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Chemical characterization of size-selected nanoparticles emitted by a gasoline direct injection engine: impact of a catalytic stripper

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Abstract

This work combines laser desorption/ionization mass spectrometry (L2MS) and advanced statistical techniques to reveal the impact of a catalytic stripper (CS) on the chemical composition (at the molecular level) of a gasoline direct injection engine exhaust, and follow the evolution of size-dependent chemical characteristics over the whole particles size range (10–560 nm). The gas phase and polydisperse particles making up the exhaust are separated and sampled on distinct substrates using an original homebuilt two-filter system, while size-selected particles are collected using a cascade impactor and separated into 13 different size bins (smallest diameters 10–18 nm). We demonstrate that a fine molecular-level characterization of the exhaust particulate matter is necessary to assess the effect of the CS, especially for the smallest ultra-fine particles carrying the largest volatile fraction.

Keywords: Nanoparticles, Carbonaceous aerosols, Size-selective chemical characterization, Internal combustion engine, Catalytic stripper

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1. Introduction

Internal combustion engine (ICE) powered vehicles constitute a major source of airborne particulate matter (PM), especially in urban areas [1, 2]. Particles emitted from vehicle engines are complex mixtures, mainly consisting of a carbonaceous core with a multitude of adsorbed compounds such as unburnt and partially oxygenated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), sulfates, and metal oxides [3, 4]. The particle's outer organic layer (the so-called surface organic fraction – SOF) exerts a considerable influence on the properties of particulate emissions (*i.e.* reactivity, toxicity, nucleation properties) and is considered a major contributor to particle-associated health hazards [5]. In this context, special attention is drawn by the ultra-fine particles (size <100 nm) due to their higher deposition fraction, deeper penetration, and higher retention rate in the lungs [6, 7]. The inhalation of these smallest particles can result in health problems beyond the lungs: the presence of combustion derived nanoparticles has been detected in the frontal cortex of autopsy brain samples [8], urine of healthy children [9], and even in the fetal side of the placenta [10]. If transported to the fetus, these particles – as carriers for potentially toxic chemical species – could significantly affect fetal health and development [10]. Most recently, a strong association between increases in PM concentration and mortality rates due to COVID-19 was evidenced [11, 12].

The automotive industry has made significant efforts to reduce the amount and impact of internal combustion engine emissions [13–15]. For this purpose, various after-treatment systems based on conversion, adsorption and trapping technologies, such as three-way catalysts, diesel oxidation catalysts, selective catalytic reduction systems and particulate matter filters have been implemented in the exhaust track of both spark and compression ignition engines [16–18]. Devices providing chemical sites for oxidation and reduction reactions (*i.e.* catalytic strippers/converters) are particularly useful as they can convert toxic by-products present in the exhaust into less hazardous substances such as carbon dioxide, water vapor, and nitrogen gas. In the meantime, recent improvements in engine technology resulted in a significant decrease in the total number and mass of PM emitted by on-road vehicles. This, however, also led to a shift in the particle diameter toward smaller sizes (lower than 100 nm [19]).

34 Although not a major contributor to the emitted particle mass, these ultra-fine
35 sizes represent an important share in the total particle number (PN), which is
36 regulated by 17 out of the 20 countries of the G-20 group (accounting for 90%
37 of the global vehicle sales [20]). Current European Union (EU) regulations limit
38 PN emissions for sizes above 23 nm. However, sub-23nm particles are produced
39 in large concentrations by both Diesel and gasoline direct injection (GDI) en-
40 gines [21] and can sometimes reach 30–40% of the total PN for vehicles equipped
41 with a GDI [22]. Based on these findings, the PMP (particle measurement pro-
42 gramme) group of the working party on pollution and energy (GRPE) of the
43 United Nations Economic Commission for Europe (UNECE) has worked on a
44 protocol to lower the PM 23 nm cut-off point to 10 nm [23], the PM referring
45 only to solid (non-volatile) particles [24], *i.e.* those which do not evaporate below
46 350°C.

47 Lowering the cut-off size of measured PM might be quite challenging, as
48 it requires more efficient aerosol conditioning technologies to remove volatile
49 and semi-volatile compounds with minimal size-dependent particle losses and
50 to avoid the creation of artifacts (*i.e.* particles generated in the sampling /
51 conditioning system). Three EU Horizon 2020 projects [25–27] have worked in
52 parallel over the past few years to propose a robust methodology and associated
53 instrumentation (portable emissions measurement systems – PEMS) for PN
54 measurements down to 10 nm. Recent assessment campaigns [28–30] confirmed
55 that the developed PEMS prototypes are ready to be introduced in the future
56 regulations. A major change proposed in the PMP draft recommendations [23] is
57 to impose the use of a catalytic stripper (CS) as volatile particle remover (VPR)
58 in the future 10-nm PEMS, which is considered a safer option [31] than the
59 evaporation tube (ET) or the thermodenuder (TD). The ET, currently used in
60 automotive particle measurement systems, is a simple and robust method when
61 measuring particles larger than 23 nm as it is able to completely evaporate most
62 hydrocarbons. However, this technology might lead to re-nucleation of semi-
63 volatile species at high hydrocarbon particle concentrations and thus higher
64 primary dilution ratios are required to reliably measure solid particles smaller
65 than 23 nm [32, 33]. Therefore, for measuring particles in the sub-23 nm range,
66 removing the semi-volatile aerosol fraction using a CS optimized for small losses

67 of ultra-fine particles can prove more efficient [34–36].

