Review on manuscript ar-2025-15 “Mass concentration intercomparison of soot generated with Mini-Cast”

This article compares several experimental methods for determining, directly or indirectly, the mass concentration of soot particles produced by a propane/air premixed flame. A mini-CAST generator was used and the total mass concentration of particles produced by this generator was determined by sampling and weighing on filters. The mass concentrations thus obtained for different operating points of the mini-CAST are then used to compare the mass concentrations determined by four methods with very different detection principles (thermo-optical analysis, analysis of the charge carried by the particles, optical analysis and extrapolation from an analysis of the particle size distribution obtained by electrical mobility analysis).

Although the experimental developments appear to have been carried out with great care and the results clearly presented, **a number of questions remain concerning the interest of such an article for the scientific community**, the generation of the mini-CAST and the comparison of various soot characterisation instruments that have already been the subject of numerous works:

- https://www.tandfonline.com/doi/epdf/10.1080/02786826.2010.482113?needAccess=true
- https://www.tandfonline.com/doi/epdf/10.1080/02786820701197078?needAccess=true
- https://doi.org/10.1089/ees.2014.0038
- https://doi.org/10.1021/es051228v

In addition, the assumptions associated with certain methods, and in particular the extrapolation from data obtained by the SMPS, are questionable, as is the transposition of the conclusions of this study to other sources of soot.

As it stands, this work, while of genuine technical quality, does not seem to me to be truly innovative, as it does not propose any new analytical strategies or corrections to be applied to the technologies investigated. What's more, the number of techniques is limited to the capacities of the two laboratories involved and does not allow us to cover a sufficient number of analysis technologies and instruments of the same technology in order to rule on possible sources of variability inherent in the different methods targeted.

Thank you for your deep and pertinent review. In the following answers, we have tried to enhance the clarity and impact of the demonstration of the scientific relevance of the paper. We have modified the title of the paper and brought some improvements. The new proposed title is “Evaluation of mass measurement techniques for soot with different size distributions and OC/TC contents”

I do not recommend this manuscript as a research article for publication in the journal ‘Aerosol Research’ and I invite the authors to submit this article in the form of a technical note.

Nevertheless, and in support of the quality of the technical work carried out and presented in this article, here are a number of comments that I feel are important to consider.

Specific comments

- **Abstract:** The authors mention that SMPS is an ‘offline’ method for determining mass concentration. As SMPS performs an on-line analysis of the particle size distribution, I do not think it is appropriate to mention this technique as an ‘offline’ method. SMPS softwares are also generally capable of directly converting particle size distributions by number into size distributions by mass (assuming spherical particles with a constant density, which is of course not relevant for soot particles), so the measurement is indeed “online”.
It has been modified in the abstract.

- **2. Experimental setup:** SMPS specifications are missing, please add them; It has been added in the text.

- **Line 68-69:** the authors mention that the measurements were carried out 3 times and that the error bars in the graphs correspond to these repetitions, but the uncertainty inherent in the measurement process (in particular the measurement of mass concentration by weighing) is not evaluated, presented or discussed in the context of this comparison of methods;
A paragraph has been added to the text to evaluate the gravimetric weighing based on the Iso 15767 standard.

- **Figure 1:** the impact of the transport line heated to 180°C, upstream of the filter sampler, on the determination of mass concentration by weighing and thermo-optical analysis was not discussed. One might wonder about a significant effect for samples with high OC/TC values. Have the thermograms been obtained and compared with and without this heated line to ensure that no volatile fraction is desorbed under these conditions? This point is important as the sample is not heated for the line upstream of the dilution system;

Indeed, this is an important point, and the aim of this experiment was to test the filter sampling procedure that is applied in direct exhaust measurements, particularly for ship engines. In such exhaust measurements where temperatures are over 200 °C depending on the sampling location, the main issue is to avoid condensation of

