ethane, propylene, propane, propadiene, 3-butadiene, 2-M-1, 3-butadiene and benzene. The second most noticeable contributions are attributed to 4-M-1-pentene, M-Cyc-pentane, toluene, E-Cyc-hexane, E-benzene, m- and p-xylene, styrene, 1-M-3-E-benzene, 1,2,4-TM-benzene and indane and with a smaller amount of naphtalene. The GC-FID analysis of the miniCAST gas phase was also performed using dodecane instead of diesel B7 for untreated exhaust, but only for the fuel-lean OP27 and the fuel-rich OP34 operating points. The results of this analysis are available in Appendix Figure I.2. At these operating points, using dodecane as a fuel was found to produce more ethylene, t-2-butene, 1-butyne and naphthalene compared to case where diesel B7 was used. Overall, it was observed that as the miniCAST was switched from fuel-lean to fuel-rich OPs, the concentration of species in the gas phase increased.

Since the GC-FID measurements were performed few months after the continuous measurement of THC using only the FID-based analyzer, the data are compared by summing the amount of all species quantified by GC-FID for each operating condition. Figures 6.3.(a,c) show the THC measured by the FID-based analyzer using either diesel B7 or dodecane, while Figures 6.3.(b,d) show the THC deduced from the GC-FID measurement.



Figure 6.2. Results of the GC-FID analysis of miniCAST gas phase obtained under OP9, OP17, OP27, OP32, and OP34 for untreated (raw) and filtered exhaust using diesel B7 (October 2021). Data not corrected for dilution (~ 19:1).



Figure 6.3. Total hydrocarbon content (THC) of the gas phase of the exhaust for different operating points (OP2, OP17, OP27, OP32 and OP34). The data are classified on the diagnostic (FID only and GC-FID, by columns) and on the fuel (diesel B7 and dodecane, by rows). THC data in (a,c) were acquired using the graphite 52-M-D (Envea) where uncertainties account for 8 minutes continuous analysis (July 2021), while measurements in (b,d) were performed using a Varian 450-GC FID (October 2021). Data not corrected for dilution (~ 19:1).

These measurements (FID-only vs. GC-FID), although distant in time, are in good agreement. In particular, the increase of THC from fuel-lean to fuel-rich OPs is respected regardless of the used fuel. The THC measured by GC-FID and FID-only were found to be generally in good agreement, with a maximum difference of ~ 40 %. These differences could have resulted from (i) day-to-day variations of the combustion conditions, (ii) the sampling protocol with a long sampling line, although heated at 180 °C, used for the graphite 52M-D analyzer compared to gas samples extraction using Tedlar bags for the GC-FID analysis, and (iii) the measurements uncertainties and recovery rate of the GC-FID.

The GC-FID analysis allows to organize the identified species in classes that are alkanes, alkenes, alkynes and aromatics. Accordingly, Figure 6.4 displays the results of the GC-FID analysis classified as such. The last class, with the lowest contributions, contains all the species with a known number of carbon atoms but that the GC-FID analysis failed to assign with certainty. This Figure also shows three studied configurations corresponding to (i) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(a)), (ii) gas phase samples obtained for CS-treated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using diesel B7 (see Figure 6.4.(b)) and (iii) gas phase samples obtained for untreated exhaust while using die



Figure 6.4. Total hydrocarbon content (THC) deduced from GC-FID analysis of the gas phase of the miniCAST exhaust obtained under (a) OP9, OP17, OP27, OP32 and OP34 (b,c) OP27 and OP34 miniCAST operating points for (a,c) untreated (raw) and filtered exhaust and (b) thermally treated (CS-treated) and filtered exhaust using (a,b) diesel B7 and (c) dodecane (October 2021). Data are organized by class of chemical species and are not corrected for dilution (~ 19:1).

Looking into Figure 6.4.(a) one can see that alkenes are the responsible for the largest contribution to the chemical composition of the gas phase. In Figures 6.4.(a,c) under fuel-lean OP27 and fuel-rich OP34, the production of alkenes is more significant while using dodecane instead of diesel B7. Moreover, while using diesel B7, Figure 6.4.(b) shows that the CS use results in the quasi-total oxidation of the gas phase obtained under OP27 and OP34 with an oxidation efficiency > 96 %. The detailed GC-FID analysis for these CS-treated cases is available in Appendix Figure I.3. Figure 6.5 displays the calculated oxidation efficiency per class of chemical species under these two OPs (OP27 and OP34) and shows that among all identified species, alkenes and alkynes were almost completely oxidized. Alkanes had the lowest removal efficiency (18 % under OP27 and 28 % under OP34). Furthermore, aromatics and other unidentified species (with 4-11 carbon atoms) seem also to be oxidized but with lower efficiency that fluctuates between 90 % and 97 %.



Figure 6.5. Oxidation efficiency calculated per class of chemical species found in the gas phase of the miniCAST exhaust obtained under OP27 and OP34 using diesel B7 (October 2021). The oxidation process results from the use of a catalytic stripper operated at 350 °C.

# 6.2 ToF-SIMS analysis of the PM chemical composition

In this section an analysis is carried out to provide more information on the chemical composition of the PM generated by the miniCAST burner under various operating conditions. To this end, the time-of-flight secondary ion mass spectrometry (ToF-SIMS) analyses described in section 3.4 were performed on a selection of operating conditions summarized in Table 6.2. As discussed in section 3.4, the sampling time was varied between 20 and 120 minutes as a function of the burner's soot production to insure that only the necessary amount of PM was deposited on the substrate surface. These conditions were selected to explore the impact of (i) adjusting the miniCAST flow rates while using diesel B7, (ii) changing the fuel composition from diesel B7 to dodecane and (iii) adding a catalytic stripper (CS) thermal treatment at 350 °C. Since using dodecane was found to produce less PN compared to diesel B7 (see section 5.1.1), the global dilution ratio was reduced to almost half of that applied for diesel B7 (see Table 6.2).

Operating point (OP)	Condition	Flame overall equivalence ratio φ	Sampling time [min]	Global dilution ratio
		Diesel B7		
OP2	Untreated	0.187	40	10:1
OP9	Untreated	0.300	40	19:1
OP17	Untreated	0.626	35	19:1
OP27	Untreated	0.933	20	19:1
OP32	Untreated	1.502	30	19:1
OP34	Untreated	1.564	20	19:1
OP2	CS-treated	0.187	90	10:1
OP9	CS-treated	0.300	60	19:1
OP17	CS-treated	0.626	45	19:1
OP27	CS-treated	0.933	40	19:1
OP32	CS-treated	1.502	50	19:1
OP34	CS-treated	1.564	40	19:1
		Dodecane		
OP9	Untreated	0.277	120	10:1
OP27	Untreated	0.862	60	10:1
OP34	Untreated	1.445	45	10:1
OP9	CS-treated	0.277	180	10.1
OP27	CS-treated	0.211	90	10.1
OP34	CS-treated	1.445	50 60	10.1
01.04	OD-mealed	1.440	00	10.1

 Table 6.2.
 Overview of the operating points and sampling conditions selected for the ToF-SIMS analysis of the miniCAST exhaust.

It is worth reminding that PM sampling was done by impaction on Ti wafers (see section 3.4). Experiments conducted by Irimiea et al. [185] and Faccinetto et al. [73] used a similar sampling system, and suggested that the used sampling apparatus offers the advantage of allowing a rough separation between (i) PM that deposits on the central of an impaction spot and (ii) the condensable gas phase that diffuses on the surface of the wafer. Accordingly, for each operating condition (see Table 6.2) mass spectra in positive polarity were acquired from 6 regions of interest (i.e., ROIs), 3 targeting the central deposit referred to here as 'on **spot**' and 3 others targeting the peripheral area around it referred to here as 'off spot'. All acquired mass spectra were then post processed following the methodology presented in section 4.4. To sum up, this post processing consisted in aligning, calibrating and detecting ion peaks in each mass spectrum. Then, a peak list was automatically built where most of the identified species (not considered as substrate) were assigned. The resulting peak list is what constitutes the initial data set used for the analysis conducted here. Figure 6.6.(a) shows a mass defect plot with all detected clusters (groups of peaks describing probably the same ion species) over the 0 - 600 m/z detection range. The use of Ti wafers as substrate offered the advantage of easy identification since Ti has a distinctive isotopic pattern and high negative

mass defect. Hence, the clusters (in black) shown in Figure 6.6.(a) identified as background (substrate) and that consists mostly of Ti oxides ions.



Figure 6.6. Mass defect plot showing all detected ion peaks across the 126 mass spectra over the entire mass detection range  $(0 - 600 \ m/z)$ , indicating ion species considered as background (substrate) (in black) and in (a) the data of interest (in blue) and in (b) the data of interest (in red) without fragment ions (in gray).

Once the contribution of the substrate is removed, one can examine the global content of each mass spectrum. As such, Figure 6.7 shows examples of mass spectra after the removal of the contribution of the substrate, and displays mass spectra measured for 'on spot' and 'off spot' ROIs under the fuel-rich OP34 condition for untreated exhaust while using diesel B7. When using the ToF-SIMS diagnostic, systematic differences in the amount of desorbed and ionized compounds are common and may originate from various sources. The overall result is a fluctuation of the ion count which does not reflect the true amount of each molecular species in the sample deposit. To compensate at least partially for these differences, the ion count was normalized to the total ion count calculated on the selected peak list, after discarding any signal attributed to the substrate. The mass spectra shown in Figure 6.7 are normalized accordingly.



Figure 6.7. ToF-SIMS mass spectra (after background substrate subtraction) for untreated exhaust obtained under OP34 while using diesel B7 and measured from (a) 'on spot' ROI and (b) 'off spot' ROI. The raw TIC (before normalization) is indicated above the legend for each mass spectrum.

The common feature these mass spectra share is that they are all dominated by low mass fragment ions in the region m/z < 150 regardless of the ROI ('on spot' vs. 'off spot') and of the operating point (not shown here). Most of the fragment ions result from postionization dissociation reactions [223, 73] of large organic molecules like polycyclic aromatic hydrocarbons (PAHs), however some of the fragment ions have been also shown to derive from the dissociation of organic contamination pre-existing on the surface of the substrate [224]. Since fragment ions having different origin are mixed in the region m/z < 150, for the statistical analysis the choice was made to limit the use of signals of organic ions to the region  $m/z \ge 150$ , as they can all and only be attributed to the samples. In the mass defect plot, the majority of the removed fragment ions are shown in gray in Figure 6.6.(b). Mass spectra displayed in Figure 6.7 also show that 'on spot' ROIs (see Figure 6.7.(a)), which are representative of PM deposits, are significantly richer in high m/z than condensable gas 'off spot' ROIs (see Figure 6.7.(b)) and exhibit an intensity maximum between 150 m/z and 500 m/z. It should be clarified that even if 'off spot' mass spectra provide chemical information on the condensable gas phase, the possibility that 'on spot' mass spectra contains contributions from condensable gas phase mixed to soot aggregates cannot be neglected. Moreover, detected peaks in the mass spectra investigated in this work. In order to distinguish differences and similarities between the mass spectra, more advanced statistical tools will therefore be needed.

As already briefly mentioned above, the fragment ions are common to all mass spectra, the choice was made to discard them from the analysis and focus on  $m/z \ge 150$  highlighted in red in Figure 6.6.(b) (i.e., data of interest without fragment ions). Accordingly, from now on the mass spectra are normalized to the total ion count calculated on the selected peak list after discarding any signal attributed to the background (substrate) and to fragment ions. The final peak list (without substrate and fragment ions) contains 484 entries. Given this large number of variables, it is difficult to easily see the m/z that are common/different from one mass spectrum to another. That is why multivariate analysis (MVA) methods are usually applied in mass spectrometry to better identify similarities and differences between mass spectra [225]. One of the widely used MVA methods is the principle component analysis (PCA). In this work, PCA is used as a statistical tool for interpretation and exploration. As such, a brief description of PCA modeling is given here, but more details can be found in the literature [226, 227].

#### Principal component analysis (PCA)

The essence of a PCA is to replace the original J = 484 peak list elements (i.e., variables) with K components, with K  $\ll$  J. From a theoretical point of view, this consists of an orthogonal transformation that projects the original mass spectra (i.e., observations) onto linearly uncorrelated variables called principal components (PCs) that explain each a percentage of the variance of the data set. This way, the initial peak list elements are replaced with few PCs weighted by contributions from the elements of the peak list. These weights are called loadings and may serve to support a chemical interpretation. Compressing the initial peak list elements into fewer PCs greatly facilitates the interpretation by highlighting similarities and differences that would not be possible to see otherwise. It should be clarified that the data set (the group of mass spectra) fed to the PCA is not the matrix of normalized ion count (NIC) that contains the peak list elements for each mass spectrum, but it is the mean center of that matrix. Such pre-processing is common before applying the PCA [225]. As such, mean-centering the data set consists of subtracting the mean value of NIC for ion species (across mass spectra) from that ion species NIC in each spectrum. Hence, getting a data set that evaluates differences between mass spectra variances instead of their means.

