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A CRYOTRAP TECHNIQUE FOR THE QUANTITATION OF MONOTERPENES IN HUMID AND OZONE-RICH FOREST AIR

F. JÜTTNER

Institut für Chemische Pflanzenphysiologie der Universität, Corrensstrasse 41, D-74 Tübingen (F.R.G.)

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SUMMARY

A cryotrap technique is described that permits the enrichment of volatile organic constituents in the air to such concentrations as to make them accessible to mass spectrometry. In combination with single ion monitoring this method allows the quantitation of monoterpenes and organic pollution products under all weather conditions. High humidity or rain do not affect the measurements. Furthermore, the actual concentrations of ozone-sensitive molecules (unsaturated monoterpenes) can be quantitated in ozone-rich air (up to 150 μg ozone/ m^3), as is often observed in forested regions at high elevations in Central Europe.

INTRODUCTION

Monoterpenes are emitted to the atmosphere by terrestrial vegetation, particularly conifers¹⁻⁸. They are involved in photochemical reactions of polluted air and are thus of current interest^{9,10}. It was originally assumed that most atmospheric volatiles are biogenic, based on data from remote regions of North America¹. However, in Central Europe and other industrialized areas, organic pollutants exceed biogenic organics in both number and concentration¹¹. In these areas the anthropogenic volatile organic compounds (VOCs) are sufficiently concentrated to interfere with terpene determination by capillary gas chromatography (GC) with flame ionization detection. Significantly lower concentrations are obtained by the more specific mass spectrometric single ion detection. However, this method requires that sufficient amounts of atmospheric constituents can be concentrated from the air.

Several adsorbents have been described for collecting VOCs: cartridges of Tenax^{6,7,12}, Carbopack¹³ and activated charcoal^{5,14}. All suffer from two disadvantages. First, high humidity often leads to water deposition in the cartridge which must be removed before GC and may cause variable losses of VOCs. Secondly, the presence of ozone in concentrations of up to 150 μg m^{-3} in forested areas¹⁵ can exceed the monoterpenes in concentrations on a molar basis and react with them on the adsorbent. Major alterations of the monoterpene pattern can result due to different rate constants for the reaction of particular monoterpenes with ozone. The accurate determination of monoterpene concentrations is clearly important for understanding

photochemical reactions in air. I have therefore developed a trapping device which performs well under all weather conditions (also during rain) and with air rich in ozone. It significantly improves the accuracy of the determination of atmospheric monoterpenes.

EXPERIMENTAL

Monoterpene trapping

The organic air constituents were collected in a cartridge filled with 500 mg of Tenax TA (60–80 mesh, Chrompack) providing a bed of 70 mm × 7 mm I.D. The bed was secured at each end by quartz wool. One end of the cartridge terminated in a ground-glass joint and the other end was fitted with a metal Luer lock. The constructional details of the cartridge which is commercially supplied by SGI/Laborbedarf (Dornstadt, F.R.G.) have already been published^{16,21}.

Sampling device

The air drawn into the Tenax cartridge was passed initially through a glass-fibre filter (Whatman GF/C) to remove aerosols. It was then passed through an ozone catalyst to remove ozone from the air (Antechnika, Ettlingen, F.R.G.) before entering a glass tube (1.8 m × 7 mm I.D.) which was arranged in three coils, 33 cm long and 10 cm wide (Fig. 1). The last coil of the glass tube terminated in a female ground joint fitted to the joint of the Tenax cartridge. Both were carefully connected after wetting the joints with water. A silicone rubber vacuum tube connected the outlet of the cartridge with a battery-operated diaphragm pump (Model 7005 D; ASF, München, F.R.G.). The resistance of the Tenax bed resulted in a gas flow of around 90 l/h. The outlet line of the vacuum pump was connected first with a flow meter and then with a gas meter. Both the coil of the glass tube and the Tenax cartridge were positioned in an insulated box and cooled with crushed ice during sampling. After completion of the sampling (1 h) the cartridge was removed and stored in a convenient small-volume glass vessel sealed with a ground-glass joint.