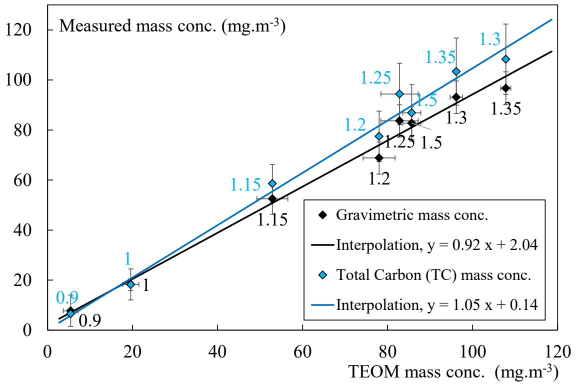
moisture and semi-volatile species. The procedure follows the ISO 8178 standard, which specifies a target temperature of 180 °C for the sampling line and a maximum residence time of 3s. With a sampling flow rate of 7.7 L/min, a line length of 1 m, and an inner diameter of 6 mm, the aerosol residence time is approximately 0.22 s. This duration is extremely short compared to the 173 s of the first temperature plateau at 140 °C on the thermogram shown below, which is required to vaporize only 1.3% of the total carbon mass.
In the revised presentation of the results from this study, the TEOM measurement is considered the reference. All measurements are performed downstream of the dilution system (TEOM, SMPS, PPS, MA300), except for the gravimetric measurement, whose results are validated by comparison with the TEOM measurements, as discussed later in the article.

- Still in connection with the impact of this line heated to 180°C, were SMPS size distributions or electron microscopy images taken before and after conditioning at 180°C? These questions are intended to shed light on the comparability of samples weighed on quartz filters and those characterised downstream of the dilution system;
All instruments are positioned behind the dilution system, so at iso sampling conditions, except the filter mass sampling. We provided elements on the previous question/remark, and believe they clarify the comparability.

- Has the actual dilution factor been evaluated for the different generation conditions? It is legitimate to wonder about possible particle losses within the dilution system and whether these losses differ according to the miniCAST settings. This point should be discussed and the uncertainty associated with determining this dilution factor should be taken into account when calculating the mass concentrations obtained downstream of the DEKATI diluter.
All the instruments used in this study are positioned downstream of the dilution system and are therefore all potentially affected by biases introduced by the dilution process, with the exception of the gravimetric filter-based sampling, as previously mentioned.

- **Line 77:** a heat exchanger is mentioned but not visible on figure 1, please add it;
Thank you. It has been added to the article.

- **Line 77:** what methodology (standard, standardised protocol) was used to determine the mass concentration from sampling on quartz filter? Has an assessment of the uncertainties (taking into account the uncertainties inherent in weighing and measuring the volume sampled) been carried out? If so, it should be added to the standard deviation associated with the three repetitions shown in Figures 4 to 8;
Indeed, the standard procedure implemented is already described in the manuscript, but we now provide a more detailed explanation of the uncertainty calculation, which is based on the combined uncertainties associated with weighing and sampled volume measurement. For this uncertainty evaluation, we followed ISO 15767 to assess the uncertainty related to weighing, evaluated the uncertainty on the sampled volume, and applied uncertainty propagation to estimate the overall uncertainty, which combines measurement uncertainty with the uncertainty associated with repeatability based on the three repetitions. The error bars shown in Figure 5 for the “Gravimetric mass conc.” result from this analysis, while the uncertainty in the determination of “Total Carbon (TC) mass conc.” determined through the thermo-optical analysis is estimated at 13%, as established through the literature review.



- **Figures 2 and 3** are not useful, as principles of the PPS and MA 300 instruments have been documented elsewhere and the present article does not introduce any significant changes to the principle of these instruments.
We wanted the reader to find all the operating principles of the devices used in this article without having to resort to additional bibliography.

- **Lines 114 to 124** seem to me to go into too much detail and could concentrate on the fact that the PPS mass calibration constant was established essentially on automobile emissions with a relatively limited range of size distribution in numbers; It has been modified in the text.