Each time the PCA was applied, the first and second components were found to explain most of the variance within a data set. As long as the number of PCs is small compared to the number of variables [226] (484 in this case) and that the data set is normally distributed as shown in Figure 6.8.(a), including additional components did not change dramatically the results. Figure 6.8.(b) shows the percentage of the explained variance up to 12 used PCs for instance for one of the studied cases shown later. Figure 6.8.(c) displays the cumulative explained variance and shows that usually the first 4 PCs explain more than 90 % of the data set variance. Nevertheless, it should be kept in mind that the impact of real phenomena on the variance can be small, yet important and non-negligible even when associated to low explained variance PCs [226].



Figure 6.8. (a) Distribution of normalized ion count of peak list entries across all mass spectra, (b) percentage of explained variance by the first 12 principal components (PCs) and (c) the cumulative variance along those PCs.

The projection of a mass spectrum in a PC space results in having coordinates ("scores", one for each mass spectrum) in the PC space indicative of the weight it has according to each PC. That is why mass spectra can be represented in a scatter score plot according to any two PCs. Data points (i.e., mass spectra) that have close scores along a given PC are similar in terms of what that PC represents which is defined by its loadings. Inversely, the higher the distance between two data points (i.e., mass spectra) along a given PC axis in a score plot the more it reveals differences between them in terms of what that PC represents. This is useful to quantify patterns within a group of mass spectra.

## 6.2.1 Impact of miniCAST OPs while using diesel B7

Focusing first on the untreated exhaust, the goal here is to explore the impact of adjusting miniCAST flow rates (i.e., OPs) on the chemical composition of condensable gas phase and PM while using diesel B7. To this end, two data sets are considered separately (i) 'on spot' mass spectra and (ii) 'off spot' mass spectra.

## Condensable gas

Figure 6.9 displays the normalized ToF-SIMS mass spectra (without the background (substrate) and fragment ions) between 150 m/z and 600 m/z at six different miniCAST operating points (OP2, OP9, OP17, OP27, OP32 and OP34). These mass spectra are acquired on the 'off spot' ROIs and only contain the contribution of the condensable gas phase and not of the PM [185, 73]. Figure 6.9 seems to indicate that the contribution of high mass species progressively increases from fuel-lean (e.g., OP2) to fuel-rich (e.g., OP34) operating points. This observation is consistent with GC-FID results shown in section 6.1.2, that although limited below 150 m/z, quantitatively demonstrated the increasing presence of organics in the gas phase from fuel-lean to fuel-rich operating points. It was also shown from GC-FID measurements that the majority of the gas phase content was attributed to low mass species and that high mass species contributed significantly less to the exhaust THC. This leads to believe that the absolute contribution to the gas phase of the high mass species detected by ToF-SIMS visible in the mass spectra up to 450 m/z remains small overall.


Figure 6.9. Processed (without the background (substrate) and fragment ions) ToF-SIMS mass spectra measured from 'off spot' ROI for untreated exhaust obtained under OP2, OP9, OP17, OP27, OP32 and OP34 while using diesel B7. The total ion count is indicated above the legend.

There are 484 peak list elements between 150-600 m/z. Revealing the specific similarities and differences between samples in Figure 6.9 is not obvious. Therefore, it is proposed to apply PCA, as explained previously, on this group of mass spectra. Accordingly, the results of the PCA are shown in Figure 6.10. As mentioned before, mass spectra can be represented by scatter points as shown in Figure 6.10.(a) where the coordinates ('scores') of each mass spectrum along each PC can be interpreted using the contributions ('loadings') of the peak list elements along each PC as shown in Figures 6.10.(b,c).



Figure 6.10. Results of the PCA performed on 484 selected m/z in the ToF-SIMS mass spectra and representing the chemical composition of the condensable gas phase ('off spot') in Figure 6.9. (a) PC2 vs. PC1 score plot. Each data point represents one mass spectrum. Color coded symbols represent the miniCAST operating point. (b) and (c) PC1 and PC2 loading plots. Red and black represent the sign of the loadings.

For this study case, Figure 6.10.(a) shows the scores of each mass spectrum along the PC2 and PC1. Here, the PC1 and PC2 explain ~ 82 % of the variance with most of it conveyed by the PC1 (~ 60 % of the explained variance). In this score plot, mass spectra

are grouped per OP shown with color coded symbols. In Figure 6.10.(a) the PC1 seems to separate OP2 and OP9 with high positive scores from the rest of the OPs (OP17, OP27, OP32 and OP34) most of which have negative PC1 scores. The loadings of the PC1 (see Figure 6.10.(b)) show that many peaks between 150-400 m/z contribute to the negative scores while only some peaks up to 250 m/z contribute to the positive scores. On the other hand, the PC2 conveys ~ 23 % of the explained variance. Along the PC2, it was not possible to find clear trends.

#### Particulate matter

Figure 6.11 displays ToF-SIMS mass spectra (without the background (substrate) and fragment ions) normalized in intensity between 150-600 m/z at six different miniCAST operating points (OP2, OP9, OP17, OP27, OP32 and OP34). These mass spectra are acquired from the 'on spot' ROIs and they mainly contain contributions from the PM and condensable gas phase [185, 73]. Since most of the assigned peaks correspond to organic ions, Figure 6.11 globally shows that for these PM samples the contribution of high m/z increases from fuelean (e.g., OP9) to fuel-rich (e.g., OP34) operating points. Mass spectra acquired under the fuel-lean condition OP2 were observed to be richer of high m/z organic compounds compared to the next in line OP9 condition.



Figure 6.11. Processed (without the background (substrate) and fragment ions) ToF-SIMS mass spectra measured from 'on spot' ROI for untreated exhaust obtained under OP2, OP9, OP17, OP27, OP32 and OP34 while using diesel B7. The total ion count is indicated above the legend.

It is proposed to apply the PCA on this data set to explore the similarities and differences in the chemical composition of PM. One can already expect that the impact of changing the miniCAST operation points would be responsible for most of the variance within this data set. What is expected from the PCA is to provide more information on the species responsible for this trend and maybe reveal other hidden trends.



Figure 6.12. Results of the PCA performed on 484 selected m/z in the ToF-SIMS mass spectra and representing the chemical composition of PM ('on spot') in Figure 6.11. (a) PC2 vs. PC1 score plot. Each data point represents one mass spectrum. Color coded symbols represent the miniCAST operating point. (b) and (c) PC1 and PC2 loading plots. Red and black represent the sign of the loadings.

Accordingly, the results of the PCA are shown in Figure 6.12. For this study case, Figure 6.12.(a) shows the score plot of PC2 against PC1. Here, the PC1 and PC2 explain  $\sim 80$  % of the variance with most of it conveyed by the PC1 ( $\sim 72$  % of the explained variance). In this score plot, the mass spectra are grouped per OP shown with color coded symbols. This grouping seems to be ordered with respect to the PC1 axis where fuel-lean OPs (OP9, OP2 and OP17) have positive scores and fuel-rich OPs (OP32 and OP34) have negative scores. The slightly fuel-lean OP27 also follows this trend despite having negative scores on PC1. This suggests that variation in the miniCAST operating point can be approximately related to what the PC1 represents. Looking into the PC1 loadings in Figure 6.12.(b), a clear separation at  $m/z \sim 220$  is made between positive (in red) and negative (in black) loadings. This means that the mass spectra of the fuel-rich OPs (OP34 and OP32) and the slightly fuel-lean OP27 are distinguishable because of the higher contribution of high mass species (m/z > 220) compared to the fuel-lean OPs (OP9, OP2 and OP17). Also, OP2 and OP17 have scores not far from the average distribution of scores. Additionally, Figure 6.13 provides a closer look to the PC1 loadings shown in Figure 6.12.(b) and indicates the assigned species that contribute the most to the negative loadings between 220-450 m/z.



Figure 6.13. Closer look into the loadings of PC1 shown in Figure 6.12.(b) indicating some of the assigned molecular formulae species that contribute the most to the negative loadings.

Overall, this PCA highlights two phenomena. First, the variance of the chemical composition is driven by the presence of high m/z organic compounds above 220 m/z that can be used to efficiently separate fuel-lean from fuel-rich OPs. Second, the condensable gas is not completely depleted of high mass species. In parallel, it is interesting to notice that, TEM observation shown in section 5.1.2 indicated that under fuel-lean conditions (OP2, OP9, OP17 and OP27), primary particles had more perceptible edges than under fuel-rich conditions (OP32 and OP34), for which primary particles exhibit more overlap and a smoother aggregate external surface. It was suggested then that such observations could be explained by a significant amount of condensed semi-volatile organic compounds overlayed all over the aggregates surface. This hypothesis is corroborated by the PCA conducted here and provides the argument that contrary to soot aggregates obtained under fuel-lean conditions, those obtained under fuel-rich conditions contain high m/z organic compounds (220-450 m/z) on their surface.

## 6.2.2 Impact of the fuel composition (diesel B7 vs. dodecane)

Here it is proposed to examine the impact of the fuel composition on the chemical composition of the PM. Accordingly, the left side of Figure 6.14 displays the normalized ToF-SIMS mass spectra (without the background (substrate) and fragment ions) between 150-600 m/zat three different miniCAST operating points (OP9, OP27 and OP34) shown previously in Figure 6.11 when diesel B7 was used. The right side of Figure 6.14 displays the mass spectra obtained when dodecane was used. These mass spectra are acquired from the 'on spot' ROI and confirm that PM contain heavier organic species under fuel-rich (e.g., OP34) than under fuel-lean (e.g., OP9) regardless of the fuel composition (dodecane vs. diesel B7). Also, under the fuel-rich condition OP34, more signals are detected above 350 m/z while using diesel B7 instead of dodecane. For OP9 and OP27 it is difficult to visually confirm such a difference. The fact that the mass spectra (under OP34) obtained while using dodecane look more intense between 250-350 m/z compared to diesel B7, is believed to be the result of the normalization to different TIC as indicated in each panel of Figure 6.14. That is why it is difficult to draw conclusions from the visual comparison of normalized mass spectra. Therefore, the PCA was performed on the data set of Figure 6.14 to hopefully provide more information on possible differences and similarities within this data set. One can already expect that the impact of changing the miniCAST operation points would be responsible for a significant part of the variance within the data set as seen before.



Figure 6.14. Processed (without the background (substrate) and fragment ions) ToF-SIMS mass spectra measured from 'off spot' ROI for untreated exhaust obtained under OP9, OP27 and OP34 while using (left) diesel B7 and (right) dodecane. The total ion count is indicated above the legend.

For this PCA, Figure 6.15.(a) shows the score plot of PC2 against PC1. These two components explain ~ 85 % of the variance. Once again, this grouping of OPs is observed with respect to the PC1 axis where fuel-lean condition OP9 have positive score and slightly fuel-lean OP27 and fuel-rich OP34 conditions have negatives scores regardless of the fuel composition. Looking into PC1 loadings, a clear separation at 220 m/z is found between positive (in red) and negative (in black) loadings similarly to what was observed before on the data set that contained mass spectra using only diesel B7.



Figure 6.15. Results of the PCA performed on 484 selected m/z in the ToF-SIMS mass spectra and representing the chemical composition of the particulate phase ('on spot') in Figure 6.14. (a) PC2 vs. PC1 score plot. Each data point represents one mass spectrum. Color coded symbols represent the miniCAST operating point and solid and open symbols indicate the used fuel. (b) and (c) PC1 and PC2 loading plots. Red and black represent the sign of the loadings.

As such, the mass spectra of the fuel-rich condition OP34 are distinguishable with their high mass (m/z > 220) organic content compared to the fuel-lean condition OP9 containing

below 220 m/z. This corroborates the previous finding that attributes the main variance to the variation in the miniCAST operating point. Furthermore, the PCA conducted here separates the samples as a function of the used fuel. This separation can be seen along the PC2 axis in Figure 6.15.(a) where regardless of the operating point (fuel-lean vs. fuel-rich) all data point representative of dodecane have negative scores while the quasi-totality of the data points representative of diesel B7 have positive scores. This separation is done on the basis of ~ 9 % of the explained variance conveyed by the PC2 whose loadings are shown in Figure 6.15.(c). These loadings suggest that the PM generated using dodecane are richer in organic compounds up to 300 m/z, while the PM generated using diesel B7 are richer in (i) different organic compounds between 150-300 m/z and (ii) additional organic compounds between 300-500 m/z. Figure 6.16 provides a closer look to the PC1 loadings shown in Figure 6.15.(b) and indicates the assigned species that contribute the most to the negative loadings between 220-400 m/z.



