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Characterization of Biogenic Emissions by Online Thermal Desorption Gas Chromatography-Mass Spectrometry

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Summary

The novel GERSTEL Online TDS G was developed to allow fast, reliable and continuous analysis of airborne compounds. For the described application the total analysis time, including GC runtime, is about 1 hour. Sampling is done in parallel with gas chromatographic analysis.

Introduction

Volatile Organic Compounds (VOCs) are important trace atmospheric gases because they participate in many chemical processes occurring in the troposphere (0 - 12 km height). During tropospheric ozone formation, the VOCs act as fuel while nitrogen oxides NO_x ($NO + NO_2$) act as catalysts. Tropospheric ozone is mainly produced during summertime smog episodes. However, car exhaust is not the only source of VOCs. VOCs are emitted from natural (biogenic) as well as from human (anthropogenic) sources. Estimates by several authors [1-3] lead to the assumption that, on a global scale, the emission strength of biogenic VOCs is about 10 times higher than that of anthropogenic sources. However, on a regional scale the contribution of

biogenic VOCs to photochemical ozone formation is not known. Some new results from field measurements made at Schauinsland (close to the city of Freiburg in southwestern Germany) indicate that biogenic VOCs are responsible for 60 % of total reactions with OH-radicals [4].

To determine the mechanisms of VOC emissions from higher plants, an experimental system was built at Forschungszentrum Jülich as part of a joint venture with GERSTEL GmbH. This experimental system allows investigations of biogenic emissions under controlled environmental conditions. The main compounds emitted by plants are 2-methyl-1,3-butadiene (isoprene, C_5H_8), monoterpenes ($C_{10}H_{16}$), including a couple of oxygenated varieties as well as sesquiterpenes ($C_{15}H_{24}$). Some of these compounds are emitted as signal molecules [5], as defense compounds against attack by herbivore or bacteria, or as signal molecules to attract natural enemies of parasites [6-7]. In order to determine these airborne compounds, a novel, automated online thermal desorption (Online TDS G) device was developed in collaboration with GERSTEL GmbH. This online thermal desorption system is used with a Hewlett Packard GC (HP 5890 Series II) that is directly coupled to a quadrupole mass selective detector (HP 5972 A, MSD). The system is now commercially available and it is described in this article.

Alternative Techniques for VOC Concentration Measurements

Measurements of biogenic VOCs require an enrichment step because their concentrations in the atmosphere are in the pptV to ppbV (pmol/mol to nmol/mol of sampled air) range. Cryogenic or adsorptive devices can be used for the enrichment. Adsorptive sample enrichment is feasible with classical adsorbents, such as charcoal, graphitized carbon black, porous polymers or novel adsorbents like polydimethylsiloxane particles (PDMS) [8]. The choice of the adsorbent depends on the method of elution. However, not all adsorbents are suitable for thermal desorption.

Solid phase extraction (SPE) of sample analytes followed by elution with solvent mixtures is a time consuming process. Furthermore, SPE can lead to large sample dilutions. Hence, large sample volumes (100 - 150 L) and often long sampling times are necessary, making the process difficult to automate. In contrast, the GERSTEL Online TDS G is highly automated, and through the use of a standby cooling mode, allows sampling at a constant temperature during the chromatographic analyses. High desorption flows (20 - 100 ml/min) are made possible by providing a split flow at the TDS G as well as at the Cooled Injection System (CIS), that acts as a cryotrap and inlet. The system configuration allows a column flow of less than 2 ml/min, which is needed to directly couple the column to the MSD. Furthermore, blank measurements and calibrations can be made at any time during the analysis.

Instrumentation

The GERSTEL Online TDS G (Figure 1) is built from a modified GERSTEL ThermoDesorption System (TDS 2), a heated Valco 6-2-way valve, and a mass flow controller. A CIS is connected to the Valco valve. The CIS is used to focus the thermally desorbed compounds before injection onto the capillary column. Figure 2 shows a schematic diagram of the adsorption-desorption cycle. An advantage of this configuration is that the direction of the gas flow is reversed between sample adsorption and desorption. This prevents the adsorbed compounds from having to pass through the entire adsorbent bed.

Figure 1. The GERSTEL Online TDS G.

