

Interactive comment on “An enhanced procedure for measuring organic acids and methyl esters in PM_{2.5}” by F. Liu et al.

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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

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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.

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.

The SPE was mainly used in preparing the samples for analysis (separation, purification, concentration), not for the analysis itself. It recovers the analyte better than traditional liquid-liquid extractions. The review we quoted (Walgraeve et al., 2010) mentioned that “Whereas PM consists for up to 50% of a complex mixture of organic compounds exhibiting a wide spectrum of physical-chemical properties (e.g. molecular weight and polarity), only approximately 10-20% of the organic fraction has been chemically identified and quantified (Alves, 2008; Mazurek, 2002). This has made molecular characterization of the organic fraction of PM become one of the priority research issues in the field of environmental analytical sciences (Alves, 2008),” and “GC-MS analysis of raw PM-extracts may cause problems in terms of uncertainty of confirmation or even undetectability of some target oxygenated PAHs, due to interfering compounds from the matrix.” “Performing this derivatization step significantly decreased the limit of detection (LOD, signal/noise =3) ranging from 0.002 (acenaphthenequinone) to 280 ng/m³ (phenanthrene-9,10-dione) without derivatization to maxi-

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mum 0.008 ng/m³ (naphthalene-1,2-dione) after derivatization. Quantitative data on the relative importance of secondary versus primary formed oxygenated PAHs are scarce.” Based on this and the polarity and nonpolarity of the targets and the extracting solvent, we noted that the PM matrix was complex, the identified organics were few, and identifying trace oxygenated PAHs in raw extracts was even harder (P2382 L4-5). SPE coupled with gas chromatography, high performance liquid chromatography, etc., has been widely applied in measuring trace organic pollutants such as PAHs, pesticide residue, and polychlorinated biphenyls in aerosol, water, and soil. Since organic acids have high concentrations in particulates, no enrichment was usually needed, and after liquid-liquid concentration and derivatization, the samples could be injected directly into the GC. So the existing methods do not mention separating the esters from the fatty acids. We used SPE to improve selectivity—important with so many compounds. We will follow your advice to discuss the limitations/disadvantages of the various methods in the paper.

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.

The procedure we developed is for pretreatment, not analysis. The review we quoted from Walgraeve et al. thoroughly described the various types of analytical equipment, including GC, GC-GC, LC, and LC-GC with different detectors. Hallquist et al. (Atmos. Chem. Phys., 2009,9,5165-5171) had detailed the measurement of SOA chemical composition. Thus we saw little need to discuss much about the equipment or analytical procedure. But we will follow your suggestion and add a brief summary of the

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relevant analytical literature.

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.

When we first used solid-phase microextraction (SPME) to identify organic compounds in PM_{2.5}, we found quite a number of FAMES that had not been reported. And when read the analytical literature about organic acids, we found that after the organic acids were extracted from aerosols, they were converted to esters with BF₃–methanol, BF₃–butanol, or N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) before they were measured by GC. Butyl- and trimethylsilyl-(TMS) derivatives have been used more often for measuring low-molecular weight organic acids, instead of the methyl esters used for high-molecular fatty acid, because they are less volatile and more convenient for GC analysis. But if the methyl esterification was used without separating FAMES from methyl derivatives of organic acid, the organic acids would have been overcalculated.

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It was reported that the regular organic solvent used for organic acids in GC-MS analysis was methanol (Graham et al., 2002; Gao et al., 2003; Pio et al., 2008; Yu et al., 2008; Kundu et al., 2010; Boucharat et al., 1998; Limbeck and Puxbaum, 1999; Nolte et al., 2002; Wang et al., 2006; Oliveira et al., 2007). We replaced the methanol after the extraction with high-purity acetonitrile so as to avoid methanol's artifact due to its reaction with $-\text{COOH}$ compounds later in the analytical procedure (Li Yun Chun, Characterization of polar organic compounds and source analysis of fine organic aerosols in Hong Kong. 2008, 84). Then we designed a set of sequential solvents with increasing polarity (hexane/DCM/ACN) in order to extract as much of the organic material as possible.

