



EVALUATION OF THE INTERACTIONS OF A TEQOYA TIP9 IONIZER WITH A MIXTURE OF TERPENES (TURPENTINE GAS) BY FT-ICR MASS SPECTROMETRY

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Confidentiality :

YES / ~~NO~~

Table of Contents

1	Materials and methods	3
1.1	Description of the test equipments	3
1.2	Seeding in Terpenes	4
1.3	Monitoring of α -pinène concentration and isomers by FT-ICR mass spectrometry BTRAP	4
2	Results	6
2.1	Fragmentation pattern of α -pinene by PTR-MS	6
2.2	Measurement of semi-volatile particulate aerosol	8
2.3	Measurement of ozone	9
3	Conclusions	10

1 Materials et methods

1.1 Description of the test equipments

A 1m³ polymethyl methacrylate (PMMA) sealed enclosure is used to accommodate the Teqoya TIP9 device to be evaluated. This enclosure has sampling and seeding ports and passages for electrical connections. A 60x60 waterproof access door provides access to the interior of the volume.

A thermometer-hygrometer makes it possible to follow the temperature and the relative hygrometry which reigns within the enclosure.

1.2 Seeding in Terpenes

The box is inoculated by placing inside the chamber a volume of 20 μ L of turpentine. The essence of turpentine is a distillation section of compounds of formula C₁₀H₁₆ whose majority species is α -pinene.

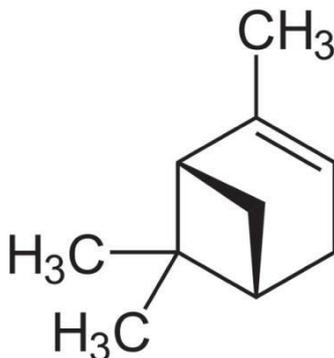


Figure 1: α -pinene (C₁₀H₁₆)

Natural evaporation leads to concentrations of between 2 and 3ppmV in the 1m³ chamber.

1.3 Monitoring of α -pinène concentration and isomers by FT-ICR mass spectrometry BTRAP

The volatile organic compounds are measured by a magnetic trap mass spectrometer using the principle of ion cyclotron resonance.

The BTrap 5 mass spectrometer, brand Alyxan, is based on FT-ICR (Fourier Transform Ion Cyclotron Resonance) whose principle is as follows. The first step is to use a gentle and selective ionization technique: PTRMS (Proton Transfer Reaction Mass Spectrometry: H₃O⁺ + MH₂O + MH⁺). This proton transfer reaction is only possible if the proton affinity of the analyte is greater than that of water (691 kJ / mol). Thus, most Volatile Organic Compounds (VOCs) can be detected except, on the one hand, alkanes, whose proton affinity is lower than that of water and, on the other hand, ionized species, who can not enter the cell because of their charge. Another precursor such as O₂⁺ may be used to detect compounds of NO, NO₂ type or sulfur organic compounds.

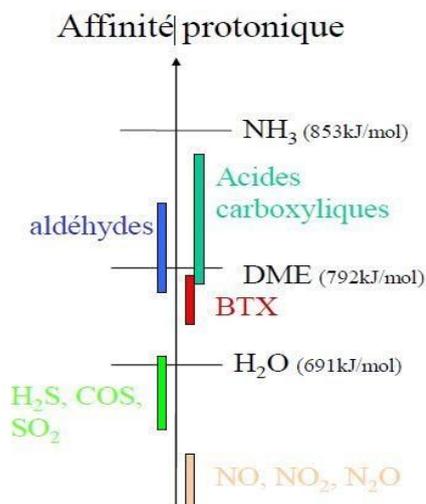


Figure 1 : Diagram of the proton affinities of some VOCs

Once formed, these ions will be collected in a magnetic trap. The application of magnetic and electrostatic fields allows the ions to confine themselves inside this trap and to acquire a cyclotron movement. The detection is based on the measurement of frequencies in the magnetic trap. For this, the ions are excited by an electric field, allowing the latter to increase the energy of the cyclotron movement and to acquire a coherent movement. The current induced by this coherent movement of the ions is then measured by the detection plates, resulting in obtaining a sinusoid damped cyclotronic frequency. Thus, the measured total induced current corresponds to the sum of the sinusoids of the cyclotronic frequencies, which after Fourier transform makes it possible to obtain a mass spectrum.

