

Introduction

- Organosulphate formation in laboratory produced SOA from BVOC oxidation [Inuma, et al., 2007a; Inuma, et al., 2007b; Ng, et al., 2008; Surratt, et al., 2008; Surratt, et al., 2007a; Surratt, et al., 2007b] and from reactive uptake of VOCs [Liggio, et al., 2007; Liggio and Li, 2006; Liggio, et al., 2005] in the presence of acidic particles
- Atmospheric relevance of organosulphate and nitroxy-organosulphate originating from isoprene and monoterpenes [Gao et al., 2006; Surratt et al., 2007; Inuma et al., 2007; Gómez-González et al., 2008; Altieri et al., 2008].
- Field evidence: organosulphates may contribute significantly to ambient SOA, ranging from 6-12% [Lukács et al., 2009] or as high as 30% [Surratt et al., 2008].
- The proposed structures of organosulphates suggest a terminal sulphate group with MW ~ 200-300.
- The reaction of epoxides with sulphuric acid is kinetically preferred over the reaction of alcohols with sulphuric acid [Minerath et al., 2008; Minerath and Elrod, 2009].
- Furthermore, epoxides containing tertiary carbon atoms react much faster with acidic sulphate than epoxides containing only primary and secondary carbon atoms [Minerath and Elrod, 2009].
- The reactive uptake of α -pinene oxide, β -pinene oxide, campholenic aldehyde and carveol onto the acidic sulphate particles is investigated to obtain information on the feasibility of organosulphate formation from these compounds.

Experimental

Leipzig Aerosol Chamber (IfT LEAK)



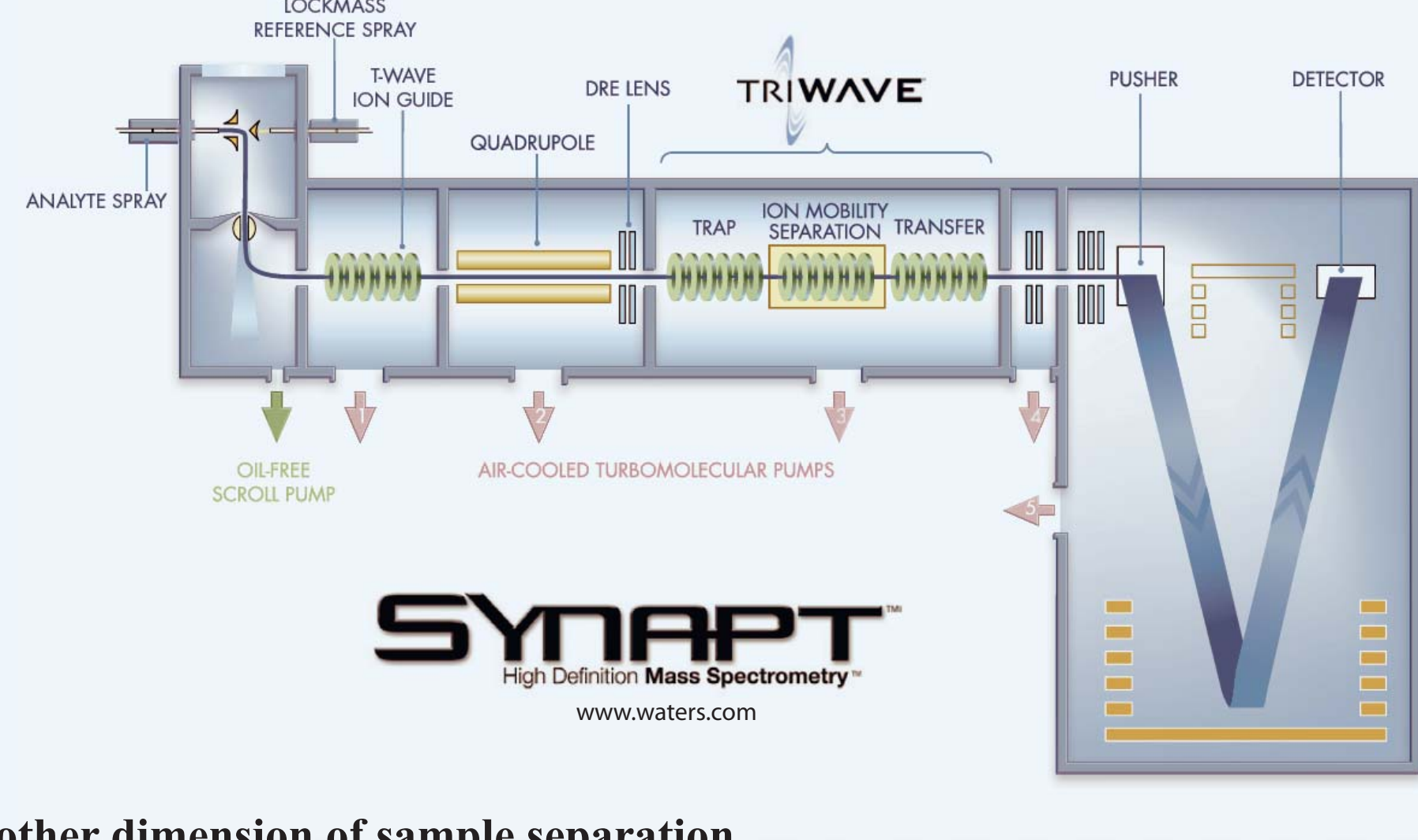
Material:	FEP-Teflon
Volume:	19 m ³
SV Ratio:	2.1 m ⁻¹
Temperature Range:	289-308K (16-35 °C)
Humidity Range:	10-85%
Gas Measurements:	O ₃ monitor, Online GC/FID, PTR/MS, Denuders
Particle Measurements:	Denuder-Filter (UPLC/IMS-QTOFMS, GC/MS), DMPS

