

## Short Communication

# Protection of terpenes against oxidative and acid decomposition on adsorbent cartridges

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### ABSTRACT

Sampling of monoterpenes from air on Tenax porous polymer may introduce analytical errors owing to oxidation and acid rearrangements on the adsorbent. Particularly terpenes which react rapidly with ozone, *e.g.* myrcene and limonene, are partially lost when sampling air with high photooxidant levels. On acidified adsorption cartridges,  $\alpha$ -pinene and  $\beta$ -pinene may be converted into camphene, limonene, *p*-cymene and several minor monoterpenes. Pretreatment of the adsorbent cartridges with thiosulphate as an antioxidant and hydrogen carbonate as a buffer were found to prevent decomposition and rearrangements. Applications to monoterpenes emitted from the kraft, thermo-mechanical and sulphite pulp industries are presented.

### INTRODUCTION

Sampling of organic air pollutants on adsorbent cartridges is a widely applied technique because of its simplicity and versatility. It suffers, however, from the inherent disadvantage that adsorbed compounds may react with each other and with active species from the air passing through the cartridge [1]. The very front of the adsorbent column is particularly susceptible to reactions because of elevated levels of all compounds adsorbed. Reactive agents in air may also affect the adsorbent, and thiosulphate treatment was introduced to protect Tenax cartridges [1,2].

Among the hydrocarbons, the terpenes are exceptionally reactive towards air pollutants such as photooxidants [3]. The atmospheric chemistry and the environmental impact of terpenes are subjects of great current interest. A favoured technique for sampling of terpenes in air is adsorption on Tenax porous polymer. Our contributions include studies

of monoterpenes from pine forests [4], logging operations [5] and pulp industries [6]. This study is based on analytical results for terpenes emitted into the air from the alkaline sulphate or kraft pulping process, from the acid sulphite pulping process and from thermo-mechanical pulp (TMP) production. Reliable results were found to depend on the techniques reported here for avoiding decomposition and rearrangements in the adsorption cartridges.

### EXPERIMENTAL

#### *Basic analytical system*

The adsorption cartridges were 80 × 2.2 mm I.D. glass liners filled with 0.1–0.2 ml of Tenax adsorbent (60–80 mesh). Field samples were taken by connecting the cartridges to conventional portable air-sampling pumps [2]. The air volumes were typically in the range 0.2–2 l.

In the laboratory, thermal desorption was effected in the injector of a conventional gas chromatograph.

graph [2]. The oven temperature was kept below 0°C during desorption and raised at 2°C/min during analysis. The analytical column was a 25 m × 0.33 mm I.D. fused-silica capillary with the cross-linked methylsilicone BP-1 as the stationary phase. Detection was by flame ionization and the same response factor was used for all monoterpenes [5,6].

#### Treatments of adsorbent cartridges

The Tenax adsorbent was kept in place by two glass pellets made from fritted glass filters, with a minimum amount of silanized glass-wool providing the required friction between the pellets and the wall of the glass liner.

A 5% aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used for antioxidant treatment. A droplet (10–20 μl) was introduced on to the front of the adsorbent layer using a micropipette. The water was evaporated cautiously at an elevated temperature and the cartridge was preconditioned in the gas chromatographic injector at 250°C with helium [2] before sampling. Pretreatment with NaHCO<sub>3</sub> as a buffer against acids was made in an analogous manner with a 5% aqueous solution.

## RESULTS AND DISCUSSION

### Oxidative decomposition

In Table I, results are given for air samples taken at ground level several hundred metres downwind of

two pulp mills. The kraft mill was Gruvöns Bruk, northwest of lake Vänern, with terpene emissions mainly from processed Scots pine. The thermo-mechanical pulp (TMP) mill was Bravikens Pappersbruk, in Norrköping on the east coast, with terpene emissions almost exclusively from processed Norway spruce. The samples taken on Tenax cartridges pretreated with thiosulphate correctly reflect the monoterpene composition, as confirmed by comparisons with many other samples. The different compositions of monoterpenes from the two mills reflect the characteristic differences between Norway spruce, with large proportions of α- and β-pinene, and Scots pine, with large proportions of α-pinene and 3-carene [5].

For duplicate samples, taken with untreated cartridges, the percentage oxidative losses given in Table I were determined. It is seen that β-pinene and the terpene-related alkylbenzene *p*-cymene are not affected, whereas the acyclic triene myrcene is lost completely. The other major monoterpenes were lost to various extents from the fairly stable α-pinene to the reactive limonene. The same order of reactivity was observed on other occasions for several different untreated duplicate cartridges, although the degree of losses varied. The greatest losses were observed during daytime in the summer, in periods of fine weather favouring high levels of photooxidants.