68 The use of CSs in emission measurement systems has been reviewed by
69 Giechaskiel et al. [31]. Up to now, the impact of CSs on the resulting emissions
70 has mostly been characterized physically, with comparisons between stripped
71 and unstripped particle mass, number or size distribution. What comes into
72 view is the current lack of information regarding its impact on the chemical
73 composition (at the molecular level) of the emitted aerosols (with the notable
74 exception of one study addressing marine exhaust aerosols [37]). As the chemical
75 composition (and thus the degree of volatility) making up the SOF layer can
76 significantly vary with engine regimes or with PM size, an extensive investigation
77 of the physico-chemical properties of the measured objects should be undertaken
78 to ensure the development of a PEMS instrument capable of maintaining its
79 accuracy and reliability for a wide range of engine operating conditions (*i.e.* in
80 real driving conditions).

81 In the frame of the EU Horizon 2020 PEMS4Nano project [25] we conducted
82 extensive measurement campaigns to thoroughly analyze the physico-chemical
83 properties of particles emitted by a single-cylinder engine in a bottom-up ap-
84 proach combining experimental [38] and theoretical studies [39] for the devel-
85 opment of a PEMS prototype. The action of a home-made (University of Cam-
86 bridge) CS on the measured aerosol (polydisperse and size-selected particles,
87 gas phase) was investigated both on-line (physical characterization by an origi-
88 nal tandem arrangement of aerodynamic aerosol classifier, differential mobility
89 analyzer, and centrifugal particle mass analyzer [40]) and off-line (laser mass
90 spectrometry chemical characterization of filter-collected samples). As on-line
91 chemical characterization by aerosol mass spectrometers is limited to particles
92 larger than $\sim 50\text{nm}$ [37], the off-line approach adopted here is the only possible
93 solution when focusing on smaller nanoparticles (10–32 nm in the present study)
94 of actual interest for the 10-nm PEMS development.

95 **2. Materials and methods**

96 *2.1. Sampling*

97 A generic single-cylinder gasoline direct injection engine was used on a test
98 bench to generate particles with various properties for building an extensive

99 database through multi-technique physico-chemical characterization [38]. The
 100 engine was described in detail in a previous publication [38], only the main
 101 characteristics are briefly reminded in Table 1, Supporting Information. For
 102 the present study, two set-points were used, called in the following low speed
 103 (LS, 1200 rpm) and high speed (HS, 2000 rpm). The IMEP (indicated mean
 104 effective pressure) was kept constant at 10 bar, λ at 1.01, and the injection
 105 at 270° bTDC (before top-dead center). The engine was operating on Euro
 106 Stage V E5 Gasoline (CEC-RF-02-08 E5) with the ignition timing set for the
 107 maximum brake torque (MBT). The temperature of both coolant and oil (Agip
 108 SIGMA, 10W-40) was kept at 80°C. To ensure the cleanliness of the combustion
 109 chamber, the engine was conditioned with methane (CH₄) before changing the
 110 operating point.

Table 1: Engine specifications (b/aTDC – before/after Top Dead Center)

Specification	Value
Cylinder head	Pentroof type
Compression ratio	12.5:1
Bore	82 mm
Stroke	85 mm
Displacement	449 cm ³
Fuel direct injection system	Central mounted generic six-hole injector
Injection pressure	150 bars
Spark plug location	Exhaust side
Intake valve timing:	Open 334 deg. bTDC
	Close 166 deg. bTDC
Exhaust valve timing:	Open 154 deg. aTDC
	Close 330 deg. aTDC

111 A custom sampling line (Figure 1) was used for the simultaneous collection
 112 of engine exhaust for offline characterization and online volatile mass fraction
 113 measurements [40]. Raw engine exhaust was sampled from the exhaust pipe 10
 114 cm downstream of the manifold. Sampled flow was then diluted using a Dekati
 115 FPS 4000 (1:30 dilution ratio) to prevent the condensation of volatile species as
 116 well as their aggregation. The main objective of this study was to assess the im-
 117 pact of the catalytic stripping on the gas phase, polydisperse, and size-selected
 118 particles. Two CSs were used: CS1 (1.5 l/min flow) for on-line measurements
 119 (Catalytic Instruments CS-015) and CS2 (presented in detail in reference [38]),

120 which was manufactured identical to CS1 by the University of Cambridge with
121 the exception that it was adapted to accept higher flows (10 l/min) to increase
122 the exhaust collection efficiency needed for the subsequent offline analysis. Both
123 CSs performances in terms of hydrocarbon removal were tested to be >99% for
124 30 nm tetracontane ($C_{40}H_{82}$) particles at a concentration of $>10^4 \text{ cm}^{-3}$. As this
125 work focuses on the offline analysis, only the corresponding experimental details
126 are given below, while information about the online measurement can be found
127 in reference [40]. The upstream (unstripped) flows were analyzed/sampled us-
128 ing bypasses (red dashed lines in Figure 1), while the downstream (stripped)
129 flows were collected after passing through the CS. The sampling of size-selected
130 particles was performed with a NanoMOUDI II cascade impactor (TSI, model
131 125R) able to separate particles into 13 different size-bins, with nominal cut
132 sizes of 10000, 5600, 3200, 1800, 1000, 560, 320, 180, 100, 56, 32, 18, 10 nm.
133 The size-selected particles were deposited on aluminum foils that were cleaned
134 and thermally treated (at 300°C) prior to the sampling to remove all possible
135 surface contaminants. The sampling time varied between 6h and 12h. An alter-
136 native (separate) sampling of polydisperse particles and exhaust gas phase was
137 performed with an original double-filter system recently developed in our labora-
138 tory [41]. This device is made of two quartz fiber filters (QFF) placed in series:
139 the front filter (FF) retains the particulate matter while letting through the
140 gas/volatile phase, which is then adsorbed by a layer of activated carbon placed
141 on the back filter (BF). This sampling system was proven to be very efficient
142 in separating the particulate (non-volatile) and the gas phases in combustion
143 emissions [41]. Both front and back filters were thermally conditioned before
144 the sampling in order to remove any possible contaminants. The sampling time
145 was adjusted (60–80 min) in accordance with the particle concentration and size
146 distribution in the exhaust to obtain a homogeneous layer of particles on the
147 FF.

