

Journal: AMT

Title: Evaluation of NO⁺ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds

Authors: A. R. Koss et al.

MS No.: amt-2016-78

MS Type: Research Article

Response to Short Comment by S. Inomata

The short comment is in black text.

Our response is in blue text.

Our group has reported product ions and their relative intensities of C3-C13 n-alkanes and C4-C10 iso-alkanes measured by NO⁺ CIMS (see Table A1 of the Supplementary Data in Yamada et al. (2015)). The present results are generally similar to ours. But it seems that the ratios of fragment ions to [M-H]⁺ ions are larger in the present study than ours. I think that the strength of the electric field of the drift tube (i.e., E/N ratio) cannot be the reason of this difference because the ratios are similar in both the studies (60 Td in the present study and 67 Td in our study). We also showed that O₂⁺ ionization of alkanes produces the same fragment ions as NO⁺ ionization (see Table A1 of the Supplementary Data in Yamada et al. (2015)). Therefore, we subtracted the contribution of O₂⁺ ionization from ion signals in order to report the detection sensitivities of alkanes by NO⁺ CIMS. Did the authors consider the contribution of O₂⁺ ionization when they measured alkanes by NO⁺ CIMS?

Yamada, H., Inomata, S., and Tanimoto H.: Evaporative emissions in three-day diurnal breathing loss tests on passenger cars for the Japanese market, *Atmos. Environ.*, 107, 166-173, 2015.

We are pleased to see a short comment from Dr. Inomata – his work (Inomata et al., 2013) has motivated us to investigate high-mass alkanes.

On comparing the contaminant O₂⁺ reported in our work (4% of NO⁺ signal) to that reported in Yamada et al. (2015) (1.5% of NO⁺ signal), it seems likely that the difference in O₂⁺ contributes to the difference in the reported product ion distributions. We have acknowledged this important consideration in two places in the revised manuscript. First, in section 3.1.2 (“Distribution of Product Ions”), we have included a comparison to Yamada et al. tridecane distribution in Figure 5, along with an explanation (see our response to Reviewer 1 for details). Second, in section 3.1.3 (“Alkane Fragmentation”), at line 297, we have added a brief consideration of the effect of contaminant O₂⁺ on sensitivity and product ion distribution.

We do not have a characterization of our instrument’s response to O₂⁺ ionization, so it is not possible for us to perform a sensitivity correction as in Yamada et al.

References

- Blake, R. S., Wyche, K. P., Ellis, A. M., and Monks, P. S.: Chemical ionization reaction time-of-flight mass spectrometry: Multi-reagent analysis for determination of trace gas composition, *Int. J. Mass Spectrom.*, 254, 85-93, <http://dx.doi.org/10.1016/j.ijms.2006.05.021>, 2006.
- Inomata, S., Tanimoto, H., and Yamada, H.: Mass Spectrometric Detection of Alkanes Using NO⁺ Chemical Ionization in Proton-transfer-reaction Plus Switchable Reagent Ion Mass Spectrometry, *Chem. Lett.*, 43, 538-540, 10.1246/cl.131105, 2013.

Španěl, P., Ji, Y., and Smith, D.: SIFT studies of the reactions of H₃O⁺, NO⁺ and O₂⁺ with a series of aldehydes and ketones, *Int. J. Mass Spectrom.*, 165–166, 25-37, [http://dx.doi.org/10.1016/S0168-1176\(97\)00166-3](http://dx.doi.org/10.1016/S0168-1176(97)00166-3), 1997.

Španěl, P., and Smith, D.: Selected ion flow tube studies of the reactions of H₃O⁺, NO⁺, and O₂⁺ with several aromatic and aliphatic hydrocarbons, *Int. J. Mass Spectrom.*, 181, 1-10, [http://dx.doi.org/10.1016/S1387-3806\(98\)14114-3](http://dx.doi.org/10.1016/S1387-3806(98)14114-3), 1998.

Wyche, K. P., Blake, R. S., Willis, K. A., Monks, P. S., and Ellis, A. M.: Differentiation of isobaric compounds using chemical ionization reaction mass spectrometry, *Rapid Commun. Mass Spectrom.*, 19, 3356-3362, 10.1002/rcm.2202, 2005.