We chose two anion-exchange SPEs to retain the organic acids and concentrate the nonpolar compounds, including FAMEs, in the solvent mixture. The retention ability depended on the interaction between $-\text{COOH}$ groups of analytes and the anionic functional groups on the surface of the adsorbent.

Your review mentioned that the pK_a of benzoic acid was 4.2 in water but 20.7 in pure ACN, and that the acidity would gradually decrease as the pK_a increased. But the solvent extract was a complex mixture, and its electron-withdrawing groups (carboxylic, cyano and nitro groups) could enhance the ionization. Adler and Siren[a] have compared the retention efficiency of α,ω -dicarboxylic acids (C2–C10 DCAs) in fine aerosols by Oasis HLB, Strata X, Isolute 101 and SAX SPE. The analytes were extracted by hot water with ultrasound, with the results shown in Figure 1.

The results showed that nonpolar retention mechanism enhanced selectivity for non-specific analytes. Oasis HLB and Strata X SPE had better extraction efficiency for C2–C10 DCAs and low inorganic matrix background for capillary electrophoresis using indirect UV detection, and Isolute 101 sorbent was superior to C7–C10 DCAs. The pK_a s of C2–C10 DCAs were given in the paper as follows:

Oxalic acid ($\text{C}_2\text{O}_4\text{H}_2$, purity 99%, $\text{pK}_{a1}=1.27$, $\text{pK}_{a2}=4.27$)

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Malonic acid (C₃H₄O₄, purity 99%, pK_{a1} = 2.83, pK_{a2} = 5.69

Succinic acid (C₄H₆O₄, purity 99%, pK_{a1} = 4.2, pK_{a2} = 5.6

Glutaric acid (C₅H₈O₄, purity 99%, pK_{a1} = 4.32, pK_{a2} = 5.54

Adipic acid (C₆H₁₀O₄, purity 99%, pK_{a1} = 4.43, pK_{a2} = 5.41

Pimelic acid (C₇H₁₂O₄, purity 99%, pK_{a1} = 4.46, pK_{a2} = 5.58

Suberic acid (C₈H₁₄O₄, purity 99%, pK_{a1} = 4.526, pK_{a2} = 5.498

Azelaic acid (C₉H₁₆O₄, purity 99%, pK_{a1} = 4.550, pK_{a2} = 5.598

Sebacic acid (C₁₀H₁₈O₄, purity 99%, pK_{a1} = 4.720, pK_{a2} = 5.450

[a]Adler, H., Siren, H.: Study on Dicarboxylic Acids in Aerosol Samples with Capillary Electrophoresis, Journal Of Analytical Methods In Chemistry, 2014

Our results showed that the retention capability of C₁₀ DCA was better than C₂–C₉ DCAs by Isolute SAX SPE even though the pK_a value was higher than the C₂–C₉ DCAs. And even if the pK_a values of oxalic and malonic acid were low, the performance enrichments of Isolute SAX were not good. So the pK_a value might not be the key factor in enriching organic acids by anion-exchange SPE.

Anion exchange SPE cartridges have been used to clean or concentrate organic acids in acetonitrile matrices. A NH₂/Carb solid phase extraction cartridge has been used to remove organic acids from indoxacarb/acetonitrile solution (Wang H.Q. et al. Enantioselective determination of the insecticide indoxacarb in cucumber and tomato by chiral liquid chromatography-tandem mass spectrometry. Chirality. 2013, 25,350-354). They thought “The NH₂/Carb SPE cartridge consists of an amino layer and a graphitized nonporous carbon layer. The former has a high capacity for removing organic acids, and the latter provides the best removal of pigments like chlorophyll and carotenoid.” This supports our idea of using the amino layer to clean organic acids, while we used the amino layer to retain and concentrate organic acids, then elute it for analyzing. It is

the same thing, but we applied it differently.

