

AR-2023-3 - Anonymous Referee #1 Comments and Reply by the authors (actions in blue)

The authors developed a procedure to identify and quantify primary and secondary alkylamines in airborne particulate matter. They applied the developed method to quantify 5 alkylamines in PM₁₀ samples collected in North Italy, and they try to investigate the sources of emission through a statistical approach. The data about the emission are not conclusive, however I think the main scope of this work is to develop and validate an analytical method rather than a study on sources and concentrations of amines in the atmosphere. The manuscript is clear and well-written, the procedure developed is simple and effective and in future it could be easily applied to a larger number of samples.

Here are some minor comments:

Line 113-114: were the filters treated before use? Please specify it.

The filters were not treated before use. In fact, very low blank values were always obtained, for instance $OC < 0.4 \mu\text{g}/\text{m}^3$, $DMA \ll LOD$. A proper phase has been added:

... equipped with 47 mm quartz filters (Whatman, QM-A quartz filters, Particle Retention Rating 98% at 2.2 μm). **The filters were not treated before use, acceptable blank values were always obtained ($OC < 0.4 \mu\text{g}/\text{m}^3$, $DMA \ll LOD$).**

Lines 119-125: mid-September is not always the cold season and the temperature difference between September and November could be relatively high. Indeed, the temperature during the campaign period ranged between 24 and 8 degree C. Please comment this in regard to the artefacts and sampling losses of volatile and semivolatile compounds.

The authors thank the reviewer for evidencing this important aspect. Although the temperature changed in the range 8-24 °C, we think that artefacts in amines determination were very limited. In fact, we focused on amines, but in PM we find their ammonium salts, rapidly formed in the atmosphere by reaction with acids, which characterized by a significantly lower volatility. The relevant phase has been rewritten.

We did not estimate these artifacts **but, considering that amines are present in PM as ammonium salts, the sampling losses of these low-volatile compounds were probably limited.**

Lines 139-140: was the test tube placed in a bath or stored in an oven? Please give more details about that.

The requested details have been provided.

... and allowed to react for 10 minutes at 50 °C **in a thermostatic block.**

Paragraph 2.4: Could you please provide the retention times of the derivatized amines? Could you please provide the resolution of the MS instrument?

Now, in section 3.1.1 are detailed the retention times of the analytes, in section 2.5 we added the Mass resolution value of the MS detector.

The order of retention times of Fmoc derivatives is as follows: methylamine (MA, $t_r=10.1$), ethylamine (EA, $t_r=12.4$), dimethylamine (DMA, $t_r=13.6$), propylamine (PA, $t_r=14.8$), buthylamine (BA, $t_r=17.4$), and diethylamine (DEA, $t_r=18.1$);

... ESI-QTOF-MS (Agilent 6545, mass resolution 35000). The UHPLC-MS analysis was performed with ...

Paragraph 3.1 - Lines 192-199: It's a bit confusing this part. Also if the derivatization of tertiary amines is possible using Fmoc, the procedure you developed is not suitable for tertiary amines. Please clearly states that the analytical procedure you developed is suitable only for primary and secondary amines.

The relevant phrase has been rewritten.

However, the derivatization of TMA is possible using Fmoc, but the reaction is very slow (Szulejko et al., 2014), especially in aqueous solutions. **As a consequence, only primary and secondary amines can be determined by the present procedure. This is confirmed by the fact that, after adding TMA to a standard**

solution or to a sample, no peak attributable to TMA was identified in our chromatograms. Moreover, regarding a possible bias in the quantification of DMA (tertiary amines derivatized with Fmoc may dealkylate, yielding a product identical to the derivatized secondary amine), no difference in the peak intensity of DMA was observed.

Lines 211-213: Both eluents have been acidified with formic acid? Please specify it also in the paragraph 2.4. How it is written now seems that formic acid was added only to water.

Many thanks, this lack has been corrected.

... using acetonitrile (eluent B) and water (eluent A), to which formic acid was added (0.05%) to both solutions,

Paragraph 3.1.1: Probably it would be better to overlap the two chromatograms in Figure 1.

Indeed, we tried to do it, but the larger FMOC peaks make the information not clear. In our opinion, the present picture allows us to make a better comparison among the signals of amines present in the sample.

Paragraph 3.1.2: Since the derivatization is quite fast already at room temperature and the unreacted Fmoc is a chromatographic interference, why have you used higher concentration of Fmoc compared to previous studies?

