

Terpenes as potential precursors of humic-like substances in the atmosphere?

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Secondary aerosol formation from 5 monoterpenes (α -Pinene, β -Pinene, Limonene, Δ^3 -Carene) and 2 sesquiterpenes (β -Caryophyllene, α -Farnesene) under various conditions was studied in a series of experiments performed in the SAPHIR chamber at Forschungszentrum Jülich in June 2008. In these simulation experiments terpene species and their concentration were varied while in most cases ozone concentration was kept at 50 ppb. Light conditions in the outdoor chamber followed the weather situation. Aerosol microphysical characterization as well as aerosol mass spectrometry were performed on-line but filter sampling was also carried out for more detailed off-line chemical characterization. In most cases filter samples were collected on the first day of reaction then the aerosol particles aged in the chamber and filter samples were collected again on the second day. Reaction products were analyzed at University of Pannonia by electrospray ionization (ESI) mass spectrometry either directly or following HPLC separation. In some cases identification of oxidation products was supported by GC-MS as well.

Extracts of the filters were analyzed by reversed phase HPLC coupled to negative electrospray ionization MS. A number of intense ions were detected in the chromatograms as shown in Figure 1.

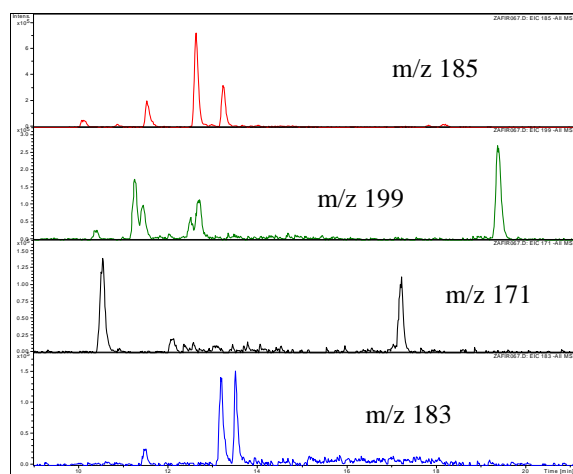


Figure 1 RP-HPLC ion chromatograms detected with ESI-MS from 9 to 21 min. Peaks with the same m/z value indicates the formation of isomers: e.g. m/z=185 can be pinic acid, caric acid or norlimonic acid.

In the mass spectra of individual peaks very often the difference between m/z values equaled 44 that is characteristic for the CO₂ loss of carboxylate ions. Furthermore, the formation of cluster ions with Na⁺ revealed the number of carboxylic groups within the molecules. Thus, numerous dicarboxylic acids were found among the terpene oxidation products. The drawback of HPLC-MS is that the sample is diluted in the chromatographic eluent and, consequently, less intense ions can be lost. Furthermore, irreversibly retained compounds will not elute from the column and therefore no information can be obtained about them. In order to avoid these problems direct injection MS was also applied to get information on the overall undiluted sample. A mass spectrum obtained with this technique is shown in Figure 2.

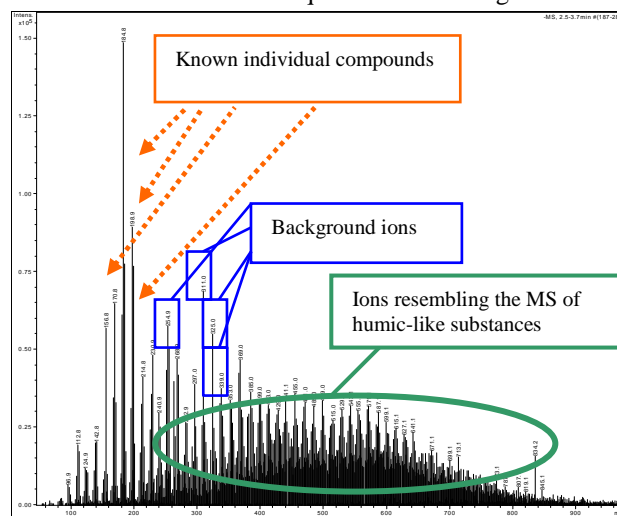


Figure 2 Direct injection ESI-MS spectrum of a filter extract recorded from m/z 50 to 1000.

Most of the known monoterpene oxidation products form ions below m/z 200 while sesquiterpene oxidation products can be detected in the m/z 200-300 range. However, periodic spectral lines ($\Delta m/z=14$) were detected from approximately m/z 300 to 800 with maximum intensity around m/z 550. The periodicity and the wide range of ions resembled those of humic-like substances found in rural aerosol although the maximum in ambient samples was around m/z 250-300.

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