148 A total of 44 samples were collected in the two engine regimes for subsequent
149 offline analysis. A sample labeling scheme is used in the following, indicating the
150 engine set-point (HS or LS), the downstream (CS) or upstream sampling point,
151 the size-bin (for size-selected particles) or the collection QFF in the double-
152 filter device (FF for polydisperse particles, BF for gas phase). For instance,

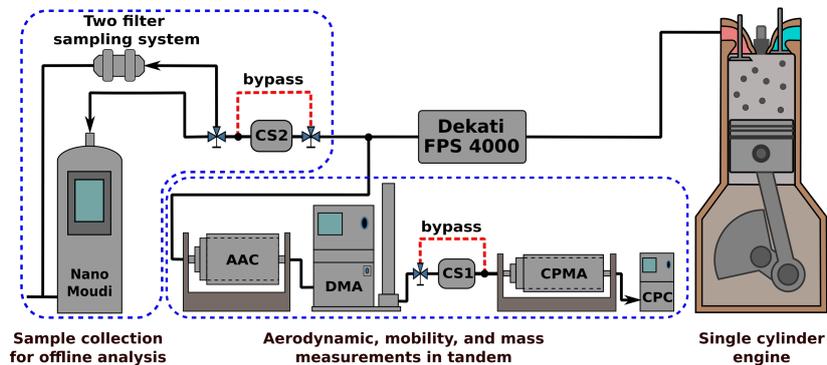


Figure 1: Schematic representation of the experimental setup. Sampling of the exhaust was conducted with a NanoMoudi II cascade impactor to size-select particles and a two-filter collection device [41] to separate the PM (polydisperse particles) and the gas phase. The collection was performed with and without the CS. The online SOF mass fraction measurements were performed with a combination of Aerodynamic Aerosol Classifier (AAC, Cambustion Ltd.), differential mobility analyzer (3080 DMA, TSI Inc.), and centrifugal particle mass analyzer (CPMA, Cambustion Ltd.) followed by a condensation particle counter (CPC, 3776, TSI Inc.) [40].

153 HS-CS_{FF} indicates polydisperse particles collected downstream the CS in HS
 154 engine regime, while LS_{10–18} labels 10–18 nm size-selected particles collected
 155 upstream the CS in the LS engine regime. In addition, a set of blank samples
 156 (aluminum foil, a neat QFF, and an activated carbon-covered QFF) were pre-
 157 pared, stored (at 4°C) and managed in a similar way than the collected samples.

158 2.2. Chemical analysis

159 The chemical characterization of collected particles was performed using a
 160 two-step (desorption/ionization) laser mass spectrometry technique (L2MS) de-
 161 scribed in detail elsewhere [42, 43]. The mass spectrometer used in this study
 162 (Fasmatech S&T) combines ion cooling, Radio Frequency (RF) guiding and
 163 Time-of-Flight (ToF) analyzer to reach a mass resolution of ~ 15000 . The sam-
 164 ple, placed under vacuum (10^{-8} mbar residual pressure), is irradiated at 30° an-
 165 gle of incidence by a frequency doubled Nd:YAG laser beam (Quantel Brilliant,
 166 $\lambda_d=532$ nm, 4 ns pulse duration, $0.10\text{--}0.22$ J cm $^{-2}$ fluence, 10 Hz repetition rate)
 167 focused to a 0.07 mm 2 spot on the surface. The desorbed compounds form a
 168 gas plume that expands in the vacuum normally to the sample surface, and are
 169 ionized by an orthogonal UV laser beam (Quantel Brilliant, $\lambda_i = 266$ nm, 4 ns

170 pulse duration, 10 Hz repetition rate, $\sim 0.3 \text{ J cm}^{-2}$ fluence). The generated ions
171 are then RF-guided to a He collision cell for thermalization and subsequently
172 mass analyzed in a time-of-flight mass spectrometer equipped with a reflectron
173 (ToF-MS). The desorption and ionization fluences were adjusted for each sample
174 to obtain the maximum signal intensity while minimizing fragmentation in the
175 mass spectra. Each mass spectrum was obtained by averaging the signal from
176 200 laser shots applied on a small ($\sim 2 \text{ mm}^2$) zone of the sample. To check the
177 homogeneity of the sample surface, the analysis was performed on four different
178 zones of each sample and all the results were used in the subsequent statistical
179 data treatment.

180 Since mass spectra of the analyzed samples contain a large number of peaks
181 its interpretation can be challenging. To optimally exploit this large amount of
182 information, the MS data treatment follows a dedicated methodology developed
183 in our group [44–46], which includes mass defect and multivariate analysis ap-
184 proaches. In this framework, a variety of advanced statistical techniques such as
185 Principal Component Analysis (PCA) [47], Hierarchical Clustering on Principal
186 Components (HCPC), and volcano plots [48, 49] can help uncover “hidden” pat-
187 terns in complex datasets, group samples based on their similarities and identify
188 the most significant mass peaks contributing to sample differentiation.

189 **3. Results and discussion**

190 *3.1. Polydisperse particles and gas phase*

191 The impact of the catalytic stripper on polydisperse PM and the gas phase
192 was assessed by comparing the chemical composition of samples collected with
193 and without the CS. Examples of mass spectra recorded for polydisperse parti-
194 cles (FF) and gas phase (BF) samples collected (in the high-speed engine regime)
195 upstream and downstream the CS are displayed in Figure 2. The spectra contain
196 predominantly polycyclic aromatic species and their fragments; their partial ion
197 count (PIC) was shown to be representative of the organic carbon content of the
198 sample [38, 46, 50]. When comparing downstream (HS_CS_{FF}) and upstream
199 (HS_{FF}) particles, a 7-fold reduction of aromatic PIC is observed, which clearly
200 demonstrates the efficiency of the CS in stripping the surface organic layer. Al-
201 though a direct quantitative comparison is not possible (different experimental

