

Dear reviewer,

we thank you for your valuable feedback to our manuscript, which we believe makes it more valuable to the readers. Within the letter, we commented on and replied to all suggestions and requests. The changes made to the manuscript are written italicized in quotation marks within the reply. Within the manuscript, we marked all changes with track changes.

Reply on “Comment on amt-2022-206” of Anonymous Referee #2

This manuscript by Pikmann et al., describes a novel automated batch sampler for aerosols and trace gases integrated into a mobile laboratory platform. The intended use of this instrument is to predefine continuously monitored trace gas measurements, aerosol measurements, and metrological data to control the sampling scheme for targeted airmasses (i.e. urban, biomass burning, cooking emissions, etc). The authors describe the hardware, software and a single source experiment to demonstrate the operation and data product this instrument can provide.

The AERTRACC system is a novel addition to the batch sampling measurement system community. This ‘smart’ sampler, allows for unattended sampling of different airmasses, without the input of an expert user. The authors describe the implementation of this system clearly and I believe this is well in the scope and interest of the AMT audience. However, I have concerns on the clarity of how this work is presented and the validity of assumptions made for this analysis:

The filters were analyzed with Iodide FIAGAREO-CIMS and the thermal desorption tubes (TDTs) were analyzed with a custom desorption unit coupled to the Iodide CIMS, however little information is given on analyte sensitivities used in this analysis. It is well known that Iodide CIMS sensitivities vary many orders of magnitude by analyte (Iyer et al., 2016; Lee et al., 2014; Bi et al., 2021) and are a function of Iodide:H₂O ratio, ion optics tuning, and ion molecule reactor (IMR) temperature (Lee et al., 2014; Lopez-Hilfiker et al., 2016; Robinson et al., 2022). Nowhere in this manuscript or SI can the reader find information on what sensitivities are applied to the detected molecular ions in the mass spectra. If the authors did not calibrate, at minimum the assumed sensitivities and dependencies to water and IMR temperature should be described or assumptions stated and the impact to uncertainty. For example, the IMR temperature dependence of sensitivity may explain the large uncertainties found for the TDT calibration samples (62%). I recommend adding sensitivities used for identified compounds from filter analysis in Table 2 and for TDT analysis in Table 3. Additional information on the temperature programmed ramp for the FIGAERO-CIMS analysis should also be included (including the IMR temperature time series). Even if sensitivities are not applied to these data, it should be made clear to the reader that reporting ion signal intensities can falsely report molecular abundance in a sample due to the widely varying sensitivities.

Answer:

Thank you for pointing us to this issue. We agree that Iodide CIMS sensitivities can vary strongly, dependent on the analyte and other parameters. In this manuscript, that deals with the design, characterization, and validation of the AERTRACC sampler, the CIMS is only used to show the enrichment of source-related compounds in the source samples in comparison to those in the background samples. Since we did not intend to determine absolute concentrations of individual compounds in this experiment, no calibrations were performed nor assumptions were made regarding

the sensitivity of the compounds. We assume that ion intensities observed during the analysis of source and background samples, respectively, were directly comparable, as the analysis settings were identical for both sample types. We made this clearer by adding the following statement to Section 4.2:

“Signal intensities for individual compounds were determined semi-quantitatively as a calibration for individual compounds was not feasible.”

As the carrier gas for thermal desorption was dried (Section 2.5) and water from the sampling media is desorbed before the organic species we do not expect a strong influence of water onto the analysis.

The temperature ramp for the CIMS analysis is already provided in Section 2.5. Based on your request, we added information regarding the ion optics tuning and the IMR temperature in Section 2.5:

“Tuning of the ion optics was performed before the analysis with formic acid and triiodide for signal intensity, mass resolution, and peak shape using the software Thuner (Tofwerk AG, Switzerland). The IMR conditions were kept constant at 130 mbar and 60 °C.”

While the discussion of sampling time delay (3.2) is interesting, I believe the magnitude of the correction to be minimal, and the discussion detracts for the clarity of the methods. I believe most of this section could be moved to the SI.