In these experiments, the ionization precursor used is H₃O⁺ and the measurements were made with concentration membrane. The mass spectrometer operates on the principle of a sampling loop of 12 normoliters per minute, the sampling is carried out in the center of the box and its return on one of the sides so as not to induce dilution of the compounds by a depression of the system.

A monitoring of the internal concentration of the ozone chamber is carried out using an environmental UV absorption analyzer O3-42m Environnement SA with a detection threshold of 1 µg / m³. The particulate numerical concentration in the chamber was also recorded using a TSI 3022 condensation ring counter which counts the particles from 0.007µm with a resolution and detection limit of 1 particle / cm³.

The Teqoya TIP9 device was then turned on after stabilizing the evaporation of turpentine.

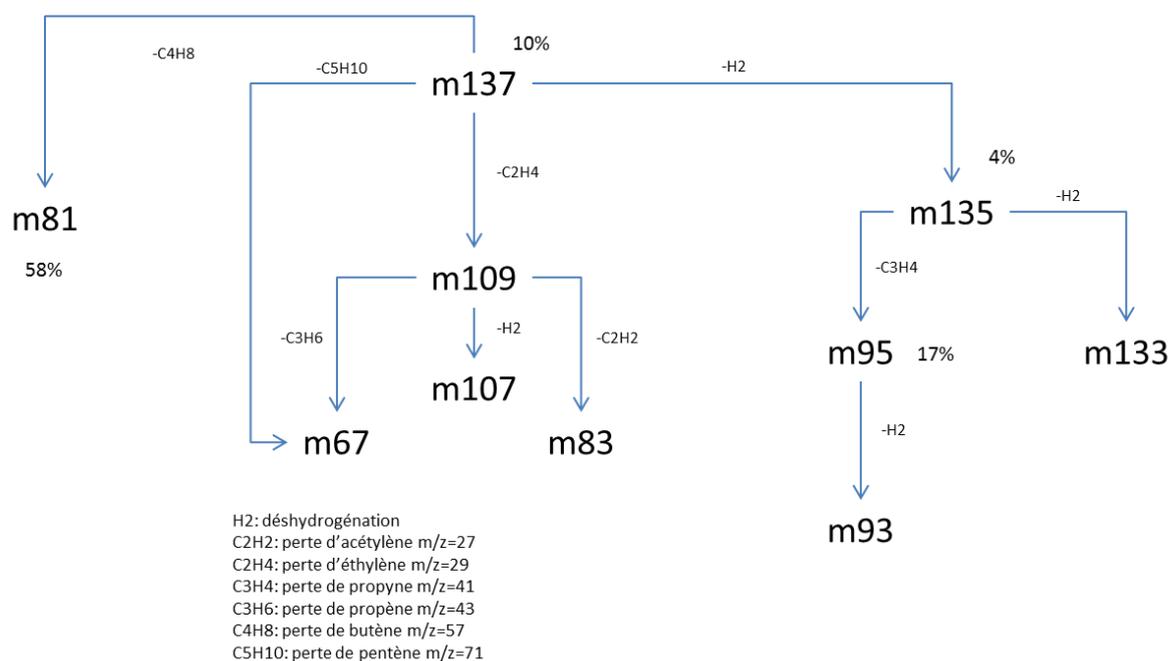
The experiment was carried out with and without the use of a halogen-UV lamp reproducing the solar light spectrum; this is to check for any interaction with ultraviolet radiation.