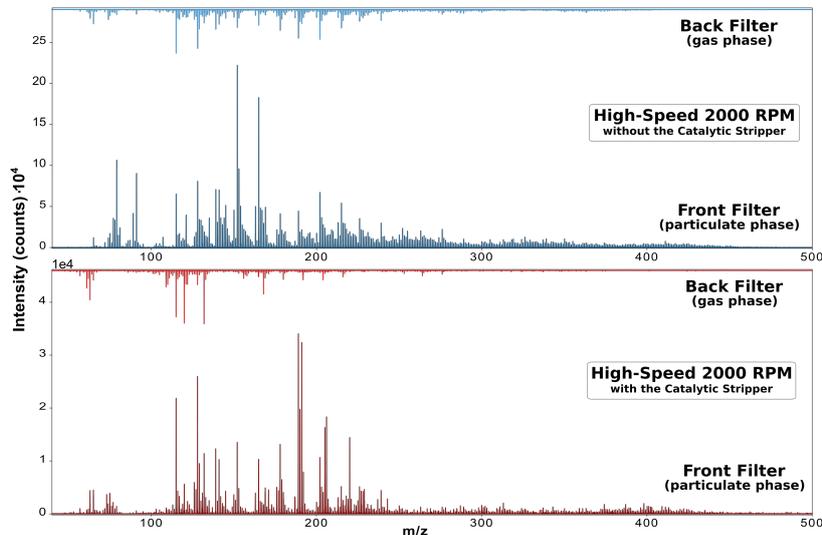


Figure 2: Mass spectra of $\text{HS}_{FF/BF}$ and $\text{HS-CS}_{FF/BF}$ samples (particulate and gas phase collected with and without the CS) obtained with L2MS.

202 configurations), we note that this efficiency is in line with previous measure-
 203 ments performed with a soot particle aerosol mass spectrometer (SP-AMS) on
 204 marine engine exhaust, where organic species reductions in the range 94-97%
 205 were observed upon stripping [37]. The relatively small difference between the
 206 results presented here and the ones reported in Amanatidis et al. [37] might
 207 be explained by the fact that the SP-AMS instrument is only able to measure
 208 particles larger than ~ 50 nm and the smallest particles below this threshold
 209 are expected to carry a higher SOF. A detailed discussion on this will be pro-
 210 vided in the section 3.2, which focuses on size-selected particles (especially the
 211 10–32 nm range). The efficiency of the CS in removing organics is even higher
 212 on the gas phase, as a 20-fold reduction in aromatic PIC was recorded down-
 213 stream (HS-CS_{BF} sample) with respect to upstream (HS_{BF}). Indeed, the mass
 214 spectrum of the HS-CS_{BF} sample contains mostly carbon clusters (C_n^+ , repre-
 215 sentative of the elemental carbon content [38, 46]) and is almost identical to the
 216 blank BF spectrum. We emphasize that the presence of carbon clusters on back
 217 filters, sampled both with and without the CS, is determined by the layer of
 218 activated carbon intended to trap the gas phase [41] and cannot be associated
 219 with the exhaust gas phase combustion by-products.

220 To properly interpret mass spectrometric data, mass defect analysis [44–46]

221 was used to assign chemical formulas to the most intense peaks. The full list
222 of assigned peaks is provided in Table S1. A volcano plot [48, 49] was used to
223 highlight the CS-induced changes in the chemical composition of both particu-
224 late and gas phases. The two phases carry chemical species of different volatility
225 and mass, and thus the separate study of these phases allows to better evaluate
226 the efficiency of the CS. The differences between the chemical composition of
227 the particulate and gas phases can clearly be seen when the front (particulate
228 phase) and the back filter (gas phase) sampled without the CS are compared,
229 Figure S1. The front filter receives a high contribution from higher-mass aro-
230 matic species, with more than 4 aromatic rings. According to Bari et al. [51],
231 the volatility of aromatic compounds can be inferred from the total number of
232 aromatic rings: compounds consisting of only two aromatic rings are considered
233 volatile, three to four – semi-volatile, and those with more than four aromatic
234 rings – non-volatile. It should be noted that all the peaks corresponding to car-
235 bon clusters (C_n^+) have been excluded from this analysis since, in this case, they
236 do not originate from the same source (soot particles for the front filters and the
237 pre-applied black carbon layer for the back filter). However, when comparing
238 only front filter samples (Figure 3a), carbon clusters provide important infor-
239 mation about the variation of the OC/EC ratio (organic carbon to elemental
240 carbon content) of sampled particles as they are commonly considered as mark-
241 ers of EC [46, 52–54]. Once the particles pass through the CS the contribution of
242 aromatic compounds, considered as good indicators of the organic carbon con-
243 tent [38, 50], is significantly reduced, effectively decreasing the OC/EC ratio.
244 Moreover, stripped particles feature a higher contribution from oxygenated and
245 nitrogenated species which can be linked to the oxidation processes occurring
246 in the CS.

247 A similar picture can be seen when the two samples corresponding to the
248 gas phase (HS_{BF} and $HS_{CS_{BF}}$) are compared, Figure 3b. The gas phase
249 sampled without the CS presents a high content of aromatic compounds (mostly
250 low-mass, up to 4 aromatic rings), while the one collected downstream the
251 stripper is characterized only by carbon clusters (coming from the underlying
252 black carbon layer). The fact that no organic species contribute in a significant
253 way to the $HS_{CS_{BF}}$ mass spectrum implies that the CS removed the majority

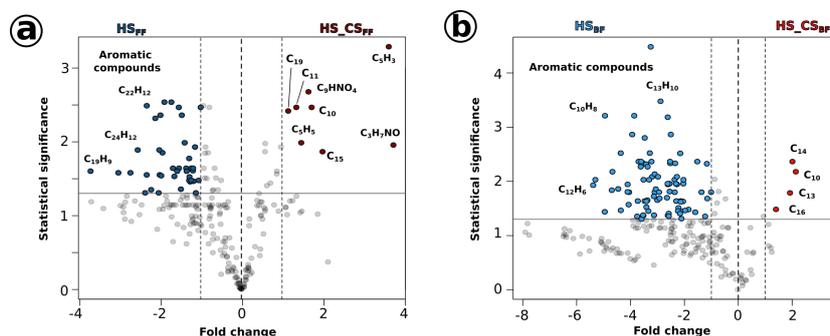


Figure 3: Volcano plots showing the “differential expression” of detected chemical species: a) comparison between the chemical composition of the particulate phase sampled with and without the CS, and b) influence of the CS on the chemical composition of the gas phase.

