Monitoring Of Terpene Emissions From Pine Trees By Auto-TDGCs

It has been established that organic aerosols (OA) makes up a major fraction of fine particulate matter in all region of the atmosphere. This fraction accounts approximately for half of the total PM2.5 dry mass.[1,2] Primary OA is directly emitted in the troposphere from anthropological and natural sources whereas secondary OA (SOA) is formed in-situ in the atmosphere from the oxidation of biogenic or anthropogenic gas-phase precursors and subsequent partitioning of the less volatile products into the particle phase. The current number is that, on a global scale, SOA would represent around 60% of the overall OA.[3] However, recent global mass-balance estimations for the removal of volatile organic compounds (VOC) suggest that this number could under-predicts SOA production.[4] Recent field measurements in urban locations are also in support of a larger share, indicating that SOA is the dominant fraction of OA, with amounts considerably 20 greater than models predictions.[2,5,6]

> *The solution is completed and defined as unique solution for VOC/Sulphurs/Odour monitoring showing the strong expertise of Chromatotec in online gas analysis.*

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Studies are being carried out by Kammer and E. Villenave (EPOC, University of Bordeaux) in French Landes forest to assess SOA formation from biogenic origins according to several parameters such as solar radiation, humidity and proximity of the ocean.[7] Landes Forest is located in the south-west of France and is one of the largest forests in Europe (1 million ha), relatively homogeneous with more than 90 % of maritime pines (pinus pinaster) and few anthropogenic inputs. The measurement of monoterpenes (MT) and MT precursors have already been reported to study seasonal variations of Mediterranean Sea emissions[8] and for the characterisation of plant-specific volatile organic compound emission rates.[9]

One of the challenges of this project was to continuously measure the concentrations of specific VOC emitted by the maritime pines of Landes Forest. The cycle time must be short enough so that the kinetics of emissions can be monitored. Also, the types of MT must be identified and quantified accurately. A field deployable analytical system designed by Chromatotec has been used for continuous analysis of VOC. We present, in this article, the methodology and the instruments used to develop the analytical system. First a laboratory study has been carried out to characterise the nature and retention times of VOCs emitted by maritime pines using a TD-GC-FID-MS. Then the method has been optimised to perform on-field measurements with an auto-TD-GC-FID. As sulphur compounds are known to contribute to the global OA mass,[10] a second system specific for sulphur compounds was developed to monitor their concentrations by auto-GC.

Materials and Methods

AUTO-TD-GC-FID-MS methodology

For the laboratory phase, an automatic thermal desorption gas chromatograph, equipped with a Flame Ionisation Detector (airmoVOCXpert from Chromatotec®) and a Mass Spectrometer (DET QMS from Chromatotec®) was used to characterise the different compounds emitted by maritime pines and to establish the complete list of compounds to be monitored during the field campaign. The list will be used to create the substance table needed in the auto-GC. The integrated TD device comprises of a mass flow controller, to control the flow and time of pre-concentration and a one phase trap specific for VOCs. It is not needed to use a drying system for such a trap, which reduces the risk of adsorption of analyst. 30 and 60 meter non-polar metallic capillary columns were tested.

AUTO-TD-GC-FID methodology

The analytical system used for the field measurements utilises an automatic thermal desorption gas chromatograph equipped with a Flame Ionisation Detector (airmoVOC C6-C12 from Chromatotec®), an air generator for the flame of the FID and valve actuation (airmopure from Chromatotec®) and a hydrogen generator 99.9999% (Hydroxychrom from Chromatotec®). The integrated TD device comprises a one phase trap specifically chosen for Terpenes analysis.

AUTO-GC-MEDOR®

Sulphur compounds were analysed in laboratory and on-site using an automatic gas chromatograph with 250 µl loop injection and equipped with a MEDOR® electrochemical sulphur specific detector (TRS MEDOR from Chromatotec®). A nitrogen generator 99.9995% was used for valve actuation and carrier gas (Nitroxychrom from Chromatotec®). The instrument can measure sulphur at ppb level in ambient air.

Calibration and results validation

As for all analytical systems from Chromatotec®, quality controls of the instruments were performed using NIST certified cylinders. TO15, TO14 and PAMS 58 (from Takachio) were used for the calibration of instruments and response factor calculations for the VOCs. PAMS 58 includes α-pinene and β-pinene. We measured experimentally that both molecules had the same response on the FID. Therefore we applied the same RF for all MT.

