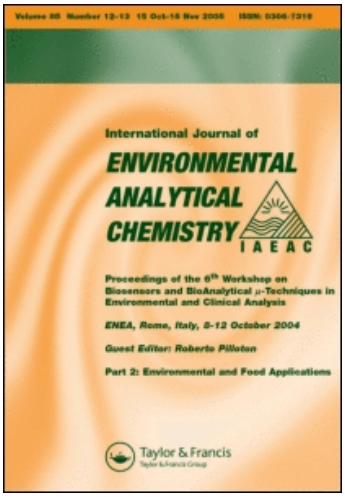

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Estimation of Volatile Substances in the Atmosphere of Forest Ecosystems by Gas Chromatography

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Estimation of Volatile Substances in the Atmosphere of Forest Ecosystems by Gas Chromatography

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Volatiles occurring in the open atmosphere of forested areas can be determined practically only by employing sample enrichment techniques of gas chromatographic trace analysis. A technique was developed of concentrating trace volatiles from large air samples (5–15 l) on trapping columns packed with Tenax GC, followed by the thermal desorption and gas chromatographic analysis of the concentrate by using a flame ionization detector. A procedure is shown of calculating the masses of the individual components of the concentrate by virtue of the basic properties of the flame ionization detector as a non-ideal coulometer, which makes it possible to estimate reliably the concentrations of the analytes in the air analysed from the parameters of the chromatogram without direct calibration for the components under determination. At the usual concentrations of the analytes in the forest atmosphere, special measures have to be taken in order to protect the samples entrapped in the Tenax column against contamination with artifacts. Several tens of volatile components with boiling

points in the range of 30–230°C at concentrations within 1–100 ng/m^3 were found in the atmosphere of various kinds of forest by the method described. With our instrumentation and under the conditions employed, the times of sampling 15 l of air, gas chromatography of the concentrate, and manual processing of the chromatogram amounted to about 150, 80 and 60 min, respectively. The method is suitable particularly for monitoring slow changes in the composition of volatile hydrocarbonaceous compounds in the atmosphere of various ecosystems.

KEY WORDS: Trace analysis, volatile metabolites, forest atmosphere, sample enrichment, gas chromatography, sample contamination.

INTRODUCTION

Plants are producers of substances creating the plant bodies, and also of substances, i.e. certain secondary metabolites, that are released to the environment. The substances released as solids or liquids always come in contact with the soil, and, especially with some species, become important growth regulators for other species occurring nearby. The metabolites released from plants in the form of gases or vapours are not confined to their close neighbourhood (except for those that are, for instance, washed out of the air by rain) and become an ecological factor even in a distant environment.

The role of the substances called allelopathics[1] has been known since as early as the Middle Ages.[2] Different authors have classified these substances from the viewpoints of their origin and the kind of their coactions, i.e. according to whether substances that are produced or substances that are absorbed, influencing higher plants or micro-organisms, are concerned, whether this effect is stimulating or inhibiting, etc. These substances are e.g. phytoncides, kolins, ekrins, phytoalexins, vivotoxins, marasmins, blastokolins and exohormones.[3–7] In addition, it has been proved that some of these substances play a role also in relations between insects and other organisms, for example, as telergons, pheromons and similar agents,[8–10] and/or as repellents. Whittaker and Feeny[11] compared different views on the function of the secondary substances. Now these substances are supposed to influence not only the metabolism, autoregulations, growth and development of organisms, but also their behaviour, social structures and creation of biocenoses.[7,12] The substances mentioned are of great importance in natural as well as

cultivated cenoses and influence the quality of the environment also from the anthropic and sanitary points of view.[13-16] The possibility of getting information on the physiological state of trees or stands by virtue of the analyses of plant volatile substances occurring in the air of forest ecosystems, similarly as e.g. insects can do it, is especially important.