Experimental Conditions

	α -Pinene oxide	β -Pinene oxide	Campholenic aldehyde	Carveol
Initial HC Conc. [ppbv]	50	50	50	50
RH%	50	50	50	50
Temp [°C]	22	22	22	22
Reaction Time [h]	1	1	1	1
Sampling [h]	1 (2 m ³)	1 (2 m ³)	1 (2 m ³)	1 (2 m ³)
Seed Particle	0.06M Na ₂ SO ₄ (Neutral) 0.03/0.05M (NH ₄) ₂ SO ₄ /H ₂ SO ₄ (Acidic)	0.06M Na ₂ SO ₄ (Neutral) 0.03/0.05M (NH ₄) ₂ SO ₄ /H ₂ SO ₄ (Acidic)	0.06M Na ₂ SO ₄ (Neutral) 0.03/0.05M (NH ₄) ₂ SO ₄ /H ₂ SO ₄ (Acidic)	0.06M Na ₂ SO ₄ (Neutral) 0.03/0.05M (NH ₄) ₂ SO ₄ /H ₂ SO ₄ (Acidic)

Sample Analysis

Aerosol samples were analysed using an ultra performance liquid chromatography coupled to electrospray ionisation ion mobility spectrometry and quadrupole time-of-flight mass spectrometry (UPLC/(-)ESI-IMS-QTOFMS, Waters Synapt HDMS).



The IMS provides another dimension of sample separation.

