

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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Reviewer # 2

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

Reviewer comment 1. Page 6008, Lines 19-20: The authors mention here that the quantification of the abundance of IVOC species is improved by the method described in this paper. But I cannot find the discussion as to what degree the detection of the IVOC was improved, for example, in comparison with the previous methods, in the paper.

Response. Good point, we are simply trying to demonstrate this technical approach

C2769

to measuring IVOC compounds. We have changed this sentence, removing the word “improved” to better state our purpose of the paper. “A new method is presented here to quantify of the abundance of IVOC species using a thermal desorption sampler integrated into a proton transfer reaction mass spectrometer (PTR-MS).”

Reviewer comment 2. Page 6010, Lines 6-8: I guess that the temperatures of the inlet tube, the ion source, and the drift tube were 50 °C, according to Jobson and McCoskey (2010). Was it okay that the desorption temperature was 230 °C? I am afraid that sticky compounds may be adsorbed on the line, resulting in the interference for the next desorption.

Response. We have made more clear the temperatures used for the heated lines and drift tube on page 6009. The inlet tube was thermostated to 80 °C and the ion source and the drift tube were 70 °C. Periodic zeros were performed and no carryover effects were observed, even at higher masses and we have noted this on page 6010.

p. 6009: “The drift tube was thermostated to 70 °C using the thermoelectric drift tube heater supplied by Ionicon. For analysis of heavier organics a high temperature resistive glass drift tube would be preferred such as used in Thornberry et al. (2009). Because of limitations on drift tube temperature, the sampling lines, either electropolished stainless steel tubing (UHP Cardinal) or silica coated stainless steel tubing (Sulfinert, Restek Corp), were heat traced to a similar temperature (80 °C), so that the drift tube didn’t act as a cold spot and become contaminated.”

and on p. 6010 Zero air was collected on the trap in the same manner as a sample and peak responses above the zero air signals were determined; no carryover effects from previous samples were observed in the zero air desorptions.

Reviewer comment 3. Page 6014, Lines 20-28: As mentioned in the abstract, the authors defined the long chain alkanes as C12-C18. However, the detection sensitivity was determined up to C16 at 120 Td and C13 at 80 Td in Fig. 3. Is there any difficulty in determining the sensitivity for C17-C18 alkanes at 120 Td and C14-C18 alkanes at

C2770

80 Td? In particular, the data for C14-C16 alkanes at 80 Td should be shown because there were data for C14-C16 alkanes at 120 Td. If the sensitivities for C14-C16 alkanes at 80 Td were not close to 1.5 Hz ppbv per MHz H₃O⁺, I am afraid that the long chain alkanes (C12-C18) were not quantified correctly by the method described in this paper.

Response. Determining sensitivities for alkanes > C16 was not attempted as these species are solids at room temperature and we couldn't inject them as neat liquids to prepare a test mixture with the dynamic dilution system as we did with the other compounds. Making mixtures by dissolving them in a non-responsive solvent is something we are working on.

We have added data for C14-C16 n-alkanes sensitivities at 80 Td and updated Fig 3. The measurements now include uncertainty shading representing the accuracy of the dynamic dilution system ; the standard deviation of the replicate measurements was better than 15%. At 80 Td the n-alkane sensitivity peaks around C12 at 1.7 Hz / MHz ppbv and decreases for larger alkanes to about 1 Hz / MHz ppbv for C16. This is in part attributed to differences in fragment ion distribution and lower transmission efficiency for heavier ions produced by the larger n-alkanes but we can not explain the significant decrease in sensitivity. Sampling methods were identical so our working hypothesis is that the differences are due to the role of water cluster ions which are in much greater abundance at the 80 Td condition. A large fraction of alkanes maybe bound as ligands in water clusters which then dissociate in the after drift pumping stages of the vacuum system. This is speculation but we are working experiments to test if water clusters influence sensitivity trends. We changed the paragraph on page 6015 adding an extra 2 sentences discussing the figure: "At 120 Td the n-alkane sensitivity is primarily determined by the ion signal at m/z 41, 43 and 57 while at 80 Td the sensitivity is determined by broader range of heavier ion masses, as illustrated in Figure 2, with most of the ion signal (>50%) at m/z 57, 71, 85. At 80 Td the dodecane sensitivity is 1.7 ncps and the sensitivity of the C14-C16 n-alkanes appears to display a decreasing trend. The decreasing trend is in part due to lower ion transmission efficiency for the

C2771

heavier ions produced by these alkanes, but the large difference between the 120 Td and 80 Td sensitivities for these alkanes can't be readily explained."