Yamada, H., Inomata, S., and Tanimoto, H.: Evaporative emissions in three-day diurnal breathing loss tests on passenger cars for the Japanese market, *Atmos. Environ.*, 107, 166-173, <http://dx.doi.org/10.1016/j.atmosenv.2015.02.032>, 2015.

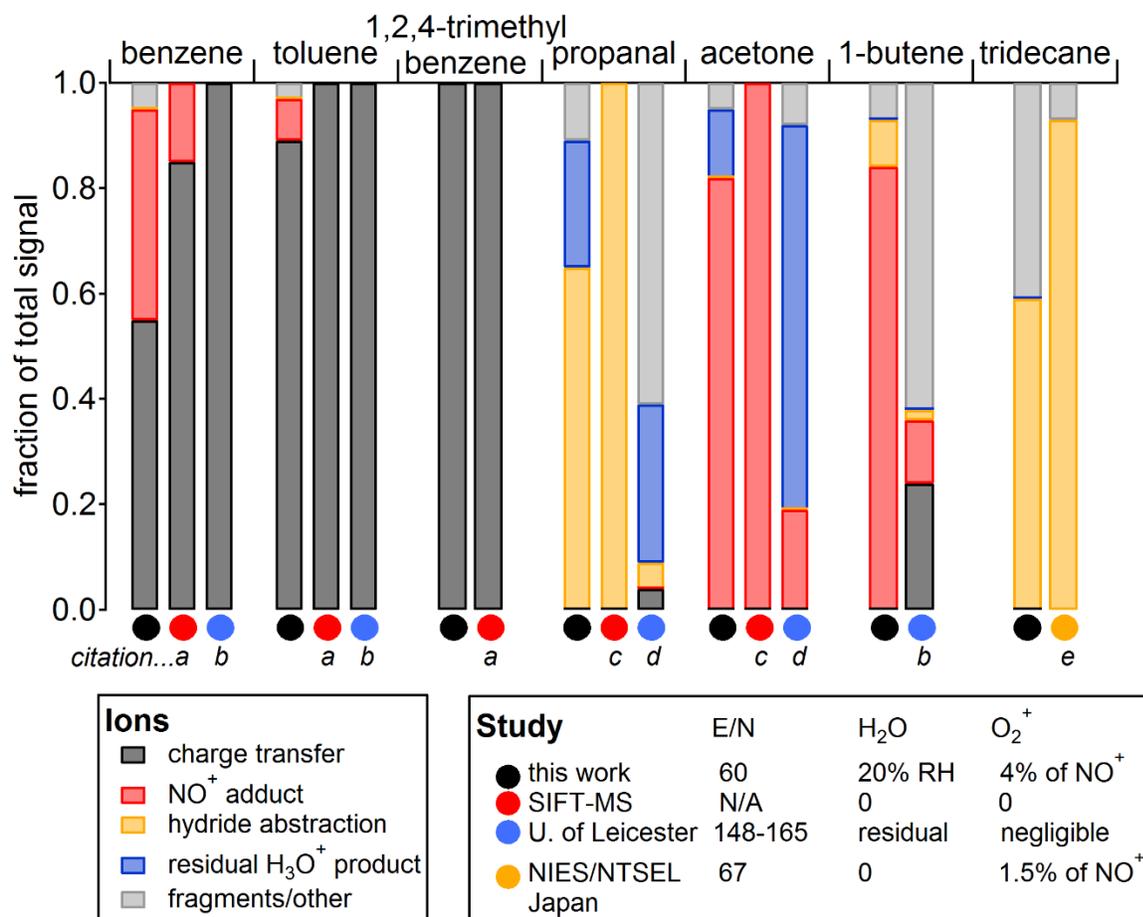


Figure 5. Comparison of product ion distributions between four sets of instrumental and environmental conditions.

a. Španěl and Smith (1998a)

b. Blake et al. (2006)

c. Španěl et al. (1997)

d. Wyche et al. (2005)

e. Yamada et al. (2015)