Gas chromatography and mass spectrometry

The air constituents collected on the Tenax were thermally desorbed at

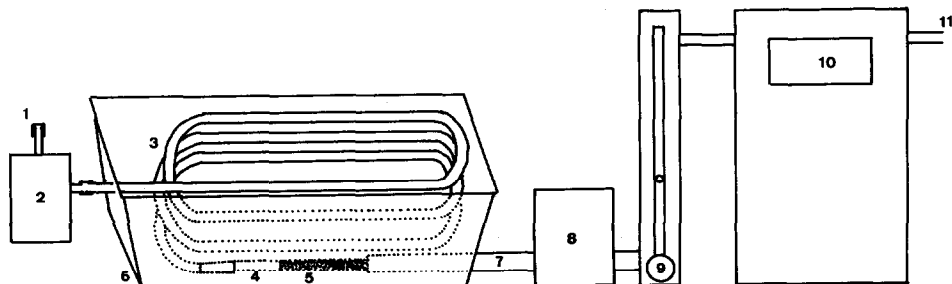


Fig. 1. Cryotrap device for the analysis of monoterpenes in humid and ozone-rich air. 1 = Whatman glass-fibre filter; 2 = ozone scrubber; 3 = glass coil for the condensation of water; 4 = cartridge provided with a ground-glass joint and a Luer lock; 5 = Tenax bed of the cartridge; 6 = insulated box with crushed ice; 7 = silicone rubber tube; 8 = diaphragm pump; 9 = flow meter; 10 = gas meter; 11 = outlet.

300°C^{16,21} for 6 min and then transferred by means of a helium gas stream (50 ml/min) into a precooled (0°C) fused-silica bonded phase capillary column (DB-1301, 30 m × 0.3 mm I.D., d_f 0.25, J & W Scientific) connected to a Hewlett-Packard gas chromatograph (Model 5790A). After the transfer was complete, a temperature programme was initiated with a rate of 5°C/min and a final temperature of 280°C. The temperature of the injection port was maintained at 300°C and the head pressure of helium at 90 kPa, which permitted a carrier gas flow-rate of 3 ml/min at ambient temperature, a septum purge of 2 ml/min and a split vent rate of 50 ml/min. The column outlet was connected directly via an interface heated at 280°C with an ion-selective detector (Hewlett-Packard 5970A). Single ion monitoring was conducted throughout this study. The intensities of the fragment ions stated in Table I were used for the quantitation of the compounds of interest. The electron multiplier voltage was 2000 V and the residence times varied between 10 and 130 ms. Calibration was performed by taking reference compounds dissolved in diethyl ether and adding them in such concentrations to a gas stream passing through the Tenax cartridge as to give integrated areas of fragment ion intensities in ranges similar to those observed for natural samples.

Reference compounds

Monoterpenes of high purity were obtained from Fluka (Neu-Ulm, F.R.G.); the pollution products were obtained from Merck (Darmstadt, F.R.G.).

RESULTS AND DISCUSSION

Cryotrapping with Tenax

At high ambient temperatures in summer, monoterpenes are insufficiently sorbed on Tenax, even when the amount of adsorbent is increased to 500 mg. Since a further increase in the amount of Tenax would lead to problems in the desorption

TABLE I

FRAGMENT IONS AND RETENTION TIMES USED FOR THE QUANTITATION OF MONOTERPENES AND POLLUTION PRODUCTS BY MASS FRAGMENTOGRAPHY

Fragment ions (m/z)	t_R (min)	Monoterpene	Fragment ions (m/z)	t_R (min)	Pollution product
93, 136	16.23	Tricyclene	50, 78	7.82	Benzene
93, 136	16.72	α -Pinene	130, 95	8.95	Trichloroethylene
93, 136	17.30	Camphene	46, 90	9.25	Isopropyl nitrate
93, 136	18.35	β -Pinene	91, 92	11.37	Toluene
93, 136	18.43	Sabinene	129, 166	12.37	Tetrachloroethylene
69, 93, 136	19.18	Myrcene	56, 73	13.77	Butyl acetate
93, 136	19.51	Δ^3 -Carene	91, 106	14.78	Ethylbenzene
68, 93, 136	20.26	Limonene	91, 106	15.99	<i>o</i> -Xylene
93, 154	20.59	Eucalyptol	85	25.55	Dodecane
		(1,8-cineole)	128	26.20	Naphthalene
93, 136	21.31	γ -Terpene			
93, 152	25.38	Camphor			

