Supplement of Atmos. Meas. Tech., 13, 951–967, 2020
https://doi.org/10.5194/amt-13-951-2020-supplement

Atmospheric Measurement Techniques
Open Access

Supplement of

Chemical discrimination of the particulate and gas phases of miniCAST exhausts using a two-filter collection method

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S1 Details on the PCA statistical method

Before PCA is performed, mass spectra are baseline corrected and all the peaks that are coming from compounds on the substrate or residual gas in the analysis chamber are identified and removed. All spectra were later normalized to the partial ion count (PIC) corresponding to the total remaining signal. The areas of the peaks, rather than their intensities, were used in order to take into account the full contribution of a certain molecule at their specific *m/z*, regardless of the mass resolution.

Scree plots representing the cumulative contribution of principal components are derived from the PCA. These are presented for each wavelength in Figure S2. These data allow us to choose the number of components to retain for further analysis while still preserving most of the information about the dataset. In this case, for the data obtained with 266 nm ionization, the first three principal components account for more than 91 % of the variation in the dataset (PC1 ~59 %, PC2 ~20 %, PC3 ~12 %), therefore in the analyzes presented here, the data can be treated as being only three-dimensional. However, the information regarding the difference between the Front and Back Filters can be derived from the first two components alone (almost 80 %), therefore from now on only the first two components will be considered. The same can be said about the other two ionization wavelengths: in the case of 157 nm ionization, the first two components account for ~76 % of the variation (PC1 ~55 %, PC2 ~21 %) and in the case of 118 nm ionization, for ~72 % (PC1 ~53 %, PC2 ~19 %).

The contribution of every mass peak in the covariance matrix to the principal components, in the form of loadings, is plotted in order to aid the interpretation of their physical meaning (Figure S3). Although all detected peaks were used in this analysis, for visualization purposes, peaks with little to no contribution are not displayed in these plots.

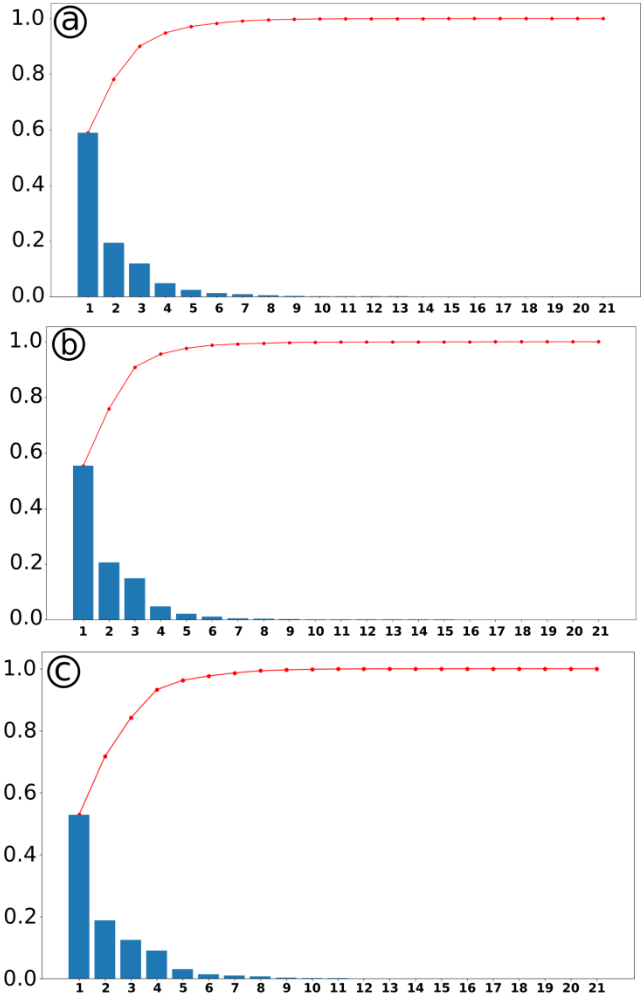

Figure S1. Scree plots representing the cumulative contribution of principal components for mass spectra obtained by L2MS at ionization wavelengths: (a) 266 nm, (b) 157 nm, and (c) 118 nm.