Figure 6.16. Closer look into the loadings of PC1 shown in Figure 6.15.(b) indicating some of the assigned molecular formulae that contribute the most to the negative loadings.

Additionally to the chemical characterization of the exhaust of the miniCAST discussed in this chapter, a two dimensional gas-chromatography - FID (GC  $\times$  GC - FID) analysis was carried out for liquid diesel B7. The results of this analysis are available in Appendix Figure K.1. Contrary to dodecane that contains one single compound, diesel B7 contains a variety of compounds including linear and branched alkanes, cycloalkanes, benzene and derivatives, PAHs and derivatives and esters. Such a complex fuel composition for diesel B7 may explain the difference in the chemical composition of the produced PM compared to dodecane. However, the chemical processes leading to this difference in the chemical composition of the PM obtained from the combustion of diesel B7 and dodecane are out of the scope of this work and remain to be explored through advanced modeling.

## 6.2.3 Impact of the catalytic stripper while using diesel B7

Here it is proposed to examine the impact of the thermal treatment (using a CS operated at 350 °C) on the chemical composition of the PM generated by the miniCAST burner. Accordingly, the left side of Figure 6.17 displays the normalized ToF-SIMS mass spectra (without the background (substrate) and fragment ions) between 150-600 m/z at six different miniCAST operating points (OP2, OP9, OP17, OP27, OP32 and OP34) for untreated exhaust when diesel B7 was used, while the right side of Figure 6.17 displays those obtained for CStreated exhaust at the same OPs. These mass spectra correspond to those acquired from the 'on spot' ROI.

The first appealing observation one can make is that the CS removes all species beyond 250 m/z regardless of the operating point. The only exception is OP32, for which some of the species up to 350 m/z survive despite being drastically reduced with respect to the untreated

samples. Also, under fuel-lean conditions OP2 and OP9 no significant difference can be seen between untreated and CS-treated mass spectra. Therefore, one can already expect that the impact of (i) CS and (ii) OPs variation on the chemical composition of PM would be responsible for most of the variance within this data set. What is expected from the PCA is to provide additional information on the nature of these differences. As for the mass spectra measured from 'off spot' ROIs, they were observed to remain fairly similar between untreated and CS-treated conditions (see Appendix Figure J.1). In the previous section GC-FID results showed that the gas phase oxidation efficiencies was  $\sim 100 \%$  for low mass alkenes and alkynes and decreased down to 90-97 % for aromatics and other unidentified heavier species (with 11 carbon atoms at most). Supposing this removal efficiency to be representative even of higher mass species, one could assume that species above 150 m/z (that the GC-FID could not measure but that the ToF-SIMS could detect) were not totally oxidized, and therefore 'off spot' mass spectra still contained high mass species. However, this hypothesis would not explain why 'on spot' mass spectra did not contained them. Consequently, the reasons why 'off spot' CS-treated mass spectra still contained high mass species are yet to be determined. On the other hand, it is proposed to focus the attention of the CS impact on 'on spot' mass spectra and perform a PCA on the data set of Figure 6.17.



Figure 6.17. Processed (without the background and fragment ions) ToF-SIMS mass spectra measured from 'on spot' ROI for CS-treated exhaust obtained under OP2, OP9, OP17, OP27, OP32 and OP34 while using diesel B7. The total ion count is indicated above the legend.

For this PCA, Figure 6.18.(a) shows the score plot of PC2 against PC1. These two components explain  $\sim 75$  % of the variance. As expected, data points are grouped along the PC1 that explains most of the variance of the data set. For untreated conditions (full symbols), once again the grouping of OPs is observed with respect to the PC1 where the scores of OPs progressively decrease from positive to negative while transitioning from fuel-lean to fuel-rich OPs. In Figure 6.18.(a) untreated OP17 have a negative PC1 score while in Figure 6.12.(a) it had a positive one. This should not be confusing since the PCA is simply not applied to the same data set. However, this does not change the conclusions on the analysis presented here. Looking into PC1 loadings shown in Figure 6.18.(b), a clear separation again at  $\sim 220 \ m/z$  is found between positive (in red) and negative (in black) loadings similarly to what was observed before on the data set that contained only untreated mass spectra while using diesel B7. As such, mass spectra of the fuel-rich conditions OP34 are distinguishable with m/z > 220 organic content compared to the fuel-lean condition OP9 containing m/z< 220. However, this time the PC1 seems to distinguish also untreated from CS-treated conditions. The quasi-totality of CS-treated mass spectra (regardless of the operating point) have positive scores along the PC1.



Figure 6.18. Results of the PCA performed on 484 selected m/z in the ToF-SIMS mass spectra and representing the chemical composition of the particulate phase ('on spot') in Figure 6.17. (a) PC2 vs. PC1 score plot. Each data point represents one mass spectrum. Color coded symbols represent the miniCAST operating point and solid and open symbols indicate the used fuel. (b) and (c) PC1 and PC2 loading plots. Red and black represent the sign of the loadings.

Figure 6.19 provides a closer look to the PC1 loading shown in Figure 6.18.(b) and indicates the assigned species that contribute the most to the negative loadings between 220-400 m/z. The separation along the PC1 attributed to increasing m/z (resulting from the variation of OPs or using the CS) is once again consistent with TEM observations shown in section 5.1.2 where primary particles boundaries became more noticeable under CS-treated fuel-rich condition OP34 compared to their respective untreated ones, while remaining fairly similar under OP9 and OP27. Thus confirming that the condensed semi-volatile organic compounds overlayed all over the aggregate surface was indeed partially removed once heated at 350 °C.



Figure 6.19. Closer look into the loadings of PC1 shown in Figure 6.18.(b) indicating some of the assigned molecular formulae that contribute the most to the negative loadings.

# 6.3 Relationship between the chemical composition and the optical properties of exhaust

In this section, the goal is to explore possible relationships between the chemical composition (sections 6.1 and 6.2) and the optical properties (section 5.1) of the exhaust. It was observed that the optical extinction coefficients, particularly in the UV spectral range, were affected by the absorbing species in the gas phase. Additionally, the PM generated under a variety of operating conditions has been described in terms of size distribution, morphology, optical extinction coefficients and Ångström absorption exponent and were found to vary from fuelean to fuel rich, untreated to CS-treated and diesel B7 to dodecane conditions. Consequently, the aim of the analysis conducted here is to understand the impact of the composition of the gas phase and of the PM on the optical extinction coefficients.

## 6.3.1 Impact of aromatic species on the optical absorption coefficients of the gas phase

The analysis presented in section 6.1 allowed to identify and quantify the contributions of different classes of chemical species to the total hydrocarbon content (THC) of the exhaust of the miniCAST. Among all of the identified species, aromatic hydrocarbons are known for their strong absorption features in the near UV [228], and therefore are suspected to give major contributions to the light absorption at low wavelengths described previously in section 5.1.3. As a reminder, a high efficiency particle arrestance filter was used to remove PM from the gas flow, and then the global absorption coefficient  $(\sum_{i} K_{abs,i})$  of the exhaust was acquired for each OP as shown in Figure 6.20.(a). The remaining gas phase was found to absorb only below 300 nm wavelength regardless of the operating point and the used fuel.  $\sum_{i} K_{abs,i}$ against wavelength in Figure 6.20.(a) has a distinctive profile with broad absorption peaks always located at the same wavelengths ( $\lambda = 204.5$  nm, 210.3 nm, 215.8 nm and 238.5 nm to name a few), the most intense of which is observed at 210.3 nm. Therefore, the choice was made to show in Figure 6.20.(b) how  $\sum_{i} K_{abs,i}$  evolves with the aromatic content of the gas phase at those distinctive wavelengths. In Figure 6.20.(b), at 210.3 nm (colored dots),  $\sum_{i} K_{abs,i}$  is observed to monotonically increase with the aromatic content of the gas phase while switching from fuel-lean to fuel-rich operating points. This remains valid for the other wavelengths (204.5 nm, 215.8 nm and 238.5 nm). Figure 6.20.(b) also shows that under OP27 and OP34 the aromatic content in the gas phase is significantly less when using dodecane instead of diesel B7 which is quasi-proportionally reflected on  $\sum_{i} K_{abs,i}$ .



Figure 6.20. Global optical absorption coefficient  $(\sum K_{abs,i})$  against aromatic content measured by GC-FID of the gas phase.

In conclusion, this measurements strongly supports the hypothesis that the aromatic content can be used as an indicator to predict the optical absorption of the gas phase. Among all the identified species (by GC-FID) in the gas phase of the exhaust of the miniCAST, the absorption cross sections of those able to absorb light above 200 nm are shown in Figure 6.21. This Figure shows the absorption cross section (ACS) of hydrocarbons adapted from the data base of Keller-Rudek *et al.* [229] with ACS that were collected from Jones *et al.* [230], Dillon *et al.* [231] and McGlynn *et al.* [232]. Among these species, the candidates that could explain the distinctive broad absorption peaks observed experimentally are small aromatics like benzene, toluene and styrene especially that are detected in significantly larger concentration (see Figure 6.2) than the rest of the species reported in 6.21. However, some non-aromatic species could also explain part of the absorption spectrum as suggested in Figure 6.21 such as 1,3-butadiene, 2-M-1,3-butadiene and propadiene.



Figure 6.21. Absorption cross section (ACS) of some hydrocarbons (at 298 K) adapted from the data base of Keller-Rudek *et al.* [229] with ACS that were collected from [230–232].

# 6.3.2 Relationship between the PM chemical composition and the optical properties

The description of chemical composition of the PM presented in section 6.2 was based on the analysis of processed ToF-SIMS mass spectra and concerned only organic compounds between 150-600 m/z. This analysis shed light on how adjusting the miniCAST OPs changes the chemical composition of PM. The change consisted in a significant contribution of high masses above 220 m/z for fuel-rich operating conditions compared to fuel-lean ones. This analysis also revealed changes in the PM chemical composition due to the change of fuel composition and suggested that regardless of the operating point, using dodecane resulted in having species up to 350-450 m/z at most in the PM; while using diesel B7, heavier species up to 500-550 m/z were found in the PM. On the other hand, it would seem that once a thermal treatment (using a CS) was applied, the quasi-totality of species above 300 m/z were oxidized.

The m/z most representative of the changes of the chemical composition of the samples as a function of the operating point, composition of the fuel and use of the CS have the highest (absolute value) of the loadings in the various PCA discussed above, and were routinely identified as PAHs, substituted PAHs and their derivatives from the assigned molecular formulae. These formulae include (i) for the low mass species (positive loadings, not shown herein):  $C_{12}H_8^+$ ,  $C_{13}H_9^+$ ,  $C_{13}H_{10}^+$ ,  $C_{14}H_{10}^+$ ,  $C_{15}H_9^+$  and  $C_{16}H_{10}^+$ , and (ii) for the high mass species (negative loadings, shown in the Figures 6.13, 6.16 and 6.19):  $C_{18}H_8^+$ ,  $C_{19}H_9^+$ ,  $C_{19}H_{11}^+$ ,  $C_{20}H_{10}^+$ ,  $C_{20}H_{12}^+$ ,  $C_{21}H_{11}^+$ ,  $C_{22}H_{10}^+$ ,  $C_{22}H_{12}^+$ ,  $C_{23}H_{11}^+$ ,  $C_{24}H_{12}^+$  and  $C_{25}H_{13}^+$ . One simple yet effective representation for the global chemical composition of the PM is by representing the H/C ratio as a function of the number of carbon atoms to facilitate the identification of classes of species that a mass spectrum contains [233].

#### Untreated

#### **CS-treated**



Figure 6.22. H/C ratio as a function of the number of carbon atoms. Calculations are based on ToF-SIMS mass spectra measured from 'on spot' ROIs for (a) untreated and (b) CS-treated exhaust obtained under OP34 while using diesel B7. The size of the data points is proportional to the log of the normalized intensity of OP.