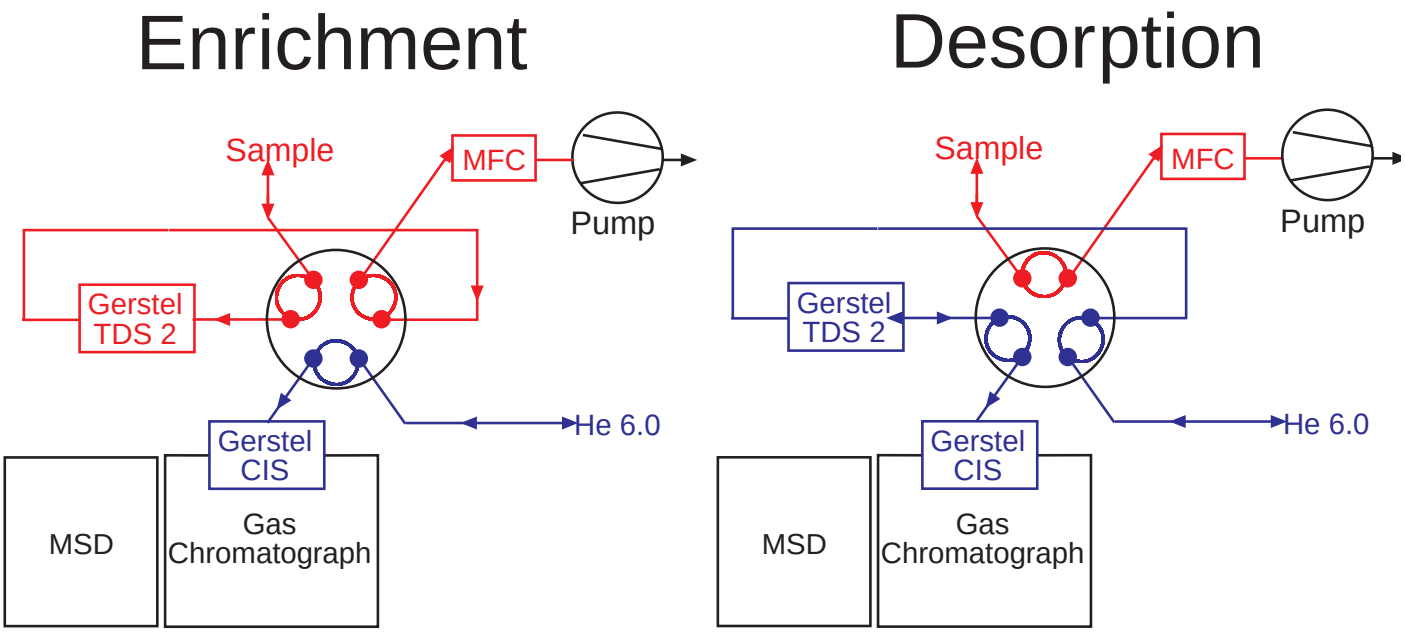

Figure 2. Schematic flow diagram of the adsorption and desorption cycle.

Material and Methods

The porous polymer Tenax TA (60/80 mesh) is a suitable adsorbent for the terpenoid compounds [9-10]. A second adsorbent phase is necessary to avoid loss of C5 - C7 hydrocarbons. The graphitized carbon black Carbotrap (20/40 mesh) is used for this application. The CIS is cooled by liquid nitrogen to -100 °C. Furthermore, the inlet liner is filled with an adsorbent. Here Tenax TA, or the graphitized carbon black sorbent Carbopack B is suitable. This increases the surface area and reduces the dead volume. A non-polar column (5 % phenyl / 95 % methylpolysiloxane) is used for the separation of the compounds. In this case, a BPX-5-capillary column (50 m x 0.2 mm x 1 µm; SGE) is used. Figure 3 shows the suitability of the column for the analysis as well as the performance of the CIS as a cryotrap.