Ozone is a major photooxidant which may cause

TABLE I

### OXIDATIVE DECOMPOSITION OF MONOTERPENES ON TENAX ADSORPTION CARTRIDGES AND REACTION RATE WITH OZONE IN AIR

Parallel air samples taken ca. 500 m downwind from pulp mills, on thiosulphate-treated cartridges (correct results) and on untreated cartridges (results reflecting oxidative losses).

Compound	Kraft mill, Scots pine, 17/8/90, 10.15–12.15		TMP mill, Norway spruce, 21/8/90, 11.15–13.00		Reaction rate with ozone in air [3], $k \times 10^{17}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated (μg/m <sup>3</sup> )	Untreated (% loss)	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated (μg/m <sup>3</sup> )	Untreated (% loss)	
<i>p</i> -Cymene	0.75	0	0.28	0	<0.005
β-Pinene	6.4	0	10.6	0	1.5
α-Pinene	33.9	6	23.8	6	9.7
3-Carene	13.9	34	2.3	33	5.2
β-Phellandrene	0.80	55	1.2	63	17
Limonene	1.70	76	1.7	80	21
Myrcene	0.33	100	0.22	100	49





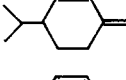
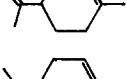
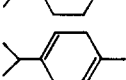
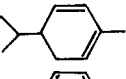
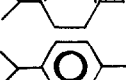


losses owing to the high reactivity of ozone with branched alkenes such as terpenes. From Table I, it is evident that the gas-phase reactivity of terpenes with ozone correlates fairly well with the sampling losses of different terpenes. Accordingly, sampling of monoterpenes with and without an ozone scrubber [7] results in differences similar to those observed

with and without thiosulphate treatment. It should be remembered, however, that terpenes also react rapidly with other photooxidants, and that decomposition in the front of the adsorption cartridges is not a gas-phase reaction.

Freshly thiosulphate-treated cartridges normally permitted a satisfactory recovery of myrcene, thus

TABLE II  
ACID REARRANGEMENTS OF MONOTERPENES ON TENAX ADSORPTION CARTRIDGES

Composition (%) of monoterpenes emitted from processed wood of Norway spruce, for parallel air samples taken on neutral cartridges (correct results) and on acid-treated cartridges (results reflecting acid rearrangements).

Compound	Structure	TMP process		Pulpwood chipping	
		Correct	Acidic	Correct	Acidic
$\alpha$ -Pinene		58	55	58	46
$\beta$ -Pinene		26	14	23	12
Camphene		1.7	6.1	1.8	9.0
3-Carene		3.5	3.3	4.9	4.2
$\beta$ -Phellandrene		3.0	2.9	3.1	2.3
Limonene		5.1	9.9	6.2	9.3
Terpinolene		0.25	1.3	0.40	2.2
$\gamma$ -Terpinene		0.10	0.6	0.11	1.1
$\alpha$ -Phellandrene		0.05	0.5	0.07	0.5
$\alpha$ -Terpinene		0.04	0.6	0.06	1.1
<i>p</i> -Cymene		0.8	3.3	0.9	8.6

ensuring that no oxidative losses of the less reactive monoterpenes were obtained. The minor monoterpenes terpinolene,  $\alpha$ -terpinene and  $\alpha$ -phellandrene are even more reactive than myrcene with ozone [3], but they are often absent from ambient air owing to their high gas-phase reactivity. Near conifers and man-made monoterpene emissions, they act as oxidant scavengers and may be sampled without oxidative losses [5].

Oxidative reactions during sampling also affect the Tenax adsorbent and cause the formation of artifacts such as benzaldehyde and acetophenone [2]. The thiosulphate treatment prevents this decomposition and therefore often provides additionally improved analytical quality.

#### Acid rearrangements

Man-made terpene emissions from the forest industry and other sources are often accompanied by emissions of sulphur dioxide, nitrogen oxides and organic acids. In these instances, acidification of the adsorbent front during sampling is an obvious consequence. However, even the acidity of ambient air in general might have a limited impact. The character of the acidic terpene reactions on the adsorbent cartridges was found to be well elucidated by parallel sampling on untreated and artificially acidified cartridges.

