

### AR-2023-3, Topic Editor's Comments and Reply by the Authors (*italic, actions in blue*)

*We thank the Editor for the comments and suggestions aimed to improve the manuscript. They have been carefully addressed, accordingly.*

#### Sampling artifacts

Responding to comments by both reviewers about potential sampling artifacts, you state that "amines are present in PM as ammonium salts". What is the evidence for this statement? What about aminium salts? Regarding the sampling artifacts, ammonium salts such as ammonium nitrate would be prone to volatilization losses during sampling, and it is not convincing to expect limited sampling losses of semi-volatile compounds. Moreover, the sampling artifacts discussed in Shen et al. (2017) are positive artifacts due to adsorption from the gas-phase or salt formation on the filter, which is not discussed at all, and particle bounce-off in impactor sampling (not relevant for filter sampling).

*We apologize for the incorrect name adopted for these chemicals. Actually, they are aminium ions, now correctly reported. Regarding the sampling artifacts, they are reported only by Shen et al. (2017); Szulejko et al. (2014) only mention artifacts in the SPME step of the analytical procedures. Moreover, in the recent work of Chen et al. (2022), the determination of amines in the gas phase appears to be not interfered by the PM sampled (at the same time) on quartz filters. In our humble opinion, the procedure adopted by Shen for the estimation of these artifacts (on filter sampling) is open to criticism (for example, only positive biases were assessed, avoiding investigation on the negative ones; formation of aminium salts on the quartz filter during the sampling is described by the same mechanisms that occur in the atmosphere). Since these aspects have not been explored in depth (neither by Shen nor by us), we suggest caution in the relevant statements, inviting more in-depth analytical studies on the matter.*

It is worth noticing that artifacts can occur in the sampling of aliphatic amines, as described by Shen et al. (2017). They are mainly due to gas/particle phase transfers and some structure rearrangements, although different hypotheses regarding DEA are proposed. **However, in studies in which gaseous amines are sampled on acidified quartz filters, significant absorption on untreated filters used for the PM sampling seems to be excluded (Chen et al.; 2022).** We did not estimate these artifacts, but considering that amines are present in PM as aminium salts, the sampling losses of these low-volatile compounds were probably limited. **In this regard, more in-depth analytical studies would be desirable.**

#### Extraction of amines

With respect to a comment by reviewer #2 about the extraction of amines, please add exemplary figures to the supplementary material showing the instrumental signals for 20 min and 10 min extraction times, and for the four different temperatures tested. These additional figures in the supplementary material will be very useful to the reader.

*Signals from different real samples extracts are not directly confrontable because they refer to different amine concentrations. Regarding the extraction time, the new Table S5 shows the signals obtained under different conditions. As for the derivatization temperature/time, the results of a significant test are now reported in Table S6. The text of the manuscript has been modified, accordingly.*

... reducing it to 10 min (Table S5). **The derivatization step was tested at different temperatures (25, 50, 60 °C) and reaction times (5-20 min) (see Table S6 as an example).**

#### Additional comments

In the abstract, with respect to comments by reviewer #2, please change lines 22/23 to "The procedure has been optimized obtaining very satisfactory analytical performances...".

*Done*

... optimized **and validated** obtaining ...

In line 55, please remove "well recognized in the review of" from the text.

*Sorry, now it has been removed.*

In line 125, please clarify by changing to: "PM10 samples were collected for 24 h, and PM10 mass concentrations were directly measured..."

*We agree, text has been modified, accordingly.*

In line 171, the duration of a chromatographic run is given as 28 min (a chromatographic run lasting 28 min), while in lines 230/231 the duration is given as 32 min (a chromatographic run lasting 32 min). Please reconcile.

*Sorry, the chromatographic run lasts 32 min.*

In lines 227/228, with respect to comments by reviewer #2, please remove the following part of the statement: ", being able to separate the analytes in about twenty minutes using an acidic mixture of water/acetonitrile as the eluent". In line 229, the qualification "slightly higher efficiency" is unclear to me. Please clarify the advantage of the selected column, or alternatively remove the comparison of the three columns.

*According to the Editor's comment, the phrase has been modified but maintaining information on the similar performances of the tested columns.*

Three RP-C18 columns were preliminary tested for the UHPLC separation of the six derivatized aliphatic amines (Shimadzu XR-ODS III C18, Phenomenex Luna Omega polar C18, Phenomenex Kinetex C18) showing similar performances in terms of selectivity. The Luna Omega column was chosen because of its slightly higher efficiency (better peaks shape).

In line 252, with respect to a comment by reviewer #2, please add possible reasons why the addition of 0.1 M hydrochloric acid might have shown better recoveries, e.g. higher fraction of protonated analytes.

*Acidic conditions are adopted in all extraction procedure described in the literature. Even if the presence of stable metal-amino complexes in PM might be hypothesized (if of interest, see our previous works in this field) for which the acidic water solution promotes their hydrolysis and the solubility of the ligands, it is probable that this effect is simply due to the higher water solubility of the aminium ions with respect to the corresponding amines.*

... in terms of recoveries (from 80-95% to >95%), [due to the higher water solubility of the aminium ions with respect to the non-protonated amines.](#)

In line 273, with respect to a comment by reviewer #2, please remove the following part of the statement: "appears faster as it"

*It has been removed.*

In line 298, with respect to a comment by reviewer #2, please remove the following part of the statement: "better accuracy, with"

*We accept this compromise; it has been removed.*

In lines 327/328, with respect to a comment by reviewer #2, please change to "while butylamine was not detected" or alternatively "while the butylamine signal was below the limit of detection".

*We agree, the phrase has been modified, accordingly.*

... while the butylamine [signal was below the limit of detection](#) and ...

In line 360, please change to "since the 1960s".

*Changed*

With respect to the comment by reviewer #2 about Table S2 in the original supplementary material, how were measurement values below the limit of detection treated and presented in Table S2?

*Table S2 contains some data below LOD (only for sulfate, and all close to LOD). For these concentrations, the values were taken as they are (without empirical correction) in the statistical analysis. This information is now reported in Table S2.*

*Concentrations below LOD (sulfate) were taken as they are (without empirical correction) in the statistical analysis.*

With respect to the comment by reviewer #2 about time series of the amine measurements for the three different sites: In my opinion it would be valuable to show a time series plot with time on the x-axis and the concentration of the five amines on the y-axis as an addition figure in the supplementary material.

*The required figure (S3) has been added to the supplementary material.*