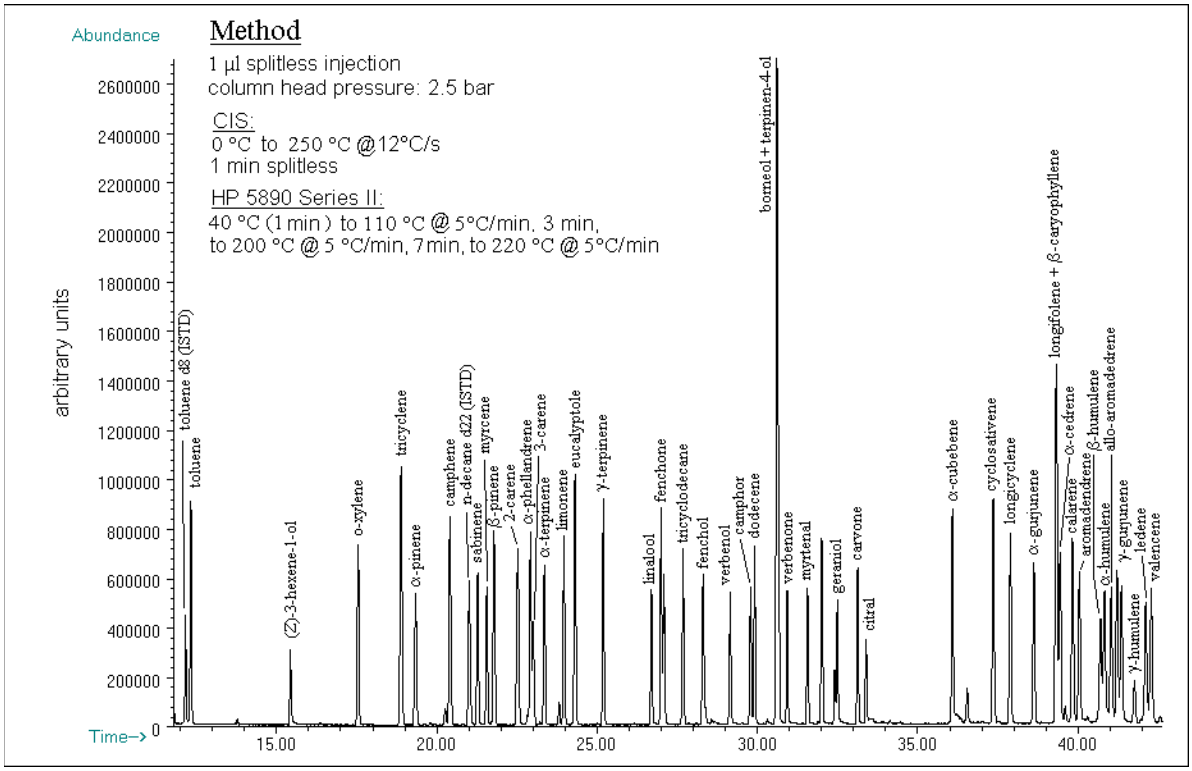

Figure 3. Chromatogram (Total Ion Current; TIC) of a complex liquid standard of monoterpenes, oxygenated terpenes and sesquiterpenes. 1 µL sample was injected into the CIS.

A permeation source that delivers the compounds at a constant concentration is used for calibration. The permeation rates are controlled gravimetrically. To determine the performance of the analytical system, deuterated decane (D22) acts as an internal standard (ISTD). This compound is provided by a separate permeation source, and is added to every sample. A schematic diagram of the setup for calibration and sampling is shown in Figure 4.