In Table II, the percentage monoterpene composi-

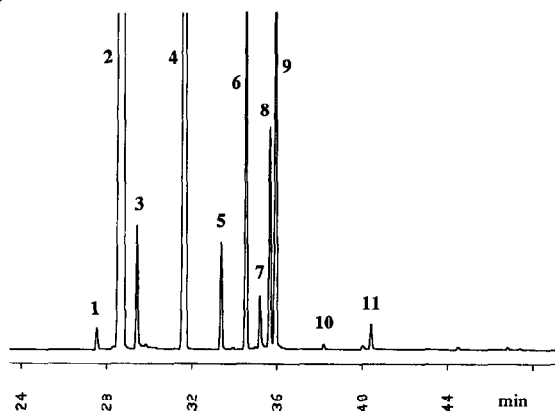


Fig. 1. Gas chromatographic separation of monoterpenes emitted into the air during industrial chipping of pulpwood from Norway spruce. Peaks: 1 = tricyclene; 2 =  $\alpha$ -pinene; 3 = camphene; 4 =  $\beta$ -pinene; 5 = myrcene; 6 = 3-carene; 7 = *p*-cymene; 8 =  $\beta$ -phellandrene; 9 = limonene; 10 =  $\gamma$ -terpinene; 11 = terpinolene.

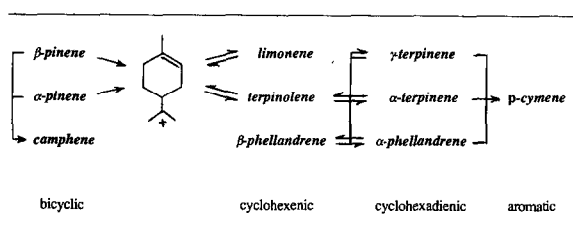


Fig. 2. Scheme of sequential acid-catalysed rearrangements of monoterpenes.

tion is given for emission samples from the processing of spruce pulpwood. The first sample corresponds to TMP refiner steam emissions passed through fresh chips before venting to air at the Braviken mill. The sample from industrial pulpwood chipping was taken at the Billerud sulphite pulp mill west of lake Vänern. It is seen that the percentage compositions are very similar. In Fig. 1, the chromatographic separation is illustrated. The total monoterpene concentrations were as high as 7 mg/m<sup>3</sup> for the TMP sample and 60 mg/m<sup>3</sup> for the chipping sample, resulting in a depletion of oxidants from the air. As a consequence, even the most easily oxidized hydrocarbon monoterpenes could be determined without oxidative losses. With the attenuation chosen for Fig. 1, the minor species  $\alpha$ -phellandrene and  $\alpha$ -terpinene are just visible in front of 3-carene and *p*-cymene, respectively.

The duplicate samples in Table II were taken on cartridges acidified with trace amounts of sulphuric acid. No significant decrease in the total amount of monoterpenes was observed, but the composition was very different, indicating acid rearrangements in the acidified cartridges. The proportions of  $\alpha$ -pinene and particularly  $\beta$ -pinene were greatly lowered and those of  $\beta$ -phellandrene and 3-carene were slightly lowered. The percentages of camphene, limonene, terpinolene and the alkylbenzene *p*-cymene were increased. The minor cyclohexadienic components  $\gamma$ -terpinene,  $\alpha$ -terpinene and  $\alpha$ -phellandrene increased considerably compared with their true proportions in the emissions. Other samples taken on acidified cartridges were found to give qualitatively the same errors, although the magnitude and proportions of the deviations varied.

The basic acidic rearrangement reactions of monoterpenes, as outlined in Fig. 2, are compatible with the deviations observed for acidified cartridges.

The acid rearrangements of  $\alpha$ - and  $\beta$ -pinene to camphene, and via the depicted carbonium ion to isomerizing monocyclic terpenes, are known from terpene chemistry [8,9]. The formation of *p*-cymene in high yield from monoterpenes is also known from the acid sulphite pulping process [10]. The deviations for limonene and other terpenes which appear as reaction intermediates were found to be irregular in magnitude for different acidic samples. Weakly acidified samples tended to give rearrangements without any significant dehydrogenation to *p*-cymene. The risk of overlooking more or less subtle analytical errors resulting from acid rearrangements is obvious.

The pretreatment of the adsorption cartridges with buffering hydrogencarbonate prevented acid rearrangements without affecting the analytical performance. After this treatment, the previously acidified cartridges worked perfectly well again. Reproducible results could be obtained even for digester

emissions from the acid sulphite pulp mill. It is concluded that the pretreatment of adsorption cartridges with a buffer may offer an improved analytical quality for a wide range of applications.

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