We have provided a detailed description of the SPE procedure in the revised manuscript as follows: "SPE was used to concentrate and purify the air samples after filtration. Two anion-exchange SPE materials: LC-NH₂ cartridge (3 mL, containing 500 mg of a silica-based matrix with bonded aminopropyl active groups, Supelco, Bellefonte, PA, USA) and LC-SAX cartridge (3 mL, containing 500 mg of a based matrix with quaternary amine active groups and Cl⁻ counterions, Supelco) were tested for the separation of the organic acids from nonacid organic compounds. Empty cartridges were stepwise equilibrated by flushing with 3 mL hexane, 3 mL dichloromethane, and 3 mL acetonitrile. The 60 mL extract was percolated through the preconditioned cartridge at a flow rate of 1–1.5 mL min⁻¹ (controlled throughout the SPE procedure by adjusting the vacuum). After the extract had been passed through the cartridge, the cartridge was washed with 8 mL hexane and then 4 mL dichloromethane, and air was passed through the cartridge to dry it. The retained organic acids were eluted with 2 mL of 5% HCl-methanol, which was collected in a conical flask. The eluents were evaporated using a rotary evaporator in reduced pressure then under ultra-pure nitrogen gas to about 100 μ L, then the organic acids in the eluent were derivatized with 14% BF₃-methanol (500 μ L, Sigma-Aldrich) to obtain the corresponding methyl esters. The mixture was placed in a water bath at 55°C for 40 min. The reaction mixture was washed with 3 mL of hexane and then 1 mL of a saturated Na₂SO₄ (aq) solution. 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 ultra-pure nitrogen gas flow before being analyzed. "

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

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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.

The sets of compounds have now been clarified in the paper, and we have moved the discussion of SPE results to a new section “3.1 Selectivity of anion-exchange SPE” under “3 Results and discussion.”

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).

We have revised the abstract and clarified the SPE extraction results. The section you mentioned was revised to: “We have developed an enhanced analytical procedure to measure organic acids and methyl esters in fine aerosol with much greater specificity and sensitivity than previously available. This capability is important because of these species and their low concentrations, even in highly polluted atmospheres like Beijing, China. The procedure first separates the organic acids from non-acid organic compounds by an aminopropyl-based solid-phase extraction (SPE) through ion-exchange interactions, then quantifies them by gas chromatography coupled with 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.”

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- 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.

We can understand doubts about the 80% figure, because it does seem high. But the literature shows that it can get this high. For example, Huang (Huang X.F. et al, Annual variation of particulate organic compounds in PM_{2.5} in the urban atmosphere of Beijing. Atmospheric Environment. 2006,40,2449-2458) showed that “fatty acids contributed as high as 82% of the total mass of all the quantified compounds,” including alkanes, PAHs, fatty acids, dicarboxylic acids, and hopanes. Table 2 below summarizes the percentages for different seasons:

But we thought this 80% might be a bit high, because the reported “82%” in the paper of Huang et al. had not included all the organic matter. So we reexamined our data, and found that on some clean days, the contributions of organic acids to OM could exceed 90% in PM_{2.5} (Table 3). We will still clarify the sentence, however.

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

We have changed “aerobic degradation” to “oxidation”.

- P2382, L9-11: Most references given here seem inappropriate in the context of environmental SPE. I suggest including atmospheric applications, which do exist for the studied compound classes.

We have removed three references that had little connection to atmospheric SPE, and added a paper that was closely associated.

- 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).

We have revised this section and added a reference that is very relevant to our usage. The discussion was focused on the use of anion-exchange SPE to clean or

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separate organic acids in different phases, as follows: “For example, solid-phase extraction (SPE) is a fast and simple method for separating, purifying, and concentrating organic compounds, and it offers clean extracts with very 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 from fine aerosol (Fraser et al. 1997; Hou et al. 2006; Duan et al. 2006). When analyzing the α,ω -dicarboxylic acids (C2–C10) in fine aerosols, Adler and Siren enriched the analytes in hot water extract by Oasis HLB, Strata X, Isolute 101 and SAX SPE. The results showed that SPE with nonpolar retention mechanism enhanced selectivity for nonspecific analytes. Anion exchange SPE cartridges have been used to clean or concentrate organic acids in various matrices. Wang et al. have used NH₂/Carb SPE to clean the organic acids in indoxacarb/nitrotrile solution (Wang et al., 2013). A kind of aminopropyl imidazole-modified silica sorbent was used as a SPE sorbent for measuring carboxylic acids in environmental water samples (Wang et al., 2014). Using ion-exchange SPE to isolate and enrich polar from non-polar organic compounds in organic solvent extract, which from our knowledge of the literature have not yet measure with these separation techniques.”