To calculate a global H/C ratio per mass spectrum one needs to account for the normalized intensities of each assigned organic compound. Thus, the H/C ratio is equal to the ratio of the atomic percentages of hydrogen [H] and carbon [C] of the species found in a each mass spectrum. Calculating the atomic percentages is performed using equation (6.1) (example is given for H) where  $N_{X,i}$  is the number of 'X' atom of the 'i' assigned species and  $w_i$  is the normalized ion count of those assigned species [234, 73].

$$\begin{split} [H]_{ToF-SIMS} &= \frac{N_H}{N_H + N_C} \\ N_X &= \sum_i w_i N_{X,i} \quad ; \quad \text{with} \quad X = H, C \quad ; \quad \text{and} \quad \sum_i w_i = 1 \end{split} \tag{6.1}$$

Among the considered 484 m/z in the peak list that were used for ToF-SIMS mass spectra analysis, only the assigned 411 species were considered in the calculation. On the basis of the assigned formulas, a global H/C ratio is calculated from each mass spectrum. Figure 6.22 shows an example of the H/C ratio as a function of the number of carbon atoms of species detected between 150-600 m/z. This example corresponds to 'on spot' mass spectra obtained under the fuel-rich OP34 for untreated (see Figure 6.22.(a)) and CS-treated (see Figure 6.22.(b)) exhaust. Similar graphs for 'on spot' mass spectra obtained under OP2, OP9, OP17, OP27 and OP32 for untreated and CS-treated exhaust are available in Appendix Figure J.2. In Figure 6.22, among all detected organic ions (shown in black dots), identified PAH are shown in red dots and are for the most part located between the two dashed and dotted blue lines that represents the limits of oligomers of benzene (high H/C values) and that of maximally pericondensed PAHs (low H/C values), respectively. In section 6.2.3 it was shown that the use of the CS resulted in oxidizing most of the species (assigned and not assigned) above 300 m/z. Figure 6.22.(a) also shows that among the detected PAHs, the H/C ratio decreases as the number of carbon atoms increases. This suggests that if H/C ratio is calculated for each mass spectrum it can be used as a descriptor for the presence of small (high H/C) and large (low H/C) PAHs.



Figure 6.23. (a) H/C ratio as a function of Ångström absorption exponent ( $\alpha$ ). H/C ratios are calculated from the assigned peak list elements of 'on spot' mass spectra, and the uncertainties account for all mass spectra measured for the same configuration.  $\alpha$  is evaluated by fitting K<sub>abs,soot</sub> between 400 nm and 1000 nm and the uncertainties account for day-to-day variations. (b) scores of 'on spot' mass spectra according to the PC1 shown in Figure 6.18.(a) as a function of  $\alpha$ .

On the other hand, the analysis of the optical absorption coefficient ( $K_{abs,soot}$ ) discussed in section 5.1.3, showed that the Ångström absorption exponent ( $\alpha$ ), that describes the wavelength decay of  $K_{abs,soot}$  measured between 400 nm and 1000 nm, increases from 1.05 under fuel-lean conditions up to 2.25 under fuel-rich conditions. Also, it was shown that

Figure 6.23.(a) shows that the H/C ratio globally decreases with  $\alpha$  for the untreated PM. Also, once the PM is thermally treated,  $\alpha$  decreases down to values between 1.2 and 1.4 while the H/C ratio increases. This leads to believe that the pronounced wavelength decay of optical absorption coefficient of PM may result from the increase of large PAHs on the PM. Moreover, the PCA shown in Figure 6.18 that evaluated differences between untreated and CS-treated 'on spot' mass spectra, allowed to evaluate the masses that distinguish the chemical composition of the surface of PM obtained (i) under fuel-lean vs. fuel-rich conditions and (ii) for untreated vs. CS-treated PM. This separation was observed along the PC1 (see Figure 6.18.(a)). As a result, the scores obtained for each mass spectra along the PC1 are used as a descriptor of the chemical composition variation. Accordingly, Figure 6.23.(b) displays these scores which are found to behave similarly to H/C evolved with respect to  $\alpha$ . This observation suggests that high mass species between 220-500 m/z (see Figure 6.18.(b)) that manifested with negative PC1 scores given to the mass spectra are the responsible for the highest values of  $\alpha$  and that when  $\alpha$  decreases, either due to switching from fuel-rich to fuellean OP or to the use the CS these mass spectra have positive scores indicating that the chemical composition of the surface of their PM contains only masses below 220 m/z.

## In conclusion :

This chapter provides a detailed characterization of the chemical composition of the exhaust of the miniCAST burner. It was found that the total hydrocarbon content (THC) of the gas phase of the miniCAST exhaust increased to 0 to  $\sim 300$  ppmC while transitioning from fuel-lean to fuel-rich operating conditions regardless of the used fuel (diesel B7 or dodecane). Thanks to GC-FID analysis, the composition of the gas phase was described in detail and allowed to identify aromatic species that were found to explain the optical absorption broad peaks that characterized the optical extinction coefficients on the UV wavelength range. Also, the use of the catalytic stripper was found to oxidize the quasi-totality of the gas phase which explains disappearance of absorption peaks of aromatics species for the CS-treated exhaust containing only soot aggregates.

The PCA allowed to reduce the complexity of the information that ToF-SIMS mass spectra contain and revealed relations between peak list elements and operating conditions that would not be possible to see by inspecting pre-processed data. Moreover, the description of the chemical composition of the exhaust was extended to masses higher than 150 m/z. This description did not only brought more information on condensable gas phase, but most importantly on the chemical composition of the soot particles. Most notably, a correlation was found between the H/C calculated from the mass spectra and the Ångström absorption exponent ( $\alpha$ ) that strongly suggests that the chemical species mainly responsible for increase of  $\alpha$  are C<sub>18</sub>-C<sub>25</sub> PAHs. This page is left intentionally blank

# Chapter 7

# Monitoring particulate emissions and some gaseous pollutants

In this chapter, an exploratory study is conducted to evaluate the feasibility of measuring the soot volume fraction and the concentration of some gaseous pollutants such as NO, NO<sub>2</sub> and NH<sub>3</sub> in the exhaust using a single one-meter long optical extinction cell. To this end, optical absorption/extinction coefficients are measured for different exhaust containing either a single or multiple pollutants. These exhaust mixtures were prepared in a laboratory test bench following the experimental protocol described in section 3.1 where (i) the PM were generated using the miniCAST burner and (ii) NO, NO<sub>2</sub> and NH<sub>3</sub> were injected at controlled concentrations using a gas mixer (e.g., Sonimix). Optical absorption/extinction coefficients were then measured between 200-1000 nm using the optical extinction cell described in section 3.5.

To investigate the possibility of simultaneously retrieving the concentrations of multiple pollutants, it is proposed to proceed with a step-by-step approach and prospect the monitoring of (i) NO, NO<sub>2</sub> and NH<sub>3</sub> in absence of particulate emissions in the exhaust, (ii) soot volume fraction in absence of the gaseous pollutants and (iii) soot volume fraction and NO, NO<sub>2</sub> and NH<sub>3</sub> all mixed together in the exhaust. This chapter is structured accordingly.

## 7.1 Monitoring some gaseous pollutants

In this section, it is proposed to discuss the measurement of the concentrations of NO,  $NO_2$  and  $NH_3$  in a gas mixture in absence of particulate emissions in the exhaust. When measuring an optical absorption coefficient ( $K_{abs}$ ) for a mixture of those gaseous pollutants only, one may write  $K_{abs}$  as a linear combination of these pollutants concentrations [i] and their absorption cross sections  $ACS_i$  as in (7.1).

$$K_{abs} = \sum_{i} K_{abs,i} = \sum_{i} [i] \times ACS_i$$
(7.1)

To evaluate a gaseous pollutant concentration [i] from measured  $K_{abs}$  using (7.1), one needs to know its absorption cross section ACS<sub>i</sub> which can be found in literature for NO [235], NO<sub>2</sub> [236, 237] and NH<sub>3</sub> [238]. The experimental conditions (gas density, spectrometer resolution etc) under which the ACS reported in literature were obtained may be slightly different that those used in this work. Therefore, the ACS of NO, NO<sub>2</sub> and NH<sub>3</sub> are reevaluated in this work by measuring  $K_{abs}$  at known concentration for each gaseous pollutant and deducing its ACS. As such, following the experimental protocol explained in section 3.1 gaseous samples containing separately NH<sub>3</sub> (i.e., mixture (a)), NO<sub>2</sub> (i.e., mixture (b)) and NO (i.e., mixture (c)) were prepared at 300 K as summarized in Table 7.1. The mixture (c) contained mostly NO but also traces of NO<sub>2</sub> (see section 3.1). Figure 7.1.(a) displays a zoom on the measured  $K_{abs}$  between 200-240 nm for NH<sub>3</sub> concentration up to ~ 42 ppm. Similarly, Figures 7.2.(a,d) show  $K_{abs}$  between 200-300 nm for NO concentration up to ~ 74 ppm and between 200-1000 nm for NO<sub>2</sub> concentration up to ~ 482 ppm. In Figures 7.1.(b), 7.2.(b) and 7.2.(e) all  $K_{abs}$  (at 208.5 nm for NH<sub>3</sub>, 226.2 nm for NO and 435.1 nm for NO<sub>2</sub>), were found to evolve linearly with respect to the injected concentrations. Care was taken to run all measurements with absorbance < 1 to avoid saturation. Hence, justifying the validity of equation (7.1) to evaluate the ACS of each gaseous pollutant. As such, the ACS shown in Figure 7.1.(c) for NH<sub>3</sub>, Figure 7.2.(c) for NO and Figure 7.2.(f) for NO<sub>2</sub> were obtained and compared to the literature. It should be clarified that the contribution of NO<sub>2</sub> traces in the calibration gas mixture was subtracted from the spectrum of NO.

 Table 7.1. Overview of the content of gaseous samples mixtures.

Gaseous	Mixtures				
$\operatorname{pollutant}$	а	b	с	d	
NH <sub>3</sub>	1	×	×	1	
$NO_2$	X	1	1	1	
NO	×	×	<ul> <li>Image: A second s</li></ul>	<ul> <li>Image: A second s</li></ul>	



Figure 7.1. (a) Optical absorption coefficients (K<sub>abs</sub>) between 200-240 nm measured at different concentrations of NH<sub>3</sub> (indicated in the legend), (b) K<sub>abs</sub> (at 208.5 nm) as a function of NH<sub>3</sub> concentration and (c) the ACS of NH<sub>3</sub> evaluated in this work (at 300 K) and the one adapted from Limão-Vieira *et al.* [238].



Figure 7.2. (a,d) Optical absorption coefficients ( $K_{abs}$ ) measured at different concentrations of NO and NO<sub>2</sub> (indicated in the legend), (b,e)  $K_{abs}$  (at 226.2 nm for NO and at 435.1 nm for NO<sub>2</sub>) as a function of NO and NO<sub>2</sub> concentrations and (c,f) the ACS of NO and NO<sub>2</sub> evaluated in this work (at 300 K) and the ones from Thompson *et al.* [235], Bass *et al.* [236] and Schneider *et al.* [237].

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The ACS obtained for NH<sub>3</sub> and NO<sub>2</sub> are found to be consistent in shape and width of the spectral bands with those reported by Limão-Vieira *et al.* [238] for NH<sub>3</sub> and Bass *et al.* [236] and Schneider *et al.* [237] for NO<sub>2</sub>. Looking into Figure 7.1.(c), one can see that our spectral spectral resolution (of ~ 1.5 nm in this work) is insufficient to resolve the peaks of NH<sub>3</sub> as reported by Limão-Vieira *et al.* [238] with a 0.075 nm resolution. Concerning NO, the obtained ACS (see Figure 7.2.(c)) is inconsistent with the one reported by Thompson *et al.* [235]. It appears that, not many works are available in the literature on experimentally measured ACS of NO. In practice, the ACS need to be evaluated for each measuring equipment to ensure an optimal measurement accuracy. Consequently, from now on, the ACS determined in this work are used and not those of the literature.

In this work, optical absorption coefficients ( $K_{abs}$ ) were measured between 200-1000 nm. This means that only some of the NH<sub>3</sub> and NO absorption peaks are detected (see Figures 7.1.(c) 7.2.(c)). These peaks are located in the UV part of the spectrum at 205 nm, 208 nm, 212 nm and 216 nm for NH<sub>3</sub> and at 205 nm, 215 nm and 226 nm for NO. In contrast with NO and NH<sub>3</sub>, NO<sub>2</sub> absorbs over a wide spectrum in the UV and visible, which means that unless NO<sub>2</sub> monitoring is done over the visible range, interference issues can be expected in the UV part with NO and NH<sub>3</sub> (that already interfere at some wavelengths). This calls for a careful selection of wavelengths at which the concentration of each gaseous pollutant is measured. Therefore, for an exhaust that contains a mixture of only NO, NO<sub>2</sub> and NH<sub>3</sub> the following procedure is proposed :

### ► Step 1 :

- Evaluate the concentration of NO<sub>2</sub> by solving  $K_{abs} = [NO_2] ACS_{NO_2}$  (7.1) at 435 nm;
- ► Step 2 :

Since NO<sub>2</sub> absorbs light in the UV part of the spectrum, it is proposed to take advantage of the shape (wide absorption band) of the absorption signature. Thus, instead of solving equation (7.1), it is proposed to solve its gradient :

$$\frac{\partial K_{abs}}{\partial \lambda} = \sum_{i} [i] \times \frac{\partial ACS_{i}}{\partial \lambda}$$
(7.2)

Indeed, pollutants that have a wide absorption band such as NO<sub>2</sub> will see their  $\partial K_{abs}/\partial \lambda$  vanish leaving only the gradient of narrow absorption peaks which is the case for NO and NH<sub>3</sub>. This is illustrated in Figure 7.3.(a) where applying the gradient on the ACS removes the wide absorption band of NO<sub>2</sub> in the visible range. It also removes it over the UV range as shown in Figure 7.3.(b) thus leaving only the issue of interference between NO and NH<sub>3</sub> to be dealt with. Therefore, in this step calculations are done using  $\partial K_{abs}/\partial \lambda$  that are used to :

- Solve equation (7.2) for i = NO between 224.3-228.1 nm (around NO A–X (0,0) vibrational band);
- Solve equation (7.2) for  $i = NH_3$  around the  $NH_3$  vibrational band from  $\stackrel{\sim}{A^1}A_2'' \leftarrow \stackrel{\sim}{X^1}A_1'$  located in the 206.8-211.1 nm spectral range;

The selected spectral bands shown in Figure 7.3.(b) allow to individually monitor these species and reduce their interference.