As reported at the end of the section "our sample pre-treatment appears faster as it does not need successive liquid-liquid extraction or preconcentration steps". These significant advantages, with respect to previous published procedures, have been obtained by using an excess of FMOC (which allow us to obtain the quantitative derivatization of all amines, also for DEA) and reducing its chromatographic interferences using acidic eluents and the optimized reaction time/temperature. In our opinion, these concepts are correctly reported and discussed in the text. Small changes make them clearer.

Using a large excess of Fmoc-Osu, the reaction was quantitative (also for DEA) and very fast even at ambient temperature, as it takes less than 5 minutes to complete.

... carried out at 50 °C, for 10 min, to completely eliminate the chromatographic peak relative to the unreacted Fmoc that coelutes with the derivatized ethylamine.

Paragraph 3.2: Have you investigate the potential effect of the matrix? How other compounds that might be present on the filter could interfere with the extraction, derivatization yield, recovery, etc.?

The matrix effect was investigated by recovery experiments in which known amounts of amines were added to PM filters. The slope of the recovery functions led to the estimation of quantitative recoveries for the amines of interest. Although it is not a measurement of the analytical bias, this result is a good indication of the negligible effect of the matrix components on the effective recovery of each analyte at various steps of the procedure, as well as on instrument response. This is also confirmed by the equivalent results obtained using an independent (and more selective) detection system (MS). A small change should make the concept clearer.

... recoveries ranged from 95% to 101%, suggesting a negligible effect of the matrix components on effective recovery of each analyte at various steps of the procedure, as well as on instrument response.

Line 319: It would be interesting to add some info about the type of emission from tanning industry
Since the 60s, tanneries in the Chiampo Valley (Vicenza, Italy) have been the main responsible for the contamination of both the surface/ground waters and the atmosphere of a larger area. In particular, large amounts of H₂S and VOCs are directly emitted into the atmosphere, with the consequence that a typical odor is always present in the valley. This is confirmed by the Regional Environmental Agency (ARPAV) that recently (2022) measured high atmospheric H₂S levels (daily average of up to 241 µg/m³, hourly average up to 1067 µg/m³). Regarding VOCs, emission inventory data (2022) show that in the Montorso municipality (in

the middle of the tanning district), VOC emissions from the tanneries amount to 87.5% of total VOC sources. Similar values are estimated for the other municipality of the district. Although the primary aerosol emissions from the tanneries are comparable to those estimated for other sources (traffic, other industries, agriculture, domestic), a significant contribution of the tanning district to the secondary aerosol production in a larger area is predictable. These phenomena are carefully monitored by ARPAV and are detailed in its technical reports.

A new sentence in the revised manuscript, with references to the ARPAV reports, summarizes these details.

In this connection, we underline that since the 60s tanneries of the district have been the main responsible for the contamination of both the surface/ground waters and the atmosphere of a larger area. In particular, high amounts of H₂S and VOCs (mainly toluene, xylenes, ethylacetate, and butylacetate) are emitted into the atmosphere by this industrial activity. This is confirmed by the Regional Environmental Agency (ARPAV) which recently measured the high atmospheric levels of H₂S (up to 241 µg/m³, daily average, and 1067 µg/m³, hourly average) and estimated that 60-88% of the total VOC emitted comes from the tanneries of the district [ARPAV, 2023; JRC, 2013]. Primary aerosol emissions from these tanneries are comparable to those estimated for other common sources, but, associated with high H₂S and VOC emissions, a significant contribution to secondary aerosol production in a larger area is predictable.

Paragraph 3.3: I think the comparison between the data obtained in this work and others reported in literature could be also summarized in a table.

As required, a new table will be added to Supplementary Materials section.

Technical comments:

All these comments have been addressed.

Line 70-71: specify that is not possible separate amines with the same molecular mass without MS2 analysis.

... HPLC-MS may fail to separate **coeluted** amines with the same molecular mass (i.e. DMA/EA and PA/TMA) (Kieloaho et al. 2013; Tzitzikalaki et al., 2021) **in absence of an suitable MS2 detection system.**

Line 71: DMA/EA PA/TMA acronyms have not been specified before. Please do it.

Sorry, they are defined in the Abstract

(i.e. DMA/EA and PA/**trimethylamine**, TMA)

Line 175: Please use the subscript for the “x” in NO_x

NO_x

Line 342: please define the acronym OC

between DMA and OC (**the organic carbon concentration in PM10**),

Line 360: Please use the subscript for the “x” in NO_x

NO_x

References

ARPAV: I Monitoraggi della Qualità dell’Aria nell’Area della Concia Anno 2022, 1–54, 2023.

JRC: Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins, 290 pp., 2013.