In view of the methodological approach to the problem, gas chromatography appears to be the most suitable choice. The modern gas chromatographic instrumentation with flame ionization detection makes it possible to determine reliably about 10^{-10}-g amounts of organic substances when the sample to be analysed is introduced directly into the gas chromatograph. In gas chromatography on normal packed columns it is possible to easily charge gaseous samples as large as 5 ml, so that concentrations of about 20 $\mu g/m^3$ can be determined in this way. Although this sensitivity is appreciably high, it is by far not sufficient to solve our problem. Preliminary experiments have shown the concentrations of volatile compounds in the atmosphere of forest growths to be about three orders of magnitude lower, which can be determined only by using appropriate sample enrichment techniques combined with gas chromatography.

Attaining an enrichment factor of 10^3 is a relatively difficult task not only in view of concentrating the components to be determined, but also in view of undesirable interferences by artifacts. Namely, a typical problem of ultratrace analysis is concerned, in which the background of artifacts may be much larger compared to the signal of the compounds under determination. In the course of the development of the analytical method the problem of interferences indeed proved to be a most important one. Also the analytical interpretation of the gas chromatographic output data is appreciably more difficult when sample enrichment techniques are involved.

The necessary increase in the analyte concentration was attained by drawing a large volume of the air analysed through a short column packed with a sorbent. The trapping column was then connected into the carrier gas circuit ahead of the inlet to the analytical column of the gas chromatograph. Upon heating up the trapping column the compounds entrapped were desorbed and the concentrate so obtained was entrained by the carrier gas into the analytical column and analysed by using a flame ionization detector.

Similarly, as in other works,[17–20] Tenax GC was used as a packing of the trapping column. In this way it was possible to determine concentrations as low as units of nanograms per m^3. In order to facilitate the characterization of the individual analytes on the basis of their retention behaviour, the chromatograms were run under isothermal conditions. The analytical procedure proper was designed so as to provide relevant, though approximate information on the nature and quantitative representation of the individual analytes with minimum reference data.

EXPERIMENTAL

Analytical method

1. Qualitative characterization of the analytes The components represented by the individual peaks in the chromatogram of the concentrate were characterized by calculating their retention indices[21] and estimating their boiling points from the respective retention data. We assumed the analytes to be altogether nonpolar compounds of hydrocarbonaceous character. In gas chromatography of such compounds on a column with a hydrocarbonaceous liquid stationary phase under constant conditions the logarithms of the adjusted retention times of the analytes are approximately linearly proportional to their boiling points. A plot of the logarithms of the adjusted retention times (t'_R) of reference *n*-alkanes against their boiling points (b.p.) was provided, and the boiling points of the compounds under determination were found by fitting their t'_R values, measured under the same conditions as with the reference hydrocarbons, to the plot. The retention indices were determined by means of a plot of $\log t'_R$ against the carbon number of the reference *n*-alkanes.

2. Quantitative analysis The method of quantification must involve the determination of the degree of accumulation of the analytes, the determination of the masses of the individual components of the concentrate from the chromatogram of the latter, and the subtraction of the interfering background. The first item is rather problematic. While drawing the air analysed through the trapping column, frontal chromatography of the components being trapped

takes place. As the concentrate is a multicomponent mixture with a pretty wide boiling-point range (i.e. wide range of sorbability), and it is necessary to draw appreciable large air volumes through the trapping column, one must reckon with the fact that the frontal zones of some weakly sorbed components will pass through the column in the course of sampling and, possibly, equilibrium between the concentrations of the respective components in the air and in the sorbent will be established, while more strongly sorbed components will be totally captured in the column. In the first case we speak of equilibration trapping and in the second of conservation trapping. In both cases it is necessary to define the so-called safe sampling volume, which equals approximately either the sum of (equilibration mode), or difference between (conservation mode) the retention volume of the given component on the trapping column and the two-multiple of the volumetric standard deviation of the respective elution zone.[22,23] The difference between the equilibration and conservation regimes of trapping must carefully be taken account of. For this reason, we have provided a plot of the logarithm of net retention volume (V_R^x) against carbon number for a series of *n*-alkanes on the trapping column (Tenax GC) at several temperatures within the range of supposed temperatures of sampling, and the analytes to be trapped were looked upon in this context as pseudoalkanes with carbon numbers corresponding to their retention indices on Apiezon L at the temperature of the analytical chromatographic column (Figure 2). In this way it was possible to quickly estimate the retention volume of a component on the trapping column and then decide whether equilibration or conservation trapping is concerned. Simultaneously, the data ($V_{R_i}^x$ in the case of equilibration trapping) necessary to calculate the results could be obtained.