254 of combustion-generated compounds from the gas phase.

255 A principal component analysis of all FF and BF samples collected (with
 256 and without the CS) in both engine regimes (HS and LS) was performed. This
 257 approach allows the differentiation between samples and highlights (through
 258 the analysis of the loading plots, Figure S2) the contribution of individual com-
 259 pounds or groups of highly correlated species to this differentiation. The PCA
 260 was able to separate all the samples with only two principal components account-
 261 ing for $\sim 72\%$ of the total variance. The first principal component ($\sim 63.9\%$) sep-
 262 arates the samples based on the OC/EC ratio (a high positive PC1 score reflects
 263 a low OC/EC ratio). The volatility of the samples can be inferred from their
 264 PC2 ($\sim 8.2\%$ of explained variance) scores. A positive PC2 score is associated
 265 with the presence of non-volatile aromatic species (more than 4 aromatic rings)
 266 with $m/z \leq 363$, while a negative PC2 score is linked to the presence of volatile
 267 and semi-volatile compounds, as well as some high-mass aromatic species (m/z
 268 > 363). Three major regions can be seen on the score plot presented in Figure
 269 4: i) particulate phase sampled without the CS (HS_{FF} and LS_{FF} , dark blue),
 270 ii) particulate phase sampled with the CS along with the gas phase sampled
 271 without it ($HS_{CS_{FF}}$, $LS_{CS_{FF}}$ – dark red, HS_{BF} , and LS_{BF} – light blue), and
 272 iii) the gas phase collected after the CS ($HS_{CS_{BF}}$ and $LS_{CS_{BF}}$ - light red).

273 It is worth noting that even though particulate phases sampled without the
 274 stripper are located fairly close to each other and can be grouped together,
 275 their chemical composition is different. The PC1 score for the front filter (par-

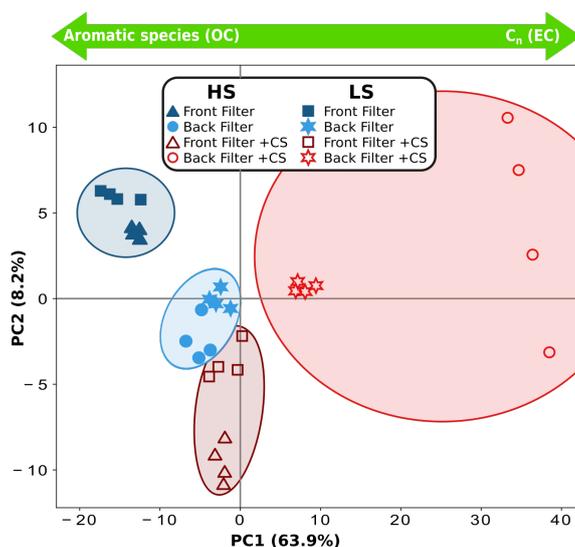


Figure 4: Score plot of the first two principal components for the particulate and gas phase samples collected with and without the CS in two different engine regimes (HS and LS). The arrows represent the meaning of the first principal component derived from the corresponding loadings plot, Figure S2.

276 ticulate phase) collected in the LS engine regime is lower, thus indicating a
 277 higher contribution from organic compounds in this regime. However, after the
 278 catalytic treatment, particles emitted in different engine regimes seem to have
 279 a more similar chemical composition, depicted by their almost identical PC1
 280 scores. Moreover, the sign of the PC2 value changes after the particles have
 281 passed through the CS, suggesting the removal of the vast majority of high-
 282 mass organic compounds. The untreated gas phase contains a much smaller
 283 amount of organic species (PC1 value close to zero) which are almost com-
 284 pletely removed by the stripper (PC1 sign changes). Therefore, mass spectra
 285 of HS-CS_{BF} and LS-CS_{BF} samples have a much larger contribution from the
 286 layer of activated carbon pre-applied to their surfaces, and thus the difference
 287 in PC1 value (*i.e.* contribution of elemental carbon) between the two samples
 288 cannot be attributed to combustion conditions and instead is determined by
 289 small inhomogeneities in the layer of activated carbon. The PC2 value for gas
 290 phase samples is close to zero, indicating a low influence from this component
 291 due to the insignificant number of high-mass organic species.

292 A volcano plot (Figure S3) was employed to compare the particulate phase

293 produced in the HS and LS engine regimes. When comparing unstripped par-
294 ticles, Figure S3a, we can see that while both samples contain a large amount
295 of aromatic compounds, the one obtained at lower speed (LS) contains more
296 high-mass species (*i.e.* non-volatile compounds [41, 51]). Unstripped parti-
297 cles collected in different regimes have a noteworthy difference in the chemical
298 composition, demonstrated by the fact that 55 compounds contribute in a sta-
299 tistically significant way to their separation. In contrast, stripped particles
300 appear to be very similar, Figure S3b. Only a few species contribute to the
301 separation between the mass spectra of stripped particles generated in different
302 engine regimes, and these mass spectra are mostly constituted of carbon clus-
303 ters (representative of EC). This is an important result, showing that the CS
304 is able to treat particles exhibiting quite different initial chemical composition,
305 effectively stripping their (different) surface organic layers and leaving them as
306 solid non-volatile PM.