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

We have added details how the SPE cartridges were equilibrated: “Empty cartridges were stepwise equilibrated by flushing with 3 mL hexane, 3 mL dichloromethane, and 3 mL acetonitrile.”

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

We have revised this section as follows: “The uncleaned extracts and the solutions that had been passed through the cartridges were concentrated under vacuum, and

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then dried under a stream of nitrogen, washed with 2 mL of dichloromethane, and evaporated to 1 mL under a stream of nitrogen before being analyzed. Before each GC injection, 50 μL of 1.0 ng μL^{-1} hexamethylbenzene/hexane (Sigma-Aldrich) internal standard was added in order to correct for evaporation and variations in injection volume)."

- 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?

We chose 55°C is because it is the optimal temperature for the derivatization step. Duan[a] used 45°C, and other researchers used 80°C when extracting organic acids with methanol. Yan Xiao-Jun[b] stated that the regular derivatization temperature was 60°C for fatty acids, and that N₂ should be used to protect the unsaturated fatty acids from being oxidized. If the temperature exceeded 60°C in our procedure, filling with N₂ ahead made it difficult for the deriving device to be sealed, and lower temperatures led to low recoveries.

[a]Duan F.K. The characteristics and sources of carbonaceous aerosols in Beijing. [D].Beijing: Tsinghua university.2006

[b]Yan Xiao Jun. The application of GC-MS in the study of Marine biological and biochemical analysis. [http:// www.science.com](http://www.science.com).2009

- 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.

Anhydrous sodium sulfate Na₂SO₄ (aq) is usually used for drying organic solvents, Pure water washing is typically applied to remove polar contaminants. But our results showed that pure water could not wash the polar contaminants and the HCl and BF₃

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from the eluent: several peaks of the silica matrix were observed in the chromatograms, which we suggested came from the SPE cartridge. Since NaCl[a] and Na₂SO₄[b] (aq) were known to remove polar contaminants, here we chose Na₂SO₄ (aq).

[a]Yan Xiao Jun. The application of GC-MS in the study of Marine biological and biochemical analysis. [http:// www.science.com.2009](http://www.science.com.2009)

[b]Duan F.K. The characteristics and sources of carbonaceous aerosols in Beijing. [D].Beijing: Tsinghua university.2006.

- 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).

The reference concentrations of MCAs, DCAs and AMAs groups in the eluent, and the FAMEs from the clean-up solution from the NH₂ and SAX cartridges, was the fine aerosol of 1 January 2013 in Beijing. The results showed that this procedure could be widely applied, even for low concentrations of air pollutants.

Under the same conditions, the extraction efficiency of the NH₂ and SAX cartridges for the same sample were measured. Each test was run three times, and the mean was used to minimize discrepancies. The goal of this experiment was to measure the extraction selectivity of cartridge rather than the extraction efficiency of sorbent. The recoveries were determined by NH₂-SPE, and then used to calculate atmospheric con-

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centrations, not obtained by both cartridges. This confusion was due to our improper sequence in the text, so we have put the comparison and discussion of SPE extraction efficiencies into “Results and Discussion.”

- 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.