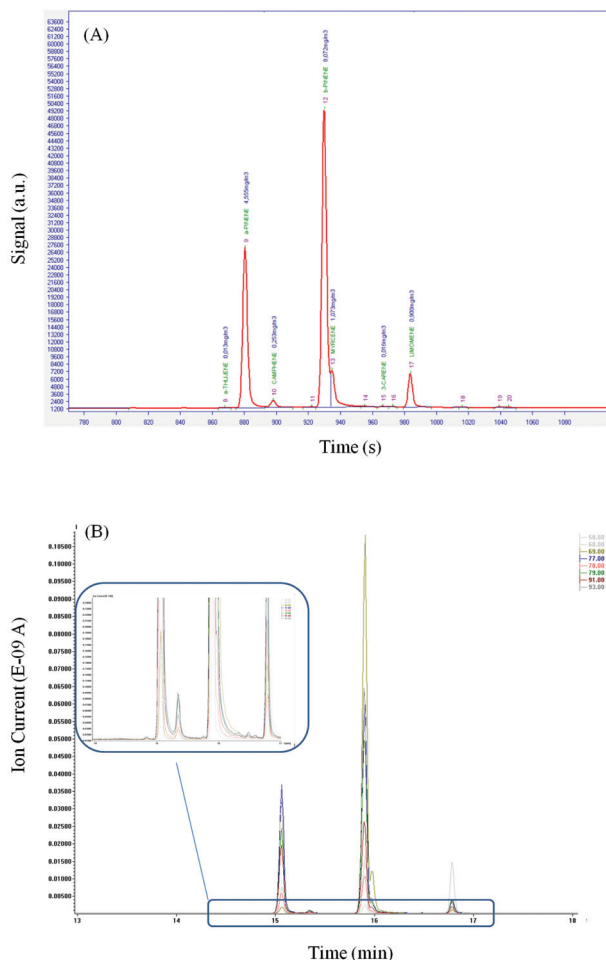*Chromatotec's New Online Monitoring Station in Andernos city*

The analytical system for sulphur measurement was calibrated with a certified sulphur compounds cylinder (from NPL London). During the measurement campaign in the forest, Benzene and Dimethyl sulfidde permeation tubes were installed in an internal oven to check the sensitivity and stability of airmoVOC C6-C12 and TRS MEDOR respectively.

Results and discussion

Laboratory phase

To optimise the method for terpenes measurement, the first step was to know what species to expect. Therefore, we collected broken pine twigs and pine needles and placed them in a glass container for laboratory analysis. The results are shown on fig.1. Several terpenes were detected, including α-thujene, α-pinene, camphene, β-pinene, myrcene, 3-carene and limonene, all well separated on the 30 m column, and all well identified on both FID (fig. 1 A) and MS (fig.1 B). The MS confirms the time at which compounds elute from the column. α-pinene and β-pinene represents 84% of the overall Terpenes mass analysed from broken pine twigs and pine needles.

Figure 1: Auto-TD-GC-FID-MS chromatograms obtained with a 30 minutes cycle time. (A) Chromatogram with FID. (B) Chromatogram with MS.

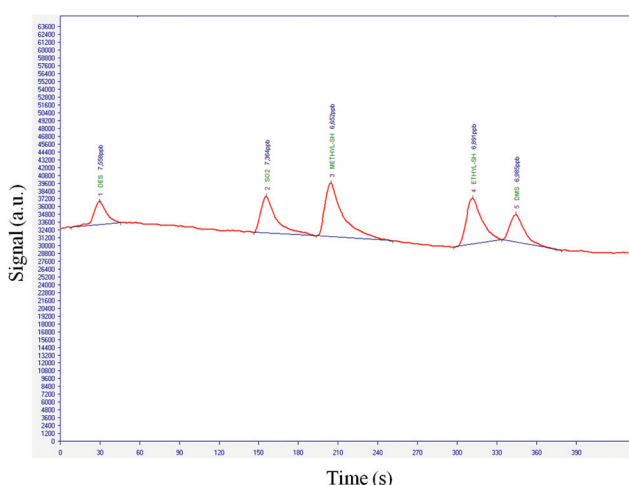As expected, the most abundant compounds are α- and β-pinene, tracers of pine trees.

To optimise the method for sulphur compounds measurement, an analytical gas standard containing five common sulphur species was used. The five species are diethylsulfide (DES), sulphur dioxide (SO_2), methylmercaptan, ethylmercaptan, and dimethylsulfide (DMS). The results are shown on fig.2. The five compounds were well separated and detected at concentrations below 10 ppb.