The absolute calibration of the detector was carried out in order to convert the areas of the peaks in the chromatogram to the masses of the respective analytes. The ionization efficiency[24] in Coulombs per a gram-atom of paraffinic carbon was determined empirically for the flame ionization detector employed under the working conditions chosen, and this detector was then utilized as a non-ideal coulometer.

In order to eliminate and/or suppress the interfering background, the trapping columns were purged by carrier gas at the temperature used to desorb the concentrate before each analysis. The course of

purging was followed by checking the chromatographic record. The purged columns were kept in hermetically closed casings with no contact with any material that could produce traces of volatile compounds.

Instrumentation and procedure

1. Sampling The air analysed was sucked through the trapping column with the aid of an MP-1 diaphragm pump (Chemoprojekt, Satalice, Czechoslovakia). The rate of air flow through the trap was controlled and measured by a needle valve and flowmeter connected to the outlet of the pump. In the sampling proper the trapping column was situated about 10 m above the ground level, approximately in the middle of the crown zone of the surrounding forest growth. The sucking rate was about 100 ml/min and the sample volumes varied within 5 to 20 litres. The temperature of the air sampled was measured with an alcohol thermometer.

2. Gas chromatograph A Chrom 2 gas chromatograph with a flame ionization detector (Laboratory Instruments, Prague, Czechoslovakia) was employed for the analyses of the concentrates obtained from the trapping columns. The analytical column was of stainless steel, 2.4 m long and 6 mm in the inner diameter, packed with a 10% Apiezon L-on-60/80 Chromosorb W packing (Carlo Erba, Milan, Italy), the mass of the column packing being 22 g. The flow rates of the carrier gas (nitrogen), hydrogen and air were 100.5, 65, and about 1500 ml/min, respectively, and the column temperature was 80°C. Under these conditions, the efficiency of ionization in the flame was 0.05 Coulomb per a gram-atom of paraffinic carbon, as determined by calibration. At the full electrometer sensitivity , an ionization current of 1×10^{-11} A produces an electrometer output voltage of 10 mV with the Chrom 2 apparatus. The recorder was set to 5 mV per full scale deflection (280 mm). All the above electrometer and recorder parameters have to be known for calculating the results when employing the method described here.

3. Trapping columns The trapping columns were 60 mm long glass tubes of 5 and 4 mm in the outer and inner diameters, respectively, each packed with 90 mg of 30/60 Tenax GC (Applied Science Labs.,

State College, PA, U.S.A.). The sorbent was fixed in the column by two quartz wool clumps. In order to minimize the possibility of contaminating the trapping columns with artifacts, they were put in brass casings and closed by screw plugs tightened up against aluminium sealings. In order to facilitate the tightening up and loosening the plug, both the casings and the plugs were manufactured from a hexagonal rod. The length of the casing and the diameter of its hexagonal cross-section were 80 and 19 mm, respectively. The casing was cylindrical, about 63 mm long and 6.5 mm in the diameter. Hence, there was minimum freedom for the column to move when closed in the casing. Before the first use the casings were washed with acetone, to remove contaminants coming from manufacture, and then heated at 400°C for 4 hours. The column was taken out of the casing only for sampling and the analysis of the concentrate. The time for which the column was exposed to the laboratory atmosphere (from the instant of opening the casing to that of completing the installation of the column in the gas chromatograph) did not exceed 10 seconds.