As discussed above, Wang H.Q. et al. have used NH2/Carb SPE to separate organic acids from indoxacarb/acetonitrile solution through ion-exchange by amino layer with organic acids. And, silica-based strong anion exchange cartridges (SAX)[a,b,c] have been used to separate AsV from organic forms. Chen, G.Y. and Chen, T.W. have discussed that “After MAD, excess acid must be neutralized to achieve adequate pH. Conventional buffer systems could well achieve this goal but resulting ionic strength would be too high for SAX sorbent to function properly,” which suggested the strong ionic strength of SAX sorbent. Copaciu et al.[d] analyzed the efficiency of the Strata NH2 and SAX by comparing the recoveries of the eluted dyes. They reported that “The best results obtained on Strata NH2 were due to the retention mechanism of polar analytes by either hydrogen bonding or weak anion exchange. It is suitable for extraction of strong and/or weak anions from aqueous samples. Strata SAX gave lower recovery levels for both dyes (57.99% for Nylosan Red N-2RBL and 80.49% for Optilan Blue MF-GL), which is a consequence of the strong interactions between the two textile

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dyes and the Strata SAX sorbent that is a strong anion exchange resin.” This result showed that the strong ionic strength of SAX sorbent reduced the extraction of weak anions. Based on this, we suggest that the separation of organic acids from FAMES and other nonpolar organic compounds by polar interactions as the retention mechanism is appropriate. From Fig. 1, different species and concentrations of MCAs, DCAs and AMAs were shown to explain the extraction behavior of LC-SAX and LC-NH₂. The high concentration of some species made the difference between the two SPE cartridges less significant.

[a]Rasmussen Rie R. , Hedegaard Rikke V., Larsen Erik H., Sloth Jens J. Development and validation of an SPE HG-AAS method for determination of inorganic arsenic in samples of marine origin. *Analytical and Bioanalytical Chemistry*. 2012, 10, 2825-2834.

[b]Rasmussen Rie R. , Qian Y.T., Sloth Jens J. SPE HG-AAS method for the determination of inorganic arsenic in rice-results from method validation studies and a survey on rice products. 2013, 405, 7851-7857. [c]Chen, G.Y.; Chen, T.W. SPE speciation of inorganic arsenic in rice followed by hydride-generation atomic fluorescence spectrometric quantification *Talanta*, 2014, 119,202-206.

[d]Copaciu, F., Coman, V., Simedru, D., Beldean-Galea, S, Opris, O., Ristoiu, D.: Determination of two textile dyes in wastewater by solid-phase extraction and liquid chromatography/electrospray ionization tandem mass spectrometry analysis, *Journal of Liquid Chromatography & Related Technologies*, 36,1646-1660,2013.

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

We have revised the experimental section to note that “50 μ L of 1.0 ng μ L⁻¹ hexamethylbenzene/hexane (Sigma-Aldrich) internal standard was added.”

- 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

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preparation will be much higher than variations in injection volume.

Internal standards refer more to correcting analytical equipment (GC) than to methods, and the recovery refers more to correcting the sample pretreatment. The internal standard was usually added before the injection. If it was injected from the very beginning of the sample-preparation procedure, evaporation during the concentration would affect its ability to correct 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.

You were right. The sentence should have read “The whole extraction and analytical procedure had a reproducibility of 9%.” We had omitted this point because the reproducibility fell below the permitted limit of 10%. We have revised the experimental section to include “Seven known pentadecanoic acid standards were spiked onto blank quartz filters to determine the limit of detection (LOD) of the analytical instrument, and the signal to noise ratios (S/N) was 3. The limit of quantification (LOQ) was calculated at S/N=10. The reproducibility of the method was determined by analyzing spiked pentadecanoic acid samples with LOQ concentration in duplicate of 7 times. The recovery of pentadecanoic acid was 96.8%, and the reproducibility was 9% with relative standard deviations (RSD) less than 8%. Mixtures of about 55 known amount organic acid standards were spiked onto blank quartz filters to determine the recoveries and the method detection limit (MDL) of the analytes, with the results shown in Table 1.” We chose pentadecanoic acid as the standard for checking the overall reproducibility because of its suitable retention time and signal strength (Figure 2).

Note that the retention times of the FAMES differed from those given in the manuscript. The corresponding oven-temperature procedure was: “The temperature of the column oven was initially set to 60 °C, then held for 1 min, increased at 6 °C min⁻¹ to 140 °C, held for 1 min, increased at 3 °C min⁻¹ to 200 °C, held for 1 min, increased at 4 °C min⁻¹ to 280 °C, and held for 5 min.”