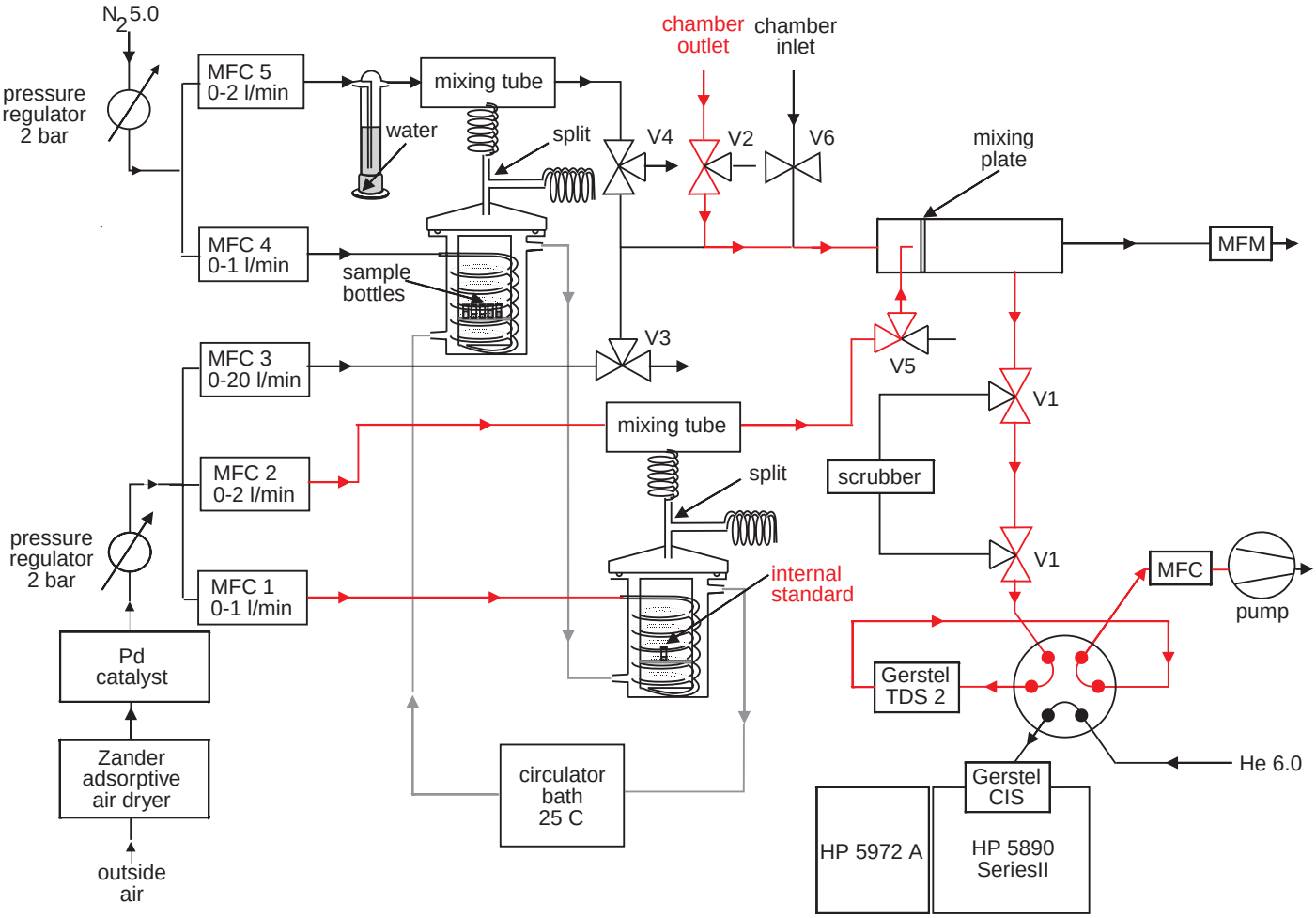

Figure 4. Schematic diagram of calibration and sampling system.

Pure chemicals are stored in separate sample bottles that are equipped with septa with different size holes. The hole size is determined by the vapor pressure of the compounds. The sample bottles are sealed with Teflonâ membranes and stored in a thermostatically controlled glass vessel. A mass flow controller is used to provide a constant nitrogen flow through the vessel. A split vent is installed at the exit of this vessel. After this, another dilution step is employed to obtain concentrations in the ppbV range. Valve V2 is used for enrichment from the exposure chamber and the ISTD is added through valve V5. Valve V1 switches the airflow over an ozone scrubber, if necessary. For calibrations, valves V2-V4 are switched. Calibration gas, which has been diluted with cleaned air (V3), is available from valve V4.

Detection limits for the compounds range from about 1 pptV to 5 pptV depending on the quantitation mass. Reproducibility is typically better than 8 %, and breakthrough does not occur for sample volumes up to 5 L. The time needed to run the entire method is about 1 hour. The thermal desorption portion takes 9 minutes while 47 minutes are necessary for the GC analytical run. These 47 minutes can be used for adsorption of the next sample.

Several authors [11-14] have already described the suitability of this method for measurements of biogenic hydrocarbons. The suitability of this method is further demonstrated by comparison of the results obtained with thermal desorption to those obtained with liquid injection (Figure 5). A series of calibration standards were measured with both methods. Sensitivities were normalized to the molar mass of the compounds for both methods. The

resulting responses were normalized to monoterpene α-pinene, because this compound is thermally stable and tends not to rearrange. Both methods show similar trends for the normalized response with deviations of about 10%. The determination of isoprene and hexane is impossible by SPE, because a solvent mixture of benzene and acetonitrile (4:1) has to be used for this application and these compounds elute during the solvent delay of the MSD. However, the quantitation of isoprene emissions is important for VOC measurements. Compared to liquid injection, some sesquiterpenes show lower responses when thermal desorption is used for the analysis. This is attributed to condensation of these high boiling compounds at the interface between the valve and the CIS. This happens because the CIS is cooled to -100°C and no auxlliary heating is supplied to the interface. Installing additional heating capabilities at the interface significantly reduced this problem.