4. Analysis of the concentrate A system was installed ahead of the sampling port of the gas chromatograph, that provided for connecting the trapping column into the carrier gas line, heating up the trapping column to the desired temperature, and switching over the carrier gas flow so as to direct it either straight to the analytical column while the trapping column was closed on both ends (heating-up period), or via the heated trapping column (purging the concentrate). This system made it possible to proceed as outlined above, while simultaneously injecting samples into the gas chromatograph by an injection syringe through the septum. A flow diagram of the arrangement is shown in Figure 1. The trapping column (1) is placed into a steel frame[25] provided with connections to the inlet and outlet of the carrier gas. Silicone rubber sealing rings are situated between the connections and the faces of the trapping column. One of the connections can be traversed by means of a screw along the projected axis of the trapping column, thus making it possible to connect the column gas-tightly into the system by simply inserting it into the frame and tightening up the screw. The sample inlet port of the gas chromatograph is modified with an adapter (2) constituted by a brass cylinder with a stainless steel capillary soldered laterally

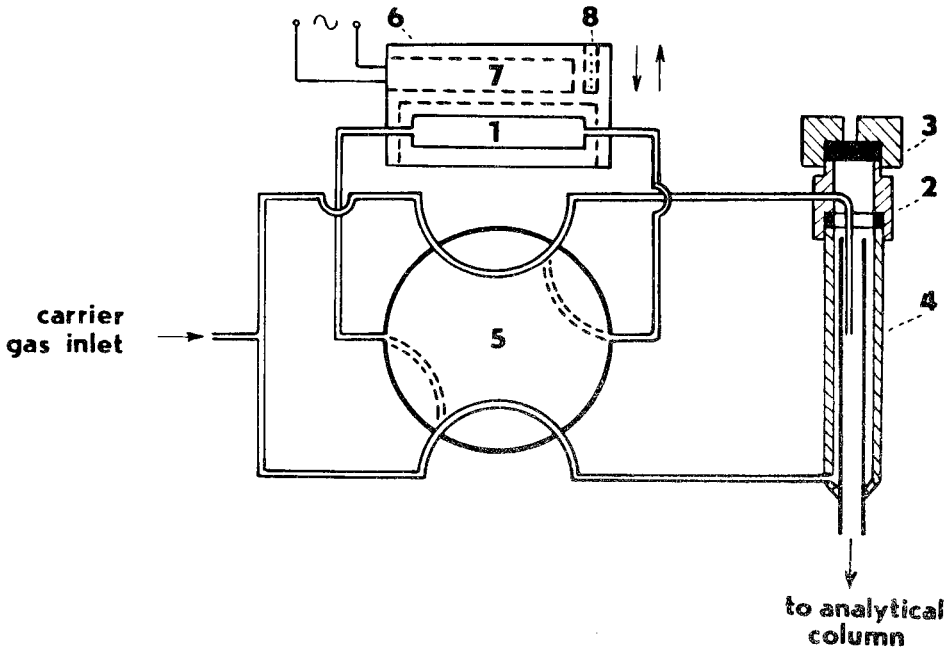

FIGURE 1 Arrangement for introducing the concentrate from the trapping column to the gas chromatograph. 1, trapping column; 2, adapter to the GC sampling port; 3, septum holder; 4, GC sampling port; 5, six-port stopcock; 6, oven; 7, heater; 8, temperature sensor.

into the cylinder and bent coaxially inside. The adapter is screwed on the sample inlet port (4) in place of the septum cap and tightened up against a silicone rubber sealing ring put on the place where the septum was originally positioned. With the adapter installed, the inner end of the capillary is inserted into the sampling port to reach about half the length of the column inlet liner. The original inlet of the carrier gas to the sampling port and the outer end of the capillary from the adapter are connected into the system as shown in Figure 1. The septum proper is situated only on the adapter and held by an appropriate cap (3). The distribution of the carrier gas is controlled by means of a six-port stopcock (5) with two mutually opposite ways in the core. Before putting the trapping column into the system, the carrier gas flows through the paths indicated by the

solid lines in the stopcock core, i.e., simultaneously both in the normal way into the sampling port and via the adapter capillary directly into the column inlet liner. In this phase, the heating oven (6) is off the system. After installing the trapping column into the system and fitting the oven into the trapping column, the latter is heated for 5 min at 200°C, whereupon the stopcock is switched over to direct the carrier gas via the paths indicated by the dashed lines in the core of the stopcock. During this phase, the concentrate is purged out of the heated trapping column and enters, via the adapter capillary, the analytical column of the gas chromatograph. The oven is heated by an electrical heating catridge (7). The electrical supply to the cartridge is controlled by a regulator comprising a resistor temperature sensor (8) situated inside the aluminium body of the oven nearby the heated trapping column.