307 3.2. Size-selected particles

308 Size-selected particles produced in the two engine regimes, and sampled with
309 or without the CS were chemically characterized. For the first engine regime
310 (HS) the stages of the cascade impactor that collected sufficient material (with
311 and without the CS) covered a quite extended size-range: from 10 nm up to
312 560 nm (HS₁₀₋₁₈ - HS₃₂₀₋₅₆₀ samples). Mass spectra of these samples are
313 presented in Figure 5. One can see that mass spectra of particles from different
314 size-bins are very different, indicating that the chemical composition of emitted
315 particles significantly changes with the size. Mass spectra of particles collected
316 without the CS show a high contribution from heavy-mass PAHs that can be
317 associated with the remnants of the fuel or lubricating oil [38]. The majority
318 of these compounds are successfully removed by the CS, which is illustrated by
319 the decrease in the absolute signal intensity. At the same time the contribution
320 of carbon clusters (C_n^+) increases, thus indicating a much lower OC/EC ratio
321 for the stripped particles. The relative contribution of low-mass PAHs and their
322 fragments increases toward smaller particle sizes which suggests an increase in
323 the overall volatility of the surface organic fraction [40].

324 PCA was applied to the mass spectrometric data to study the impact of CS
325 on the size dependent chemical composition. The first two principal components

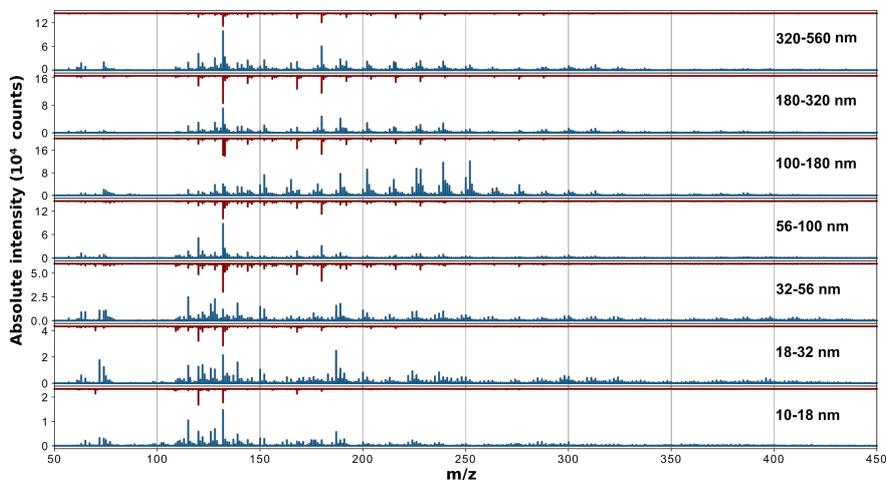


Figure 5: Mass spectra of size-selected particles produced in the HS engine regime and sampled with (red line – HS_CS) and without (blue line – HS) the catalytic stripper. The labels indicate the corresponding NanoMOUDI size-bin.

326 account for $\sim 60\%$ of the variance in the dataset and are able to discriminate
 327 between different samples (with particles of a different size and collected with or
 328 without the catalytic stripper), Figure 6a. The meaning of each component was
 329 determined from its corresponding loadings plot, Figure S4. The first principal
 330 component (PC1) separates samples based on the contribution to mass spectra
 331 of aromatic species (OC – positive PC1 scores) and carbon clusters (C_n^+ , EC
 332 – negative PC1 scores). Therefore, this component enables the discrimination
 333 between particles with a different OC/EC ratio. The HS samples have mainly
 334 positive PC1 scores while HS_CS ones – mostly negative, thus indicating that
 335 a significant amount of the organic fraction was removed from the particles
 336 by the CS. It is worth noting that the smallest analyzed particles (10–32 nm,
 337 HS_{10–18} and HS_{18–32}) are the most affected by this treatment (revealed by the
 338 large separation between HS_{10–18,18–32} and HS_CS_{10–18,18–32} data points in
 339 the score plot, Figure 6a). This separation can be associated with the high
 340 relative content of organic species present on smaller particles which is almost
 341 completely removed by the CS and leading to a significant change in the PC1
 342 score (OC/EC). Once the organic fraction is removed, the signal related to the
 343 elemental carbon (EC) becomes more important (C_n^+ ions), leading to a negative
 344 PC1 score.

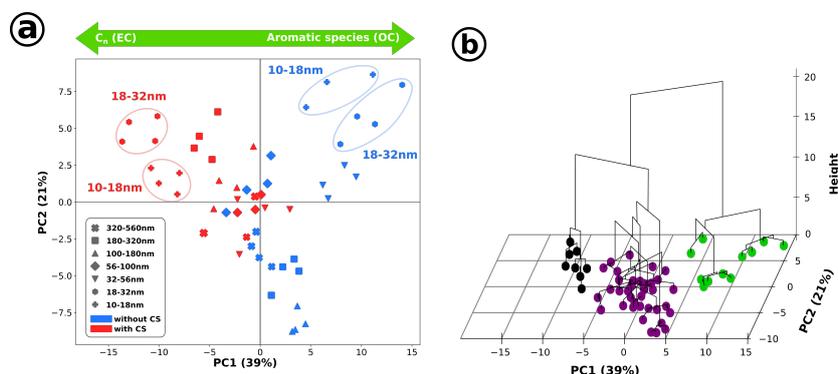


Figure 6: Impact of the CS on size-dependent PM chemical composition: a) Score plot of the first two principal components obtained from mass spectra of size-selected particles collected with (red symbols) and without (blue symbols) the CS in the HS engine regime; the arrows show the meaning of the principal components obtained from their loadings, and b) HCPC performed on the first five principal components (explaining more than 82% of the variance); three biggest clusters correspond to: small particles collected with the CS (HS_CS₁₀₋₁₈ and HS_CS₁₈₋₃₂) – black markers, small particles collected without the CS (HS₁₀₋₁₈, HS₁₈₋₃₂, and HS₃₂₋₅₆) – green markers, and bigger particles collected in both regimes (HS and LS) – purple markers.

