## Responses to the Reviewers' comments

### Reviewer 1

**(1)** The work faces the challenge of measuring the chemical composition and physical properties of ultrafine particles on-line and continuously. The authors propose an original approach for selecting $PM_{0.1}$ using an aerodynamic aerosol classifier (AAC) sending then the size-resolved sample to a HR-ToF-AMS, an SP2-XR and a Xact625i to achieve a full chemical composition characterisation. The topic is of broad interest for the scientific community and the research networks. The paper is clear, the description of the methodologies is fine, and only a few comments are reported below to improve it. The Reviewer suggests to accept the paper after minor revisions.

We appreciate the helpful suggestions and comments of the reviewer. Our responses (in black font) and the corresponding changes in the manuscript follow each comment of the reviewer (in blue font).

**(2)** Line 257: please add a more detailed description of what do you mean with "positive/negative" artefacts (i.e., on which elements? Why?) and how much these artefacts affect X-ray fluorescence analysis. Indeed, the authors mention "These components included the tubing, the $PM_{2.5}$ cyclone, the AAC, and one MFC." (line 264-264) but it is not specified how each of these parts are impacting on positive/negative artefact and which are the elements gained/lost.

By using the broad term "positive/negative artifacts," we aimed to include all potential interferences that could occur in this complex, multi-component system and increase/decrease the various measured concentrations. In multi-element ambient samples, spectral line interferences are common and can hinder the detection of a specific element when another is present at high concentrations (Furger et al., 2017). To minimize the risk of contamination and to reduce aerosol losses during sampling, we used stainless steel tubing. However, the ambient samples also passed through the mentioned additional components (the $PM_{2.5}$ cyclone, the AAC, and an MFC) all of which are constructed from different metallic materials and could potentially introduce contamination for elements like Fe and Ti. We have added a brief discussion to better clarify this point and included a table in the supplemental material showing the measured field blank values to illustrate the background levels observed for each detected element.

**(3)** As for the LOD: please add a table with the calculated values for all detected elements. From e.g., Figure S8 in most of the cases the concentrations were below or next to the LOD. The authors should discuss further this limitation of the Xact instrument when aiming at the on-line quantification of the elemental composition in the ultrafine PM fraction. Of course, some results could be also affected by the element's size distribution so that – being the first application of the Xact to ultrafine particle samples – it is desirable to have information from parallel measurements of the elements size distribution (see e.g., https://doi.org/10.1016/j.aca.2021.339367) to better characterise its performance in the ultrafine size range.

We have added a table to the supplementary material that includes the calculated LOD values for the detected elements, as suggested by the reviewer. Additionally, we have provided a table showing both the uncorrected and corrected values (accounting for blank and dilution corrections) for the detected elements, to illustrate how close each measurement was to its respective LOD. The limitations of the Xact, particularly regarding real-time quantification, should be carefully considered for each specific field application, regardless of the results presented here. This is because LODs can vary considerably depending on factors such as the sampling lines, the cleanliness of the Xact tape, and other operational parameters, as well as the degrees of freedom and confidence levels applied in the LOD calculation formulas. Therefore, blank measurements and LOD calculations should be performed for every field deployment to ensure proper assessment of the Xact's performance and to enable accurate data interpretation. That being said, the Xact provided quite reliable data in this study and demonstrated robust overall performance.

We agree about the importance of the ultrafine elemental size distribution. Our primary objective in this study was method verification, and as such, an in-depth analysis of size distribution was considered beyond the current scope. This issue clearly deserves attention in future work.

**(4)** Line 299-301: the authors report that "When measured concentrations are close to the LODs the lighter elements Si, S, Cl, K, Ca are more susceptible to self-absorption effects" which should be better explained as it sounds quite strange in X-ray spectrometry. Indeed, the self-absorption effects do not strictly depend on the light element concentration closeness to LOD while they are known to depend on the matrix, on the energy of the fluorescence X-ray emitted, and potentially on the position of the light element inside the sample thickness if it is not a thin sample.

We agree with this point raised by the reviewer. As with most analytical techniques, matrix effects in ambient samples, by interactions between different elements and varying analyte concentrations, can lead to higher and more variable LODs across samples. Measurement uncertainties are particularly pronounced near the LOD for elements susceptible to spectral interferences in multi-element samples, as well as for lighter elements (Si, S, Cl, K, and Ca), which tend to be more affected by self-absorption effects (Furger et al., 2017). Therefore, multiple factors, beyond self-absorption alone, can influence the LODs of lighter elements. We have clarified this in the revised manuscript.

**(5)** Line 314-315: while the S concentration comparison is fairly good, the assessment of Cl by Xact is almost half of the value given by AMS. This result should be underlined and better explained.

We appreciate the reviewer's observation and agree with the point raised. Nevertheless, we would like to emphasize that chloride contributed less than 2% of the total $PM_{0.1}$ mass (0.7 µg $m^{-3}$), indicating that both Cl and chloride concentrations were very low. In this context, the fact that the two measurements are of the same order of magnitude and differ by only a few nanograms is still a satisfactory outcome. We have added a brief discussion in the manuscript to better underline this result.

