

Investigations on the influence of drift field and humidity on sesquiterpene product ion distributions in a PTR-MS instrument and implications for sesquiterpene detection sensitivity.

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Abstract

The effects of the ratio of the electric field strength to the buffer gas number density (E/N) in the drift tube of a commercial high sensitivity PTR-MS (Ionicon Analytik GmbH) on the product ion distributions of the sesquiterpenes β -caryophyllene, α -humulene, α -cedrene and longifolene have been investigated. Product ion distributions of α -cedrene and longifolene have also been determined at different water vapour pressures in the inlet line.

Chemical ionization of the sesquiterpenes resulted in important fragmentation of the nascent excited ion/molecule complex at the highest E/N values. The yield of the protonated molecule increased on average by a factor 1.6 by decreasing E/N from 140 to 80 Td. Taking into account the influence of E/N on the reaction time and on the reactant ion mobility, it is estimated that this decrease in E/N may lead to an overall increase in the PTR-MS detection sensitivity of sesquiterpenes (based on the ion signal at m/z 205) by a factor 3.5.

This increase in detection sensitivity was confirmed through branch enclosure PTR-MS BVOC flux measurements on a beech tree in natural conditions in the framework of the IMPECVOC project [1].

Introduction

Terrestrial vegetation is known to be an important source of non-methane volatile organic compounds (NMVOC, about 1150 Tg C yr⁻¹ worldwide). Among these biogenic VOCs isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) are generally found to have the highest emission rates and therefore they have received a lot of attention in the past. However, oxygenated BVOCs and sesquiterpenes (C₁₅H₂₄) are also known to be emitted directly by vegetation in non-negligible amounts. Quantification of sesquiterpene emissions is an experimentally difficult task because of the low vapor pressure of these compounds and their ability to react very rapidly with atmospheric oxidants (mainly O₃), which results in atmospheric lifetimes of only a few tens of seconds for some compounds. Because of their high potential to contribute to net oxidant and secondary organic aerosol (SOA) formation and in order to decrease the uncertainties on regional

and global sesquiterpene emissions, there is a growing need for more precise and reliable sesquiterpene flux data using standardized experimental protocols [2].

Important efforts have been carried out lately to develop and improve analytical techniques for sesquiterpene detection and quantification [3]. Proton Transfer Reaction Mass Spectrometry instrumentation (PTR-MS) has also been used recently to measure sesquiterpene concentrations, e.g. in smog chamber studies focusing on sesquiterpene ozonolysis [4] and in VOC emission studies from herbivore infested branches [5].

In order to optimize sesquiterpene quantification with a PTR-MS it is interesting to know how sesquiterpene product ion signals vary with changing instrumental and environmental parameters.

Experimental

The experiments were carried out with a hs-PTR-MS instrument (Ionicon Analytik GmbH). The drift tube pressure and temperature were kept at 2.2 mbar and 333 K respectively. The contribution of O_2^{+} impurity ions to the sum of reactant ions was limited to 2 %. Stable sesquiterpene flows were produced by sending high purity nitrogen (40 sccm) over the liquid sesquiterpene contained in a glass reservoir, which was completely immersed in a temperature controlled water bath [6]. The resulting sesquiterpene/ N_2 flow was further diluted in a large (1000 sccm) laboratory air flow, scrubbed from dust, ozone and VOCs and humidity controlled by means of an LI-610 dew point generator (LI-COR). Part of this diluted flow was introduced into the PTR-MS through a heated PEEK capillary (333 K). PTR-MS mass discrimination measurements were performed regularly by using a commercial dilute mixture of a set of aromatic compounds (RESTEK #34432-PI).

Branch enclosure measurements were carried out on a 85 years old *Fagus sylvatica* L. tree in the framework of the IMPECVOC project [1]. Ambient air, scrubbed from ozone, dust and VOCs was sent into the enclosure, in which it was enriched with biogenic VOCs. Part of the air leaving the enclosure was pumped towards the PTR-MS inlet through slightly heated insulated Teflon tubing. At the end of June 2008, when some branches were visually infected with aphids, sesquiterpene ion signals were continuously monitored at m/z 205 and m/z 149.

Results and discussion

Sesquiterpene product ion distributions were obtained at E/N values ranging from 80 to 140 Td, in steps of 10 Td. For all four sesquiterpenes studied, the major product ion is the protonated molecule with yields ranging from 30 to 65% at the highest E/N values. The nascent excited complex, that is formed upon reaction of the proton hydrates with the sesquiterpenes, partially decomposes into a large variety of product ions, the distribution of which is strongly dependent on the E/N value of the drift tube region. Unfortunately, these product ions are common to all sesquiterpenes and therefore cannot be used as sesquiterpene-specific fingerprints.

Interestingly, the distributions are not affected by changing relative humidities, and therefore the sensitivity of the PTR-MS for sesquiterpene detection based on specific fingerprint ions (e.g. at m/z 205) is not expected to be humidity-dependent either.

The product ion distributions also show that one should be careful when quantifying monoterpenes in the presence of sesquiterpenes, since the typical monoterpene product ion signals (at m/z 137 and 81) are also typical PTR-MS fragment ions of sesquiterpenes.

Detailed results of these laboratory studies will be presented in [7].

The laboratory results also show that the yields of the protonated sesquiterpenes on average increase by a factor 1.6 when decreasing the E/N value from 140 Td to 80 Td. By using this information and by taking into account the E/N dependence of the reactant ion residence time in the drift tube (including variations of the ion mobility), we estimated the overall PTR-MS sensitivity for sesquiterpene detection to increase by a factor 3.5 when decreasing E/N from 140 to 80 Td.

This estimation was confirmed in a recent dynamic branch enclosure field experiment (on a *Fagus sylvatica* L. tree), during which sesquiterpene emissions were clearly noticed (see Fig. 1), probably as a result of aphid infestation. A decrease of E/N in the drift region of the PTR-MS analyzer from 140 to 80 Td resulted in an increase of the sesquiterpene ion signal at m/z 205 by a factor 3.2.

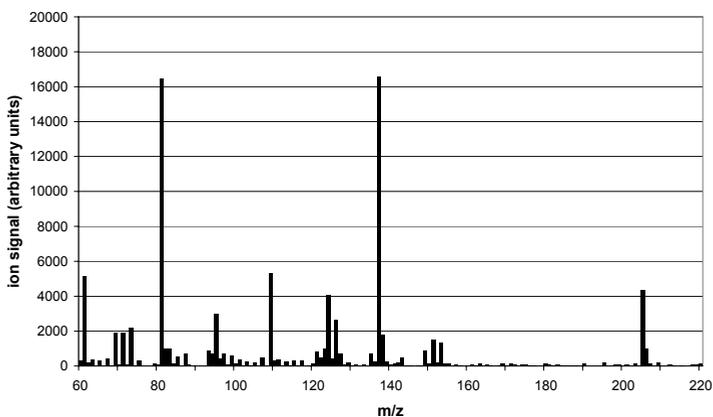


Figure 1: PTR-MS mass spectrum showing sesquiterpene emissions in a dynamic branch enclosure study on *Fagus sylvatica* L. (taking into account mass discrimination).

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