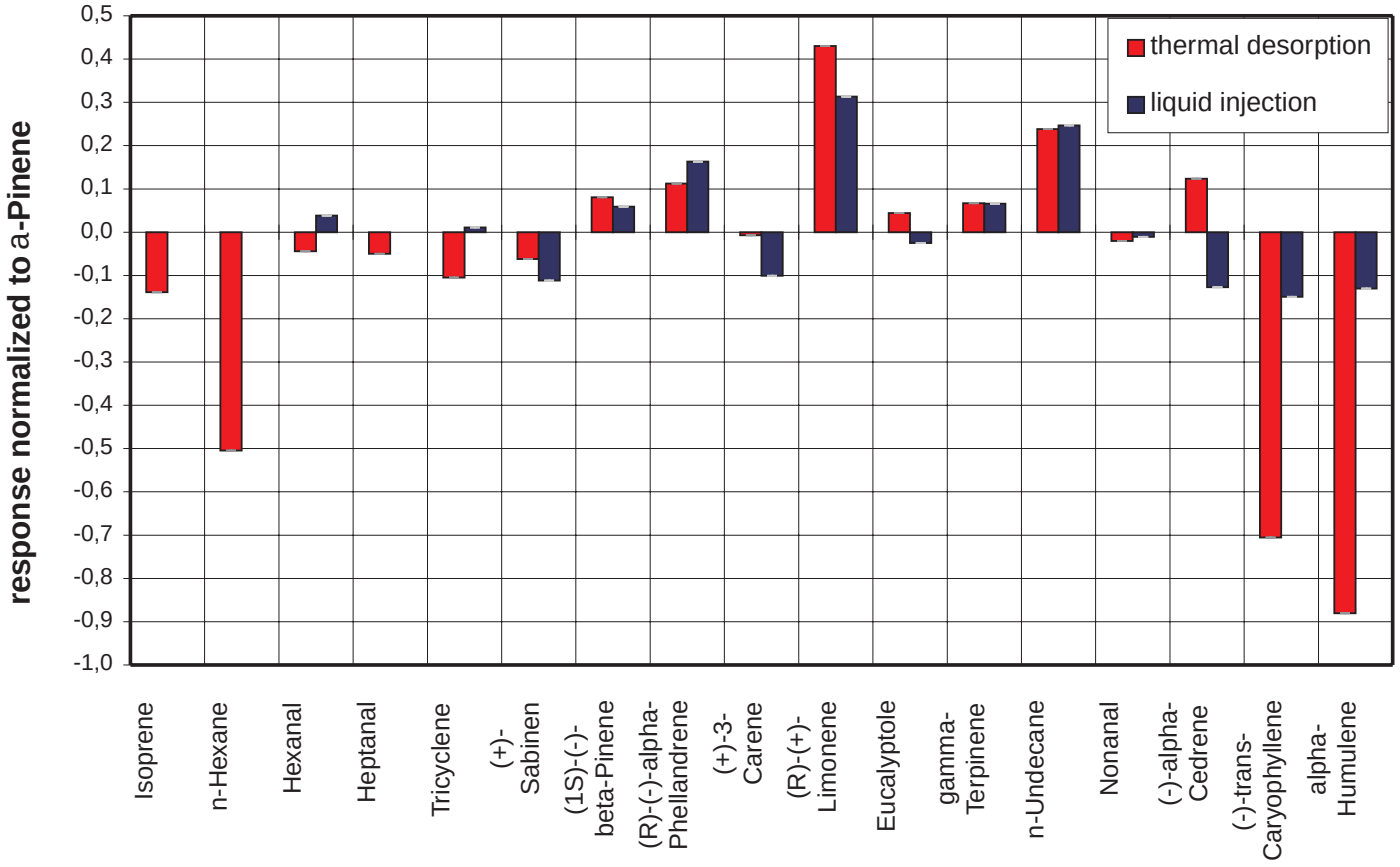

Figure 5. Comparison of liquid injection and thermal desorption methods. Compounds are first normalized to their molar mass and then normalized to the monoterpene α-pinene internal standard.