**(6)** Figure 4, panel (c): AMS data time-series with this y-scale are almost not visible for most elements, please modify it in order to see the patterns for all components. These AMS data appear very much "smoothed" due to the 4-h average representation? It would be useful to show the AMS data time-series on higher time resolution to compare their pattern with also rBC. Please add a comment on the time-series variability and the possibility of identifying episodic emissions.

We have followed the reviewer's suggestion by adjusting the y-axes in Figure 4 and separating the organic and inorganic data to enhance clarity. As for the 4-hour averaging, we chose to present this resolution in the main results as it still effectively illustrates the temporal trends of each species. To support a more detailed examination, we have included a supplementary figure displaying both AMS and rBC data at hourly resolution, as recommended. A corresponding discussion has been added to the revised manuscript.

**(7)** Line 370-371: the authors summed up Ca, Fe, K, Zn, and Ti as elemental concentrations to the refractory components and to rBC. The Referee wonders about the chemical form of these elements in the ultrafine PM fraction: are they present as pure metals or oxides or others? Are there literature data to confirm that the pure elemental form is the right one in this size fraction? What are the sources?

Refractory components such as Ca, Fe, K, Zn, and Ti typically exist in the form of oxides, although their exact chemical form is quite uncertain (Seinfeld and Pandis, 2016). For this reason, we chose to report only their elemental concentrations, as this is the direct output of the Xact measurements. Any further interpretation would be an assumption at this stage. Elements such as Ca, Fe, K, Zn, and Ti can originate from a wide range of sources, including coal and oil combustion, biomass burning, steel production, boilers, smelters, and waste incineration (Seinfeld and Pandis, 2016). A brief discussion of these points has been added in the revised manuscript.

**(8)** Line 438-441: the terminology used here is confounding. Indeed, the bilinear PMF model can be solved by different algorithms contained in both the PMF2 and ME-2 programs. The authors should specify that they used the algorithm of the PMF2 program for the unconstrained run and they should use the terminology "SoFi" when they are referring to the constrained run with fixed profiles using the algorithm contained in the ME-2 program. Indeed, also EPA-PMF v.5 uses ME-2 as a program to solve the PMF bilinear model but not necessarily the profiles must be constrained to obtain a reliable solution.

We followed the suggestion of the reviewer and have clarified this point in the revised manuscript.

**(9)** Why the source apportionment was not performed including rBC and the elements?

A reliable source apportionment analysis using Positive Matrix Factorization (PMF) typically requires at least 400–500 temporal data points to ensure statistical robustness. Under the 4-hour sampling interval of the Xact, this would correspond to approximately 12 weeks of continuous data collection. Given the shorter duration of our measurement campaign, we did not attempt source apportionment of the elemental data in this study. Regarding refractory black carbon (rBC), while the temporal resolution would allow for such analysis, the suburban sampling site is dominated by the local traffic—making source apportionment less interesting. Instead, we focused on organic $PM_{0.1}$, which yielded more interesting results. Nonetheless, the chemical characterization system demonstrated robust performance overall, and its deployment for extended monitoring periods (for elemental source apportionment) and in locations with more diverse sources remains a feasible and promising application. Use of the elements and rBC in the source apportionment is clearly a worthwhile task in future longer campaigns. This point is now made in the revised paper.

**(10)** Conclusions: more comments on the limitations of the Xact performance in this setup should be added. What about possible improvements?

The main limitation of the Xact at this point is the high dilution factor needed in our system. While this can be partially addressed through blank measurements and element-specific limits of detection (LOD), performance is still constrained. One potential improvement would be to reduce the Xact's inlet sampling flow, which is factory-set at 16.7 L min$^{-1}$. This flow rate is appropriate for ambient sampling of $PM_1$, $PM_{2.5}$ or $PM_{10}$, which is the instrument's original purpose. However, for the $PM_{0.1}$ measurements investigated in this study, the high inlet flow proved to be a limiting factor. Enabling the Xact to operate effectively at lower sampling flows would significantly enhance its performance for $PM_{0.1}$ analysis. A brief discussion of this point has been added to the revised manuscript.

**Reviewer 2**

**(1)** This is an interesting paper presenting time resolved measurements of the chemical composition of ultrafine particles (UFP) in a Mediterranean city - it's generally speaking a well written manuscript with some interesting observations and certainly some innovative parts - I do have some mostly minor comments which I outlined below.

We appreciate the helpful suggestions and comments of the reviewer. Our responses and the corresponding changes in the manuscript (in black font) follow each comment of the reviewer (in blue font).

**(2)** Lines 148-158: I assume these losses were taken into consideration in the rest of the calculations regarding concentration and composition of UFP- moreover it's not clear to me why visualizers increase with particle size I would expect that because of diffusional losses it would be the other way around.

We assume that the referee refers to the results in the 50-70 nm of Figure S2. Please note that this figure illustrates the penetration efficiency, therefore it does behave like the reviewer expects: losses increase with particle size in the 50-70 nm size range. We have clarified this point to avoid confusion.

