

Short communication

Decomposition of α -pinene and sabinene on solid sorbents, Tenax TA and Carboxen

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Abstract

Laboratory experiments were performed to examine potential in situ decomposition of α -pinene and sabinene on Tenax TA and Carboxen. Reactions between monoterpenes and the sorbent surface were observed with sabinene showing lower recoveries than α -pinene. The identified degradation products were monoterpenes and aromatic compounds. © 1997 Elsevier Science B.V.

Keywords: Carboxen; Tenax TA; Sabinene; α -Pinene; Terpenes

1. Introduction

Biogenic volatile organic compounds (BVOCs), mostly isoprene and terpenes, play an important role in global tropospheric chemistry/regional photochemical oxidant formation, global carbon budget and atmospheric organic acid production [1]. To determine their influence, in-field and laboratory works were performed. In-field measurements consisting of flux quantification [2–7] and laboratory experiments performed in atmospheric simulation chambers (ASCs) allow one to determine their degradation products and rate constants [8–14].

The BVOCs may not be directly measured and their analysis requires a preconcentration step. Tenax is a widely used adsorbent in many environmental studies [15–19]. Tenax TA is a further development of Tenax GC, stable up to 280°C, and produces less artifacts than Tenax GC [20]. Like all solid sorbents, it suffers however, from the inherent disadvantage

that adsorbed compounds may react with each other and with active species (NO_x, ozone...) from the air passing through the cartridge [13,21–26]. Tenax TA is claimed to be inert with respect to sampled compounds [19,25,27–29], but recent studies have shown monoterpene degradation on this adsorbent [13]. Such decompositions require degradation product identification to differentiate them from effectively sampled compounds.

In this paper, we present and discuss recovery data of α -pinene and sabinene after adsorption on Tenax TA and Carboxen 569.

2. Experimental

2.1. Recovery measurements

α -Pinene and sabinene were individually injected with a syringe (0.02 to 10 μ l) through a septum onto a glass container (13 l) under vacuum. Then, purified and dry nitrogen was added until atmospheric pres-

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sure was reached. Various masses of each terpene were then sampled, 20 to 200 ng onto Tenax and 0.2 to 0.5 mg onto Carboxen. To determine the standard deviation, sampling and analysis per single test compound were performed six times.

Monoterpenes of high purity (>99%) were obtained from Fluka (France).

2.2. Analysis

Gaseous samples were collected onto steel or glass tubes (9 cm×0.4 cm I.D.) filled with 200 mg of Tenax TA 60–80 mesh and onto glass tubes (16 cm×0.3 cm I.D.) filled with 100 mg of Carboxen 569. The packed tubes were preconditioned by heating at 300°C for 12 h with continuous inert gas flow (nitrogen 20 ml/min).

Compounds sampled on Tenax TA were thermally desorbed for 10 min at 300°C onto a 20 mg Tenax TA cold trap at –30°C (ATD 400, Perkin-Elmer). Then the cold trap was heated at 300°C for 5 min and the compounds were flushed into the chromatographic column. Compounds trapped on Carboxen 569 were eluted by hexane (2 ml) and directly introduced (0.2 µl) into the chromatographic injector (250°C).

The compounds were separated on a CP-Sil PONA CB (100 m×0.25 mm) fused-silica capillary column, 0.5 µm film, installed in a Perkin-Elmer GC

(Model Autosystem) and equipped with a flame ionisation detector (FID, 300°C) or installed in a Carlo Erba GC (Model QMD 1000) and detected with a mass spectrometer for peak identification.

3. Results and discussion

The recovery data obtained for about 200 ng of α -pinene or sabinene sampled onto Tenax TA are shown in Table 1. α -Pinene and sabinene were partly decomposed in steel or in glass tubes filled with Tenax TA and we could note a good reproducibility between replicated cartridges. Sabinene, showed lower recoveries ($28.3\pm 2.9\%$) than α -pinene ($95.9\pm 0.5\%$). Moreover, higher degradation was observed on old Tenax than on fresh one. Additional compounds identified on the chromatograms were terpenes and aromatic compounds, suggesting rearrangement and dehydrogenation reactions. Such decompositions were already observed on Carbotrap for α -pinene and β -pinene that were partly or completely decomposed [13,19,25]. Other degradation products identified were terpenes [13,19] and aromatics [13].

We have performed different experiments to determine how these monoterpene decompositions occurred: (i) a desorption at lower temperature (200°C instead of 300°C), (ii) a storage duration

Table 1
Recoveries (%) of α -pinene and sabinene on Tenax TA for about 200 ng sampled

| Compound | Recovery ^a (%) | Degradation products | Degradation products ^b (%) |
|------------------|---------------------------|------------------------|---------------------------------------|
| α -Pinene | 95.9 ± 0.5^c | Camphene | 2.3 ± 0.2 |
| | | Limonene | 1.0 ± 0.3 |
| | | α -Thujene | 0.5 ± 0.1 |
| | | β -Pinene | 0.4 ± 0.1 |
| | | Sabinene | <0.1 |
| | | α -Terpinene | <0.1 |
| Sabinene | 28.3 ± 2.9 | <i>p</i> -Cymene | 25.6 ± 3.3 |
| | | γ -Terpinene | 14.4 ± 0.4 |
| | | α -Terpinene | 12.6 ± 0.4 |
| | | α -Thujene | 9.8 ± 0.5 |
| | | Limonene | 5.3 ± 1.5 |
| | | α -Phellandrene | 2.3 ± 0.4 |
| | | β -Pinene | 0.6 ± 0.1 |

^a Recovery (%) = experimental chromatographic area of the tested monoterpene / theoretical chromatographic area of the tested monoterpene.

^b Degradation product (%) = chromatographic area of the degradation product / theoretical chromatographic area of the tested monoterpene.

^c Mean \pm standard deviation.

reduction (from 48 h to a few minutes), (iii) the reduction of the trap quantity (20 ng instead of 200 ng), (iv) the sampling on Carboxen 569 followed by a solvent elution.

However, all these attempts did not reduce the artifact.

4. Conclusions

This study shows monoterpene decomposition on Tenax TA and on Carboxen, especially with sabinene. As we observed degradations on both sorbents, we can assume that monoterpene degradation on Tenax TA does not occur during the thermodesorption step. It certainly takes place during the sample step, directly when the compounds are adsorbed. The effect of both adsorbents can be confirmed.

Moreover, as the degradation products are also emitted by the vegetation, such degradations can lead to erroneous qualitative estimations on BVOC flux measurements. It would be interesting to trap sabinene onto another sorbent or directly onto a cooled fused-silica capillary placed in a chromatograph (on-line system). This last solution requires sampling with low flow-rate and water condensation before the trapping step.

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