Figure 7.3. The gradient of the absorption cross sections  $(\partial ACS/\partial \lambda)$  of NO, NO<sub>2</sub> and NH<sub>3</sub> (a) between 200 nm and 1000 nm and (b) a closer look (zoom area in red rectangle) between 200-230 nm. The wavelength windows used to measure the concentrations of NH<sub>3</sub> and NO are indicated in shadow areas.

An additional mixture (d) (see Table 7.1) containing all three NO, NO<sub>2</sub> and NH<sub>3</sub> at once was prepared to test the proposed measurement procedure. As such, Figure 7.4.(a) displays  $K_{abs}$  measured for this mixture, where variable concentrations of NO up to ~ 80 ppm were injected simultaneously with variable concentration of NH<sub>3</sub> up to ~ 45 ppm. The small concentrations of NO<sub>2</sub> in the mixture come from traces in the NO gas cylinder used for these experiments. Figure 7.4.(b) displays  $\partial K_{abs}/\partial \lambda$  between 200-300 nm that are used to calculate the concentrations of NO and NH<sub>3</sub> as proposed in step 2.



Figure 7.4. (a) Optical absorption coefficients (K<sub>abs</sub>) measured for the mixture of all three pollutants between 200-300 nm and (b) the ∂K<sub>abs</sub>/∂λ between 200-300 nm.

Figure 7.5 displays the measured concentrations of NO, NO<sub>2</sub> and NH<sub>3</sub> vs. those injected (i.e., actual). In Figure 7.5.(a) one can see that the measurements are generally in good agreement except for the underestimation of the actual (.i., injected) concentration of NH<sub>3</sub> above 30 ppm. This will be discussed in section 7.3. The measurement of NO<sub>2</sub> concentrations shown in Figure 7.5.(b) are also satisfying for such low NO<sub>2</sub> concentrations. Even though no additional tests were performed on other mixtures of these gaseous pollutants, these results

still show that retrieving NO,  $NO_2$  and  $NH_3$  is feasible using a one-meter optical absorption cell between 200-1000 nm over these ranges of concentrations.



Figure 7.5. Measured (retrieved by the inversion process) vs. actual (injected) concentrations of (a) NO and NH<sub>3</sub> and (b) NO<sub>2</sub>.

## 7.2 Monitoring particulate emissions

The ultimate goal of the work conducted here is to propose a measurement procedure to simultaneously monitor the concentrations of NO, NH<sub>3</sub> and NO<sub>2</sub> and soot volume fraction in a combustion exhaust. In this section it is proposed to initiate this development for monitoring soot volume fraction and anticipate possible interference issues with gaseous pollutants. In fact, the main difficulty of such measurement that uses a single optical extinction cell is the interference between pollutants (gaseous and particulate). In the previous section, it was shown that NO<sub>2</sub> has two broad absorption bands, one between 200-250 nm and between 260-700 nm. Meanwhile, soot aggregates absorb light - and scatter it - in the whole range 200-1000 nm. Consequently, the issue that needs to be addressed here is how to decorrelate the contributions of soot aggregates from those of the gaseous pollutants, particularly NO<sub>2</sub>.

In Chapter 5, a total of 34 operating points under various conditions (untreated and CStreated and using diesel B7 and dodecane) were described in terms of their size distribution, morphology and optical extinction coefficient. This data was then used to evaluate the soot volume fraction ( $f_v$ ) comparing methods based on aggregate size (combining mobility size distribution and morphology) and optical extinction. It was then concluded that  $f_{v_{(optical)}}$ evaluated optically agreed within 13 % with  $f_{v_{(SMPS + STEM)}}$  measured adopting the fractal aggregate approach which is considered here as a reference measurement for  $f_v$ . It is worth reminding that  $f_{v_{(optical)}}$  was evaluated using equation (7.3) at  $\lambda = 700$  nm while neglecting the total scattering (K<sub>ext,soot</sub>  $\approx K_{abs,soot}$ ) and assuming E(m) = 0.35 [199].

$$f_{v_{(Optical)}} = \frac{K_{abs,soot}\lambda}{6\pi E(m)}$$
(7.3)

Using these assumptions, Figure 7.6 shows the comparison between  $f_{v(Optical)}$  determined at different wavelengths and  $f_{v(SMPS+STEM)}$ . Though this approach appears relatively satisfying when determining  $f_v$  at high wavelength (> 700 nm), maintaining E(m) constant all over the spectrum (in the UV and visible) leads to underestimate  $f_v$  as shown in Figure 7.6. However, to decorrelate the contributions in  $K_{ext}$  of soot aggregates and NO<sub>2</sub>, it is necessary to consider the spectral dependence of E(m) with OP.



Figure 7.6.  $f_{v_{(Optical)}}$  calculated vs.  $f_{v_{(SMPS + STEM)}}$ .  $f_{v_{(Optical)}}$  is calculated assuming a constant absorption function (E(m) = 0.35)  $\forall \lambda$ . Uncertainties for  $f_{v_{(Optical)}}$  are calculated from the standard deviation over a measurement period of 400 s. Data not corrected for dilution (~ 19:1).

In section 4.3, it was shown that E(m) can be quantitatively predicted using equations (7.4) and (7.5). Accordingly, E(m) is expressed as a wavelength dependent function where  $\alpha$  is the Ångström absorption exponent and  $C_E$  is a function of  $\alpha$  only. In section 5.1.3,  $\alpha$  was evaluated for all the 34 OPs investigated in this work (see Table 5.3). It is worth reminding that  $\alpha$  was obtained by fitting  $K_{abs,soot}$  (accounting for total scattering contribution) between 400-1000 nm. Therefore, it is proposed to use the values of  $\alpha$  to calculate E(m) using equations (7.4) and (7.5) and re-evaluate  $f_{v_{(Optical)}}$  using equation (7.3) with variable E(m). The result of this calculations are shown in Figure 7.7.(a).

$$E(m) = \frac{C_E}{\lambda^{\alpha - 1}}$$
(7.4)

$$\ln(C_E) = -a \times a + b$$
;  $a = 13.98 \pm 0.66$ ;  $b = 12.47 \pm 1.06$  (7.5)

Figure 7.7.(a) shows, considering the spectral variability of E(m) at each OP, a more satisfying estimation of  $f_{v(Optical)}$  with respect to  $f_{v(SMPS + STEM)}$ . This means that,  $\alpha$  is an important parameter to reconstruct K<sub>abs,soot</sub> between 400-1000 nm. Because of the spectral interference between NO<sub>2</sub> and soot extinction below 700 nm, the feasibility of determining  $\alpha$ on the limited interference free spectral range 700-1000 nm has been explored. The Rayleigh approximation remains valid above 700 nm thus total scattering is less likely to affect  $K_{ext}$ . Moreover, in section 4.3.3 it was shown that equation (7.5) remains valid if  $\alpha$  is evaluated by fitting K<sub>abs,soot</sub> between 700-1000 nm instead of 400-1000 nm. As such, for all the investigated operating conditions,  $\alpha$  was re-evaluated by fitting K<sub>ext</sub> between 700-1000 nm, and f<sub>v(Optical)</sub> was re-calculated using equations (7.4) and (7.5). The results of this calculation is shown in Figure 7.7.(b). Figures 7.7.(a,b) look very similar demonstrating that  $\alpha$  can be evaluated with high accuracy on the narrow spectral range 700-1000 nm and that equation (7.5), resulting from K<sub>abs,soot</sub> fit between 400 and 1000 nm, can still be used between 700 and 1000 nm. Thus, this approach is made simpler and more powerful. Furthermore, the results shown in Figure 7.7.(b) show that the use of a one-meter optical extinction cell, allows the measurement of soot volume fractions as low as 0.7 ppb.



Figure 7.7.  $f_{v_{(Optical)}}$  calculated vs.  $f_{v_{(SMPS + STEM)}}$ .  $f_{v_{(Optical)}}$  is calculated using variable E(m) using equations (7.4) and (7.5) with  $\alpha$  obtained from (a) fitting K<sub>abs,soot</sub> between 400-1000 nm and (b) K<sub>ext</sub> between 700-1000 nm. Uncertainties for  $f_{v_{(Optical)}}$  are calculated from the standard deviation over a measurement period of 400 s. Data not corrected for dilution (~ 19:1).

# 7.3 Monitoring of complex mixtures containing PM and gaseous pollutants by optical extinction

In this section it is proposed to address the issue of monitoring simultaneously the concentration of some gaseous pollutants (i.e., NO, NO<sub>2</sub> and NH<sub>3</sub>) and particulate emissions that a combustion exhaust could contain. In practice, an easier solution although expensive, would be to monitor these pollutants using two distinct optical cells. The first one for gaseous pollutants only, while using a high efficiency particulate filter to remove PM. In this case, one can even consider using a different spectrometer that covers lower wavelengths for better sensitivity for the detection of NO and NH<sub>3</sub> for instance. In parallel, the second optical cell would still contain all pollutants but could only be used to monitor PM by exploiting  $K_{ext}$ between 700-1000 nm as explained in the previous section. Yet, what it is proposed in this section is to evaluate the possibility of still using a single optical cell in evaluating all of NO, NO<sub>2</sub> and NH<sub>3</sub> concentration as well as soot volume fraction simultaneously over wavelength between 200 nm and 1000 nm which is economically a more interesting solution.

To accomplish this, the exhaust mixtures summarized in Table 7.2 containing gaseous pollutants and PM were prepared following the experimental protocol explained in section 3.1. These mixtures were prepared to evaluate the possibility of retrieving pollutant concentrations when the exhaust contains PM mixed only with (i) NH<sub>3</sub> (i.e., mixture (a)), (ii) NO<sub>2</sub> (i.e., mixture (b)) and (i) NO (i.e., mixture (c)) or when the exhaust contains all of these pollutants at once (i.e., mixture (d)). The gaseous pollutants mixtures were prepared by following the usual protocol using the Sonimix gas mixer and injecting simultaneously the PM generated by the miniCAST burner. However, it should be made clear that for the experiments presented here, the miniCAST was only and always operated under the same OP17. Under this condition, it was shown previously in section 6.3.1 that the miniCAST exhaust contained gas phase species that absorb in the UV wavelength range. Also, it was shown that once the exhaust of the miniCAST was thermally treated with a catalytic stripper (CS) at 350 °C, the quasi-totality of the gas phase was oxidized leaving only soot aggregates in the exhaust. Therefore, the choice was made to prepare the mentioned mixtures downstream the CS. This was done mainly to avoid the absorption of hydrocarbons that interfere with NO and NH<sub>3</sub> in the UV part of the spectrum. Also, it should be kept in mind that this way of preparing complex exhaust mixtures is somewhat representative of real vehicle exhaust under steady conditions [57].

Accordingly, Figure 7.8 shows all the optical extinction coefficients (K<sub>ext</sub>) that were measured. Each panel corresponds to an exhaust mixture where the injected concentration of each pollutant is indicated in the legend. For the PM, the reported concentration corresponds to the soot volume fractions  $f_{v_{(SMPS + STEM)}}$  that were calculated as explained in section 5.2.1.

Pollutant	Mixtures				
	а	b	с	d	
NH <sub>3</sub>	1	×	×	1	
$NO_2$	×	1	1	1	
NO	×	×	1	1	
$\mathbf{PM}$	1	1	1	1	

Table 7.2. Overview of the content of exhaust sample mixtures.



Figure 7.8. Optical extinction coefficients ( $K_{ext}$ ) of the prepared mixtures summarized in Table 7.2. The PM exhaust corresponds for CS-treated exhaust obtained under OP17 while using diesel B7.