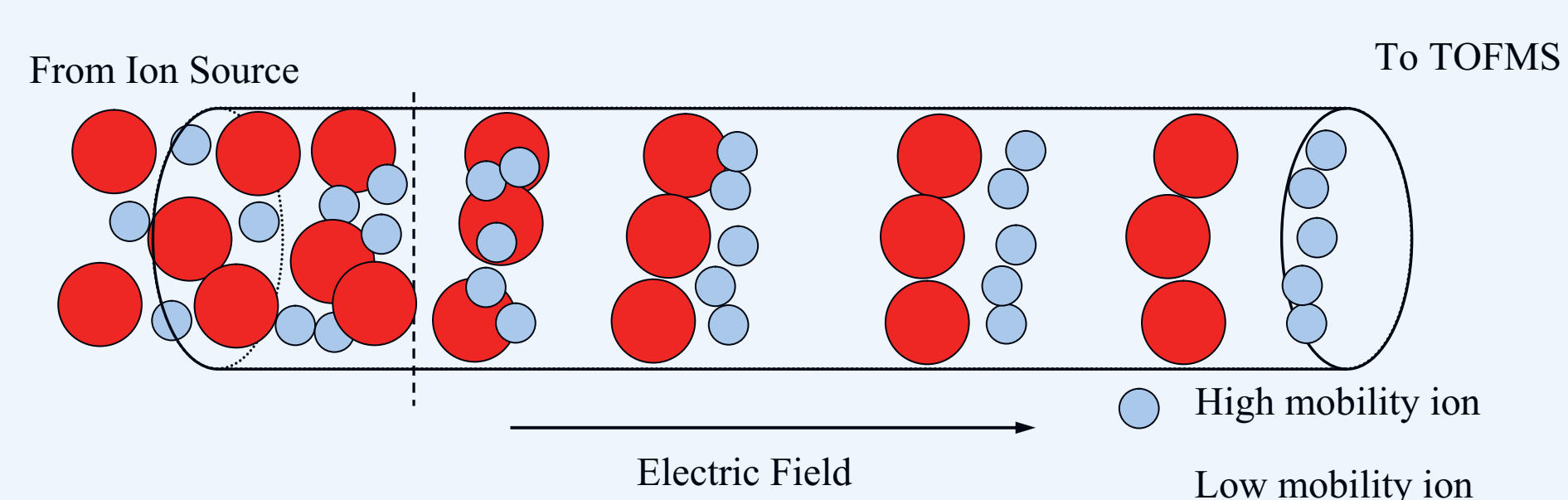
- Ions are separated as they drift through a gas under the influence of electric field.
- Drifting time depends on the mobility of ions.
- Ions of identical mass can be separated based on size, shape and charge.

Mobility can be expressed as follows:

$$K = \frac{\sqrt{18\pi}}{16} \sqrt{\frac{1}{m} + \frac{1}{m_B}} \frac{q}{\sqrt{kT}} \frac{1}{N\Omega}$$

where

q : ion charge
 m : mass of ion, m_B : mass of buffer gas
 k : Boltzmann constant
 T : temperature
 N : buffer gas number density
 Ω : collision cross section



Results

Figure 1: Time series of particle volume increase (ΔV) for all 10 experiments. 'N' and 'A' denote neutral and acidic sulphate seed particles, respectively.

- Particle volume growth was observed for all organic precursors in the presence of acidic seed particles.
- No particle volume growth was observed for all neutral seed experiments regardless of the organic precursors.