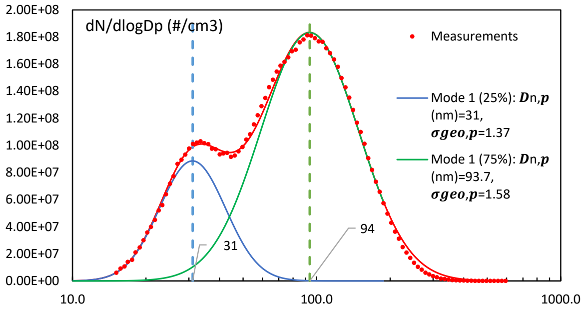
- **Figure 4 right:** the characterisation of the mini-CAST size distribution has already been the subject of numerous publications, so it does not seem useful to illustrate this with a figure (or at least to place this figure in an appendix to the article);
In the bibliography, the intermediate points have not been investigated. It is interesting to show the intermediate size distributions.

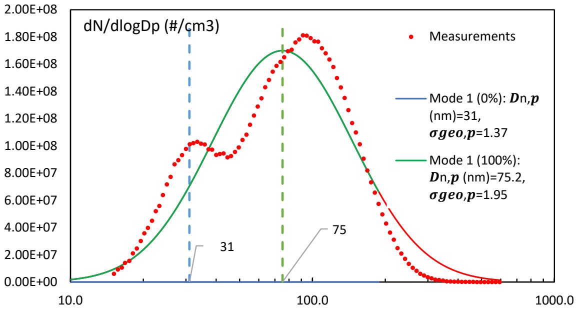
- With regard to **bimodal distributions**, are TEM images of the particles available in order to determine whether they are bimodal?
No TEM images have been done. The study was conducted at eight different oxidation air flow settings and involved several instruments or analytical protocols requiring significant analysis time. The analysis and statistical processing of the large number of TEM images that would have been required did not seem reasonable to us, although such an approach would indeed have enriched the experimental investigation.

- **Table 1:**
○ The first line requires an explanation of the 1% mentioned after the mode at 24.5 nm. If this is a monomodal distribution, shouldn't it be 100%?
Thank you. It has been corrected in the article

○ On what criteria do the authors conclude that the particle size distributions produced within the range of oxidation flow rate 1 to 1.35 L.min-1 are bimodal? Is monomodal smoothing totally unsuitable and on what criteria was bimodal smoothing preferred?

The procedure implemented to perform a least-squares minimization aimed at representing the measured distribution as the sum of two log-normal distributions is presented on the left-hand side. On the right, it is clearly visible that a single log-normal distribution fails to accurately represent the measured distribution produced by the miniCAST at the 1.25 L/min oxidation air flow condition.





- **Figure 5:** have the measurement uncertainties of the total carbon mass concentration based on thermooptical analysis been determined?
For the Total Carbon (TC) mass concentration based on thermo-optical analysis, Sipkens et al. (2024) evaluated the TC uncertainties to 13%, based on bibliography. Brown et al. (2017) reported combined standard error below 13% for a reproducibility between four laboratories and Schmid et al. (2001) reported an uncertainty on their TC measurement between 6.7% and 11%. We therefore decided to take the conservative value of 13%, as reported in Figure 5.

- **Line 196 :** “we considered a so-called true density for the aggregates that varies depending on the considered point” ➔ clarification of the method used to determine the mass concentration from the particle size determined by SMPS is required. Did the authors consider a single density value for the entire particle size distribution? If so, a discussion appears necessary and must be confronted with the notion of effective density of soot particles. Conversion models, including the fractal morphology of soot, have been developed and are available in the literature. Why not consider them in this article to achieve a conversion from number to mass size distributions?
○ https://doi.org/10.1016/j.carbon.2024.119197
○ https://www.tandfonline.com/doi/full/10.1080/02786826.2019.1577949
○ https://www.sciencedirect.com/science/article/abs/pii/S0010218018304310
○ https://www.sciencedirect.com/science/article/abs/pii/S0021850215000701