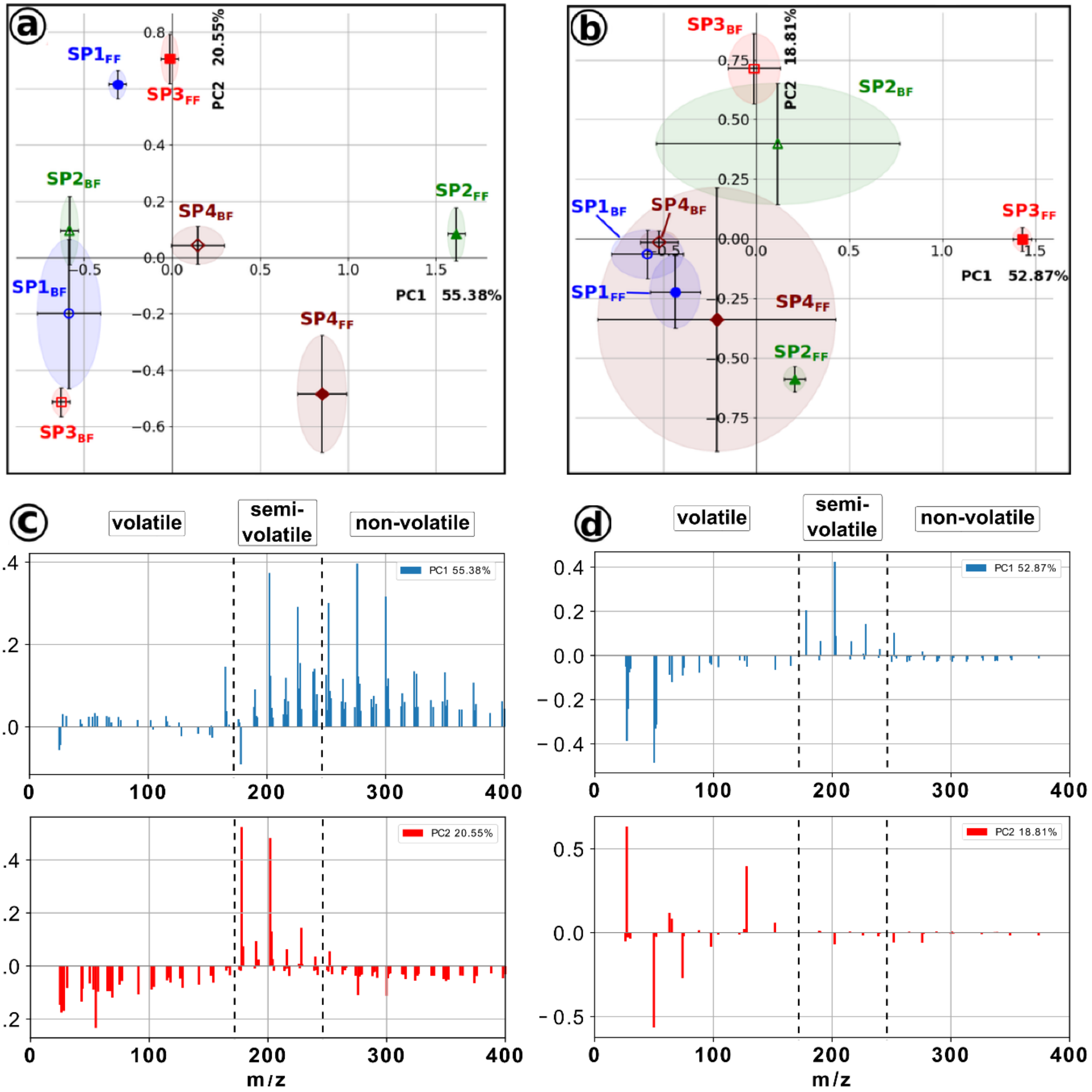

Figure S2. Score (a, b) and loading (c, d) plots corresponding to the contribution of various species to PC1 (blue) and PC2 (red) derived from L2MS spectra at ionization wavelengths: 157 nm (a, c) and 118 nm (b, d). Dashed lines indicate the limits of the three aromatic categories defined in the main text: non-volatile (*m/z* ≥ 252), semi-volatile (*m/z* 176–242), and volatile (*m/z* 78–166) fractions.