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- 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.

The lab blank experiments analyzed seven blank filters in duplicate. The results showed that minor concentrations of palmitic acid ($0.0037 \text{ ng } \mu\text{L}^{-1}$) and stearic acid ($0.0012 \text{ ng } \mu\text{L}^{-1}$) were common. These results have been added to the manuscript as follows “Seven blank filters were analyzed in duplicate to monitor the contamination.”

- P2386, L3-8: It is not clear to me what can be concluded from the 2 integrated peaks in Fig. 2d (I cannot even 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.

The caption of Fig. 2 has been revised to “Integrated areas of palmitic acid in the eluent (top) and methylhexadecanoate in the clean-up extracts (bottom).”

“Palmitoleic acid” in the caption has been revised to “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.

The clean-up extracts and the solutions that had been used to wash the cartridges were merged and concentrated by rotary evaporation under reduced pressure until nearly dry, then washed with 2 mL of dichloromethane, and then reduced to 1 mL under ultra-pure nitrogen before being analyzed. FAMES were in the clean-up extracts phase, which had passed through the cartridge, the solvent phase was dichloromethane,

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whose polarity was lower than ACN.

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

The measured average concentration of phthalic acid was 54.1 ng μL^{-1} (13.3 to 187.2 ng μL^{-1}). The measured average concentration of dimethyl phthalate was 11.4 ng μL^{-1} (8.1 to 18.8 ng μL^{-1}). If the phthalic acid was taken as dimethyl phthalate, the uncertainty would be about 20%.

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

The reproducibility was 9%. The RSD was 8%. We have revised it to “Seven known amounts of pentadecanoic acid standards were spiked onto blank quartz filters to determine the limit of detection (LOD) of the analytical instrument, and the signal to noise ratio (S/N) was 3. The limit of quantification (LOQ) was calculated at S/N = 10. The reproducibility of the method was determined by analyzing spiked pentadecanoic acid samples with LOQ concentration in duplicate 7 times. The recovery of pentadecanoic acid was 96.8% and the reproducibility was 9% with relative standard deviations (RSD) less than 8%. Mixtures of about 55 known amounts organic acid standards were spiked onto blank quartz filters to determine the recoveries and the method detection limit (MDL) of the analytes, which were shown in Table 1.”

- 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.

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The unit of the MDL should be “ng m⁻³.”

MDL in solvent (MDLS) to MDL in air (MDLA)

Let MDLS be 0.1 ng μl^{-1} (typical value, 1 ml of extract for injection)

Volume of air extracted = $[40 \text{ cm}^2/500 \text{ cm}^2] \times 1.13 \text{ m}^3 \text{ min}^{-1} \times 60 \text{ min} \times 24 \text{ h} = 130.17 \text{ m}^3$

The MDLA from which this was drawn: $[0.1 \text{ ng } \mu\text{l}^{-1} \times 103 \mu\text{l}]/[130.17 \text{ cm}^3] = 0.7682 \text{ ng m}^{-3}$

Conversion factor = $[0.7682 \text{ ng m}^{-3}]/[0.1 \text{ ng } \mu\text{l}^{-1}] = 7.682$

So to get the MDLA, multiply the MDLS by 7.682 and change the units to ng m⁻³.

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

We will split Figure 2 into four individual figures or adjust the labels and text size in Figure 2 bigger.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/8/C880/2015/amtd-8-C880-2015-supplement.pdf>