2 Results

2.1 Fragmentation pattern of α -pinene by PTR-MS

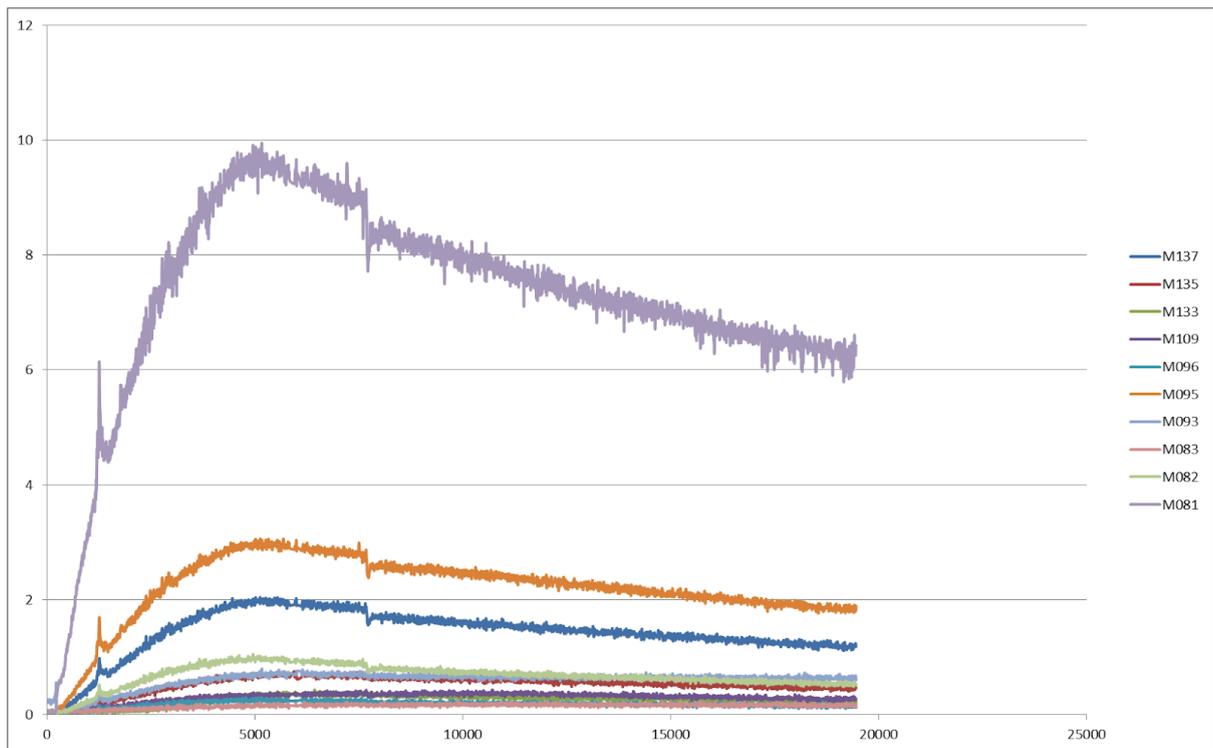
Despite the low ionization energy, turpentine isomers fragment after protonation. Thus, the FT-ICR technology allows the tracking of different fragments over time.

The following fragmentation scheme was determined during the experiments and confirmed by existing bibliographic resources¹.



The evaporation of 20 μ L of turpentine is maximum after 4800s.