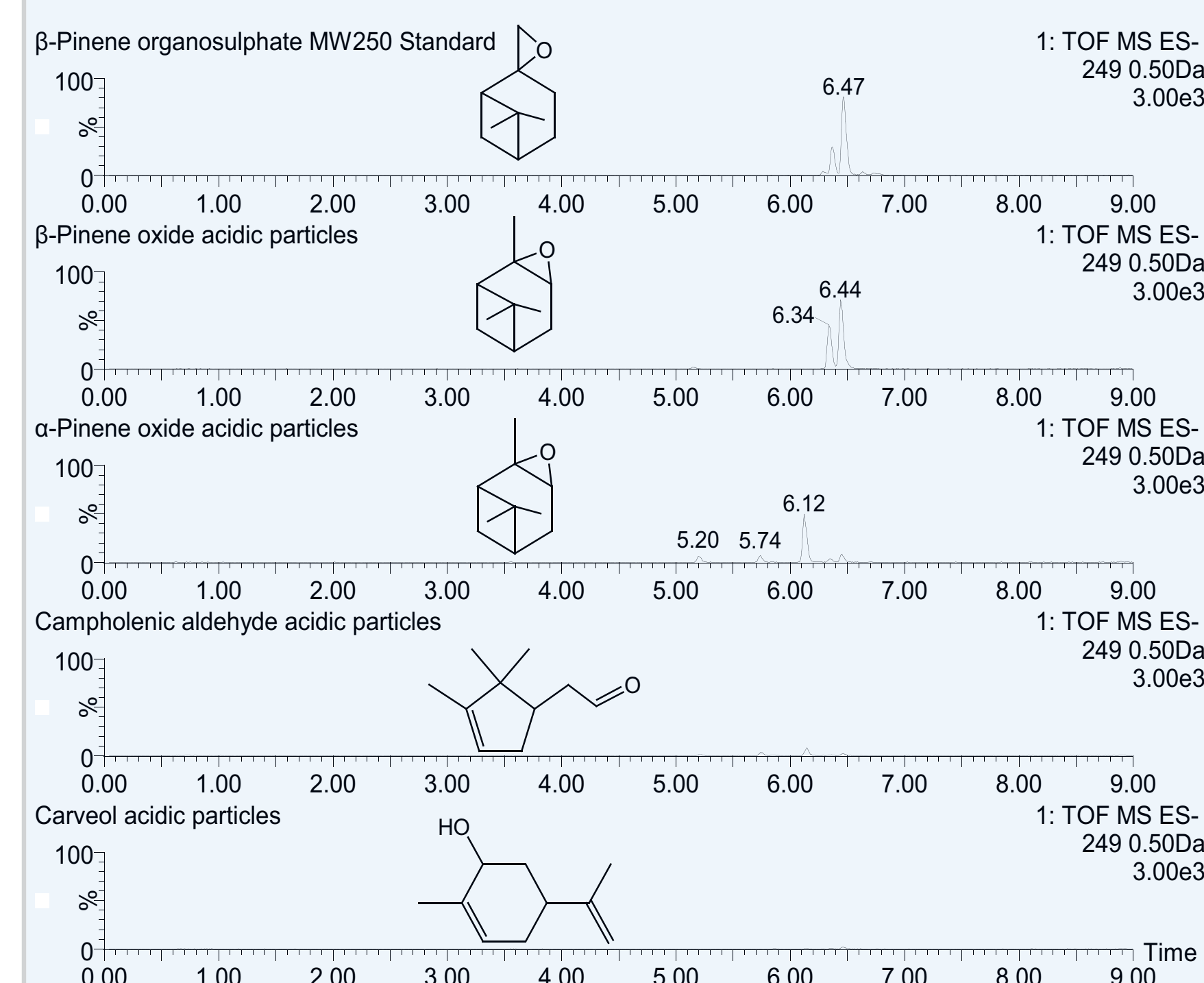