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

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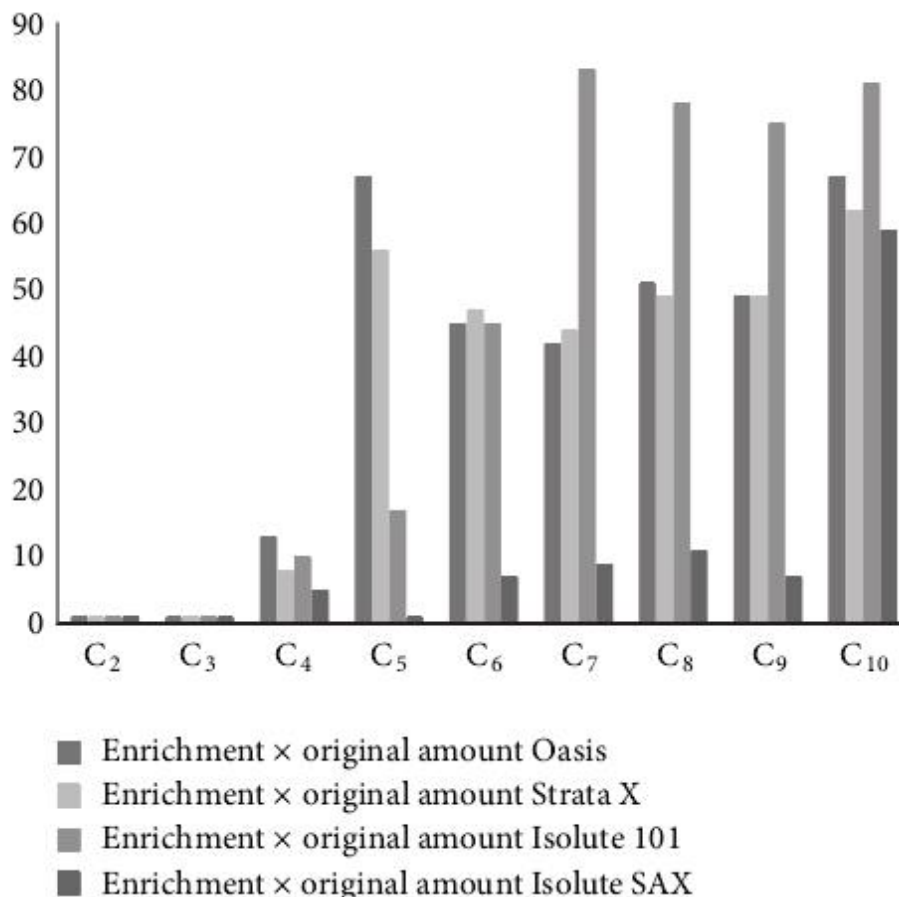


Fig. 1. Figure 1. Comparison of the performance enrichment of SPE materials in extraction of the C2–C10 DCAs. DCA concentration is 5 mg/L. The results are averages of six replicates.

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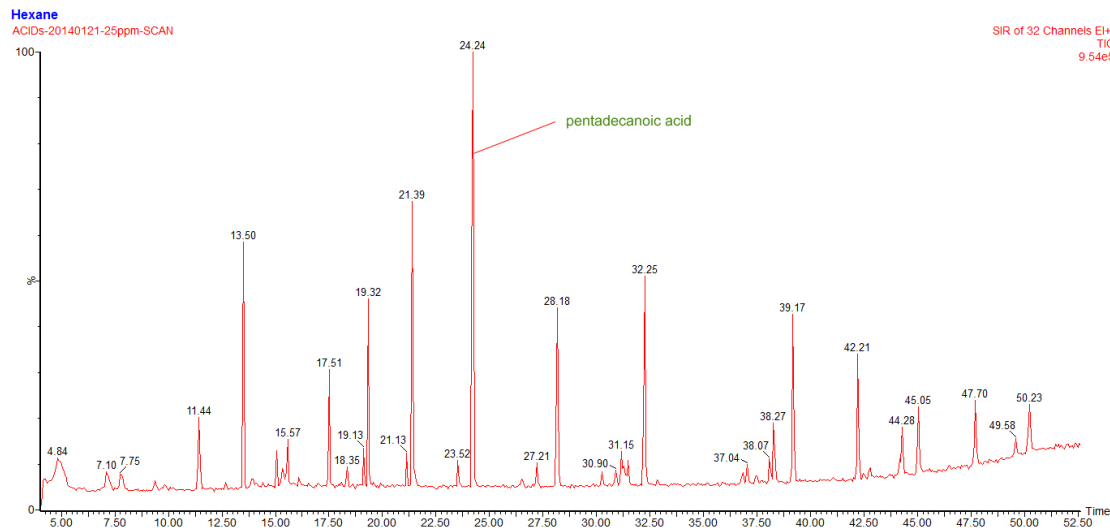
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Fig. 2. Figure 2. The Chromatograms of Mixtures of about 55 known amount organic acid standards (pentadecanoic acid was marked)