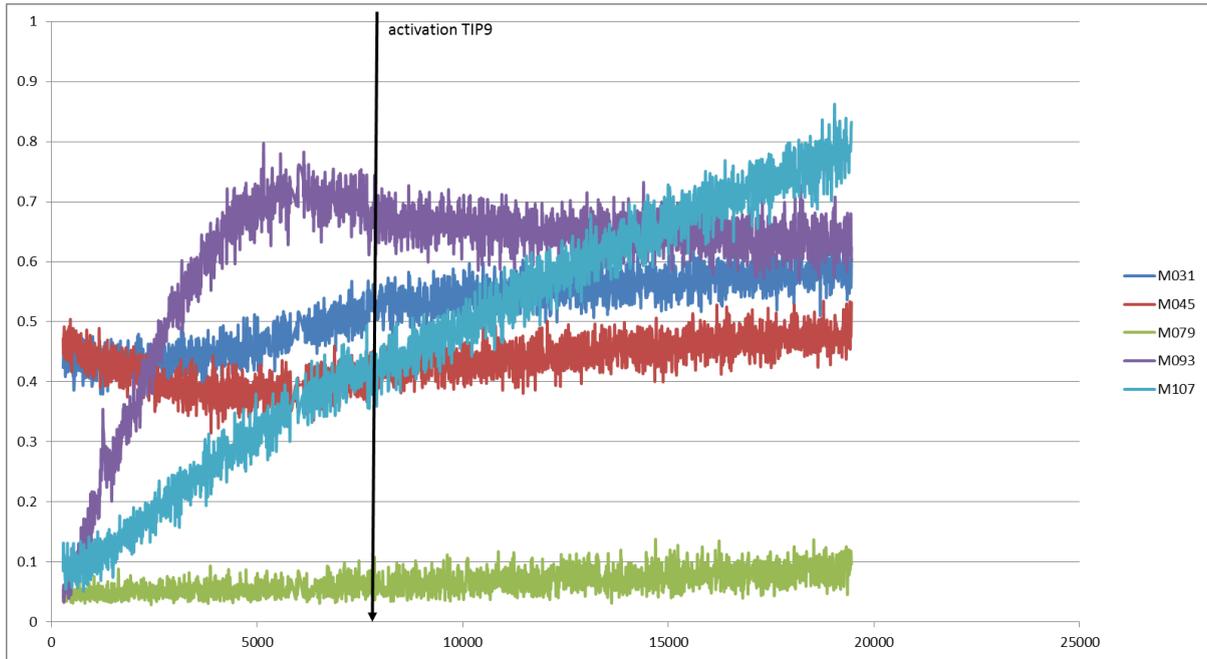
¹ Müller et al. MS/MS studies for the selective detection of isomeric biogenic VOCs. Atmos Meas Tech, 2, 703-712, 2009.



The artefacts observed at $t = 1200$ and $t = 8000$ s correspond to the removal of a low-pressure electrostatic impinger ELPI + in order to determine the size of the particulate aerosol observed (Cf following paragraph).

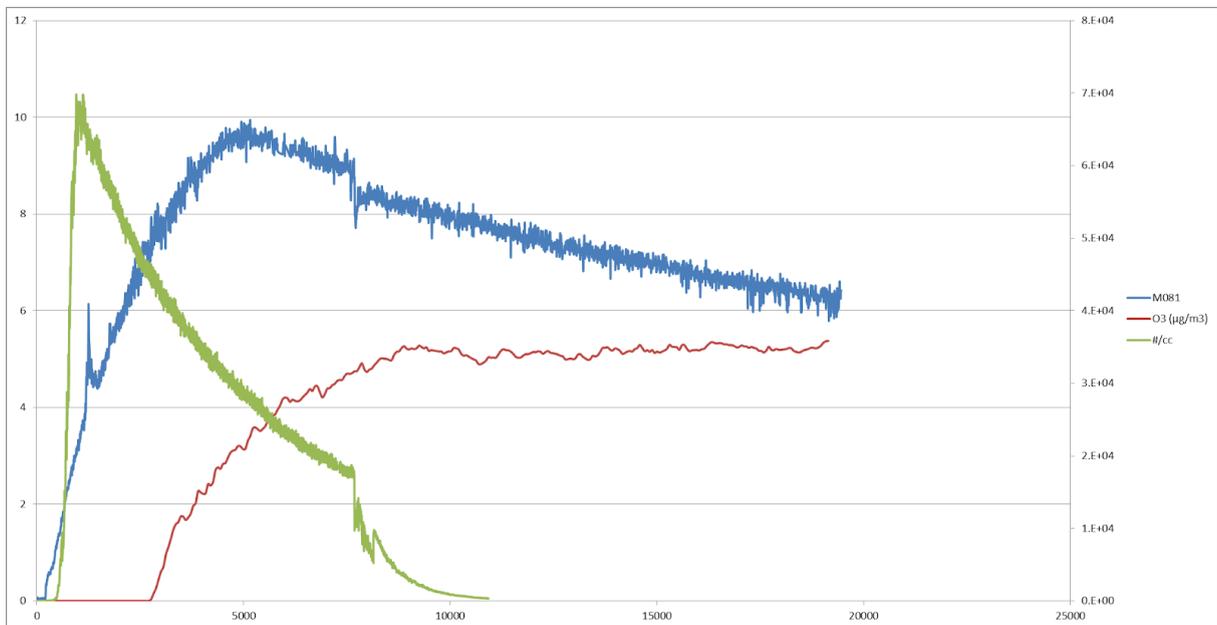
The Teqoya device was turned on at $t = 7678$ s at full power (3/3). No significant impact could be observed on vapors of turpentine.