**(3)** A general comment: So the real innovation of the presented tandem technologies is the measurements of rBC and elements - the rest of the analysis is done by the Aerodyne spectrometer- without necessarily wishing to downplay the significance of this work, what is actually measured by the tandem of the aerodynamic aerosol classifier (AAC) and the single particle soot photometer (SP2-XR, for black carbon) and an Xact625i (for elements) are also used needs to be stressed in the abstract and possibly title - as it stands one gets the impression that the authors have invented an instrument that provides real time size resolve chemically speciated data and ultrafine particles when in fact they combine commercial available instruments to do that the measurements themselves are innovative.

We would like to emphasize that our use of the AMS is also novel. We use the AMS after the AAC allowing for the first time the continuous source apportionment of the organic aerosol (second experimental set-up; Figure 3). This is necessary to measure the AMS spectra of only the ultrafine particles, in order to perform then the source apportionment analysis. So, while the instruments themselves are commercially available, the novel aspect of our work lies in their integrated application for simultaneous quantification of rBC and elements, as well as enabling source apportionment of the organic $PM_{0.1}$. We have followed the suggestion of the reviewer and have now clarified this point in the manuscript.

**(4)** Some of the data plotted in Figure 4 are literally illegible- perhaps the organic data needs to be separated from the inorganic ions to get a better idea or a better picture of how things look in the reported time series.

We have followed the suggestion of the reviewer and separated the organic data from the inorganic in Figure 4 and also changed their y-scales.

**(5)** Figure 5: I find it very interesting and somewhat counterintuitive that we do not see a clear photochemical signal in the OA (and sulphate) concentrations given that the measurements were conducted in the summer in Greece - this observation is substantially different than many other cited studies by the authors on the diurnal profiles of the chemical composition of UFP in summer- moreover this is contradicted by the discussion that follows in subsequent paragraphs reporting that most of the organic aerosol in the study period is either entirely or partially oxidized, as one might expect considering the location and season of the measurements. Any explanations or thoughts?

We appreciate the reviewer's insightful comment and agree with the point raised. Both OA and sulfate exhibit relatively stable diurnal profiles, with small increases in the morning and evening, and a slight decrease around midday. These morning and evening increases are accompanied by increases in BC, indicating that traffic in the area may be a contributing source. An additional plausible explanation involves boundary layer dynamics. During midday, the boundary layer height typically increases, leading to enhanced vertical mixing and dilution of pollutants, which in turn reduces their near-surface concentrations. In suburban environments, this dilution can outweigh midday photochemical production unless there is a significant influx of SOA precursors.

The diurnal chemical behavior at the $PM_{0.1}$ scale remains largely unexplored. To our knowledge, this is among the first studies reporting such data for ultrafine particles. Therefore, it is unclear whether diurnal patterns of $PM_1$ are the same as those of $PM_{0.1}$, highlighting the need for further investigation. We have added a discussion of this point in the revised manuscript.

**(6)** Why have the authors not attempted source apportionment of trace elements or metals and refractory black carbon in addition to the organic aerosols? Do they not have sufficient data to do this analysis? Indeed, this would have provided some very interesting and potentially valuable data regarding the sources of these species in the ultrafine range.

A robust source apportionment analysis using Positive Matrix Factorization (PMF) generally requires at least 400–500 temporal data points to ensure statistical reliability. With the Xact's 4-hour sampling interval, this equates to about 12 weeks of continuous monitoring. Since our measurement campaign was shorter in duration, we did not pursue source apportionment of the elemental data in this study. Regarding refractory black carbon (rBC), while the temporal resolution would allow for such analysis, the suburban sampling site is dominated by the local traffic—making source apportionment less interesting. Therefore, we focused on organic $PM_{0.1}$, which provided more informative results. Overall, the chemical characterization system demonstrated strong performance, and its use for longer-term monitoring (for elemental source apportionment) and in environments with more diverse emission sources remains both feasible and promising. Use of the elements and rBC in the source apportionment is clearly a worthwhile task in future longer campaigns. This point is now made in the revised paper.

**(7)** Have the authors attempted to determine size -resolved acidity of UFP given that they have all the necessary information to do these calculations? Several studies have shown that this size range is acidic, and it would be interesting to see whether the presented data here corroborate or refute this notion, and more importantly provide for the first time at least to the best of my knowledge in the peer reviewed literature this kind of information.

The chemical form of the various elements in $PM_{0.1}$ introduces significant uncertainties in acidity estimates using aerosol thermodynamic models. There are also issues arising from the uncertainty of the measured concentrations of ammonium and nitrate, the lack of measurements of gas-phase ammonia or nitric acid, etc. Addressing these limitations would require a study targeted at the pH estimation of $PM_{0.1}$ . We have opted not to include acidity estimates in this manuscript, as it lies beyond the scope of the current study. Nonetheless, we agree with the reviewer that this is an important and compelling topic deserving of further investigation.