

High resolution mass spectrometry characterisation of peroxy-carboxylic acids as ROS and ELVOC proxies

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A large number of epidemiological studies show that ambient aerosols are correlated with a wide range of respiratory and cardio-vascular diseases. The particle components that cause these negative health effects are not known, but reactive oxygen species (ROS) are thought to be a main contributor to the toxicity of particles in ambient air. Peroxy acids are a subtype of ROS shown to be present in secondary organic aerosol (SOA) (e.g. Reinnig *et al.*, 2009). Recent studies also suggest that extremely low volatility organic compounds (ELVOCs), strongly involved in the initial stages of SOA formation, often contain peroxy acid functionalities (e.g. Rissanen *et al.*, 2014). Mass spectrometry in principle provides a powerful tool to characterize peroxy acids in organic aerosol. However, for unambiguous identification of peroxy acids, an improved understanding of their ionization and fragmentation behaviour is needed. To our knowledge, the only systematic investigation of peroxy acid MS/MS fragmentation was conducted by Harman *et al.* (2006). Their study focusses exclusively on aromatic peroxy acids, which are of limited relevance considering the type of peroxy acids thought to be present in SOA. Our study aims to fill this gap and provide insight into the characteristic fragmentations of atmospherically relevant organic peroxy acids.

To study the fragmentation patterns of organic peroxy acids, we synthesized 11 peroxy acids with C₈ to C₁₀ carbon backbones and mono- or diperoxy acid functionality. All peroxy acids were synthesized by reacting the corresponding carboxylic acid with 50% hydrogen peroxide in concentrated sulfuric acid. The following carboxylic acids were used: caprylic acid, pelargonic acid, capric acid, suberic acid, azelaic acid, sebacic acid and D(+)-camphoric acid.

All analyses were performed using an Accela HPLC system with a T3 Atlantis C18 column coupled to an LTQ Orbitrap Velos mass spectrometer via electrospray interface. Both positive and negative ionization mode were employed to analyse the samples. In positive mode, sodium formate was added to enhance the peroxy acid signal intensity through sodium adduct formation.

A chromatogram of a mixture of four dicarboxylic acids and seven of their corresponding peroxy acids is shown in figure 1, demonstrating that the optimised HPLC method is capable of separating a wide range of mono- and diperoxy acids and carboxylic acids in a single chromatogram. We will discuss the specific and characteristic fragmentation patterns of the

synthesized peroxy acids in both positive and negative ionisation mode, highlighting similarities in fragmentation between the different peroxy acids and contrasting their fragmentation patterns with those of the corresponding acids.

The chromatographic separation and mass spectrometry fragmentation patterns (MS/MS) determined in this study will allow characterization of an important but largely neglected compound class, peroxy acids, in atmospheric simulation chamber experiments and in ambient samples with increased confidence.

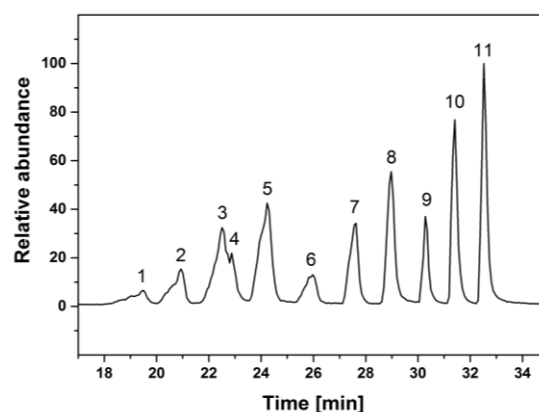


Figure 1. Separation of four dicarboxylic acids and their corresponding peroxy acid analogues: suberic acid (1), monopersuberic acid (2), dipersuberic acid (3), camphoric acid (4), monopercamphoric acid (5), azelaic acid (6), monoperezelaic acid (7), diperezelaic acid (8), sebacic acid (9), monopersebacic acid (10) and dipersebacic acid (11)

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