345 The second principal component is related to the presence of PAHs (*i.e.*
 346 stabilomers [55], negative PC2 score). Smaller particles (<100 nm) show a
 347 high contribution from fragments and PAH derivatives (positive PC2) while
 348 bigger particles (100–560 nm) contain a larger number of stabilomer PAHs that
 349 are removed by the CS (PC2 score changes from being negative to positive or
 350 almost zero). It should be noted that the spread between data points across
 351 the second dimension (PC2) is much smaller for particles collected with the CS
 352 (HS_CS), indicating that, when it comes to the organic fraction, the chemical
 353 composition of stripped size-selected particles is not very different.

354 HCPC was performed on the first five principal components, accounting for
 355 more than 82% of the variance within the data set, to identify the clusters
 356 that form in the principal component space and discriminate between particles,
 357 Figure 6b. Three separate clusters can be identified: small particles collected
 358 with the CS (HS_CS₁₀₋₁₈ and HS_CS₁₈₋₃₂) – black markers, small particles col-
 359 lected without the CS (HS₁₀₋₁₈, HS₁₈₋₃₂, and HS₃₂₋₅₆) – green markers, and
 360 bigger particles collected in both regimes – red markers. This shows that the
 361 chemical composition of the smallest particles was significantly changed by the

362 CS, thus supporting our previous conclusion that small particles contain a high
363 surface organic fraction which makes them more susceptible to a catalytic treat-
364 ment. This conclusion is also supported by online aerodynamic-mass-mobility
365 measurements that show that the volatile mass fraction increases for smaller
366 particles, Figure S8.

367 The compounds that are efficiently removed from the smallest particles (10–
368 18 nm) by the stripper were identified with a volcano plot, Figure S5. The
369 CS removes the organic fraction from these particles, leading to the decrease
370 of the OC/EC ratio. It is worth noting that, for this particular size-bin, the
371 CS effectively removes PAHs from the entire mass-range and particles end up
372 showing only a negligible contribution from organic species.

373 As the chemical composition of the emitted particles depends on the engine
374 set-point, the CS may impact differently particles belonging to the same size-bin
375 but generated in different engine regimes (LS or HS). To identify the (possible)
376 change in CS efficiency, the differences between the initial (unstripped) chemical
377 compositions of size-selected particles produced in the two engine regimes must
378 be first identified with PCA (Figure 7a). The first two principal components
379 account for 61% of the variation in the data set and will be used to explain the
380 differences in the chemical composition. From the loadings plot (Figure S6a),
381 PC1 can be linked to the contribution of PAHs (positive value), fragments, and
382 carbon clusters (negative PC1), while PC2 can be used to separate samples
383 based on the OC/EC ratio. For instance, samples with a low OC/EC ratio have
384 a negative PC2 score, while the ones with a high amount of organic species
385 exhibit a positive PC2 value. On the score plot (Figure 7a) the data points
386 corresponding to the two engine regimes are well separated by PC1. Therefore,
387 it is possible to distinguish between particles produced in these two regimes
388 based only on the contribution of PAHs, fragments, and carbon clusters. PM
389 collected in the LS engine regime features a much higher contribution from
390 PAHs, with particles from all size-bins having a negative PC1 score (except for
391 LS_{10–18}). In contrast, particles emitted in the HS engine regime exhibit a higher
392 signal coming from fragments and carbon clusters. Note that the fact that HS
393 samples show a positive PC1 score cannot be linked to a missing organic fraction
394 and should only be seen as a lower relative contribution of the peaks attributed

395 to organic species compared to that observed for LS samples. PC2 shows that in
 396 the LS regime, the smallest particles yield the highest OC/EC ratio, also higher
 397 than that of the corresponding HS sample. The biggest particles (56–560 nm)
 398 produced in the HS regime show the highest contribution from carbon clusters,
 399 *i.e.* the lowest OC/EC. In addition, smaller particles from the HS regime (10–
 400 100 nm) show the highest partition of organic species. Particles in the size range
 401 of 100–320 nm produced in both regimes display a similar PC2 score, implying
 402 that they are the least affected by the change in engine operating conditions.

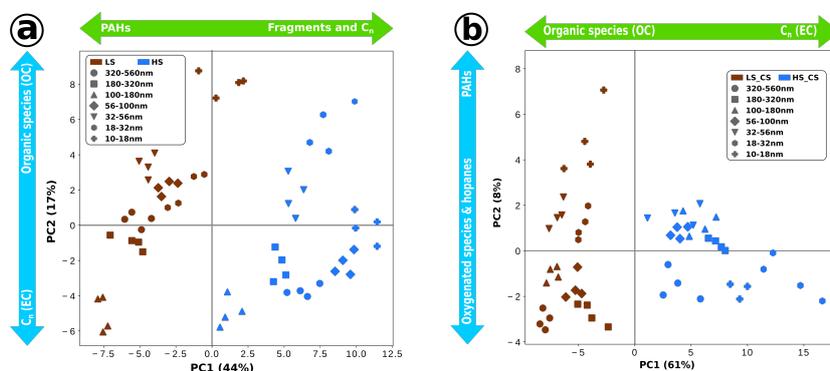


Figure 7: Score plot of the first two principal components obtained from the mass spectra of size-selected particles collected in the LS and HS engine regimes without (a) and with (b) the catalytic stripper. The arrows indicate the meaning of principal components obtained from their corresponding loadings.