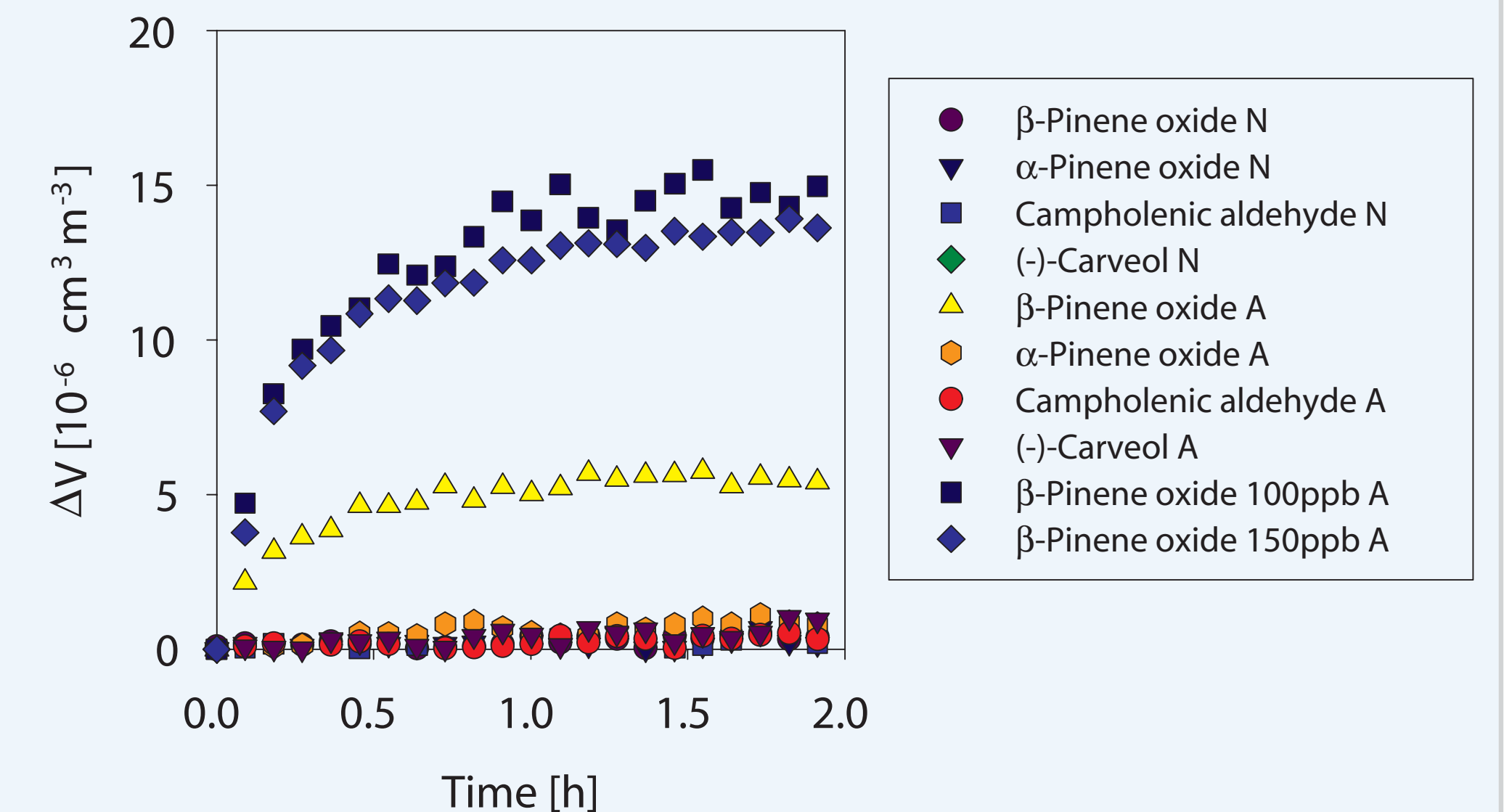