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Table 1 Summary of the relevant references

Reference	Analytes	Samples	Solvents	Volume	Extraction Method	SPE	Recoveries (%)
^a Huang X.F. (2006)	Organic compounds	69.4 cm ²	DCM/Methanol	20mL/20mL	Ultrasonic	no	70-110
^b He L.Y.(2006)	(organic acid)						
^c Hou X.M.(2006)	Fatty acids	63.6 cm ²	DCM	20mL(thrice)	Ultrasonic	Silica	75-96
^d Duan et al. (2006)	Fatty acids	75 cm ²	hexane/ DCM	20mL/20mL	Ultrasonic	Silica mixed alumina	78-95
^e Zhao X.Y. et al. (2014)	organic acids	37.5 cm ²	hexane/DCM- DCM/Methanol	15mL/15mL-1 5mL/15mL	Sonication	no	>70
Liu et al. (2014)	organic acids and FAMEs	40 cm ²	hexane/ DCM/HCN	20mL/20mL/2 0mL	Ultrasonic	Silica-based aminopropyl	74-114

^aHuang, X.F. ; He, L.Y. ; Hu, M.; Zhang, Y.H. Annual variation of particulate organic compounds in PM2.5 in the urban atmosphere of Beijing. *Atmospheric Environment*, 2006, 40, 2449-2458

^bHe, L.Y. ; Hu, M. ; Huang, X.F.et al. Seasonal pollution characteristics of organic compounds in atmospheric fine particles in Beijing. *Science of the Total Environment*, 2006, 359,167-176.

^cHou, X.M. ; Zhuang, G.S.; Sun, Y. ; An, Z.S. Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in PM2.5 aerosols in dust season in China. *Atmospheric Environment*, 2006,40,3251-3262.

^dZhao, X.Y. ; Wang, X.M. ; Ding, X. et al. Compositions and sources of organic acids in fine particles (PM2.5) over the Pearl River Delta region, south China. *Journal of Environmental Sciences*, 2014, 26,110-121.

^eDuan F.K. The characteristics and sources of carbonaceous aerosols in Beijing. [D].Beijing: Tsinghua university.2006.

Fig. 3. Table 1 Summary of the relevant references

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Table 2. Summary of concentrations of the identified organic compounds in PM_{2.5}, Beijing

Compounds	Spring	Summer	Autumn	Winter	One year
Fatty acids	260.1±77.2	369.87216.9	482.7±233.9	465.9±201.4	384.6±206.4
Total	358.7±88.4	451.8±232.7	791.5±404.5	1283.2±457.7	669.4±464.0
Percentage (%)	72	82	61	36	57

Fig. 4. Table 2. Summary of concentrations of the identified organic compounds in PM_{2.5}, Beijing

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Table 3. Summary concentrations of organic acids, OC, and PM_{2.5} in Beijing in our study

Date	Total organic acids (µg m ⁻³)	OC (µg m ⁻³)	PM _{2.5} (µg m ⁻³)	TOA/ PM _{2.5} (%)	TOA/OM ^a (%)
2013-1-1	5.12	6.93	13.43	36.12	72.24~(>)90
2013-1-8	4.95	16.47	20.27	22.63	45.26-75.43

^aWe took the average 40%, since organic matter (OM) constitutes a major fraction (30%-50%) of the total PM_{2.5} in all cities studied in China in 2013 by Huang R. J. et al.(Huang R. J. et al. High secondary aerosol contribution to particulate pollution during haze events in China. Nature, 2014, 514, 218-222).

Fig. 5. Table 3. Summary concentrations of organic acids, OC, and PM_{2.5} in Beijing in our study

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