EXPERIMENTAL

The investigation of factors that control the emission of biogenic VOC's requires an experimental system that allows well defined variations of single parameters. Such a system is installed at Forschungszentrum Jülich. A schematic diagram is shown in Figure 6.

The upper part of the chamber, containing stems and leaves of the plants, is separated from the lower part, containing the plant's roots and the nutrient solution, by sheets of Teflon. The plant stems are fed through holes in the sheeting. Illumination is provided by twelve gas discharge lamps. A mass flow controller adjusts the flow of cleaned air (Pd-catalyst) through the chamber. Concentrations of important compounds (CO2, H_2O, NO, NO_2, O_3 and VOCs) are measured at the chamber inlet and chamber outlet. The hydroponic system [15] provides reproducible amounts of nutrients to the plants as well as determining the uptake of main nutrients by the plants. The whole system is fully automated and data are collected by a central data acquisition system.

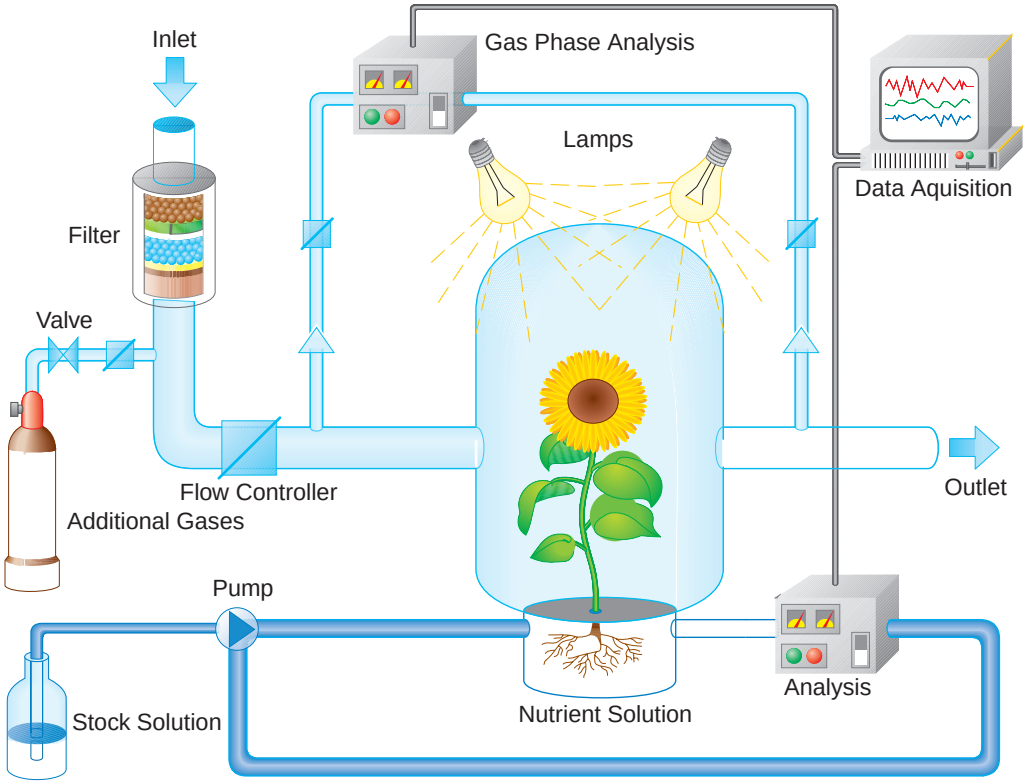

Figure 6. Setup of the exposure chamber.

Results

VOC emission from plants is affected by temperature, light intensity and several stress factors. These are; wounding (e.g. by parasites), air pollutants, and the availability of water and nutrients. Plants commonly react to stress factors by increasing emissions of VOCs [16, 17]. An example is shown in Figure 7.