- https://www.sciencedirect.com/science/article/pii/S0021850223000769#sec5

Indeed, other approaches have been developed to estimate an "effective density" of soot particles, considering their fractal nature. And based on an analysis of various data sets available in the literature, Olfert and Rogak proposed a model that expresses the effective density as a function of mobility diameter. This model allows the evaluation of the decrease in effective density with the mobility diameter of soot aggregates and is expressed using two parameters: a negative exponent and a reference density defined at a mobility diameter of 100 nanometers. The data used to develop this model originates primarily from studies of particles produced by internal combustion engines or gas turbines, and a value of 510 kg.m^{-3} for the effective density at 100 nm was proposed for this model. However, Yon et al. reported higher effective density values at 100 nm for the miniCAST and reported values ranging from 1100 to 765 kg.m^{-3} for oxidation air flow rates between 1 and 1.5 L/min. Although only three operating points were investigated, the decrease in effective density with increasing oxidation air flow rate was found to be linear. And we observed that the decay in OC/TC with oxidation air flowrate is also linear. We therefore conducted a 'best fit' identification procedure to obtain the values of $\rho_{\text{eff},100}$, the density at 100 nm that would allow us to recover the TEOM reference mass concentrations from the SMPS analysis together with the Olfert and Rogak model. We obtained a set of values $\rho_{\text{eff},100}$ "Best fit analysis" (see Fig. 7 right) and observed that the change in this density at 100 nm with the OC/TC ratio that can be represented by a linear interpolation, expressed as:

$$\rho_{eff,100}(x) = 932 + 661 \cdot x \qquad (4)$$

with x the OC/TC ratio.

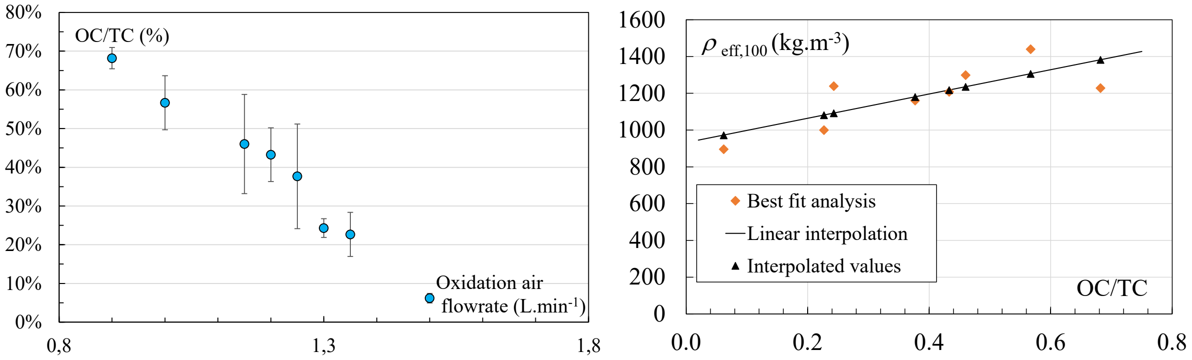


Figure 7 – Evolution of the OC/TC ratio as a function of the oxidation air flowrate (left). Identification of $\rho_{\text{eff},100}$ as a function of OC/TC ratio.

From this Equ. (4), interpolated values of $\rho_{\text{eff},100}$ can be evaluated. These effective densities at 100 nanometers determined through this procedure are reported in Table 2, and the corresponding mass concentrations, labeled "SMPS effective density," are shown in Fig. 8: the use of this effective density model combined with the measured size distributions results in a good estimation of the mass concentration.

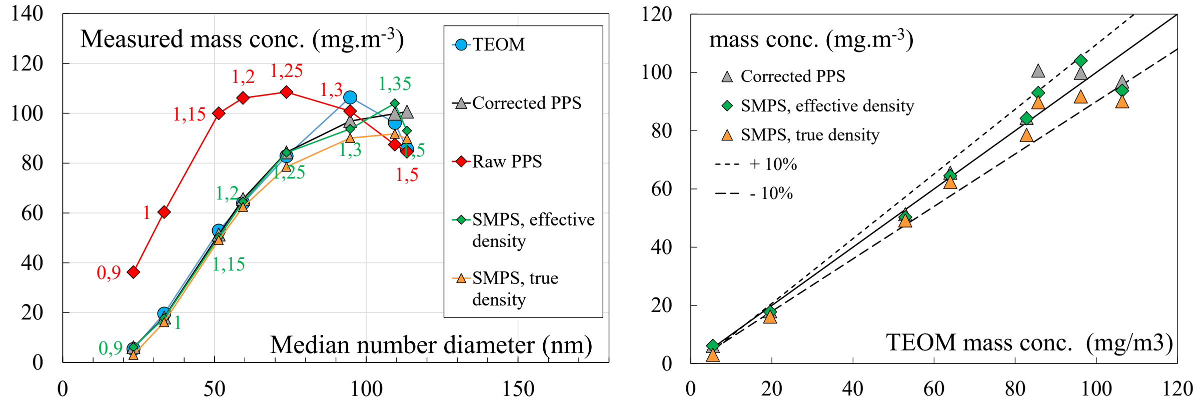


Figure 8 – Comparison of gravimetric mass concentrations with evaluations based on PPS and SMPS measurements.