TABLE II

RETENTION OF MONOTERPENES AND POLLUTION PRODUCTS IN THE TENAX CARTRIDGE

Two Tenax cartridges were arranged in series. The concentrations of air constituents are given in ng/m³. The percentage of the total found in the second cartridge is indicated (n.d. = below detection threshold in the second cartridge). The data represent the means for three replicate samples taken on August 7th, 1987 at 2 p.m. in the Schönbuch forest near Tübingen.

<i>Monoterpene</i>	<i>Amount</i>		<i>Pollutant</i>	<i>Amount</i>	
	<i>ng/m³</i>	<i>%</i>		<i>ng/m³</i>	<i>%</i>
Tricyclene	24	n.d.	Benzene	1396	8.7
α -Pinene	974	1.9	Toluene	3284	n.d.
β -Pinene	776	0.7	Ethylbenzene	875	0.9
Camphene	197	2.3	<i>o</i> -Xylene	669	2.0
Sabinene	330	n.d.	Dodecane	221	6.2
Myrcene	78	n.d.	Naphthalene	260	2.1
Δ 3-Carene	387	n.d.	Isopropyl nitrate	12	n.d.
Limonene	286	7.5	Butyl acetate	735	2.1
γ -Terpinene	78	n.d.	Trichloroethylene	1135	1.0
Eucalyptol (1,8-cineole)	131	n.d.	Tetrachloroethylene	1133	n.d.
Camphor	139	n.d.			

procedure, a reduction in the trapping temperature was preferred. At a temperature of 0°C (which can easily be achieved with crushed ice under field conditions), retention of the monoterpenes is sufficient to permit reliable measurements. The amounts of monoterpenes found in a second Tenax cartridge arranged in tandem were usually in the range of 1–2% and never exceeded 7.5% (limonene) of the total (Table II). Similar amounts were observed for C₂-benzenes and higher aromatic compounds. Low-boiling compounds such as benzene and some halogenated hydrocarbons (1,1,1-trichloroethane, dichloromethane) were less efficiently retained.

Retention of water

When air was collected during rain or high atmospheric humidity, considerable amounts of water condensed on the bed of the cartridge. Attempts to remove water by various techniques, such as vacuum drying, drying over phosphorus pentachloride and/or in a dry helium or hydrogen gas stream, failed and resulted in irreproducible losses of compounds. When placed in crushed ice, a glass tube (180 cm \times 7 mm I.D.) was sufficient to cool the air when a gas flow of 1.3 ml/min was applied. To permit convenient handling, this water trap was arranged in a coil. The installation of such a glass coil in front of the cartridge led to heavy water deposition, leaving the cartridge free of all but negligible amounts of water. Without further drying being necessary, the cartridge could be thermally desorbed directly and the organic compounds transferred to a polar capillary column. No loss of monoterpenes by this cooling coil was observed. This is consistent with the observation that volatile organic compounds are poorly retained by capillaries¹⁷. When carbon dioxide cooling was applied, significant losses of terpenes were observed in the cooling coil.

TABLE III

QUANTITATION OF MONOTERPENES AND POLLUTION PRODUCTS IN OZONE-RICH ($120 \mu\text{g}/\text{m}^3$) FOREST AIR (SOUTHERN BLACK FOREST/KÄLBELESCHUEER) WITH AND WITHOUT THE USE OF AN OZONE SCRUBBER ON APRIL 22nd, 1987 AT 1 p.m.