The challenge now is not only to retrieve soot volume fraction  $(f_v)$  from  $K_{ext}$ , but also to retrieve it in addition to the concentrations of NO, NO<sub>2</sub> and NH<sub>3</sub> mixed with particulate emissions. To meet this need, it is proposed to combine both of the measurement procedures presented in the previous two sections and to proceed as follows:

► Step 1 :

- Fit  $K_{ext} \approx K_{abs,soot}$  between 700-1000 nm with a power law of the form  $\lambda^{-\alpha}$  to evaluate  $\alpha$ . Here, the contribution of total scattering is assumed negligible;
- Calculate  $E(m) = C_E (\alpha) / \lambda^{\alpha-1}$  at 700 nm;
- Calculate  $f_v = K_{abs,soot}\lambda \ / \ 6 \ \pi \ E(m)$  at 700 nm;

► Step 2 :

- Reconstruct the contribution of  $K_{abs,soot}$  between 300-700 nm (using the previously determined value of  $\alpha$ );
- Subtract K<sub>abs,soot</sub> from K<sub>ext</sub> (This assumes that total scattering is still neglected between 300-700 nm);
- Evaluate NO<sub>2</sub> concentration by solving  $K_{ext}$   $K_{abs,soot} = [NO_2] ACS_{NO_2}$  at 435 nm;

► Step 3 :

Here, the calculation starts over by considering  $\partial K_{abs}/\partial \lambda$  in order to remove the contribution from pollutants that have a wide absorption band (NO<sub>2</sub> and PM in this case). Thus, leaving only the gradient of narrow absorption peaks of NO and NH<sub>3</sub>. Therefore, in this step calculations are done using  $\partial K_{abs}/\partial \lambda$  that are used to :

- Solve equation (7.2) for i = NO between 224.3-228.1 nm;
- Solve equation (7.2) for  $i = NH_3$  between 206.8-211.1 nm;



Figure 7.9. Measured (retrieved by the inversion process) vs. actual (injected) concentration of (a) NO, NH<sub>3</sub> and NO<sub>2</sub> and (b) PM obtained under OP17 for CS-treated exhaust while using diesel B7.

Processing the measured  $K_{ext}$  shown in Figure 7.8 with this strategy rendered the results shown in Figure 7.9. Figure 7.9.(a) displays the retrieved concentrations (i.e., measured)

vs. the injected concentrations (i.e., actual) of gaseous pollutants NO, NH<sub>3</sub> and NO<sub>2</sub>, that are overall in excellent agreement. The measurement of NH<sub>3</sub> concentrations for mixture (a) when  $NH_3$  was mixed only with PM was found to be very accurate. Also, a deviation above 30 ppm is observed between measured and actual (i.e., injected) NH<sub>3</sub> concentrations in Figure 7.9.(a) that come from the mixture (d). This deviation was observed previously (see Figure (7.5) when NO and NH<sub>3</sub> were mixed together. However, the source of this discrepancy have not been identified. Considering the overall very good agreement for all the experimental conditions, except those occurring when mixing  $NH_3$  with NO above 30 ppm, it is supposed that this discrepancy could be due to an error in the setting control of these two pollutants using the Sonimix. Therefore, further tests will need to be performed. The measured concentrations of NO<sub>2</sub> were also found to be consistent for concentrations as high as  $\sim 60$  ppm. In parallel, the measured  $f_{V(Optical)}$  is in good agreement with the reference  $f_{V(SMPS+STEM)}$  as shown in Figure 7.9.(b). These results are very promising and provide a proof of concept for a measurement protocol to optically monitor the concentration of particulate emissions, NO, NO<sub>2</sub> and NH<sub>3</sub> that a combustion exhaust typically contains and opens the way for improving this measurement procedure to render more accurate results.

#### In conclusion :

The exploratory study conducted here, proves that monitoring simultaneously gaseous pollutants such as NO, NO<sub>2</sub> and NH<sub>3</sub> and the soot volume fraction is possible using a single one-meter long optical extinction cell. In this work, this was demonstrated for concentrations up to ~ 80 ppm for NO and NO<sub>2</sub>, to ~ 45 ppm for NH<sub>3</sub> and as low as 0.7 ppb for soot aggregates. However, it should be clarified that factors impacting the measurement quality such as lens fooling or the presence of water vapor in exhaust have not been addressed. Consequently, more development is needed to improved the hardware and software of this experimental procedure for better accuracy and sensitivity. This page is left intentionally blank

# Conclusions and summary

As mentioned in the introduction of the manuscript, there is a need for a next generation mobile and low-cost measurement devices to monitor, characterize and control the particle matter (PM) and gaseous pollutant emissions from combustion systems, for instance in transportation and power generation. This need is even more urgent as in the near future companies will have to adapt to highly variable fuels, many of them obtained from renewable sources. It is therefore necessary to test beforehand the emission characteristics of these fuels before considering their large-scale use.

To meet this need, the initial objective of this thesis was to progress in three important areas: (1) to have a simple combustion device capable of burning liquid fuels (regular, renewables, surrogates) in a reproducible manner; (2) to characterize the performance of the source in terms of PM variability in size, morphology, chemical composition and optical properties; and (3) to develop a mobile optical device to monitor these PM.

A liquid fuel miniCAST burner (from Jing Ltd) has been used for aerosol generation. At the beginning of this work, there was no available characterization of this burner in the literature. 34 operating points (OP) have been selected offering a wide range of liquid fuel, oxidation and fuel flow rates, resulting in a large range of global equivalence ratios. Two fuels were analyzed: dodecane and diesel B7. Four different aspects have been investigated for each OP:

- ▶ The physical characterization of the emissions, in terms of morphology and size of the soot aerosols produced. The soot nanostructure was investigated using high-resolution transmission electron microscopy (TEM), the size distribution of the primary particles and of the aggregates and the fractal dimension using scanning transmission electron microscopy (STEM), and finally the size distribution of the aggregates using scanning mobility particle sizer (SMPS).
- ▶ The chemical composition of the emissions, both at the level of the gas phase using gas chromatography (GC-FID) and at the level of the chemical composition of the surface of the soot using time-of-flight secondary ion mass spectrometry (ToF-SIMS).
- ▶ The optical properties of the emissions using an extinction-based approach.
- ▶ And finally, the soot volume fraction as a metric of comparison between different measurement methods and OP.

To reach this extensive characterization, a complex experimental test bench was set up and optimized during this PhD work in order to meet the requirements of stability and repeatability of the emissions and associated measurements. This bench was composed of the miniCAST burner and a gas mixing system (Sonimix) whose exhaust is introduced into a dilution vein from which the instruments draw their samples, allowing the above mentioned measurements on both the soot particles and the gas phase. The experimental protocol was carefully designed to adjust the dilution levels to the range of the used instruments and the sampling time on the filters for each investigated OP to avoid overloading, while taking care to avoid problems of saturation or pollution of the vein or burner. To refine the characterization, a particle filter and a catalytic stripper were also installed, which allowed the separation of the respective contributions of the PM and of the gas phase. Due to time constraints, only six OPs were fully characterized (for both fuels, with and without catalytic stripper), the other being analyzed only with online instrumentation.

Once the protocol was established, the analysis of the results led to significant methodological developments:

- ► Based on the literature, STEM images were analyzed by applying a post processing based on image segmentation using a semi-automatic SLIDER method followed by the EDM-SBS method) allowing for accurate extraction of key morphological parameters  $(D_{geo,p}, \sigma_{geo,D_p}, D_f \text{ and } k_f)$  via a real-soot calibration approach.
- ► The optical extinction coefficient of soot was evaluated from extinction measurements performed in a one-meter long portable absorption cell, allowing the use of a compact spectrometer to measure light attenuation through an absorbing medium containing possibly a gas mixture. The contribution of scattering, which can reach 12 % at 400 nm for the richest OPs, was evaluated using the RDG-FA theory and subtracted. The spectral analysis showed that the absorption function E(m) had a power-law spectral dependence, a behavior previously shown in the literature:  $E(m) = C_E/\lambda^{\alpha-1}$ , where  $\alpha$  is the Ångström absorption exponent and  $C_E$  a constant (independent on  $\lambda$ , to be determined for each OP). While  $\alpha$  can be easily determined from the fit of the spectral absorbance, the originality of this work was to introduce  $\alpha$  in RDG-FA to quantify  $C_E$  and thus E(m). It is shown for the first time that  $C_E$  and  $\alpha$  are related in semi-log scale by  $\ln(C_E) = -13.98 \ \alpha + 12.47$  not only on the selected OP but also to several documented studies in the literature including those obtained with propane-CAST. At 700 nm, E(m) is found to vary from 0.10 for the leanest cases to 0.50 for the richest ones. The use of the catalytic stripper seems to decrease both  $\alpha$  and  $C_E$ .
- ▶ Concerning the chemical analysis, in addition to the thorough gas phase description using GC-FID, this thesis work contributes to a significant improvement in the analysis of ToF-SIMS mass spectra. In particular, a new methodology based on the mass defect analysis was developed for the automatic construction of unique peak lists, which addressed the need for fast and efficient post-processing of low-resolution datasets.

Once the methodology was established, the characterization of the particle morphology, size distribution and surface chemical composition as well as of the composition of the gas phase could be generalized to all OPs.

 $\blacktriangleright$  D<sub>geo,p</sub>,  $\sigma_{geo,D_p}$ , D<sub>f</sub> and k<sub>f</sub> describing soot aggregates morphology were successfully evaluated for the selected OP as well as the total number of soot aggregates (PN). It was found that PN increased with the global equivalence ratio  $\varphi$ . The behavior of the mobility-equivalent geometric mean diameter  $D_{\text{geo},m}$  with  $\varphi$  depended on the mixing air and oxidation air flow rates and ranged from 45 to 105 nm. While its sizedistributions looked like the one of diesel B7 fuel, dodecane was found to provide smaller aggregates in comparison. On the contrary, the interposition of a catalytic stripper in the sampling line was found to flatten the shape of the size distribution. The Angström absorption exponent was found to increase with  $\varphi$ . The higher the organic content of the soot particles, the higher  $\varphi$ , reflecting a stronger dependence with the wavelength. The soot volume fraction  $f_v$  was determined by three independent methods: optical extinction, mass deposit and SMPS, coupled with morphology data issued from STEM analysis. The main conclusions of this study are (i) that  $f_v$  evaluated on the basis of size mobility data alone overestimated by  $\sim 70$  % the one accounting for morphological aspects (fractal aggregate approach), (ii) that  $f_v$  evaluated optically agreed reasonably well with both  $f_v$  measured adopting the fractal aggregate approach (within 13 %) (iii) and  $f_v$  evaluated from mass concentration measurements was also in good agreement

with the fractal aggregate approach (within 25 %) assuming a soot bulk density of 1800 kg/m<sup>3</sup>. This characterization concluded with the delivery of a table of physical data (PN,  $D_{geo,m}$ ,  $\sigma_{geo,D_m}$ ,  $\overline{D_p}$ ,  $D_f$ ,  $\alpha$  and  $f_v$ ) for all the OPs studied, which can be useful as a reference database for the community.

- ▶ The chemical composition of the exhaust gas phase was investigated by GC-FID that allowed the identification and quantification of the contributions of several individual species up to C10-C11 as well as the total hydrocarbon content (THC). Most notably, a correlation was found between the optical absorption coefficient and the THC at several wavelengths in the near UV that strongly supported the hypothesis of small aromatic compounds as the major contributors to the UV absorption bands.
- ▶ The chemical composition of the exhaust soot particles was investigated by ToF-SIMS. Mass defect analysis allowed the identification of polycyclic aromatic hydrocarbons (PAHs) and their derivatives up to C30-C40 (roughly 400-500 m/z) as the main contributors to the chemical composition at the surface of the soot particles. Given the high complexity of the database (over 2000 different m/z having signal-to-noise ratio > 3), principal component analysis was required for classifying the samples and extracting chemical information from the mass spectra. In particular, the presence of PAHs and their derivatives on the soot particles was found to be strongly affected by the burner OP, by the chemical composition of the fuel and by the use of the catalytic stripper. The presence of high mass PAHs was also found to be correlated to morphological changes of the particles identified by TEM. Additionally, a global H/C ratio was calculated from the assigned molecular formulae. This global H/C ratio was found to be correlated to the Angström absorption exponent: the operating points generating the samples having lowest H/C and thus the largest relative contributions from high mass PAHs and their derivatives, are also systematically characterized by the highest Angström absorption exponent. To the best of our knowledge, this correlation was never observed in the literature before this work.

