Atmospheric
Measurement
Techniques
Open Access
Discussions

Interactive
Comment

Interactive comment on "An enhanced procedure for measuring organic acids and methyl esters in PM$_{2.5}$" by F. Liu et al.

Anonymous Referee #1

Received and published: 27 March 2015

The authors describe a modified method for the determination of carboxylic acids and fatty acid methyl esters (FAMEs) from extracts of atmospheric particulate matter applying solid phase extraction (SPE) and GC-MS. The compound groups targeted in this study are of relevance due to their abundance and their possible importance in atmospheric oxidation reactions. Methods for their determination exist since several decades already and they have been analyzed in numerous studies around the world, as correctly indicated by the authors in their introduction. In their study, the authors aim at an improvement of an existing method, mainly by introducing an SPE clean-up step during sample preparation. While in principle, AMT is an appropriate journal choice for such a study, I have several major issues with the manuscript as presented and therefore suggest a major revision before the paper can be reconsidered for publication.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1. The authors do not provide a convincing motivation for their introduction of an SPE step into the established sample preparation approach. They vaguely indicate that "it is difficult to use GC-MS to identify the trace oxygenated PAHs in raw extracts" (P2382 L4-5), but beyond I am left wondering what the actual benefit of the SPE step really is. I suggest including a thorough discussion on limitations/disadvantages of existing methods and – based on this – clearly elaborating on how the proposed approach addresses them.

2. Related to the first issue, there is a severe lack of method comparison. While the authors do give some (even though not complete, see below) information on their method, they do not compare it at all with existing methods. I suggest to include a comparison of important method parameters (e.g. recovery, precision, limit of detection) with published data on the targeted compound classes both for established GC-MS, as well as for liquid phase separation methods (LC-MS, CEMS, there is such data available, especially in the analytical chemistry literature). Only this would allow for a proper assessment of possible benefits of the proposed method.

3. The SPE "method development" part of the study – which I would consider the core of the manuscript – is poorly described and discussed. It starts with the choice of the SPE sorbents: Why were two anion exchange materials chosen, when the extraction of analytes from PM took place in non-polar, aprotic solvents? Ion-exchange SPE can be highly efficient in aqueous solutions of organic acids, but in a rather non-polar solvent mixture I would not expect significant acid dissociation (e.g. benzoic acid has a pKa of 4.2 in water, but 20.7 in pure ACN, see Sarmini and Kenndler, J. Biochem. Biophys. Methods 38 (1999) 123–137; I doubt there is much dissociation in a hexane/DCM/ACN mixture as used by the authors). On P2384 L29 the authors speculate that some analytes might be irreversibly retained by the LC-SAX sorbent. Given the above considerations I would strongly doubt this. In fact, I am surprised to see that even neutral and comparatively unpolar compounds (i.e. low polar interaction with the sorbent) such as the FAMEs are claimed to have recoveries of approx. 80-110 % from

the applied SPE sorbents. No details are given, however, how exactly these recoveries were obtained and whether they really include the SPE step. Much more details need to be given here on how the SPE procedure has been evaluated, see also further comments below.

4. The general structure of the manuscript needs to be revised, in my opinion. The experimental section should describe the individual steps of the method in a precise way. From the present manuscript version, I am for example not fully clear about which compounds are analyzed from which fraction within the sample preparation procedure (see comments below). This ambiguity might in part be due to the experimental section containing some discussions of SPE results, which would actually belong to the results section. In contrast, the results section only discusses observed ambient concentrations and correlations of the analytes during January 2013 in Beijing in a somewhat lengthy way. Given the choice of journal I would expect much more methodological results in this section.

Further comments:

- Abstract: Needs to be revised to include more hard facts on the developed procedure and its strengths/weaknesses compared to existing methods. Also, the description of the method is confusing. In L6-7 it says that acids and esters are separated from further organics by anion exchange SPE and then quantified, while in L9-10 the authors state that acids are actually separated from esters on the aminopropyl SPE cartridge (i.e. weak anion exchange sorbent).

- P2381, L4: Without having checked the references, I doubt organic acids can account for up to 80 % of particulate organic matter. Please verify the given numbers.

- P2381, L15: "aerobic degradation" is unusual terminology in the context of OH radical oxidation.

- P2382, L9-11: Most references given here seem inappropriate in the context of en-

vironmental SPE. I suggest including atmospheric applications, which do exist for the studied compound classes.

