

## **Interactive comment on “An enhanced procedure for measuring organic acids and methyl esters in PM<sub>2.5</sub>” by F. Liu et al.**

### **Anonymous Referee #2**

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This is potentially a worthwhile manuscript. The authors claim to have developed improved methods based on solid-phase extraction (SPE) for measuring organic acids and methyl esters in PM<sub>2.5</sub> aerosols. Improved methods for such compounds are certainly very welcome. However, the current manuscript is rather vague and not very convincing. It is not clear whether the SPE methods used are novel and what the basis was for selecting them. In the Introduction (page 2382) it should be mentioned which specific SPE techniques have been used in previous work.

*We have rewritten the discussion of the previous SPE techniques in the introduction as follows: “For example, solid-phase extraction (SPE) is a fast and simple method for separating, purifying, and concentrating organic compounds. It provides clean extracts with good recoveries and good enrichments (Rosenfeld, 1999; Ericsson and Colmsjo, 2003; Hou et al., 2006; Zhao et al., 2014). Adsorption-type SPE, such as polyurethane foam (PUF), silica-based, and silica-alumina mixtures, have been used to concentrate organic analytes in fine aerosol (Fraser et al. 1997; Hou et al. 2006; Duan et al. 2006). When measuring the  $\alpha,\omega$ -dicarboxylic acids (C<sub>2</sub>–C<sub>10</sub>) in fine aerosols, Adler and Siren enriched the analytes in hot water extract by Oasis HLB, Strata X, Isolute 101, and SAX SPE (Adler and Siren, 2014). The results showed that SPE with nonpolar retention mechanisms enhanced the selectivity for nonspecific analytes. Anion-exchange SPE cartridges have been used to clean and concentrate organic acids in various matrices. Wang et al. have used NH<sub>2</sub>/Carb SPE to clean the organic acids in indoxacarb/nitrotrile solution (Wang et al., 2013). A modified aminopropyl imidazole-silica sorbent was used as an SPE sorbent for measuring carboxylic acids in environmental water samples (Wang et al., 2014). It used ion-exchange SPE to isolate and enrich polar from nonpolar organic compounds in organic solvent extracts, which according to our knowledge from the literature have not yet been analyzed with these separation techniques.”*

Specific comments:

Page 2380 – lines 8-9 (and on many occasions elsewhere): the number of carbon atoms in a molecule should be indicated in subscript.

*The number of carbon atoms in each molecules has been indicated by a subscript.*

Page 2380 – lines 10-12: this sentence is incomprehensible; there is something missing in it. It should be rephrased.

*We have revised this section as “The procedure first separates the acids and esters from nonacid organic compounds by an aminopropyl-based solid-phase extraction (SPE) cartridge through ion-exchange interactions, then quantifies them by gas chromatography/mass spectrometry. The aminopropyl active groups based on the silica surface form hydrogen bonds with hydroxyl in the solvent*

*extracts. This selective retention with polar adsorption and weak ion exchange isolates and enriches more organic acids than the SAX cartridge can. This procedure prevents the fatty acids and dimethyl phthalate from being overestimated, and so allows us to accurately quantify the C<sub>4</sub>-C<sub>11</sub> dicarboxylic acids and the C<sub>8</sub>-C<sub>30</sub> monocarboxylic acids. The resulting correlations between the aliphatic acids and fatty acid methyl esters (FAMEs) suggest that the FAMEs had sources similar to those of the carboxylic acids, were formed by esterifying carboxylic acids, or that aliphatic acids were formed by hydrolyzing FAMEs.”*

Page 2380 – line 20: “indicated” is too strong; I recommend replacing it by “suggested”.

*We have replaced “indicated” by “suggested.”*

Page 2381 – line 28: acronyms and abbreviations, here “GC”, should be defined (written full-out) when first used.

*We have revised the section to “Organic acids are commonly extracted from aerosol samples along with other organics by sequential solvents, then converted to esters with BF<sub>3</sub>-methanol, BF<sub>3</sub>-butanol, or N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) before they are measured by gas chromatography (GC) (Kawamura, 1985; Kawamura, 1993; Fu et al., 2009.) Here “gas chromatography” has been abbreviated to “GC,” following the rules of acronyms and abbreviations.*

Page 2382 – line 1: acronyms and abbreviations, here “GC-MS”, should be defined (written full-out) when first used.

*We have revised the sentence to “Gas chromatography mass spectrometry (GC-MS) have been used to identify organic compounds (mainly organic acids, alkanes, cycloalkanes, PAHs, oxy-PAHs, and steranes) in atmospheric aerosols.” “Gas chromatography mass spectrometry” has been abbreviated to GC-MS, following the rules of acronyms and abbreviations.*

Page 2382 – line 21: replace “product-ion mass spectrum for” by “product-ion mass chromatogram for”.