Figure 2: Auto-GC-MEDOR chromatogram obtained with the mix of sulphur compounds (NPL certified cylinder).
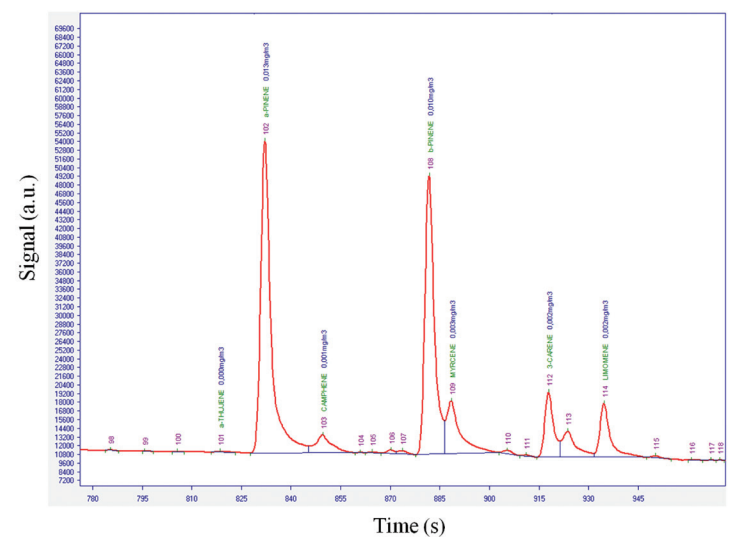

Terpenes concentrations at Landes Forest border

Measurements in the Landes Forest have been carried out by J. Kammer and E. Villenave (EPOC, University of Bordeaux). Part of the results have already been presented by E. Villenave at the 12th workshop on Air Quality in Urban and Remote Areas and its Impacts on Climate Change and a scientific article will be published soon with all results from this study. In this article, we do not show results from this campaign but we focus on the capability of the instrument to identify and quantify accurately maritime pine emissions continuously.

In fig.3 is shown a chromatogram obtained at 50 km from the Landes Forest (Saint-Antoine, France). The main compounds measured are α-pinene, camphene, β-pinene, 3-carene and limonene. α- pinene and 3-carene are the most concentrated compounds monitored in the forest.
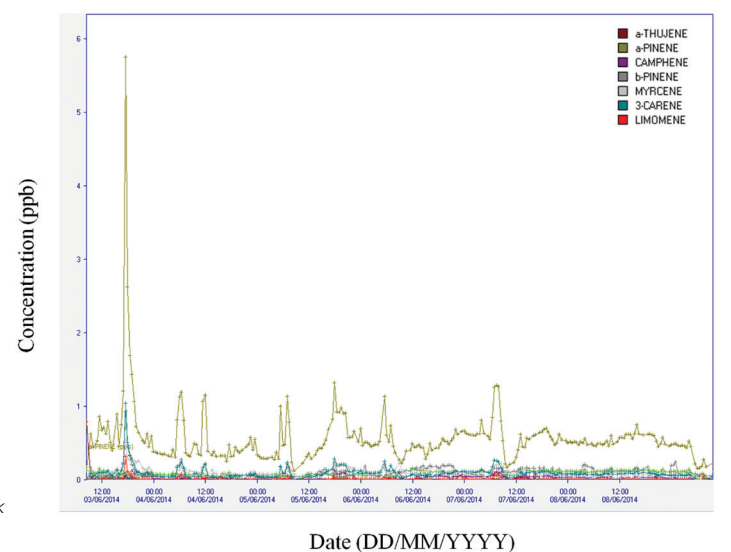

Figure 3: Auto-GC-FID chromatogram obtained at 50 km from the forest.

In fig.4, the concentrations of MT are displayed for one week. α- pinene represents 58% of the overall MT mass measured with a concentration varying from 0.72 to 32.7 µg/m3. The ratio α- pinene/β-pinene is more important when we measure at 50 km from the forest than directly above pine twigs and pine needles. In fig.4, we do not have a clear variation of concentrations from day to night. This might be due to the weather conditions that may impacts the MT production and transport.

The sulphur compound measurements were not relevant for this study. The concentrations were below the limit of quantification of the instrument (below 1 ppb). The station was probably too far from the sea which is the main source of sulphur emissions. Another campaign will be carried out using an AUTO-GC-MEDOR equipped with a thermal desorber specific for sulphur compounds.

Figure 4: Concentration of MT measured every 30 minutes for one week

Conclusion

Thanks to this study, it was possible to identify and quantify accurately the levels of α-thujene, α-pinene, camphene, β-pinene, myrcene, 3-carene and limonene emitted by maritime pine trees. Other MT have been analysed in laboratory but were not measured with the pine trees. Chromatotec solutions are clearly designed to follow the concentration variations of each Terpene with a cycle time of 30 minutes. These solutions complete the portfolio of the product line dedicated for Air Quality monitoring. The solution is completed and defined as unique solution for VOC/Sulphurs/Odour monitoring showing the strong expertise of Chromatotec in online gas analysis.

Chromatotec are celebrating 40 years of expertise in gas analysis. An inauguration of dedicated online monitoring station in Andernos city (close to the sea) will provide more information on the method of innovative solutions for such study.

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