403 Once the differences between the chemical compositions of unstripped parti-
 404 cles produced in the two engine regimes have been identified, the effect of the CS
 405 on size-selected PM with different chemical composition can be determined by
 406 PCA, as shown in Figure 7b. The first two principal components explain 69%
 407 of the observed variance and are able to distinguish between stripped particles
 408 generated in the two engine regimes based on the few chemical species left on
 409 the surface. The first principal component (61%) groups samples based on their
 410 OC/EC ratio, determined from the corresponding loadings plot (Figure S6b). It
 411 should be noted that PCA is emphasizing the variance in the dataset, and thus
 412 the separation between particles observed on the score plot (Figure 7b) cannot
 413 be used to quantify, for instance, the difference in the organic content. The ma-
 414 jority of organic species present on raw particles are successfully stripped by the
 415 CS, making their chemical composition comparable, similar to what was shown

416 before for polydisperse particles. However, the high sensitivity of the analyt-
417 ical technique [43] used here reveals distinct features in size-selected stripped
418 particles collected in different engine regimes. For instance, when comparing
419 the smallest treated particles (10–18 nm) collected in different engine regimes
420 with a volcano plot (Figure S7) we can see that only a few species contribute
421 to the separation between the samples. Due to their small mass, the chemical
422 information related to these particles is usually lost when polydisperse PM is
423 collected, thus illustrating the importance of size-selective analysis. The spread
424 between data points on the PC1 axis is rather small, suggesting that stripped
425 particles of different sizes have a comparable amount of OC.

426 The second principal component is linked to the amount of aromatic species
427 (positive PC2 score), oxygenated, and hopanoid compounds (negative PC2
428 score). The latter group of compounds is often used as marker species for rem-
429 nants of lubricating oil [38]. The CS successfully removes these compounds
430 from particles smaller than 100 nm, however, bigger LS_CS particles (100–
431 560 nm) still contain residues of these compounds. Even though particles in
432 three size-bins sampled in the HS_CS engine regime (HS_CS_{320–560}, HS_CS_{18–32},
433 HS_CS_{10–18}) also show a negative PC2 score, they do not exhibit a high hopanoid
434 content but are instead characterized by a higher content of oxygenated species
435 (identified from volcano plots). The HS_CS cluster is located very close to the
436 PC2 axis, suggesting, once again, their lower OC/EC ratio compared to LS_CS
437 particles.

438 4. Conclusions

439 To the best of our knowledge, this is the first study to tackle a detailed,
440 molecular-level characterization of the impact of a CS (in a PEMS context) on
441 the chemical composition of an ICE exhaust. Most of the studies test the CS
442 removal efficiency on tetracontane (C₄₀H₈₂) particles, following the recommen-
443 dations of the PMP protocol [20]. Amanatidis et al. [35] used liquid decane
444 (C₁₀H₂₂) and toluene (C₇H₈) injected in a 10% v/v O₂ in N₂ gas mixture to
445 measure efficiencies >90% for the removal of these hydrocarbons by a CS, while
446 preliminary tests with a heavier (C₁₆) species led to artifacts and inconclusive
447 results. In another study, Amanatidis et al. [37] measured stripping efficiencies

448 of organics in the range 94-97% from particles (>50 nm) emitted by a marine
449 engine. The results of the present study on polydisperse particles and gas phase
450 emitted by a single-cylinder GDI are well in line with those previous findings
451 and foster the use of a CS-based VPR system in future PEMS.

452 A specificity of our work is the study of the chemical composition of particles
453 selected by size. Indeed, the composition of engine exhaust PM can significantly
454 change not only with the engine set-point but also with the particle size [38].
455 When polydisperse PM is studied, a weighted average composition of particles
456 of various sizes is obtained, with individual weights related to the initial par-
457 ticle size distribution which can significantly change depending on the engine
458 set-point. This is clearly illustrated here by analyzing PM emitted in two engine
459 operation regimes. The fine statistical analysis of the CS action on size-selected
460 particles revealed (despite the high removal efficiency) the “memory” of the
461 initial (unstripped) composition of the particles, which was not possible with
462 the polydisperse PM. This further stresses how important it is to sample and
463 characterize size-selected particulate matter, especially since the chemical com-
464 position of the smallest particles (with low contribution to the total mass in a
465 polydisperse sample) cannot be otherwise inferred. Deposition on filters/sub-
466 strates and offline analysis seems to be the only option here, as aerosol mass
467 spectrometers are typically limited to sizes above ~ 50 nm.

468 This work also showed that the smallest particles (10–32 nm) are the most af-
469 fected by the CS, indicating that particles in this size range carry a larger volatile
470 fraction. This conclusion concurs with the results of online aerodynamic-mass-
471 mobility tandem measurements [40] performed in parallel with the collection of
472 samples described here: on-line (physical) and off-line (chemical) investigations
473 are in excellent agreement. The online measurements revealed an increasing
474 contribution of the particle-bound volatile mass fraction toward smaller parti-
475 cles sizes, as illustrated in Figure S8. The excellent agreement between these
476 two completely independent (chemical and physical) characterization methods
477 demonstrates the reliability of the used experimental approaches and validates
478 the main conclusions of the study, which is also supported by theoretical in-
479 vestigations [39] conducted in the PEMS4Nano project and showing the same
480 trend of the SOF with size. Moreover, the obtained trend also matches previous

481 dynamometer and on-road testing showing that semi-volatile particles represent
482 a significant fraction of the smallest nanoparticles [56, 57].

483 We demonstrated that a fine molecular-level characterization of the exhaust
484 PM is necessary to precisely evaluate the effect of a CS, especially for the small-
485 est ultra-fine particles. As the particles' outer organic layer consists of a mul-
486 titude of chemical species (*e.g.* PAHs) and that the smallest particles tend to
487 exhibit a larger volatile fraction, the ultra-fine PM could present a double risk –
488 due to their small size they penetrate deeper in the respiratory system while also
489 carrying a larger amount of potentially toxic compounds. This not only shows
490 how important is the addition of oxidation catalysts in after-treatment systems
491 of modern vehicles to remove the (potentially toxic) organic fraction from the
492 engine exhaust, but also how crucial is the regulation of the small sub-23 nm
493 particles.

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