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DETERMINATION OF MONOTERPENE HYDROCARBONS IN THE ATMOSPHERE

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SUMMARY

A gas chromatographic–mass spectrometric technique for the analysis of trace concentrations (sub-ppb*) of monoterpenes in the air is described. Samples were collected on Tenax GC adsorbent and thermally desorbed onto the analytical column for separation and detection by selected ion monitoring. Experimental results are given for different kinds of forests in the Tsukuba district of Japan. The diurnal variation of the monoterpene concentration in the atmosphere was also measured in a pine forest.

INTRODUCTION

It has been reported that approximately 175 million tons of hydrocarbons are emitted into the atmosphere annually from tree foliage sources on the earth[1]. Terpenes are best known as the group of compounds produced in significant amounts by conifers. The influence of the terpenes emitted from plants on environmental air and their geochemical fate are of great interest. Went[2] suggested that volatilization of terpenes from tree foliage results in a "blue haze" which surround forests particularly in summer on sunny and windless days. He asserted that terpenes polymerize into particles through chemical reactions in a manner similar to those resulting in urban and industrial smog. This theory of particle formation is now generally accepted. Zimmerman *et al.*[3] pointed out that the oxidation of terpenes could make an important contribution to the atmospheric sources of CO and H_2, and to organic species soluble in rain-water. Recent investigations[4,5] have shown that ozone concentrations in remote rural locations often exceed 80 ppb* for extended periods. Naturally emitted hydrocarbons are considered to be photochemical oxidant precursors in those areas because terpenes have a high reactivity in NO_x photooxidation as demonstrated by Grimsrud *et al.*[6].

However, information concerning terpenes and their importance in atmospheric chemical processes is sparse, and terpene concentrations in the air are not

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* Throughout this article, the American billion (10^9) and trillion (10^{12}) are meant.

known with sufficient precision or accuracy to permit reliable estimation of their geochemical cycle. Rasmussen and Went[7] identified α-pinene, β-pinene, myrcene and isoprene in the countryside air using gas chromatography. Whitby and Coffey[8] obtained a first-order determination of the total terpene concentration typically observed during the summer in the Adirondack Mountain region. But it is difficult to determine terpene compounds from only comparisons of retention times because the peaks of many terpenes and non-terpene hydrocarbon derivatives may overlap on the chromatogram. Recently, Holdrene *et al.*[9] detected α-pinene at a level between 10 and 730 ppt and β-pinene, 3-carene and limonene in the Moscow Mountain region with capillary gas chromatography–mass spectrometry (GC–MS).

This paper reports a sensitive GC–MS procedure for the determination of monoterpenes in the atmosphere based upon trapping of the compounds on Tenax GC adsorbent and selected ion monitoring (SIM) detection. The technique was used to measure monoterpene concentrations and compositions in different kinds of forests in the Tsukuba district of central Japan.

EXPERIMENTAL

Apparatus

A microprocessor-controlled Hewlett-Packard 5992A GC–MS instrument equipped with a SIM function (Fig. 1) was used to perform analyses. The system contains a two-way valve to switch over the carrier gas, and a block heater (FLS-3 flush sampler; Shimadzu, Kyoto, Japan) for desorption of the sample from the sampling tube.

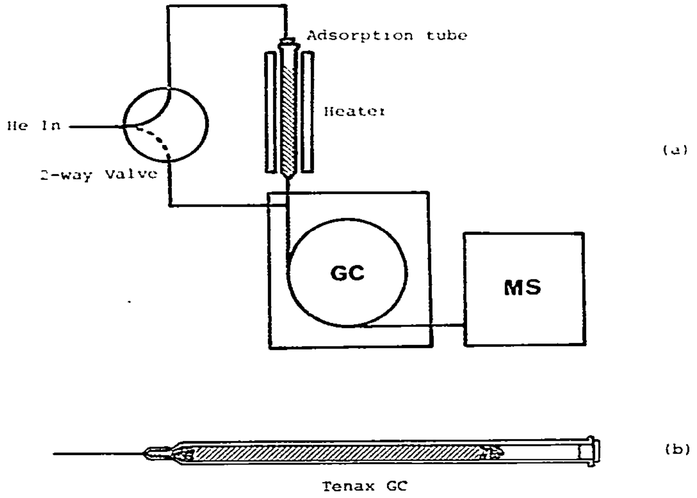

Fig. 1. Experimental GC–MS system (a) and adsorption tube (b).

Sampling tube

Sampling tubes filled with Tenax GC adsorbent were employed for collecting samples. A 0.3-g amount of Tenax GC (80–100 mesh) was packed into a Pyrex tube (15 cm × 4.5 mm I.D.) to form a bed *ca.* 10 cm long, and the tube was secured at both ends with glass-wool plugs. A diagram of the adsorption tube is presented in Fig. 1.