In L2MS data generated with 157 nm ionization wavelength, the scree plot and loadings displayed in Fig. S2b and S3c, respectively, show that PC1 (55.38 %) can be interpreted as the relative contribution of semi- and non-volatile PAHs and fragments (positive contribution) to fragments at *m/z* 25 and 26 and the very few volatile aromatic species (*m/z* 104, 128, 142, 152, 154, and 178, negative contribution), whereas PC2 (20.55 %) exhibits a positive contribution solely from semi-volatile species (*m/z* 176–242). Fig. S3a shows no clear separation between Front and Back Filters at this ionization wavelength. This is expected as the ionization energy (157 nm, 7.9 eV) is not enough to ionize naphthalene or its methyl derivatives, representative of the volatile compounds expected to be present in the gas phase (Bari et al., 2010). However, $SP2_{FF}$ once again exhibits the highest PC1 score, meaning that its mass spectrum contains a large amount of semi- and non-volatile species. $SP3_{FF}$ displays the highest PC2 score which translates into a high contribution from semi-volatile compounds. Low oxidation air flow conditions (SP3) result in the production of more semi-volatile compounds, while SP2 conditions generate a higher relative contribution from non-volatile compounds, resulting in more homogeneous mass spectra. While this ionization wavelength did not provide information on lightweight or volatile organic compounds, it yet confirmed the separation between semi and non-volatile compounds with CAST set points.

In L2MS data generated with 118 nm ionization wavelength, the scree plot and loadings displayed in Fig. S2c and S3d, respectively, show that PC1 represents the contribution from aromatic compounds (*m/z* 178–252), while lower masses (*m/z* 50–98) largely influence PC2, and in particular $C_{2n}H_2^+$ and $C_{2n}H_4^+$. $SP3_{FF}$ is the only sample with a relatively high contribution of aromatic compounds compared to low masses, resulting in a large PC1 score as seen in Fig. S3b. All other samples show a relatively low amount of aromatic species, and hence they do not diverge significantly in terms of PC1. Nevertheless, there is a clear trend in the aromatic contribution (AC), which increases ($AC_{SP1} < AC_{SP4} < AC_{SP2} < AC_{SP3}$) as the oxidation air flow decreases. $SP2_{FF}$ contains the most $C_{2n}H_2^+$ and $C_{2n}H_4^+$, followed by $SP4_{FF}$. For the SP2 and SP3 regimes, it appears that $C_{2n}H_2^+$ and $C_{2n}H_4^+$ are mostly found on the PM, while for other working points the difference between their concentrations on Front and Back Filters is minimal.

