

Responses to Reviewer #1

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.

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.

*We thank reviewer #1 for the constructive comments. Our point-by-point responses can be found below, with reviewer comments in **black**, our responses in **blue**, alongside the relevant revisions to the manuscript in **red**.*

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

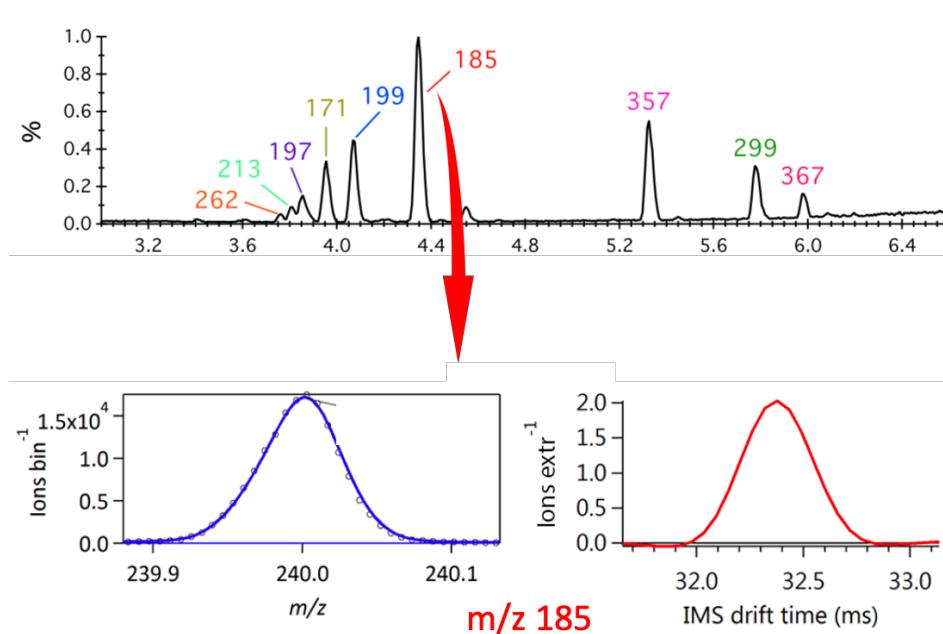
ionizing sources to analyze both gas- and condensed- phase products. Although it might not be convenient to change the ionization source, could a similar strategy (or a different one) be used to detect all the alkyl nitrates in a system?

[Response] Krechmer et al. (2016) employed the same IMS instrument for the SOAS field campaign as the one used in the current study, but with different ionization source, i.e. the NO_3 -ionization source for the gas-phase measurement. However, there is a major challenge in coupling the NO_3 -ionization inlet to the IMS chamber, that is, the voltage applied to the NO_3 -ionization inlet needs to be over 10K volts in order to push the ions through the entrance of the IMS, thereby significantly limiting the ionization efficiency of analytes of interest. To our knowledge, this technique is no longer pursued by the manufacturer. The electrospray ionization method, on the other hand, has no such limitation as it inherently requires high voltage to produce ions and/or ion clusters. We think one potential strategy to detect all the alkyl nitrates in a system is to combine the secondary electrospray ionization (SESI) for the analysis of trace concentrations of vapors with the extracted electrospray ionization (EESI) for the analysis of particle-phase constituents.

2) Quantification

The qualitative identification of different alkyl nitrates with this technique is already very valuable, as alkyl nitrates 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?

[Response] The quantitative characterization of alkyl nitrates by IMS-MS is limited by the ESI process because one critical issue in quantitative ESI is the suppression of ionization due to matrix interference. For example, a particle filter sample would give significantly lower ionization signals compared to pure standard solutions with similar analyte concentrations. To overcome the matrix interference, separation such as adding a liquid chromatography column prior to the entrance of the ESI unit is desired. The resulting spectra should be something similar to the sketch given below: for any given peak on the chromatograph, there are correspondingly one plot of ion mobility spectra and one plot of mass spectra showing the major ion (analyte) constituting this chromatographic peak.



3) There were 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..."

[Response] Revised as suggested.

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

[Response] Revised as suggested.

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

[Response] Revised as suggested.

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

[Response] Revised as suggested.