*We have replaced “product-ion mass spectrum for” with “product-ion mass chromatogram for” in “The second MS detector is also used in SIM mode. It monitors the daughter ions (the selected fragments of the precursor ions), and generates a unique product-ion mass chromatogram for quantification.*

Pages 2383-2386, section 2: it should be indicated how many samples were subjected to the analysis, so that the significance of the correlation coefficients in Table 3 can be assessed. Were it 30 samples? The number of samples should also be indicated in the heading of Table 1.

*Section “2.1 PM<sub>2.5</sub> sample collection,” on the number of samples, has been revised in the manuscript to “Samples of PM<sub>2.5</sub> were collected between 1 June 2012 and 30 April 2013. The 30 samples discussed here came from 1–30 January, which contained the periods of heaviest haze.”*

Page 2384 – line 10: there is something missing after “vial and”.

*This sentence has been revised to “The hexane layer (containing the derivatized analytes) was transferred to a clean 2-mL vial (Millex, Billerica, MA, USA), and then reduced in volume to 1 mL under an ultra-pure nitrogen stream before being analyzed.”*

Page 2385 – line 4: replace “purifying nonpolar groups” by “purifying nonpolar compounds”.

*We have replaced “purifying nonpolar groups” by “purifying nonpolar compounds”*

Page 2386 – lines 7-8: reference is made here to the “targeted analysis section”, but there seems to be no such section.

*The reference “shown in the targeted analysis section” means the MRM parameter in Table 1. We have revised this sentence as “The MS system was operated in MS-MS (MRM) mode using the parameters shown in Table 1”*

Page 2386 – line 14: “electron impact” is an old term that is not recommended by IUPAC; it should be replaced by “electron ionization”.

*We have replaced “electron impact” by “electron ionization.”*

Page 2387 – line 1: “daughter ions” is old terminology that is not recommended by IUPAC; it should be replaced by “product ions”.

*We have replaced “daughter ions” by “product ions”*

Page 2388 – line 11: there is something missing after “in the”.

*The sentence should be “in the tested fine aerosol sample.” Our mistake.*

The references are a real disaster. I strongly recommend that authors of manuscripts pay much better attention to the references.

The following references, which are mentioned in the text, are missing from the Reference list:

Barbara and Ho (2001), mentioned on page 2381, line 4. There is “Barbara et al. (2001)” in the Reference list, to which not is referred in the text.

*Reference deleted.*

Duan et al. (2013), mentioned on page 2387, line 23.

*Reference deleted.*

Grosjean et al. (1978), mentioned on page 2391, line 11.

*Reference added:*

*Grosjean, D., Van Cauwenberghe, K., Schmid, J. P., Kelley, P. E., Pitts Jr., J. N.: Identification of C<sub>3</sub>-C<sub>10</sub> aliphatic dicarboxylic acids in airborne particulate matter; Environ. Sci. Technol., 12, 313–317, 1978.*

Guillard (1993), mentioned on page 2390, lines 21-22. There is “Guillard et al. (1993)” in the Reference list, to which not is referred in the text.

*“Guillard, 1993” replaced by “Guillard et al.1993.”*

Ho et al. (2011), mentioned on page 2388, line 26.

*“Ho et al., 2011” replaced by “Ho et al., 2010.”*

Kawamura (1985), mentioned on page 2381, line 23.R

*Replaced “Kawamura ,1985” by “Kawamura et al. ,1985” and added reference to list:*

*Kawamura, K., Ng, L.L., Kaplan, I. R.: Determination of organic acids (C<sub>1</sub>-C<sub>10</sub>) in the atmosphere, motor exhausts, and engine oils. Environ. Sci. Technol., 19, 1082-1086, 1985.*

Kawamura and Gagosian (1987c), mentioned on page 2381, lines 28-29, and on page 2384. line 8. There is “Kawamura and Gagosian (1987b)” in the Reference list, to which not is referred in the text. Kawamura and Kaplan (1987a), mentioned on page 2381, line 8. I presume that this should be “Kawamura and Kaplan (1987)”, which is in the Reference list; incidentally, there is no Kawamura and Kaplan (1987b).

*We have rewritten the reference list about Kawamura’s papers because of the different co-authors: (1) “1987a” was replaced by “1987”, and cited as “Kawamura and Kaplan, 1987,” (2) “1987b” was replaced by “1987a”, and cited as “Kawamura and Gagosian, 1987a,” (3) “1987c” was replaced by “1987b” and cited as “Kawamura and Gagosian, 1987b.”*

*Reference list:*

*Kawamura, K., Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. Environ. Sci. Technol., 21,105-110, 1987.*

*Kawamura, K., Gagosian, R.B.: Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, Nature, 325, 330-332, 1987a.*

*Kawamura, K., Gagosian, R.B.: Identification of ω-oxocarboxylic acids as acetal esters in aerosols using capillary gas chromatography-mass spectrometry, Journal of Chromatography, 390, 371-377, 1987b.*

Kawamura and Ikushima (1993), mentioned on page 2390, line 22, and on page 2391, lines 11 and 16.

