GENERAL COMMENTS

The authors report on the development of supercritical fluid chromatography for the separation of polar products of the atmospherically important reaction between methylglyoxal and ammonium sulfate. The reaction itself has already been widely investigated. New molecular/fragment ions were found, however identification of the corresponding analytes was not in focus of the study (is also not expected due to the unit mass resolution of mass spectrometric detection). The presented SFC is an attractive and greener alternative to commonly applied LC and GC methods, but the motivation why it was developed for the analysis of the investigated reaction is not clear. Also, its better performance in comparison to conventional analytical techniques is not well justified (see below). Moreover, the use of C18 and HILIC columns seems fundamentally inappropriate; one does not expect any good results when applying nonpolar-to-polar gradient on C18 or operating HILIC without a certain amount of water.

It should be made clear, by corrections throughout the manuscript, that there is no chromatographic method that is unique and can be used for the detection of any analyte in any mixture. In this regard, it should be clearly shown at the end of the manuscript why the new chromatographic method is better performing than the conventional LC/GC separations (best by comparison of SFC, LC and GC chromatograms, a real sample analysis would be above expectations). I believe that the new identified peaks cannot be unambiguously attributed to the better separation, but may also arise from different MS detection (different instrument/ESI source, lower LOD, etc.). Please revise the manuscript addressing these issues in particular.

SPECIFIC COMMENTS

P1L3: *These methods (GC and LC) can be time-consuming and do not easily separate highly polar aqueous molecules.* -> The presented method obviously also doesn't assure separation of highly polar products (broad peak after 11 min).

P2L13-17: First, use of ion-pairing reagents enables/improves separation of polar analytes on RP columns and has for instance been successfully applied to the detection of ambient organosulfates. Second, how long the method has to be is very much dependent on the complexity of the sample (simulated reactions are usually less demanding than real aerosol extracts). Thirdly, many peaks co-elute also in your case (broad peak after 11 min).

P2L35-P3L1: not strictly true, revise

Section 2: a summary (table) of all tested conditions is missing (best to put it in SI).

2.3.1: four different BEH columns were used and only one is shortly named BEH. This may be misleading. I suggest changing this acronym.

P6L11 and Fig.2: Amide column does not seem any better than C18 and HILIC – improve data representation or revise the text.

P6L13-14: how do you know how many compounds elute after 12 min? It is better to say that most compounds efficiently separate within 12 min...

P6L20-29: As already stated above, the usage of C18 and HILIC seems fundamentally inappropriate. If they were treated differently, explain in detail how.

P6L26: BEH Amide and 2-EP are not HILIC columns, but rather contain polar stationary phase.

P8L1: I don't understand: *elute much more cleanly from the column*

P8L6: the reaction was left for 1 month to get sufficient amounts of products for the detection, so I don't expect that a few minutes of reaction between the carbonyls and ammonium on the column can produce the measured artefacts.

P8L16-17: same also for LC and GC

P10L29: the newly identified low-intensity signals are not always separated on the column (see for instance m/z 83,87,98,139 etc.) – they probably appear because of better performing MS detection. Also, when EIC is measured, the quality of chromatographic separation often doesn't need to be supreme; selectivity is already assured with the selection of the ion.