- **Line 211:** the following sentence: “We report in table 2 the values obtained for the OC/TC ratios as determined by thermo-optical analysis and the corresponding evaluated true densities, that were used to evaluate the SMPS mass concentrations reported on Fig. 7” is not clear;

Indeed we clarified this sentence. But first we mentioned earlier in the text that the density is considered as constant for a given point of the mini cast: “For this evaluation, we initially considered a constant so-called “true density”, independent of the particle mobility diameter, but varying with the OC/TC ratio and therefore dependent on the selected operating point of the miniCAST”

Then the sentence itself is clearer and we explain that the true density is calculated.

“We report in table 2 the values obtained for the OC/TC ratios as determined by thermo-optical analysis and the corresponding evaluated true densities calculated with the Park mixing model (Eq. 2), that were used to evaluate the “SMPS true density” mass concentrations reported on Fig. 7”

- **Lines 213-221:** this paragraph questions the capacity of the mini-CAST to be act as a reference generator, the authors stating at the beginning of their article that they wanted to use this generator for its stability. If the composition of soot varies from one mini-CAST to another, how can the conclusions of this article be generalised to other mini-CASTs
Indeed, the “S” in miniCAST was introduced by its designer to indicate "standard." It is therefore a generator that is intended to be reproducible. However, the setup installed downstream of the generator can lead to variations in the soot size distributions, due to mechanisms such as agglomeration and deposition. Moreover, to our knowledge, no intercomparison between different miniCAST generators is available, so strict equivalence from one generator to another cannot be guaranteed. Nevertheless, we emphasize here the generator’s stability, which is well established: it can produce soot with stable concentration and size distribution over relatively long periods, thus enabling gravimetric measurements and downstream characterization under dilution, using a steady source.

- **Table 2:** It is not easy to know whether the density values given in this table are calculated or determined to give the best agreement with the weighing measurement.
Indeed, we now detail that “true densities calculated with the Park mixing model (Eq. 2)”. And it is also mentioned in table 2 itself. Since an effective density is also used now, it is also mentioned that it is calculated with Equ. 4.

- **Lines 224-228**: this sentence is not easy to understand;
Indeed, we tried to clarify, and modified the sentence, as proposed below

The measured values of the OC/TC organic fraction contained in soot compare well with those obtained in the previous study by (Marhaba et al., 2019a) for equivalent operating conditions of the Mini-CAST. For the considered points named CAST1, CAST2 and CAST3 in Marhaba et al. study (CAST3 corresponds to 1 L/min, CAST2 to 1.15 L/min and CAST1 to 1.5 L/min of oxidation airflow), Marhaba et al. reported OC/TC ratio values of 87%, 46.8% and 4.1%, respectively. In the same operating conditions, we measured corresponding OC/TC values of respectively 56.7%, 46 % and 6.2%. For the point CAST3, our measured value is significantly lower, while the two other points are coherent. However, as highlighted by (Moore et al., 2014), soot production conditions can vary with parameters other than the overall carbon/oxygen ratio of the flame, and variations in mode size or OC/TC ratio have already been observed between different studies using different Cast or Mini-CAST generators.

- **Figure 8, left**: error on the x-axis legend « Gravimteric »

Thank you. It has been modified.

- **Figure 8, right**: I don't think this figure is useful, as the OC/TC ratio can be mentioned in the left part of the figure.
We understand your recommendation to limit the number of figures. However, to maintain the clarity, we were not able to modify the manuscript in this direction.

- **Figure 8 right**: oxydation ➔oxidation :

Thank you. It has been corrected in the article.