The tube was connected to the analytical column by inserting the needle end into the injection of the gas chromatograph. Prior to use, the tubes were conditioned overnight at 280°C with passage of nitrogen gas at a flow-rate of 30 ml/min.

Procedure

A 1-l volume of air was drawn through an adsorption tube by a portable pump (Charles Austen Pumps). The sampling flow-rate of 100 ml/min was controlled by a needle valve. The adsorption tubes were sealed with silicone rubber and GC–MS analysis was performed as soon as possible after sampling. Chromatographic separations were accomplished on 5% silicone DC-200 + 5% Bentone 34 on Chromosorb W AW DMCS (60–80 mesh) packed in a glass column (8 ft. × 2 mm I.D.). Desorption of the sample from the adsorbent was carried out at 200°C with the carrier gas (high-purity helium) flowing at a rate of 16 ml/min for 2 min. The monoterpene transferred onto the analytical column was temporarily trapped at the top of it for 2 min at a temperature of 0°C and the carrier flow was then switched from the bypass to the GC. The SIM chromatograms of the ions having *m/e* 93, 136, 68, 41, 78 and 91 were obtained by temperature programming at 16°/min to 100°C. Positive identifications of monoterpenes were made on the basis of a combination of retention times and the ratio of peak heights at *m/e* 93, 136, 68 and 41 which are the main peaks in the mass spectra of many monoterpenes. The concentrations of monoterpenes in the samples were usually determined from the peak heights of the SIM chromatogram at *m/e* 93 using a calibration curve prepared from standard solutions. The ions at *m/e* 41, 78 and 91 were monitored to determine other aliphatic and aromatic hydrocarbons for reference.

RESULTS AND DISCUSSION

Analytical

Breakthrough volumes for α-pinene, β-pinene and limonene were determined using two adsorption tubes connected in series. Standard gases of each compound at 100 ppb were passed through the tubes at 100 ml/min. After a known volume of air had passed through the adsorption tubes at ambient temperature, the second tube was analyzed to determine whether the compound had eluted from the first tube, indicating breakthrough. The sampling tube containing 0.3 g Tenax GC adsorbent had breakthrough volumes of more than 4 l for these three compounds. As α-pinene is one of the most volatile monoterpenes, it is reasonable to assume that all monoterpenes are trapped in the sampling tube without any loss when the sampling volume is less than 3 l.

A study was made to determine the desorption efficiency of the sampling tube: 1 ng each of α-pinene, β-pinene and limonene in 1 μl hexane were injected directly onto the analytical column and analyzed using SIM. These results were compared to those obtained when the test mixture was injected into the sampling tube and then analyzed using the technique described above. A quantitative result was achieved for three runs: the recoveries of α-pinene, β-pinene and limonene were 96 ± 3%, 94 ± 1% and 96 ± 2%.

The detection limit of this analytical method for α-pinene was 0.1 ng at a signal-to-noise ratio of >3.

Measurements of monoterpenes in forested areas

Atmospheric monoterpene concentrations were measured at several forests during the late autumn, spring and summer months of 1979–1980. The forests are situated in the Tsukuba district and rapid analysis after sampling was possible. Primary objectives of this field-sampling program were to provide both qualitative and quantitative information concerning monoterpenes in the forests of pine (*Pinus densiflora*), hinoki (*Chamaecyparis obtusa*) and sugi (*Cryptomeria japonica*) which are the predominant species in Japanese mountain areas.

Fig. 2 shows the SIM chromatogram at *m/e* 93 of a 1-l sample collected in a pine forest. Monoterpenes identified in the atmosphere of coniferous forests are listed with their retention times in Table I.

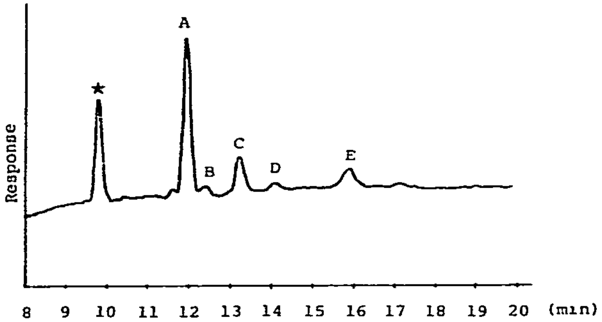

Fig. 2. Selected ion chromatogram (*m/e* 93) of an air sample collected in a pine forest. Peaks: A = α-pinene; B = camphene; C = β-pinene; D = myrcene; E = β-phellandrene; the asterisk indicates an isotope of the molecular ion of toluene.