*The reference of Kawamura and Ikushima has been added to the list.*

*Reference list:*

*Kawamura, K., Ikushima K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Envir. Sci. Technol., 27, 2227-2235, 1993.*

Kawamura et al. (1996), mentioned on page 2381, line 12, and on page 2390, line 17.

*We have replaced “Kawamura et al., 1996” by “Kawamura and Kasukabe, 1996.”*

Kawamura et al. (2005), mentioned on page 2389, line 15.

*We have replaced “Kawamura et al., 2005” by “Kawamura and Yasui, 2005.”*

Pio et al. (2008), mentioned on page 2381, lines 9-10.

*Pio et al. has been added to the list.*

*Reference list:*

*Pio, C.A., Legrand, M., Alves, C.A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A., Gelencsér, A.: Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. Atmospheric Environment, 42,7530-7543, 2008.*

Reid et al. (1998), mentioned on page 2381, line 9. There is “Reid and Hobbs (1998)” in the Reference list, to which not is referred in the text.

*We have replaced “Reid et al., 1998” by “Reid and Hobbs, 1998.”*

Rogge et al. (1991), mentioned on page 2389, line 5.

*The reference of Rogge et al. has been added in the list.*

*Reference list:*

*Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T.: Sources of fine organic aerosol. I. Charbroilers and meat cooking operations, Environ. Sci. Technol., 25, 1112-1125, 1991.*

Simoneit and Mazurek (1982), mentioned on page 2389, line 14.

*We have replaced “Simoneit and Mazurek, 1982” by “Simoneit and Mazurek, 1981” and added it to the list.*

*Reference list:*

*Simoneit, B.R.T., Mazurek, M.A., Jones, P.W. : Air pollution: The organic components, C R C Critical Reviews in Environmental Control, 11, 219-276, 1981.*

Sochor (2000), mentioned on page 2382, line 10. There is “Sochor et al. (2000)” in the Reference list, to which not is referred in the text.

*Sochor et al. deleted.*

Tan et al. (2013), mentioned on page 2381, line 10.

*Tan et al. (2013 ) added to the list.*

*Reference list:*

*Tan, J.H., Zhao, J.P., Duan, J.C., Ma, Y.L., He, K.B., Yang, F.M.: Pollution characteristics of organic acids in atmospheric particles during haze periods in autumn in Guangzhou, Chinese Journal of Environmental Science, 34, 1982-1987, 2013.*

Yu et al. (2008), mentioned on page 2381, line 10.

*Yu et al. (2008) deleted.*

Further references not referred to in the text:

He et al. (2001).

Nicol et al. (2001).

Simoneit and Mazurek (1989).

*These three deleted.*

There are two references “Rogge et al. (1993)” in the Reference list; it is unclear to which of them the “Rogge et al. (1993)”, mentioned on page 2389, lines 5 and 14, and on 2391, line 21, refers. In case both references have to be retained, they should be renamed into “1993a” and “1993b”.

*We have rewritten the reference list about Rogge et al. (1993) as follows:*

*Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T.: Sources of fine organic aerosol. 3. road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks, Environ. Sci. Technol., 27, 1892-1904, 1993a.*

*Rogge, W. F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B. R. T.: Sources of fine organic aerosol. 4. particulate abrasion products from leaf surfaces of urban plants, Environ. Sci. Technol., 27, 2700-2711, 1993b.*

*The corresponding reference method has also been revised.*

Finally, the journal names in the Reference list should be abbreviated for “Limbeck and Puxbaum (1999)” and for “Simoneit (1986)”.

*We have replaced “International Journal of Environmental Analytical Chemistry” by “Int. J. Environ. Ana. Chem.” for “Limbeck and Puxbaum (1999) and for “Simoneit (1986).”*

Grammatical and other minor technical corrections:

Page 2382 – line 6: replace “with problem” by “with the problem”.

*Done.*

Page 2387 – line 28: replace “contributed” by “it contributed”.

*Done.*

Page 2388 – line 2: replace “contributed” by “it contributed”.

*Done.*

Page 2390 – line 19: replace “Yasu” by “Yasui”.

*Done.*

Page 2390 – line 23: replace “indicators” by “and are indicators”.

*Done.*

Page 2391 – line 6: replace “acid, which” by “, which”.

*Done.*

Page 2392 – line 6: replace “strongly” by “strongly to”.

*Done.*

Page 2392 – line 11: replace “use determining” by “use for determining”.

*Done.*