Answer:

The relevance of the time delay is dependent on the typical length of sampling intervals. During our validation experiment, typical sampling periods were in the order of 2-10 s and thus in the same order of magnitude like the time delays. Therefore, knowing the exact time delay is crucial as otherwise due to sampling significant amounts of “wrong” aerosol on the source and background filters/TDTs, the separation of different aerosol types cannot be achieved anymore.

To highlight the importance of the time delay, we added a short paragraph at the end of Section 3.2

“For comparison, sampling periods during the in-field validation (see Section 4) were in the order of 2-10 s. Especially under such conditions, where the sampling periods are in the same order of magnitude as the time delays, it is crucial to consider the time delays for sampling. Otherwise, a significant fraction of the aerosol which does not fulfil the various sampling criteria would nevertheless be sampled and the separation of different aerosol types would not be given anymore.”

On a similar note as above, I found the introduction of the AMS PMF analysis to be abrupt and confusing. I believe a more thorough description of the AMS would be useful to introducing these data. It is not clear to the reader if the AMS is a part of the MoLa or was deployed at a different location. I recommend a separate section describing the AMS measurements to make this clear.

Answer:

Thank you for this comment. To make the introduction of the PMF analysis less abrupt, we added a short introduction at the beginning of Section 4.3.1:

“During the field measurement period the AMS provided quantitative data on chemical composition of the non-refractory sub-micron particle fraction. For in-depth analysis of the organic fraction, a PMF analysis was performed for source apportionment. The identified aerosol types were biomass burning organic aerosol (BBOA), cooking organic aerosol (COA) and oxygenated organic aerosol (OOA).”

In addition, we added the AMS to Table 1 showing that it is regular part of the MoLa instrumentation. Also, based on comments of reviewer #1, we focus in our manuscript on the description of the AERTRACC sampler and its development and characterization and treat the applied analysis methods rather as auxiliary contributions. Therefore, we did not add in-depth information on AMS and CIMS analysis but rather point the reader to the available literature for these methods.

A discussion of the detection limits for several important compounds (i.e. Levoglucosan, IPN1, IPN2) which appear in large abundance or are close to the $I_{\text{source}}/I_{\text{background}} = 1$ would be helpful to the reader, as it appears the 10% or 62% error bars are applied to all compounds detected (either by filter or TDT analysis). Furthermore, a more rigorous discussion of how these errors are determined would be useful.

Answer:

Thank you for mentioning this important point. As stated in our reply to your first comment, we did not determine the sensitivity of individual compounds and only used relative signal intensities for source and background samples. The detection limit, in terms of ion signal intensity, was determined based on the signal intensity variability during times of the filter/TDT analysis process when no sample was desorbed for each ion individually. Ion signal intensities measured during desorption of the samples were all above the detection limit ($3 \cdot \sigma(\text{background})$) for the individual ions, for most of them more than an order of magnitude above LOD. We added this information to Section 4.2.

“Independently of the sampling media, the ion signal intensities during desorption of the samples exceeded the limit of detection (three times the standard deviation of the molecular background) for all reported samples and ions, with the majority of samples and ions showing an excess by at least an order of magnitude.”

Concerning the determination of the errors we added more information in Section S4 how these errors were determined and in Section 2.5 a reference to Section S4 was added.

“To determine the reproducibility, several samples were prepared with equal sample amounts by simultaneously sampling the same aerosol onto multiple filters and TDTs. For the overall reproducibility, the standard deviation over all samples for all individual compounds, which were identified in this study (Section 4), was calculated and then these standard deviations were averaged over all compounds.

As error for the signal intensity of individual compounds the uncertainty, derived from the reproducibility determination, and the error from a Gaussian error propagation of the standard deviation of the blanks and the samples were compared and the larger one was chosen. The signal intensity from compounds found on blank filters was negligible in contrast to source and background samples. The error for the ratios was calculated using Gaussian error propagation from the errors of signal intensity of source and background samples. Error bars of the overall source ratios represent the standard error of the ratios of all ions assigned to the respective sources.”

Do the sample media (filters and TDTs) have to be manually changed and at what frequency? It is unclear to the reader if this system can sample for several hours/days unattended or only short timescales (hours/minutes).

Answer:

Thank you for pointing that out. Yes, the sample media have to be changed manually.