TABLE I

RETENTION TIMES OF MONOTERPENES IDENTIFIED IN THE ATMOSPHERE OF CONIFER FORESTS

Compound	*Retention time (min)*
α-Pinene	12.0
Camphene	12.4
β-Pinene	13.2
Myrcene	14.1
3-Carene	14.5
Limonene	15.6
β-Phellandrene	15.9

Terpene concentrations measured in the several kinds of forests in the Tsukuba district are presented in Table II. All the samples were collected under the forest canopy at a level of 1.5 m above the ground. The most noticeable feature of Table II is that the ambient terpene concentrations vary greatly from day to day. This suggests that there may be a close relationship between the monoterpene concentration in the air and climate. Concerning the monoterpene compositions, characteristic patterns for particular classes of forests were found. In the case of pine, α-pinene was domi-

TABLE II

TERPENE CONCENTRATIONS (ppb) IN SEVERAL KINDS OF FORESTS

n.d. = Not determined.

Date	*Location*	*Type of forest*	*α-Pinene*	*Camphene**	*β-Pinene*	*Myrcene*	*3-Carene*	*Limonene*	*β-Phellandrene**	*Weather*
Nov. 14, 1979	1	Pine	0.10	+	0.03	n.d.	n.d.	n.d.	+	Fine
Nov. 16, 1979	2	Pine	0.18	+	0.05	0.02	n.d.	n.d.	+	Fine
	3	Hinoki	0.19	+	0.14	0.03	0.02	0.07	n.d.	Fine
	4	Sugi	0.10	n.d.	0.07	0.02	0.02	0.27	n.d.	Fine
Nov. 22, 1979	2	Pine	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	+	Rain
	3	Hinoki	0.06	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	Rain
	5	Sugi	0.06	+	0.03	n.d.	n.d.	0.09	n.d.	Rain
Nov. 29, 1979	1	Pine	1.30	+	0.54	0.12	0.04	0.09	+	Cloudy
Mar. 24, 1980	4	Sugi	0.13	+	0.08	0.02	0.01	0.03	n.d.	Fine
	3	Hinoki	0.07	+	0.09	0.03	0.02	0.06	n.d.	Fine
May 15, 1980	1	Pine	0.20	+	0.03	0.01	0.01	n.d.	+	Cloudy
June 13, 1980	1	Pine	0.20	+	0.07	0.01	n.d.	n.d.	+	Cloudy
July 19, 1980	1	Pine	0.35	+	0.12	0.04	n.d.	n.d.	+	Fine
Aug. 21, 1980	4	Sugi	0.22	+	0.10	n.d.	n.d.	0.09	n.d.	Cloudy
	6	Pine	0.38	+	0.13	n.d.	n.d.	n.d.	+	Cloudy
	7	Hinoki	0.05	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	Cloudy

* Camphene and β-phellandrene were not quantified and only their existence (+) is noted.

nant, and β-pinene, β-phellandrene and myrcene were detected. In hinoki and sugi forests, α-pinene and β-pinene prevailed, and limonene and 3-carene were also detected, but β-phellandrene was not observed. The differences in monoterpene composition depending on forest type suggest that the composition of the leaf oil is responsible for the atmospheric concentrations.

The diurnal variation of monoterpene concentration in the atmosphere was measured in a pine forest (*ca.* 20,000 m^2) in the grounds of our institute on June 5–June 6, 1980. The weather was fine with little wind during the sampling time, so that the washout and wind effects can be neglected. The result for α-pinene is shown in Fig. 3. In the daytime, monoterpene concentrations were low (α-pinene 0.07–0.30 ppb), while extremely high concentrations were observed at night, when the ozone concentration is lower and photochemical reactions are negligible. This result supports the theory that terpenes emitted from plants undergo ozonolysis and photochemical reaction with nitrogen oxides.

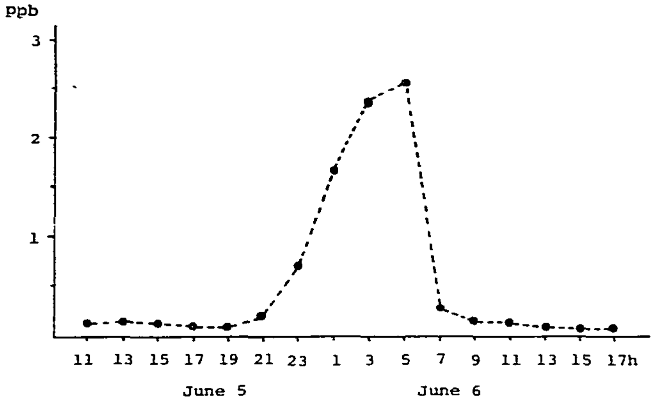

Fig. 3. Diurnal variations of the concentration of α-pinene in the air of a pine forest at Tsukuba (June 5–June 6, 1980).

In this study, we found that there are differences in monoterpene compositions in forests depending on the kinds of trees, and that at night the concentrations were about ten times greater than those in the daytime.

However, to establish the role of terpenes in atmospheric reactions, further field studies of the correlation of monoterpene concentrations in the atmosphere with external factors such as weather, NO_x and O_3 are necessary.

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