The final chapter investigates the possibility of simultaneously quantifying soot volume fraction and the concentrations of some well-known gaseous pollutants such as NO, NO<sub>2</sub> and NH<sub>3</sub>, using a one-meter long optical extinction cell. The experiments consisted of introducing known amounts of these nitrogenous pollutants, representative of engine emissions individually or mixed with the miniCAST exhaust downstream a catalytic stripper. The analysis of the absorption cross section of nitrogen species allowed to identify the optimal spectral bands to detected each gaseous pollutant and propose a measurement procedure to retrieve the concentrations of NO, NO<sub>2</sub> and NH<sub>3</sub> and soot volume fraction. The analysis of measured extinction optical coefficients for complex mixtures was performed following an inversion strategy the results of which are very promising and provide a proof of concept for a measurement protocol to optically monitor the concentration of particulate emissions, NO, NO<sub>2</sub> and NH<sub>3</sub> that a combustion exhaust typically contains and opens the way for improving this measurement procedure (hardware and software) to render more accurate results. This page is left intentionally blank

# Appendices

# A Fuels characteristics (Supplement)

The combustion of a premixed (e.g., mixture of fuel and oxidizer) flame can be generally described by the reaction below where the flame equivalence ratio ( $\phi$ ) is defined as the ratio of the actual fuel-to-air mass fraction ratio to the stoichiometric fuel-to-air mass fraction ratio. It can also be written as the product of stoichiometric air-to-fuel ratio (AFR<sub>st</sub>) and the ratio of air and fuel mass flow rates as in (A.1) [239]. In this case, an operating point is said fuel-rich when  $\phi > 1$  and fuel-lean when  $\phi < 1$ .

$$\mathrm{C_nH_m} + (\mathrm{n} + \tfrac{\mathrm{m}}{4})(\mathrm{O_2} + 3.76 \times \mathrm{N_2}) \quad \longrightarrow \mathrm{nCO_2} + \tfrac{\mathrm{m}}{2}\mathrm{H_2O} + 3.76 \times (\mathrm{n} + \tfrac{\mathrm{m}}{4})\mathrm{N_2}$$

$$\phi = AFR_{st} \times \dot{m}_{fuel} / \dot{m}_{air} \tag{A.1}$$

- $\dot{m}_{fuel}$ : Fuel mass flow rate ;
- $\dot{m}_{air}$ : Air mass flow rate ;

In contrast to premixed flames where the mixing between the fuel and oxidizer occurs well ahead of the flame area, fuel consumption in a diffusion flame is determined by the rate at which the fuel and oxidizer are brought together in proper proportions for reaction [240]. For diffusion flames, unlike premixed ones, the flame equivalence ratio has no practical meaning [240]. Instead the mixture is described by the mixture fraction (Z) which distinguishes the fuel stream from the oxidizer stream (See Glassman *et al.* [240] for more details). Despite, the distinctive characteristic between the two combustion modes (premixed vs. diffusion), for miniCAST's flames, which are for the majority of cases laminar diffusion flames, it is a common use (for comparison purposes) to refer to an operating condition with an overall equivalence ratio rather than mixture fraction. Accordingly, overall flame equivalence ratios reported in the main text (in section 4.1.1) were calculated using (A.1) and fuels characteristics summarized in Table A.1.

Table A.1. Some of the characteristics of propane, diesel B7 and dodecane fuels (+: [241]; \*: [242])

Fuel	Air	$\begin{array}{c} \text{Propane} \\ (\text{C}_3\text{H}_8) \end{array}$	Diesel B7 $(C_{12}H_{23})$	$\begin{array}{c} \text{Dodecane} \\ (\text{C}_{12}\text{H}_{26}) \end{array}$
Density at 15° C $[kg/m^3]$ AFR <sub>st</sub>	1.225 -	$1.877 \\ 15.60$	$831.5^+\ 14.59$	750* 14.94



## B RDG-FA sensitivity study (Supplement)

Figure B.1. Sensitivity study of the RDG-FA model in respect to (a) soot particles number (PN) and (b) mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ) variation. The left (1), middle (2), and right (3) plots corresponds to the absorption, the scattering, and the extinction coefficients, respectively. For each parameter the sensitivity is considered in contrast to a reference aggregate (corresponding to the green curves) that has the following characteristics:  $PN = 1.37 \times 10^7 \ \#/cm^3$ ,  $D_{geo,m} = 75 \ nm$ ,  $\sigma_{geo,D_m} = 1.7$ ,  $\overline{D_p} = 25 \ nm$ ,  $D_f = 1.851$ , and  $k_f = 1.970$ .

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Figure B.1. Sensitivity study of the RDG-FA model in respect to (c) standard geometric deviation ( $\sigma_{\text{geo},D_m}$ ) and (d) primary particle diameter ( $\overline{D_p}$ ) variation. The left (1), middle (2), and right (3) plots corresponds to the absorption, the scattering, and the extinction coefficients, respectively. For each parameter the sensitivity is considered in contrast to a reference aggregate (corresponding to the green curves) that has the following characteristics:  $PN = 1.37 \times 10^7 \ \#/cm^3$ ,  $D_{\text{geo},m} = 75 \text{ nm}$ ,  $\sigma_{\text{geo},D_m} = 1.7$ ,  $\overline{D_p} = 25 \text{ nm}$ ,  $D_f = 1.851$ , and  $k_f = 1.970$ .



Figure B.1. Sensitivity study of the RDG-FA model in respect to (e) fractal dimension ( $D_f$ ) and (f) fractal pre-factor ( $k_f$ ) variation. The left (1), middle (2), and right (3) plots corresponds to the absorption, the scattering, and the extinction coefficients, respectively. For each parameter the sensitivity is considered in contrast to a reference aggregate (corresponding to the green curves) that has the following characteristics:  $PN = 1.37 \times 10^7 \ \#/cm^3$ ,  $D_{geo,m} = 75 \text{ nm}$ ,  $\sigma_{geo,D_m} = 1.7$ ,  $\overline{D_p} = 25 \text{ nm}$ ,  $D_f = 1.851$ , and  $k_f = 1.970$ .


### C Soot production repeatability for CS-treated exhaust (Supplement)

Figure C.1. (a, b, c): SMPS measured aggregates number (PN), mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ), and geometric standard deviation ( $\sigma_{geo,D_m}$ ) as function of flame overall equivalence ratio ( $\varphi$ ) for 6 operating points over time for a CS-treated exhaust. (d, e, f) Their respective deviations to the mean curve accounts for repeatability over 5 months. Uncertainties account for 3 size distributions measured consecutively. Data not corrected for dilution (~ 19:1).



D Segmentation process (Supplement)

Figure D.1. Segmentation process showing (a) raw STEM images, (b) aggregates contours obtained using SLIDER method [189], (c) the corresponding binary images and (d) isolated aggregates after being inverted.

## E Fractal analysis (Supplement)



Figure E.1. Evolution of number of primary particles per aggregate  $(N_p)$  as a function of  $D_g/D_p$  ratio based on EDM-SBS analysis as discussed in section 4.2.2.4.



Figure E.1. Continued



# F Measured vs. modeled optical extinction coefficient (Supplement)

Figure F.1. Optical extinction coefficients ( $K_{ext,soot}$ ) obtained under (a) OP2, (b) OP9, (c) OP17, (d) OP27, (e) OP32 and (f) OP34 for an untreated (raw) exhaust while using diesel B7, (g) OP9, (h) OP27 and (i) OP34 for a CS-treated exhaust while using diesel B7 and (j) OP34 for an untreated (raw) exhaust while using dodecane. RDG-FA modeled  $K_{ext,soot}$ ) are obtained using (4.8) assuming E(m) = 0.35 and F(m) = 0.31, for  $400 < \lambda$  [nm] < 1000.



Figure F.1. Continued.

 ), mobility-equivalent geometric mean diameter $(D_{geo,m})$ and geometric standard deviation of size	and Figure 5.4, for both diesel B7 and dodecane, and for untreated and CS-treated conditions.	distributions measured consecutively (July 2021). Data not corrected for dilution ( $\sim$ 19:1).
regates number (PN), mobility- $\epsilon$	olayed in Figure 5.2 and Figure	is account for 3 size distribution
able G.1. $Agg$	stributions disp	Uncertaintic

<b>Table G.</b> distributio Unce	<ol> <li>Aggre ons displε prtainties</li> </ol>	gates number (PN wed in Figure 5.2 account for 3 size	<ul> <li>V), mobility-equivant</li> <li>and Figure 5.4</li> <li>distributions m</li> </ul>	valent geometric m , for both diesel B neasured consecutiv	ean diameter (D <sub>geo</sub> 7 and dodecane, ar ely (July 2021). Di	,m) and geometric stand for untreated and at not corrected for e	ndard deviation of size CS-treated conditions. filution ( $\sim$ 19:1).
OP	9	D <sub>geo,m</sub>	[mm]	σ <sub>gec</sub>	$0, D_{m}$	PN [#	$\cdot/\mathrm{cm}^3$ ]
	-	Untreated	CS-treated	Untreated	CS-treated	Untreated	CS-treated
Diese	91 B7						
OP2	0.187	$60.3 \pm 3.6$	$57.6\pm1.0$	$1.746\pm0.035$	$1.738 \pm 0.034$	$3.9\pm0.6\times10^{6}$	$2.3\pm0.1\times10^6$
OP9	0.300	$79.3\pm0.2$	$79.1\pm0.8$	$1.612 \pm 0.007$	$1.604 \pm 0.007$	$1.1\pm0.0 imes10^7$	$7.9\pm0.1 imes10^{6}$
OP17	0.626	$96.0\pm0.6$	$63.7\pm0.5$	$1.632 \pm 0.006$	$1.845 \pm 0.007$	$1.3\pm0.0 imes10^7$	$1.1\pm0.0 imes10^7$
OP27	0.933	$92.9\pm0.9$	$88.3\pm0.9$	$1.661\pm0.0$	$1.708 \pm 0.004$	$1.9\pm0.0 imes10^7$	$1.3\pm0.0 imes10^7$
OP32	1.502	$74.2\pm0.2$	$62.6\pm0.9$	$1.643 \pm 0.002$	$1.877 \pm 0.024$	$1.7\pm0.0 imes10^7$	$1.2\pm0.0 imes10^7$
OP34	1.564	$62.3\pm0.7$	$54.9\pm0.3$	$1.597\pm0.004$	$1.797 \pm 0.004$	$1.5\pm0.0 imes10^7$	$1.2\pm0.0 imes10^7$
Dode	cane						
OP9	0.277	$36.6\pm0.2$	$34.6\pm0.3$	$1.666\pm0.005$	$1.688 \pm 0.010$	$8.8 \pm 0.1 \times 10^{6}$	$5.0\pm0.1 imes10^{6}$
OP17	0.578	$47.47\pm0.24$	$41.6\pm0.3$	$1.660 \pm 0.003$	$1.756 \pm 0.002$	$1.4\pm0.0 imes10^7$	$8.9\pm0.1\times10^6$
OP27	0.862	$40.9\pm0.1$	$38.1\pm0.2$	$1.737 \pm 0.003$	$1.766 \pm 0.001$	$1.4\pm0.0 imes10^7$	$9.0\pm0.1 imes10^6$
OP32	1.387	$28.5\pm0.0$	$23.3\pm0.0$	$1.607 \pm 0.001$	$1.688 \pm 0.005$	$1.3\pm0.0 imes10^7$	$6.5\pm0.1 imes10^6$
OP34	1.445	$47.2 \pm 0.1$	$39.5\pm0.1$	$1.702\pm0.003$	$1.857 \pm 0.003$	$1.5 \pm 0.0 \times 10^7$	$9.4\pm0.0 imes10^6$

#### Soot aggregates size distributions statistical descriptors (Sup- $\mathbf{G}$ plement)

### H Impact of adjusting miniCAST flow rates while using diesel B7 on a CS-treated exhaust (Supplement)



Figure H.1. SMPS measured aggregates number (PN), mobility-equivalent geometric mean diameter ( $D_{geo,m}$ ) and geometric standard deviation ( $\sigma_{geo,D_m}$ ) as function of flame overall equivalence ratio ( $\varphi$ ) for 34 OPs for thermally treated (CS-treated) exhaust using diesel B7. OP2, OP9, OP17, OP27, OP32 and OP34 are indicated in colors. ( $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ) oxidation air = 2 L/min and ( $\mathbf{d}, \mathbf{e}, \mathbf{f}$ ) mixing air = 0.1 L/min. Uncertainties account for 3 size distributions measured consecutively (May 2021). Data not corrected for dilution (~ 19:1).

### I Gas chromatography - Flame ionization detection (GC-FID) analysis of the gas phase (Supplement)



Figure I.1. Results of the GC-FID analysis of the gas phase of blank samples prepared while running the miniCAST under idle condition (October 2021). Data not corrected for dilution (~ 19:1).
1.1



Figure I.2. Results of the GC-FID analysis of miniCAST gas phase obtained under OP27 and OP34 for untreated (raw) and filtered exhaust using dodecane (October 2021). Data not corrected for dilution ( $\sim 19:1$ ).



Figure I.3. Results of the GC-FID analysis of the miniCAST gas phase obtained under OP27 and OP34 for CS-treated and filtered exhaust using diesel B7 (October 2021). Data not corrected for dilution ( $\sim$  19:1).

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#### Untreated

**CS-treated** 



Figure J.2. H/C ratio as a function of the number of carbon atoms. Calculations are based on ToF-SIMS mass spectra measured from 'on spot' ROIs for (left) untreated and (right) CS-treated exhaust obtained under OP2, OP9, OP17, OP27, OP32 and OP34 while using diesel B7.