There is no general upper time limit for unattended sampling. However, the maximum filter load for the selected analysis method (to avoid contamination of the instrument) and the breakthrough volume of the TDTs (to avoid loss of sample material), together with the selected sampling flow rates, constitute an upper sampling time limit. These limits are mentioned in Section 2.4.

We added to Section 2.4 the information on manual change for clarification.

“These limits can be included as sampling conditions to stop sampling automatically when the limits are reached. Afterwards the sampling media need to be changed manually. In our experiment, sampling media were changed after typically 1-1.5 h.”

Why does AERTRACC not measure sample flows in real time with MFCs or use a more robust flow control system than needle valves such as critical flow orifices in the sample paths? It seems as though flow drift could be a significant uncertainty in this measurement.

Answer:

Thank you for this suggestion. Indeed, it would be a valuable addition to AERTRACC to avoid any drifts and to minimize uncertainties of the sample flows and to simplify flow settings by using mass flow controllers instead of needle valves. For cost reasons this was not implemented yet, but will be considered for future studies. We added to the manuscript in Section 2.2 that the flow rate did not change during control measurements and that mass flow controllers would avoid any fluctuations of the flows.

“No change of flow rates was observed during test measurements. Replacing the needle valves by mass flow controllers for future studies to ensure constant flow rates and to simplify flow settings is planned.”

Adding the exact masses, chemical formula, and sensitivities used in this analysis to Table 2 and Table 3 would be useful, rather than putting most of that information in the SI.

Answer:

As mentioned above, the sensitivities for the substances have not been determined and are therefore unfortunately not available. The chemical formula and the exact masses can be derived from the compound names and, in addition, are listed in the SI. To make the link to this information easier, we added this information also to the table captions.

“Table 2: Selected identified compounds, measured as iodide cluster, from filter analysis and acronyms used for Fig. 4a. For further details see Table S1.”

and

“Table 3: Selected identified compounds, measured as iodide cluster, from filter analysis and acronyms used for Fig. 4a. For further details see Table S2.”

Could the authors not have driven the MoLa setup to an appropriate background air mass sampling location and manually sampled in order to confirm the automated determination of background air masses?

Answer:

In principle, such an approach would be desirable for verification purposes; however, with our available instrumentation it is unfortunately not feasible. Due to the transient nature of background aerosol, especially in the complex urban environment of our sampling location, measured background aerosol before/after the hours-long sampling time downwind the pizza oven would likely not have been representative of the background aerosol prevailing during the measurement time. In order to obtain representative values, rather a parallel measurement upwind of the source would have been needed, which however would require numerous additional instrumentation which was not available to us during the measurement time. Such a verification experiment could be envisioned in the future as part of a dedicated measurement campaign with numerous partners.

A source/site map and MoLa sampling location, with Hysplit trajectories would improve the clarity of how these air masses were sampled. It could be put in the SI if the authors do not believe it adds clarity to the main text.

Answer:

Thank you for this suggestion. We added a map showing the location of the institute within the city and a magnification to show the location of MoLa and the pizza oven during the experiment in the SI as Fig. S1. A wind rose plot indicates the predominant wind direction. We added a reference to the map in the SI in the manuscript Section 4.1:

“A site map with the measurement location with respect to the city and to the micro-environment including a wind rose plot showing the predominant wind direction can be found in the supplementary information (Fig. S1).”

Since local wind direction changed on a few second basis during the field measurement, HYSPLIT trajectories, which are available on an hourly basis only, likely do not reflect the local transport situation well. Therefore, we refrained from additionally adding HYSPLIT trajectories.

Minor comments:

The manuscript often begins a sentence with a conjunction or preposition:

Line 51 : “For chemical analysis, this approach...”

Line 64: “To obtain data with high time ...”

Stylistically, these sentences read better without beginning them with a conjunction or preposition.

Answer:

Thank you for pointing this out. Wherever feasible, we changed this throughout the paper.

Line 79: “Currently, no instrument offers detailed chemical analysis...”, I believe there are many instruments which provide this capability, one of which you are using (FIAGERO-CIMS), EESI, CHARON, VIA, all come to mind, so I believe this sentence needs to be reworded to more accurately describe the work you are presenting (Lopez-Hilfiker et al., 2019).

