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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measuring long chain alkanes in diesel engine exhaust by thermal desorption PTR-MS" *by* M. H. Erickson et al.

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Thank you for your time and helpful comments to make this paper more clear.

Reviewer comment 1. While it is clear that the PTR-MS can detect alkanes, the authors should be clearer about its ability to quantify alkanes. From the manuscript it seems that quantification is based on fragment ion signals, which are non-unique among different carbon numbers. Therefore it seems to me that at this stage, the authors can only quantify "total alkanes" but not speciated compounds, like a standard GC/MS can.

Response. This is correct. The PTR-MS quantifies total alkanes. What we lose in the PTR-MS approach is potential for speciation since there is no chromatographic separation as you point out. However the ability of GC-MS to speciate the C12-C18

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alkane isomers found in diesel fuel and exhaust is limited given GC column resolutions and the very large number of alkane isomers and other co-eluting compounds. This gives rise to the unidentified complex material "hump" observed in diesel exhaust and fuel GC chromatograms. The PTR-MS can potentially have an easier job of quantifying the total abundance of alkanes in a fuel mixture than GC methods. We have made the PTR-MS information content more clear by editing the last sentence on page 6008 to read:

"The PTR-MS identifies organics by molecular weight (MW) and could provide valuable information on the relative abundance by molecular weight of C12-C18 compounds associated with diesel engine exhaust."

Reviewer comment 2. What is the interference of cycloalkane signal on the linear alkane ions (e.g. 57, 71etc.)?

Response. In general cycloalkanes do not fragment at 80 Td and yield M-1 ions so are not interfering compounds. However, cyclopentane, cyclohexane, and methylcyclopentane are the exceptions and produce M+1 ions that are interferences for alkane detection. These compounds are not problematic because they are volatile and thus purged from the Tenax trap. Fragmentation patterns of cycloalkanes and other hydrocarbons associated with engine exhaust are the subject matter of a manuscript we are in the process of submitting to Int. J. Mass Spectrometry.

We have reworded the cycloakanes fragmentation section on page 6016 to read: "Laboratory tests confirmed that cyclopentanes and cyclohexanes yield these ions at 80 and 120 Td drift tube conditions. At 80 Td these compounds yielded an M-1 ion as the major fragment ion. Exceptions were cyclopentane, cyclohexane, and methylcyclopentane where M+1 ions were observed to be the major ions. These compounds are removed during the trap purge and would not interfere with TD-PTR-MS analysis of alkanes. Methylcyclohexane, dimethylcyclohexanes isomers and trimethylcyclohexanes isomers yielded M-1 ions at greater than 95% yield. At 120 Td the M-1 ion is

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produced but at significantly lower yields and many more fragment ions are observed including m/z 69."

Reviewer comment 3. - Minor comment Pg. 6016 line 18: Typo n>n

Response. This was fixed, text now reads "n $\geq$ 5"

Reviewer comment 4. - Pg. 6025 line 20, "VOC mixing ration" should be "VOC mixing ratio"

Response. Typo was fixed.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6005, 2013.