The monitoring of the masses 31 (formaldehyde), 45 (acetaldehyde), 79 (benzene), 93 (toluene) and 107 (xylene, ethylbenzene) do not make it possible to show an inflection of the kinetics of these species during the use of the TIP9 device. It should be noted that species m93 and m107 are ionization fragments of turpentine compounds.

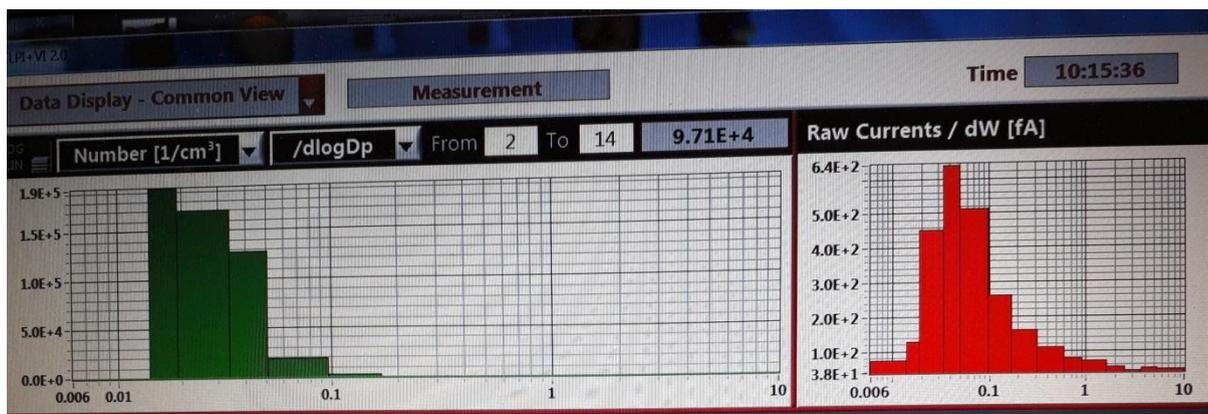


2.2 Measurement of semi-volatile particulate aerosol

Under certain experimental conditions, a semi-volatile particulate aerosol appears during the evaporation of turpentine. This aerosol is composed of ultra-fine particulate droplets and occurs during the evaporation phase.

