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Atmospheric Measurement Techniques Discussions

Interactive comment on "Molecular Characterization of Alkyl Nitrates in Atmospheric Aerosols by Ion Mobility Mass Spectrometry" *by* Xuan Zhang et al.

Anonymous Referee #1

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General Comment:

This is a short manuscript reporting the development of a new technique based on Ion Mobility Mass Spectrometry (IMS-MS) for the analysis of alkyl-nitrates in atmospheric and laboratory-generated aerosols. Although the analysis of water soluble organic compounds in atmospheric aerosols by coupling of IMS-MS with Electrospray Ionization (ESI) has already been demonstrated, this work presents the first development focusing on organic nitrates. This new technique addresses important challenges in atmospheric chemistry by aiming at separating the many alkylnitrate isomers present in atmospheric samples and identifying each of them by collision-induced dissociation.

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Even if this analysis is only qualitative for now, it is very relevant for atmospheric chemistry as alkylnitrates are key tracers for atmospheric oxidation mechanisms but can be separated by only few techniques and are notoriously sensitive to decomposition.

One of the main findings in this work is that, while alkylnitrates alone do not ionize easily with ESI, their ionization is considerably enhanced by clusterization with anions such as chloride, nitrate, iodine, and acetate, thus providing a new way to detect them. The systematic work presented here led to an increase of the alkylnitrate ion signals by 2 orders of magnitude.

As underlined by the authors themselves, the technique is still in an early stage of development. For instance, its application to the analysis of secondary aerosols produced by the oxidation of isoprene in a reaction chamber did not allow to detect first-generation hydroxy-nitrates.

In spite of these limitations, this technique is very relevant for atmospheric chemistry, therefore I recommend the publication of this manuscript.

Minor comments:

1) Combining the analysis of volatile and non-volatile compounds

One of the main limitations underlined by the analysis of the SOA produced by the oxidation of isoprene is that first-generation hydroxyl-nitrates could not be detected due to their volatility. Previous applications of IMS-MS (for instance Krechmer et al. 2015, 2016) have used different ionizing sources to analyze both gas- and condensed-phase products. Although it might not be convenient to change the ionization source, could a similar strategy (or a different one) be used to detect all the alkylnitrates in a system ?

2) Quantification

The qualitative identification of different alkylnitrates with this technique is already very valuable, as alkylnitrates are tracers for specific reaction pathways. Thus this technique

could already lead to the identification of previously unknown pathways. But quantification would certainly be a plus. Would quantification be possible, for instance from the ion mobility spectra, in a similar way as in chromatographic techniques ?

3) There was a few minor mistakes in the text:

- p.5, Li. 126: shouldn't it be "with the assistance of. . ." instead of "with the assistant of. . ."

- p. 7, Li. 170, "ubiquitously" does not seem to be the right word here. "systematically" might be more appropriate.

- p. 7, Li. 192: it should probably be "constant" instead of "consistent". Or "the same at all anion concentration".

- p. 9, Li.252: the reference "Wennberg et al., 2018" is not in the reference list, please check.

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