Figure 2: Extracted ion chromatograms (EICs) of m/z 249 obtained for synthesised β -pinene organosulphates and aerosol chamber generated SOA samples. The samples were analysed using Acquity UPLC HSS (high strength silica) T3 column (2.1 × 100 mm, 1.8 μ m particle size, Waters). The eluent composition used was (A) 0.1% acetic acid in Milli-Q grade water and (B) methanol.

- Organosulphates (m/z 249) were present in the SOA produced from the reactive uptake of α -pinene oxide, β -pinene oxide and campholenic aldehyde in the presence of acidic sulphate seed particles.
- No organosulphates were detected in the samples collected from all neutral seed experiments.
- Carveol did not yield organosulphates regardless of seed particle acidity.

Figure 3: MS² data for the peaks from β -pinene oxide originating organosulphates (left) and α -pinene oxide originating organosulphates (right).

- Formation of sulphate radical anion (m/z 95) \rightarrow A sulphate group at a tertiary carbon atom

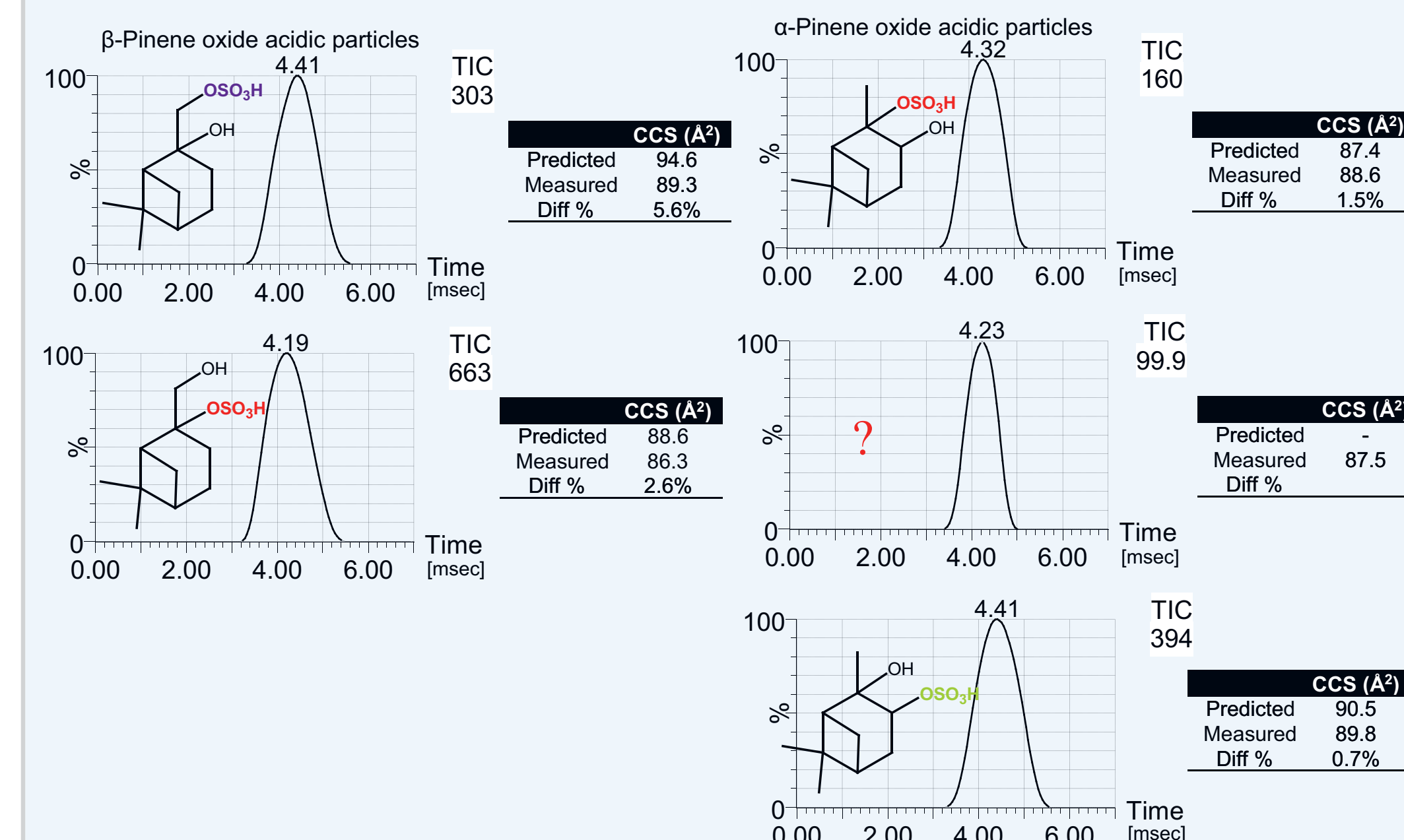
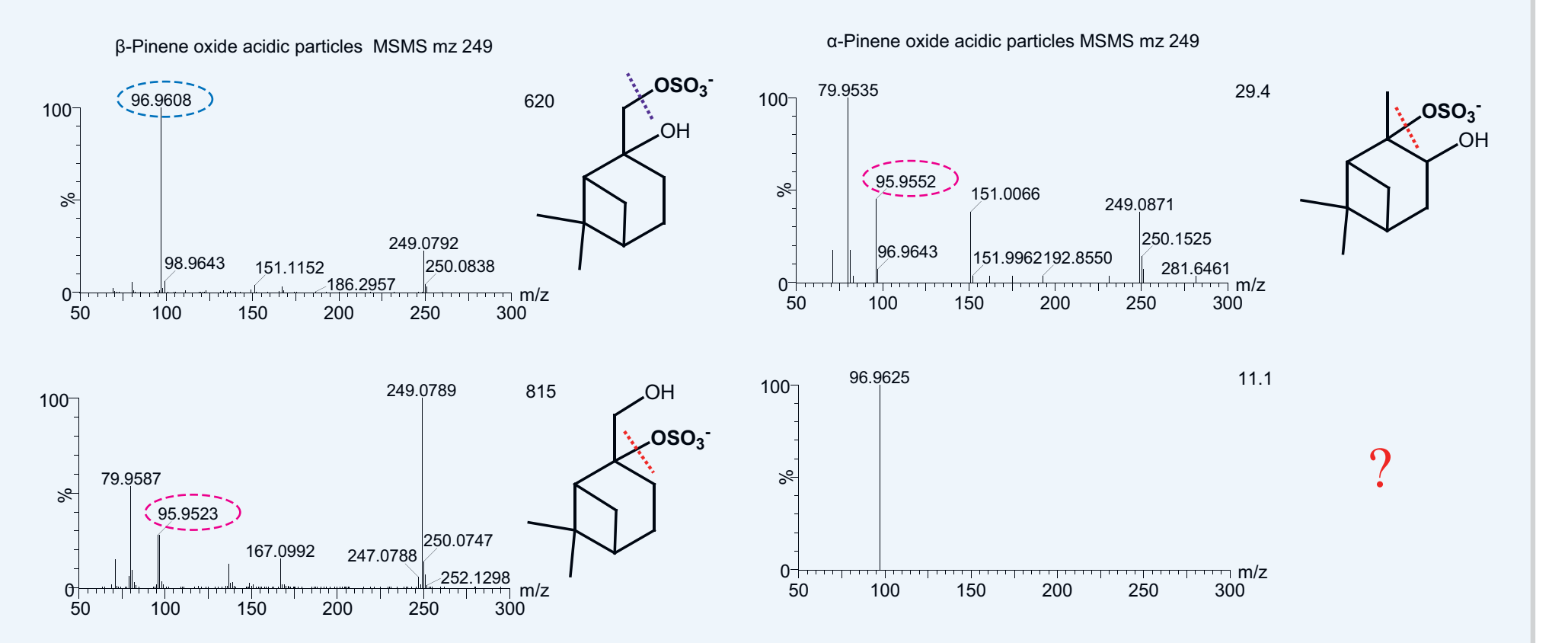
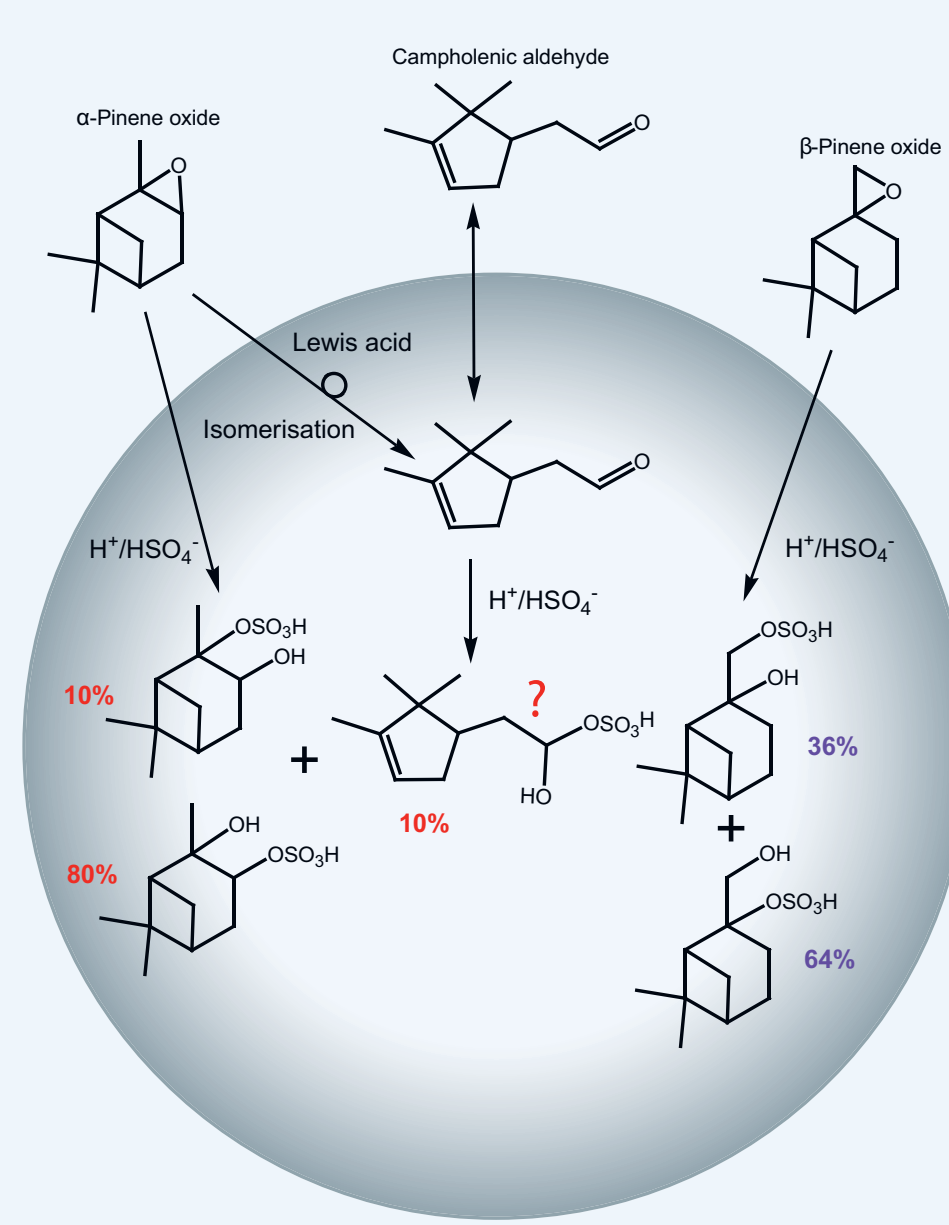


Figure 4: Drifting time obtained from the IMS analysis for the β -pinene oxide originating organosulphates (left) and α -pinene oxide originating organosulphates (right). Collision cross sections (CCS) were predicted using MOBICAL [Mesleh et al., 1996; Shvartsburg and Jarrold, 1996].

- Drifting times correspond well with the positions of a sulphate group
- Measured collision cross sections (CCS) agree well with estimated CCSs.

Summary

- Organosulphate yields
 - β -Pinene oxide > α -pinene oxide >>> campholenic aldehyde >>>>>>> carveol
- β -Pinene oxide
 - A tertiary carbon substituted organosulphate > a primary carbon substituted organosulphate
- α -Pinene oxide
 - A secondary carbon substituted organosulphate > a tertiary carbon substituted organosulphate
 - Lewis and Brønsted acid catalysed isomerisation



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