- P2382, L13: It should be mentioned that Wang et al., 2014, performed anion exchange SPE from water samples, different to what is done by the authors (solvent extraction).

- P2383, L26: Please include details on how preconditioning of the SPE cartridges was performed.

- P2384, L5: Please include details on the volume reduction step: What vacuum was applied? Was the extract evaporated to dryness?

- P2384, L9: A reference Kawamura and Gagosian, 1987c does not exist in the reference list of the manuscript. In Kawamura and Gagosian, 1987b, the derivatization takes place in a boiling water bath. Why did the authors choose a 55 °C temperature instead in their derivatization?

- P2384, L9: Washing with saturated Na2SO4 (aq) solution seems unusual. Pure water washing is typically applied to remove polar contaminants, while Na2SO4 salt removes water traces from solvents. Please clarify, what exactly has been done.

- P2384, L12-21: The comparison and discussion of SPE extraction efficiencies is i) not part of the experimental section, and ii) done in an odd way. Comparing total atmospheric concentrations of several substance groups obtained from the two cartridges does not tell much on the extraction efficiency of the actual sorbent (it's simply a wrong measure for the purpose). Also, it is unclear, how quantification was done. Were recoveries determined for both cartridges and then used to calculate atmospheric concentrations? If so, why not directly compare the SPE recoveries, obtained from standard solutions which are applied to the sorbents and eluted in a similar way than real sample extracts? This would yield a more meaningful assessment of SPE extraction efficiencies and should be given in an appropriate way for all analytes (not in stacked bar plots

where data for individual compounds is difficult to compare).

- P2384, L22 – P2386, L4: The discussion of analyte retention on the different sorbents is weak and not convincing. As stated above, strong ionic interactions with the anion exchange material seem unlikely in the given solvent mixture (in my understanding), which would leave polar interactions as retention mechanism. Are these strong enough for the compounds studied (e.g. FAMEs)? Are there any references for normal-phase SPE with the compound classes of the present study? In addition, most conclusions drawn on extraction behavior of the two sorbents do not seem to be fully supported by the data given in Fig. 1. For example, many compounds, including MCAs and DCAs, seem to yield similar concentrations from LC-SAX than LC-NH2 (which would not be surprising if ionic interactions were indeed small in both sorbents). A much more profound and differentiated discussion of extraction efficiencies is needed here.

- P2385, L8: Please give volume of added internal standard.

- P2385, L10-12: Have the authors considered to apply an internal standard from the very beginning of the sample preparation procedure? I assume variations in sample preparation will be much higher than variations in injection volume.

- P2385, L23: A reproducibility of 96.8 % would be a very high value. Is recovery meant here? If so, for which analyte? Please make sure to use correct analytical terminology throughout the whole manuscript.

- Section 3.2.: No information on blank values is given. Especially for fatty acids and related compounds contamination of lab material and/or filters can be high. A discussion of blank values and how they relate to measured sample concentrations would be important.

- P2386, L3-8: It is not clear to me what can be concluded from the 2 integrated peaks in Fig. 2d (I cannot event tell which one belongs to which extract). Please rephrase for clarification. Also, in the Figure caption it says palmitoleic acid is shown, while in the

text it says palmitic acid.

- P2387, L24-28: I don't understand how polarity of the solutions had been decreased. The polarity of the applied ternary solvent mixture should be the same before and after SPE. In addition, it is stated here that FAMEs were analysed from the "residual solutions" (the effluent during sample application, as far as I understand) which seems to be contradictory to section 2.2, where FAMEs are discussed together with MCAs and DCAs in the context of SPE retention efficiency.

- P2390, L3: How is the value of 20% uncertainty derived? And how is uncertainty defined here?

- P2392, L7: "satisfactory precision": I cannot find any data of measurement precision (i.e. RSD of repeated analyses) in the manuscript.

- Table 1: Caption is incomplete. Next to detection parameters and measured concentrations, the Table also contains recovery and detection limits. Data on measurement precision is missing and should be included. Please also indicate, how MDL was determined. In addition, it would be interesting to know, how the given MDL (as solute concentration) would translate into atmospheric concentration (for typical sampling volumes and the described extraction and enrichment procedure). Similar considerations apply for Table 2.

- Fig. 2: Labels and text are very small.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 2379, 2015.