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Atmospheric
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Discussions

Interactive comment on "A method for stable carbon isotope ratio and concentration measurements of ambient aromatic hydrocarbons" *by* A. Kornilova et al.

Anonymous Referee #1

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This paper presents a method to precisely measure concentrations as well as stable carbon isotope ratios of aromatic VOC present in low pptV to ppbV levels in ambient samples. A new sampling equipment, suitable for highly accurate measurement of light aromatic hydrocarbons, is described here together with its numerous advantages and very few limitations. The use of carbon isotope ratios for the study of atmospheric pollution and the chemistry of organic compounds in the atmosphere is a newly emerging tool. The introduced sampling method supports the application of isotopic measurements as a standard technique in atmospheric chemistry.

The experimental work is of high quality and excepting some points, that need to be addressed, both description and discussion of measurements are well founded. The manuscript contributes to scientific progress within the scope of the journal, therefore it is suitable to be published in AMT.

Specific comments:

- Page12Lines24-26: The authors state: *'The methodology has been specifically developed and tested for the purpose of accurate measurement of light aromatic hydrocarbons, but this does not exclude its use for analysis of other VOC'.* Yet, the systematic bias of up to 2 ‰ , which was found between the n-alkane off-line and on-line δ values and which is definitively beyond the hitherto reported uncertainty range for compound specific isotopic measurements, indicate the necessity of completely revising the method suitability for VOC classes other than aromatics. The first hypothesis explaining this bias on Page8Lines14-17: *'One possibility is that for heavy alkanes isotopic fractionation might have taken place inside the stainless steel canisters where the mixtures were stored and since ^{12}C containing molecules are more reactive compared to ^{13}C molecules, it is expected that any loss of n-alkanes with time will result in enrichment of ^{13}C.'* infers that ca. 60% n-hexane have already 'reacted' when exhibiting a fractionation from -31 to -29‰ . Is this likely to happen? The authors may want to comment this issue. The second hypothesis needs to be similarly discussed (Page8Lines17-20: *'Another possible explanation for the bias between off-line and on-line is incomplete oxidation during off-line combustion. This also would result in a decrease of the isotope ratio in the CO2 formed, since ^{12}C containing VOC will oxidize more readily than ^{13}C containing VOC.'*)

- Page33Figure6: Additionally to the discussion above, the chromatogram of the test mixture shows at a glance two different discrimination trends for the alkane separation, given that the mixture contains, as usual, similar concentration of all components: the peak areas seem to first increase for compounds 2 to 4, then decrease from 4 to 6, 10 and 11. If that is the case, the authors may consider revising the GC oven temperature program. Losing the 'lighter' alkanes from the mixture due to too high GC starting temperature might incidentally explain their ^{13}C enrichment in the on-line data. As it is now, the method is excellent for ambient measurements of aromatics, yet unsuitable for alkanes.

Other comments:
- Page4Line8 and Page6Line10: revise the different furnace temperature values.
- Page21Figure1: insert 'VOC sample' between furnace and valve.
- Pages33-34Figure6: revise the different retention time values for benzene (compound 3), given that the same GC temperature program was used for test and ambient samples.

Editorial revisions:
- Page7Line19: replace 'd' by 'δ'(=delta)

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 1365, 2015.