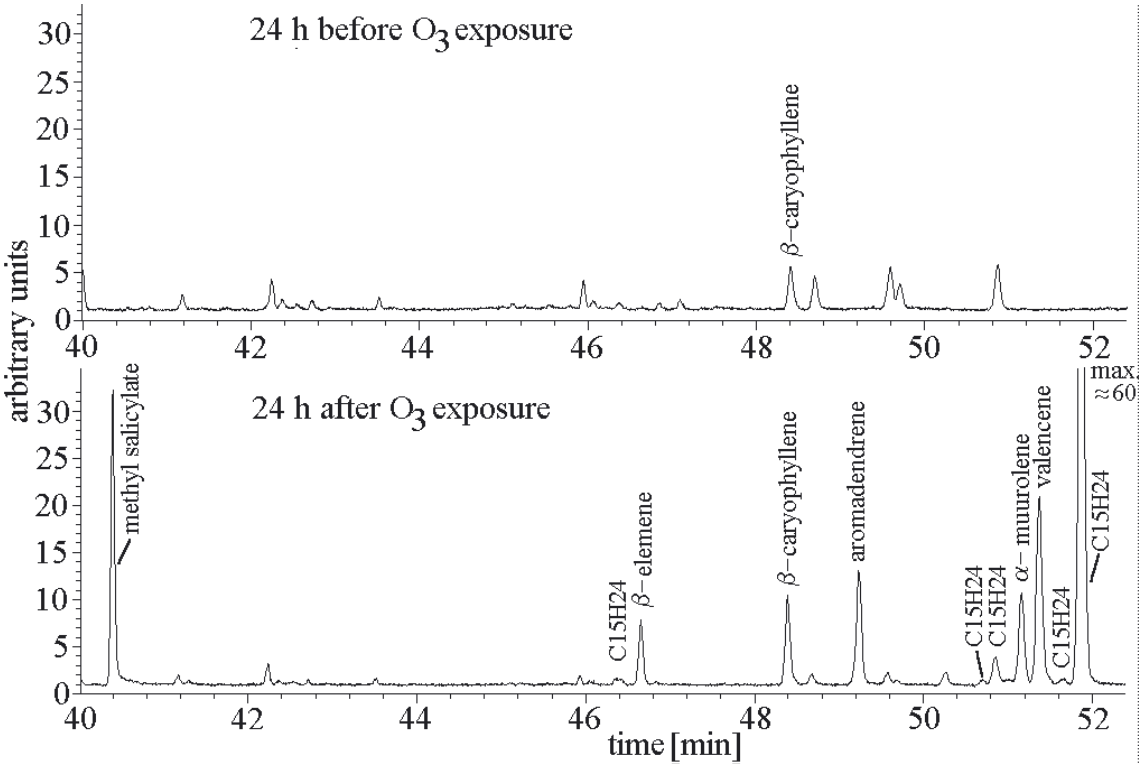

Figure 7. Chromatogram (TIC) obtained from tobacco plants one day before (upper figure) and one day after ozone exposure (lower figure).

In this context it is interesting that different kinds of stress lead to different VOC emissions [18]. For example, wounding leads to emission of (Z)-3-hexenol but not to emission of methyl salicylate. In some cases of stress, compounds are produced de novo. Furthermore, the time at which the emissions occur is different for different stress factors.

Emission rates are calculated from the measured concentrations. After normalization to the chamber flow and leaf area of the plants, they are given in units of [mol·cm^{-2}·s^{-1}]. Figure 8 shows a time plot of emission rates of valencene and methyl salicylate from tobacco plants after exposure to ozone. The plants are fumigated for 5 h with an ozone pulse of 150 ppbV. This is equivalent to a concentration of about 300 µg/m^{-3}, a value far above ozone concentrations during ozone alerts. However, the effect of ozone fumigation as well as the different timing of the emissions is clearly demonstrated by the figure. The maximum emissions of both compounds are displaced in time, and the increased emission of sesquiterpene starts during ozone fumigation, but decreases in the evening. In contrast, wounding of tobacco plants results in spontaneous emissions of different VOCs.