# K GC x GC - FID analysis of the chemical composition of liquid diesel B7 (Supplement)



Figure K.1.  $GC \times GC$  - FID analysis of the chemical composition of liquid diesel B7 in terms of iso-paraffins, normal-paraffins, monoaphthenes, di-naphthenes, di-aromatics, naphenic-di-aromatics, monoaromatics, naphenic-monoaromatics, tri-aromatics, tetra-aromatics and methyl esters.

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## List of Abbreviations

$\mathbf{AMS}$	Aerosol Mass Spectrometry
$\mathbf{APM}$	Aerosol Particle Mass analyser
BC	Black Carbon
CPMA	Centrifugal Particle Mass Analyser
CPC	Condensation Particle Counter
DMA	Differential Mobility Analyser
DPF	Diesel Particle Filter
DOC	Diesel Oxydation Catalysts
$\mathbf{ELPI}$	Electrical Low Pressure Impactor
EEPS	Engine Exhaust Particle Sizer
$\mathbf{PM}$	Particulate Matter
EC	Elemental Carbon
GC-MS	Gas Chromotography - Mass spectrometry
HACA	H Abstraction $C_2H_2$ Addition
HRTEM	High Resolution Transmission Electron Microscopy
LII	Laser Induced Incandescence
L2MS	Two-steps Laser Mass Spectrometry
$\mathbf{MS}$	Mass Spectrometry
OC	Organic Carbon
PAH	Polycyclic Aromatic Hydrocarbons
$\mathbf{PM}_{10}$	$PM$ whose aerodynamic diameter is less than or equal to 10 $\mu \mathrm{m}$
$\mathbf{PM}_{2.5}$	$PM$ whose aerodynamic diameter is less than or equal to 2.5 $\mu \mathrm{m}$
$\mathbf{SMPS}$	Scanning Mobility Particle Sizer
<b>ToF-SIMS</b>	Time-of-Flight Secondary Ion Mass Spectrometer
$\mathbf{SCR}$	Selective Catalytic Reduction
$\mathbf{SP2}$	Single Particle Soot Photometer
$\mathbf{SEM}$	Scanning Electron Microscopy
$\mathbf{TC}$	Total Carbon
TEOM	Tapered Element Oscillating Microbalance
$\mathbf{TEM}$	Transmission Electron Microscopy
$\mathbf{UV}$	Ultra-Violet
VIS	Visible
NIR	Near infrared
RDGFA	Rayleigh Debye Gans for Fractal Aggregates

## Physical Quantities

D	Diameter	nm
$\overline{\mathrm{D}}$	Mean diameter	nm
$D_{m}$	Mobility diameter	nm
$D_g$	Gyration diameter	nm
$D_{p}$	Primary particle diameter	nm
$\dot{D_a}$	Aerodynamic diameter	nm
$D_{ve}$	Volume equivalent diameter	nm
$D_{me}$	Mass equivalent diameter	nm
f <sub>v</sub>	Volume fraction	ppm
1	Mean free path	m
Np	Number of primary particles per aggregates	
PN	Aggregate number concentration	$\#/\mathrm{cm}^3$
Cs	Aggregate mass concentration	$\mathrm{mg/m^3}$
Rg	Gyration radius	nm
$\mathbf{V}^{\mathbf{a}\mathbf{g}\mathbf{g}}$	Volume of an aggregate	$\mathrm{m}^3$
$V_{m}^{agg}$	Volume of aggregate material	$\mathrm{m}^3$
v	Velocity	m/s
v <sub>r</sub>	Relative velocity	m/s
$v_{TE}, v_{TS}$	Terminal velocity	m/s
k <sub>f</sub>	Fractal pre-factor	,
$D_{f}$	Fractal Dimension	
$D_{\mathrm{fm}}$	Mass mobility exponent	
Р	Pressure	Pa
Т	Temperature	Κ
F <sub>Drag</sub>	Drag force	Ν
Ze	Electrical mobility	$m^{2}V^{-1}s^{-1}$
n <sub>e</sub>	Number of elementary charges	
e	Elementary charge	С
$m^p$	Primary particle mass	kg
$m^{agg}$	Mass of an aggregate	kg
k $2\pi/\lambda$	Wavenumber	$\mathrm{m}^{-1}$
$C_{\text{ext}}$	Extinction cross-section	$\mathrm{m}^2$
$C_{abs}$	Absorption cross-section	$\mathrm{m}^2$
$C^{p}_{abs}$	Absorption cross-section of a spherical particle	$m^2$
$C_{abs}^{agg}$	Absorption cross-section of an aggregate	$m^2$
$C_{sca}$	Scattering cross-section	$m^2$
$C_{sca}^{p}$	Scattering cross-section of a spherical particle	$m^2$
$C_{sca}^{agg}$	Scattering cross-section of an aggregate	$m^2$
f	Structure factor for differential angular scattering	
g	Structure factor for total scattering	
xp	Shape factor	
L	Optical path	m
# List of Symbols

i	Imaginary unit	
m	Complex refractive index	
n	Complex refractive index real part	
k	Complex refractive index imaginary part	
ρ0	Standard density	$ m kg/m^3$
ρp	Bulk density	$ m kg/m^3$
Peff	Effective density	$ m kg/m^3$
μ	Dynamic viscosity	Pa.s
ν	Kinematic viscosity	$\mathrm{m}^2/\mathrm{s}$
λ	Wavelength	nm
χ	Dynamic shape factor	
φ	Overall equivalence ratio	
$\sigma_{\rm geo}$	Geometric standard deviation of a lognormal size distribution	

## **Dimensionless Numbers**

- $C_c$  Cunningham slip correction factor
- Kn Knudsen Number
- Re *Reynolds* Number

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### Abstract

#### Development of optical and chemical diagnostics to characterize and control particulate and gaseous emissions from combustion systems

#### by Mouad DAOUDI

Combustion is one of the main contributors to both particulate matter (PM) and several gaseous pollutants which may have harmful effects on human health, environment, and climate. The main goal of this PhD is to develop a measurement procedure based on optical extinction to monitor PM and/or some gaseous pollutants emissions produced by a combustion system (e.g., internal combustion engine, turbine, or industrial burner). This work also aims to shed the light on the relationship between the chemical composition and the optical extinction coefficient measured for these emissions. To succeed in this measurement challenge and avoid the complexity of a real powertrain setup, a modular combustion bench has been built in which gaseous pollutants and PM can be monitored independently. This experimental setup was equipped with a version of the miniCAST soot generator that has the ability to burn liquid fuels, thus allowing the study of the impact of the chemical composition of the fuel on the physico-chemical properties of PM. A total of 34 operating points were characterized, spanning a wide range of flame overall equivalence ratio (i.e., 0.104 - 1.673) using two different fuels (diesel B7 and dodecane). The soot particles produced by this burner were characterized in terms of morphological key parameters, size distributions, mass concentrations, and optical extinction coefficients. All these data were then used to evaluate and intercompare the soot volume fraction using three different methods: granulometric (combining size measurement and morphology), mass, and optical.

Furthermore, the chemical composition of the combustion products of the miniCAST was studied in order to characterize the organic content of the gas phase and the particulate phases. This study was carried out by combining gas chromatography (GC), to examine low mass polycyclic aromatic hydrocarbons (PAHs) in the gas phase, and time-of-flight secondary ion mass spectrometry (ToF-SIMS), to characterize the heavy PAHs in both the gas and particle phases. These experiments allowed to identify the operating points associated with the highest content of organic compounds. Then, a correlation was observed between the presence of that organic content (mostly attributed to organic PAHs) and the optical extinction coefficient. The use of an oxidation catalyst (catalytic stripper) on the burner exhaust gases allowed to evaluate the impact of this thermal treatment at 350 °C on the chemical composition of the exhaust gases, on the size and morphology characteristics of soot aggregates, and consequently on the measurement of the optical extinction coefficient. Finally, the measurement of the optical extinction coefficient for PM and gaseous pollutants such as NO, NO<sub>2</sub>, and/or NH<sub>3</sub> injected first separately and then simultaneously was performed to evaluate the interference of gaseous pollutants with PM and to propose a procedure allowing their simultaneous control.

In conclusion, this thesis provides for a soot generator's PM emissions a detailed description of soot particles sizes, morphologies, soot volume fractions and optical extinction coefficients, as well as a detailed characterization of the chemical composition of the gas and particulate phase produced by this generator, under different operating conditions. Thanks to the experimental database obtained, this thesis proposes a methodology of measurement and analysis for optical extinction coefficients and for ToF-SIMS mass spectra which can be transposed to the study of biofuels or synthetic fuels (e-fuels) in the near future.

**Keywords**: Optical extinction, chemical composition, morphology, volume fraction, soot particles, gaseous pollutants, PN, PM, ToF-SIMS, miniCAST

### Résumé

#### Développement de diagnostics optiques et chimiques pour caractériser et contrôler les émissions particulaires et gazeuses des systèmes de combustion

par Mouad DAOUDI

La combustion est l'une des principales sources d'émissions particulaires (PM) et de plusieurs polluants gazeux qui peuvent avoir des effets néfastes sur la santé humaine, l'environnement et le climat. Les travaux réalisés dans cette thèse visent à développer une procédure de mesure basée sur l'extinction optique pour contrôler les PM et/ou certains polluants gazeux produits par un système de combustion (e.g., moteur à combustion interne, turbine ou brûleur industriel). Ces travaux visent également à comprendre les liens qui peuvent exister entre la composition chimique et le coefficient d'extinction optique mesurés pour ces émissions. Pour réussir ce défi de mesure et éviter la complexité d'une configuration réelle de moteur, un banc de combustion modulaire a été construit dans lequel les polluants gazeux et les PM peuvent être contrôlés indépendamment. Ce dispositif expérimental a été équipé d'une version du générateur de suie miniCAST ayant la capacité de brûler des carburants liquides, permettant ainsi l'étude de l'impact de la composition chimique du carburant sur les propriétés physicochimiques des particules de suie. Au total, 34 points de fonctionnement ont été caractérisés, balayant une large gamme de richesses globales de flamme (i.e., 0.104 - 1.673) en utilisant deux carburants différents (diesel B7 et dodecane). Les particules de suie produites par ce brûleur ont été caractérisées du point de vue des grandeurs morphologiques, des distributions de taille, des concentrations massiques, et enfin des coefficients d'extinction optique. L'ensemble de ces données ont ensuite servi à évaluer et intercomparer la fraction volumique des suies par trois méthodes différentes à savoir granulométrique (combinant la mesure de taille et la morphologie), massique, et optique.

Par ailleurs, la composition chimique des produits de combustion du miniCAST a été étudiée afin de caractériser le contenu organique de la phase gazeuse et de la phase particulaire. Cette étude a été réalisée en combinant la chromatographie en phase gazeuse (GC), pour examiner les hydrocarbures aromatiques polycycliques (HAP) de faible masse dans la phase gazeuse, et la spectrométrie de masse par analyse de temps de vol d'ions secondaires (ToF-SIMS), pour caractériser les HAP cette fois-ci lourds dans les deux phases gazeuse et particulaire. Tout d'abord, cette étude a permis d'identifier les points de fonctionnement associés à la plus forte teneur en composés organiques. Par la suite, une corrélation a été observée entre la présence de ces HAP et le coefficient d'extinction optique. L'utilisation d'un catalyseur d'oxydation (catalytic stripper) sur les gaz d'échappement du brûleur a permis d'évaluer l'impact de ce traitement thermique à 350 °C sur la composition chimique des gaz d'échappement, sur les caractéristiques de taille et de morphologie des agrégats de suie, et par conséquent sur la mesure du coefficient d'extinction optique. Enfin, la mesure du coefficient d'extinction optique de PM et de polluants gazeux tels que NO, NO<sub>2</sub>, et/ou NH<sub>3</sub> injectés d'abord séparément, puis simultanément a été réalisée pour évaluer l'interférence des polluants gazeux avec les PM et proposer une procédure permettant leur quantification simultanée.

En conclusion, ce travail de thèse restitue une métrologie des émissions particulaires d'un générateur de suies du point de vue de la taille, la morphologie, la fraction volumique et le coefficient d'extinction optique, ainsi qu'une caractérisation détaillée de la composition chimique de la phase gazeuse et particulaire que ce générateur produit, et ce, sous différentes conditions opératoires. Grâce à la base de données expérimentale obtenue, ce travail de thèse propose une méthodologie de mesure et d'analyse des résultats pour le coefficient d'extinction optique et les spectres de masse ToF-SIMS pouvant être transposée à l'étude des bio-carburants ou des carburants synthétiques (e-carburants) dans un futur proche.

Mots-Clés: Extinction optique, composition chimique, morphologie, fraction volumique, particule de suie, polluants gazeux, PN, PM, ToF-SIMS, miniCAST