S2 L2MS spectra

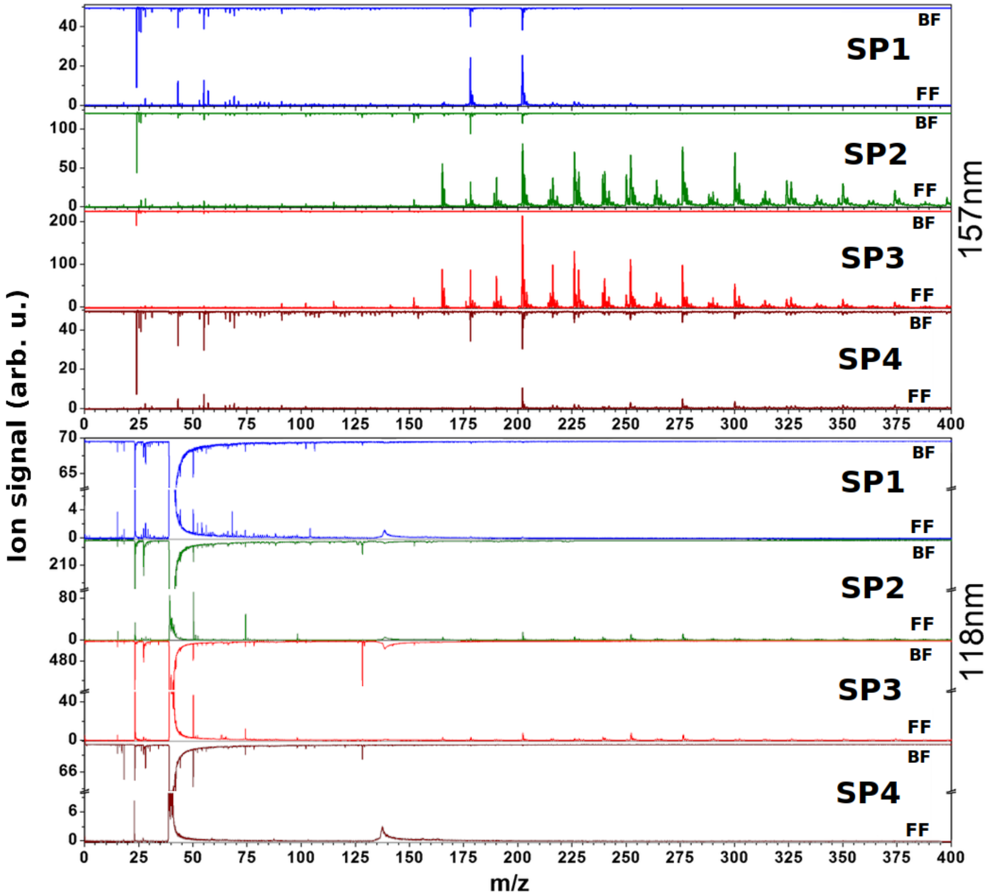

Figure S3. Comparison between mass spectra for SP1, SP2, SP3, and SP4 samples recorded with $\lambda_i = 157$ nm and $\lambda_i = 118$ nm for Front Filters (lower spectra) and Back Filters (upper spectra).

S3 SIMS spectra and details on the PCA

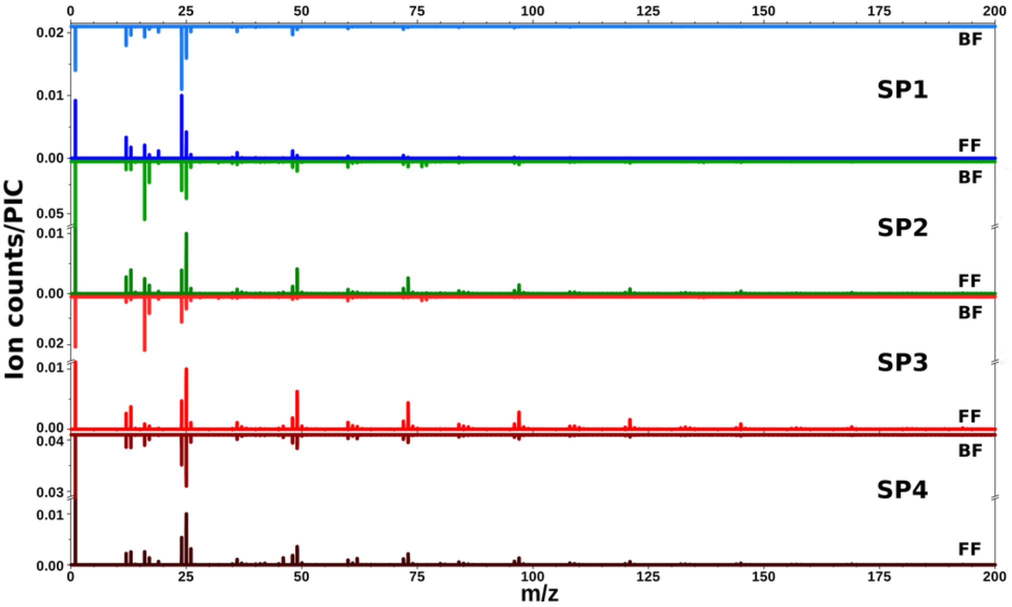

Figure S4. ToF-SIMS mass spectra of samples SP1, SP2, SP3, and SP4 obtained in negative polarity for Front Filters (lower spectra) and Back Filters (upper spectra).

When applying PCA to the SIMS data, 89 mass peaks including all PAHs and their fragments up to *m/z* 300 were selected in the positive polarity mass spectra. As the ToF-SIMS analysis procedure was performed under the same conditions for all samples, the SIMS mass spectra were not normalized before using the PCA method in order to avoid losing information. The two first principal components represent almost 81 % of the variance on the samples.