Compound	Concentration (ng/m^3)	
	With scrubber	Without scrubber
α -Pinene	770	108
β -Pinene	120	53
Camphene	40	70
Tricyclene	11	17
Myrcene	35	0
Δ^3 -Carene	30	90
Limonene	2154	69
Eucalyptol (1,8-cineole)	29	33
Camphor	8.9	63
Benzene	690	546
Toluene	803	898
Ethylbenzene	193	211
<i>o</i> -Xylene	144	139
Trichloroethylene	157	189
Tetrachloroethylene	289	367
Butyl acetate	84	167

Retention of ozone

In rural areas at high elevations, extremely high ozone concentrations occur on fine days, concentrations as high as $150 \mu\text{g}/\text{m}^3$ frequently being observed¹⁵. Since ozone readily reacts with unsaturated monoterpenes, reactions of Tenax-sorbed compounds with ozone passing through the cartridge can be assumed to be of great importance. In initial experiments, indigo-carmin-coated glass beads were used to remove ozone before it could enter the cartridge¹¹. However, a severe problem developed in the form of water clogging when humid air was analyzed. A considerable improvement was obtained with the aid of an ozone catalyst normally used to obtain ozone-free air in the calibration of ozone analyzers. This ozone scrubber can be used for long periods of time. After 3 months of continuous use it was still active. The effect of ozone in the air ($120 \mu\text{g}/\text{m}^3$) on the recovery of monoterpenes is presented in Table III. Monoterpenes with high ozone rate constants¹⁸⁻²⁰ which are, however, strictly valid only for gas-phase reactions, are eliminated to within extremely high percentages as is indicated by the concentrations of myrcene and limonene obtained. α -Pinene, which exhibits a greater ozone rate constant than β -pinene, also shows a higher loss. Non-polar compounds not subjected to ozone degradation are only slightly reduced in their concentrations, as could be shown for several alkylbenzenes and halogenated compounds. However, polar compounds such as camphor, butyl acetate and isopropyl nitrate exhibited significant losses with the ozone scrubber and corrections were needed. As an exception among the unsaturated monoterpenes, camphene was retained in slight amounts by the ozone scrubber.

These data obtained on untreated natural air were confirmed when air from

TABLE IV

QUANTITATION OF MONOTERPENES (SOUTHERN BLACK FOREST/KÄLBELESCHUEER) AND POLLUTION PRODUCTS IN THE AIR OF AN OPEN-TOP CHAMBER CONTAINING A STAND OF SPRUCE AND FIR TREES

The air of the chamber had passed through an activated charcoal filter to remove ozone and other air pollutants. One air sample was taken with, the other without, an ozone scrubber on april 22nd, 1987 at 1 p.m.

Compound	Concentration (ng/m ³)	
	With scrubber	Without scrubber
α -Pinene	319	323
Camphene	39	45
β -Pinene	36	36
Limonene	136	68
Eucalyptol (1,8-cineole)	14	18
Camphor	4.0	17
Benzene	297	247
Toluene	233	235
Ethylbenzene	54	50
Trichloroethylene	71	81
Tetrachloroethylene	97	106

open-top chambers was used. This air was purified by passage through activated carbon filters before gassing a stand of coniferous trees (*Picea abies* and *Abies alba*). Air samples taken in these chambers with and without an ozone scrubber are presented in Table IV. Since the air contained only low ozone concentrations, the ozone scrubber was found to have no effect on the α -pinene and β -pinene concentrations. Only limonene with its extremely high rate constant was protected by the ozone scrubber against the traces of ozone still present in the air. Again, little effect was observed on stable pollution products. Camphene and camphor gave higher values without the ozone scrubber.

In rural and forested areas the natural emission of terpenes is an important control mechanism for the ozone concentrations in the air. On the one hand, olefinic monoterpenes can be regarded as a sink for ozone due to their chemical reactivity, on the other hand, together with nitrogen dioxide they are precursors of photochemical reactions leading to the formation of ozone during the day. To enable the kinetics of natural air masses to be calculated, the actual concentrations of olefinic compounds in the air must be known. The technique presented here allows the determination of these components under all weather conditions and clearly differentiates between concentrations of monoterpenes actually present in ozone-rich air and concentrations obtained when both monoterpenes and ozone are trapped together on an adsorbent and are allowed to react with each other.

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