The sensitivity factor we used was fuel based using the IVOC sampler to account for branched alkane sensitivities and compound loss in the 150 °C purge. The paragraph on p. 6023 was poorly written, confusing the 2.6 Hz / ppbV sensitivity with the 1.5 Hz / ppbV sensitivity. The 2.6 Hz / ppbV was our calculation of what the PTR-MS sensitivity would be to diesel fuel alkanes in the C12-C18. It was calculated by correcting the measured 1.5 Hz / ppbv for mass loss of compounds from the 150 °C purge. We don't use this 2.6 Hz / ppbv value and has lead to confusion. We have removed this value from this paragraph and from the conclusion as well. We are satisfied that the 1.5 Hz / ppbv value is a reasonable estimate of the alkane sensitivity for our device; it is similar to what we observed for the n-alkane sensitivity. The paragraph on page 6023, line 5 now reads: "Given the complexity of alkane composition in diesel fuel and exhaust, whole diesel fuel might be a better standard to calibrate PTR-MS sensitivity to alkanes. Using the mass composition of alkanes in diesel fuel reported by Gentner et al. (2012), a sensitivity of 1.5 ncps at 80 Td was determined from the sum of the C_nH_{2n+1} ions observed from diesel fuel evaporated in the dynamic dilution system and measured by the IVOC sampler under the 150 °C purge condition. Since alkanes < C11 are either completely or mostly removed in the purge, this value represents the method sensitivity to IVOC alkanes at 80 Td and was used to estimate IVOC alkane abundance in exhaust. This value is in reasonable accord with the n-alkane sensitivity values shown in Fig 3 but perhaps higher than expected given C14-C16 n-alkane responses. Further investigation of branched alkane response and their molar abundance in diesel fuel is required to reconcile differences between whole fuel and n-alkane sensitivity factors."

In the conclusion we removed the 2.6 Hz / ppbv reference and restate the method sensitivity found with the fuel based approach using the thermal desorption sampler. On page 6028 we added this sentence in conclusion: "Diesel fuel was used to calibrate the

C2772

thermal desorption sampler sensitivity to total alkanes in the C12-C18 range, yielding a value of 1.5 Hz ppbv⁻¹ per MHz H₃O⁺. “

Reviewer comment 4. Page 6024, Lines 10-16: I cannot follow the derivation of the numbers of 18%, 2%, 1%, and 26%. Were these numbers determined from the data in Fig. 6 or from the data in the previous papers?

Response. Yes the fractional abundance figures were taken from Schauer 1999 and 2002. We have simplified the text to better make our point that IVOC mode sampling won't measure light alkanes and alkenes found in gasoline exhaust. This now reads as follows: "Alkanes and alkenes are major constituents of engine exhausts making up about 60% of gasoline exhaust (Schauer et al., 2002) and 12% of the diesel exhaust non-methane organic gas mass emission rate (Schauer et al., 1999). The IVOC sampling mode discriminates against alkanes and alkenes < C9. It is thus estimated that less than 1% of the total alkane and alkene emissions reported by Schauer et al. (2002) from gasoline engine exhaust is measurable by IVOC mode sampling. For diesel engine exhaust, IVOC mode sampling measures approximately 21% of the total alkane and alkene emissions."

Minor Comments (1) Page 6032, Line 7: ...sources, 2. > ...sources, 5. Response: This typo was fixed.

(2) Page 6032, Line 13: The paper of Schulz et al. (1999) is not referred in text. Response: Reference was removed from text.

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C2773

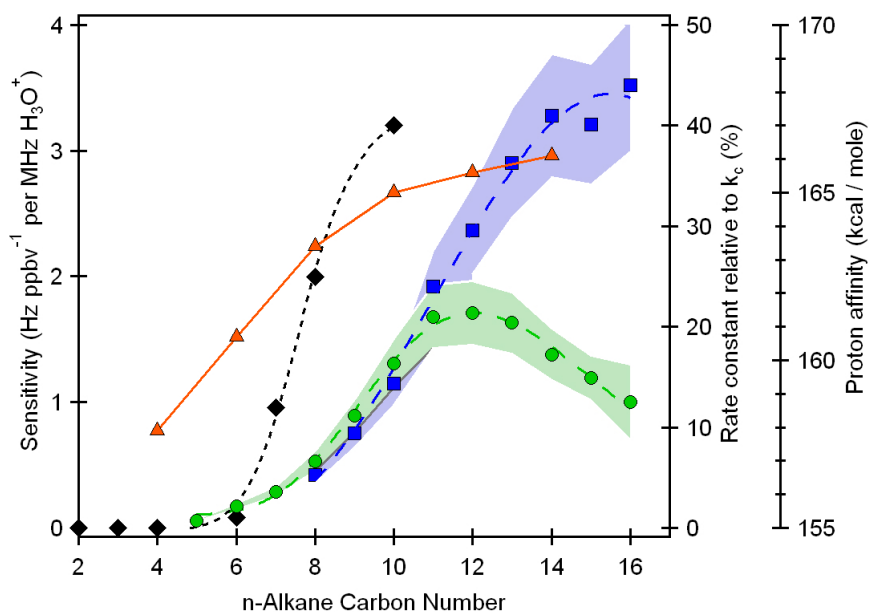


Fig. 1. Figure 3. n-Alkane sensitivity (left axis) for 120 Td (blue squares) and 80 Td (green circles) with shading representing the 15% estimated accuracy of the test mixture preparation. Measured H₃O⁺ + n-

C2774