Answer:

Thank you for this comment. We agree and removed the mentioned statement. Instead we added the mentioned instruments as current high time resolution instruments.

“A few instruments with high time resolution in the order of seconds, sufficient for the analysis of transient aerosol occurrences, combined with detailed analysis were developed in recent years, such as the EESI-ToF (electrospray ionization time-of-flight mass spectrometer) (Lopez-Hilfiker et al., 2019; Pagonis et al., 2021) and the CHARON-PTR-MS (chemical analysis of aerosol online proton-transfer-reaction mass spectrometer) (Eichler et al., 2015; Piel et al., 2019).”

Line 84: “Since offline methods or highly species-resolving semi-online methods...”, this should be reworded, as written it is confusing.

Answer:

As suggested, we reworded the sentence.

“Offline and semi-online methods offering highly resolved speciation data do not provide the required temporal resolution and quick online methods do not provide in-depth chemical analysis capability. Therefore, we developed the AERosol and TRACe gas Collector (AERTRACC), which combines the advantages of both approaches.”

Line 110: "Table 1...", The AMS should be included in this table.

Answer:

We included the AMS in Table 1, however, for technical reasons the AMS data are not yet used for AERTRACC control. Therefore, we added a statement to the footnote that the AMS data are currently not used for AERTRACC control but might be implemented in the future.

Line 135: "Downstream of the cyclone..."

Answer:

Thank you for the hint. We rephrased this sentence.

"Inside MoLa the inlet tube is split into two main paths, which are both split again, in total into four sampling paths. Main path 1 (see Fig. 1b) contains a PM1 cyclone (URG, USA, flow rate 16.7 L min⁻¹). Downstream the cyclone, main path 1 and is connected with to main path 2 with a cross tube downstream of the PM1 cyclone."

Line 175: "The two available sampling modes for AERTRACC are either all four sampling paths collecting PM1 aerosol or two...", I believe this has been stated clearly already and is a somewhat redundant sentence.

Answer:

Thank you for the remark. We removed the redundant part and combined this sentence with the following one.

"Two sampling modes are available, PM₁ and PM₁+PM₁₀. For the PM₁+PM₁₀ sampling mode, the same sampling conditions are used for each PM₁ / PM₁₀ sampling path pair."

Line 182: "...EDM", has this been defined somewhere already?

Answer:

The acronym EDM is defined in Table 1, in which the MoLa instruments are listed.

Line 226: "...CIMS", has this been defined already?

Answer:

CIMS is defined in the introduction.

Line 364: “..is only based on a literature review.” The literature review methodology referenced here is not clear to the reader. Please provide references and more detail in the SI.

Answer:

Thank you for this comment. Apparently, the word “review” is misleading here, as we did not attempt a complete literature survey. We rather searched through the literature whether the individual substances of interest were previously reported with relation to a specific aerosol type.

To clarify, we exchanged “review” with “search” in Section 4.3.2 and mentioned the criteria for identification of the substances in Sect. 4.2:

“The molecular formula of identified ions was determined for individual peaks; and individual species were identified through the molecular formula, detectability by Iodide-CIMS and occurrence in literature references (further details see Table S1).”

Line 376: “... the ratio is expected to be *on* the order of one.”

Answer:

Thank you for the remark, we corrected it.

Line 384: “In absolute concentrations...”, please provide more information on how absolute concentrations are determined in this work or remove the sentence.

Answer:

We removed the sentence, as we did not determine the CIMS sensitivity for measuring levoglucosan.

Line 394: “Some of those species, associated with cooking and biomass burning, can also originate from various other emissions sources and were assigned to the mixed group.” Couldn’t this also be due to improperly assigning sampling criteria? This assumes the authors perfectly setup the sampling criteria, does it not?

Answer:

The reason these species were assigned to the mixed group is because we found in the literature that these species were previously also measured related to other types of emissions apart from cooking and biomass burning. To clarify this, we added that the assignment of this species to the mixed group is based on the literature search.

“Based on a literature search, some of those species, associated with cooking and biomass burning, can also originate from various other emission sources and were therefore assigned to the mixed group.”

Line 404: "...have partially ratios *on* the order of one..."

Answer:

Thank you for the remark, we corrected it.