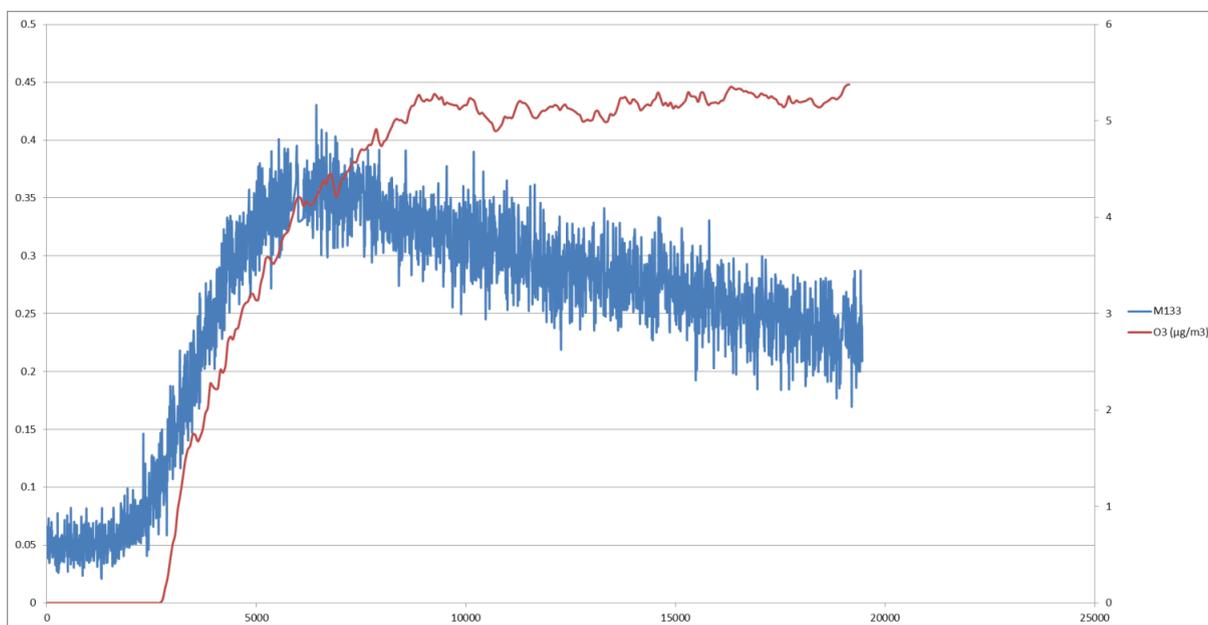


This aerosol, measured with ELPI, has a size between 40 and 60nm at the maximum particle concentration ($t = 1050$) and then forms droplets of greater size (100-300nm) by coalescence phenomena thus explaining the decrease of the concentration in number observed. Activation of TIP9 at $t = 7678$ s causes a sharp rupture in the observed natural particle decay, thus confirming its action on suspended particles.



2.3 Measurement of ozone

A monitoring of the ozone concentration was also carried out in order to determine if the device TIP9 could generate this product and whether it was likely to cause under-reactions of oxidation with the terpenes leading to the formation of other molecules.



During the evaporation phase of the terpenes, the ozone concentration measured in the caisson increases from 0 to 5.5 $\mu\text{g} / \text{m}^3$ and stabilizes at $t = 9180\text{s}$.

Activation of TIP9 at $t = 7678\text{s}$ does not cause a statistically significant increase in ozone concentration.

However, it is not excluded, the terpenic compounds absorbing in the ultraviolet radiation, that there may be an interference between certain evaporated compounds and measurement of ozone by the analyzer (measured at 260 nm). Indeed, the compound $m / z = 133$ identified as 1,2,3,4-tetrahydronaphthalene has absorption maxima of ultraviolet radiation at 259, 266, 274 and 286 nm and has an appearance kinetics correlated with the ozone measurement.

3 Conclusions

The use of the Teqoya TIP9 device under the experimental conditions mentioned above:

- Does not cause the appearance of third-party compounds within the detection limits of the analytical devices used
- Does not produce ozone that can induce side reactions and / or the appearance of secondary organic aerosols
- Exacerbates the decay of the particulate aerosol observed during evaporation of terpenes.

The use or not of a UV lamp does not modify these behaviors.