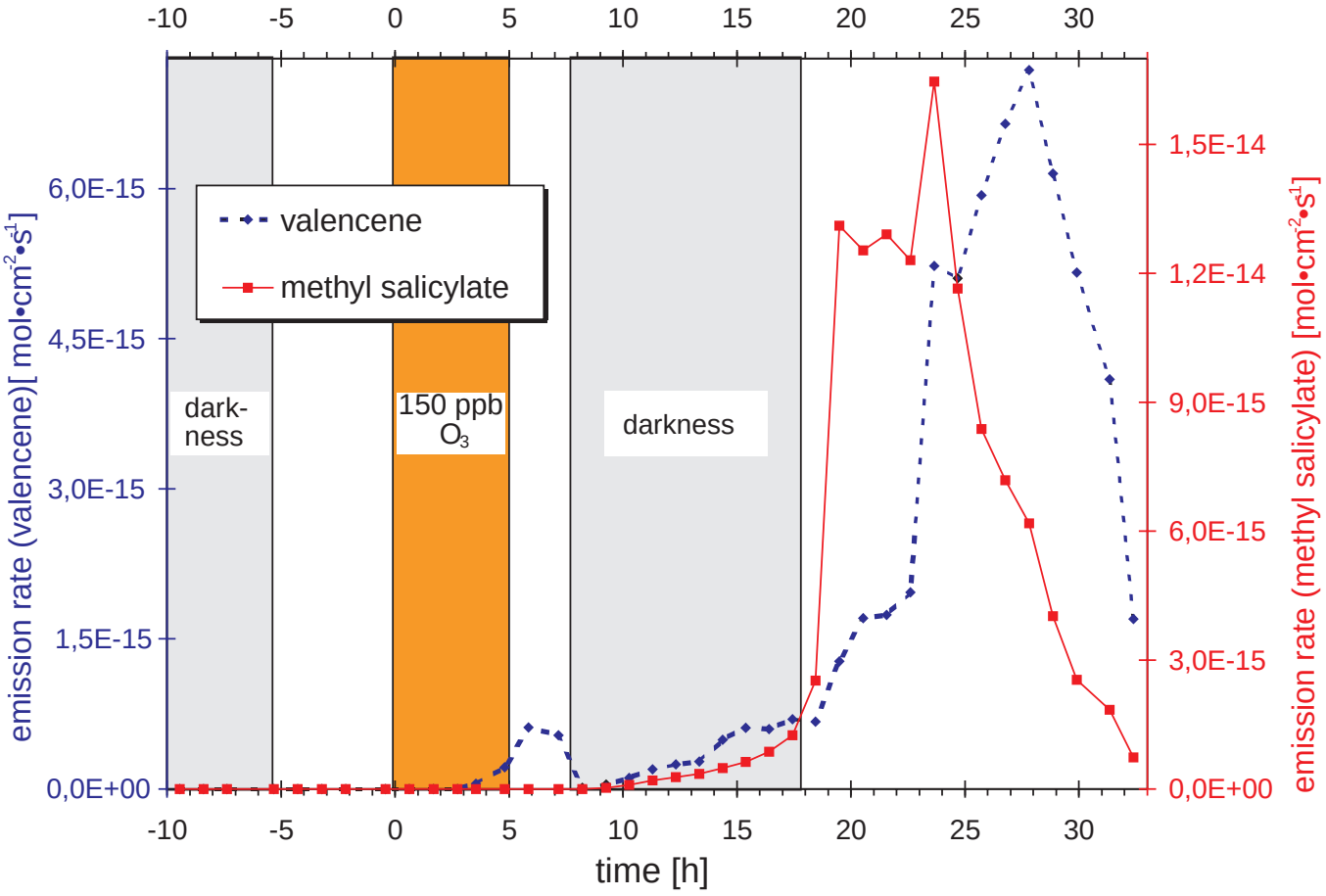

Figure 8. Time plot showing compounds emitted from tobacco after ozone fumigation. The plants were exposed to 150 ppbV ozone between 0 and 5 h. Emission rates of valencene are scaled to fit axes.

Conclusion

The applicability of the GERSTEL Online TDS G for this type of analysis is demonstrated by the results presented in this article. Comparison of results obtained using the method of liquid injection to the Online TDS G method shows them to be essentially equivalent. Off-line sampling to corroborate data from laboratory experiments with field measurements can easily be conducted with this flexible system. In addition, the GERSTEL thermal desorption autosampler (TDS A) can be used to further enhance the system's flexibility. The method can easily be transferred to other applications, for example, measurement of traffic emissions (BTX) from a mobile laboratory. Furthermore, the system is modular in design, and can be easily removed from the GC to allow the CIS to be used for injection of liquid or headspace samples.

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