Processing of experimental data

Retention data From the chromatogram of a series of model *n*-alkanes the dependences of the adjusted retention time on the carbon number and boiling point of the solutes were defined for the conditions chosen. These dependences are represented graphically in Figure 2. Under the given experimental conditions, there was a distinct negative air peak in each chromatogram, the retention time of which was taken as the dead retention time. The plots in Figure 2 served to determine the retention indices and estimate the boiling points of the compounds represented by the individual peaks in the chromatogram of the concentrate from the trapping column. The adjusted retention times (t'_{R_i}), retention indices (I_i), and boiling points (b.p.) of the individual analytes, together with their average (8 measurements carried out in the course of 6 months) concentration (c_i) and the respective concentration ranges, as found by this method in the atmosphere of a mixed forest under different climatic conditions, are summarized in Table I. Symbol n_i denotes the serial number of the peaks of the analytes in the chromatogram of the concentrate.

Quantitative evaluation of the chromatogram

1. Calculation of the masses of the analytes in the concentrate The

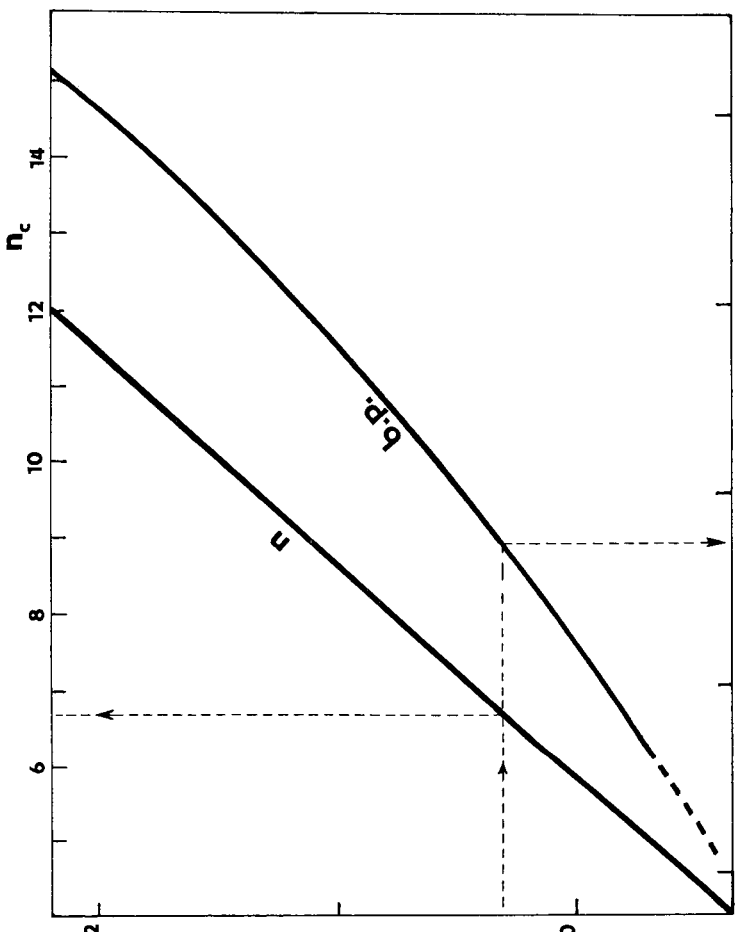

FIGURE 2 Plot of the boiling point (b.p.) and carbon number (n_c) of *n*-alkanes against their adjusted retention time (t'_R) on the analytical column used.

TABLE I

Adjusted retention times, t'_{R_i}, retention indices, I_i, boiling points, b.p., and the concentrations, c_i, of the compounds determined in the atmosphere of a mixed forest. All the data are averages of eight determinations; the respective ranges are given in parentheses. The estimate of the average percentage standard deviation of t'_{R_i} is 6.8%. n_i denotes the serial number of the peaks in the chromatogram of the concentrate.

n_i	t'_{R_i} (min)	I_i	B.P. (°C)	c_i (ng/m^3)
1	0.26	408	0	9.7 (1–15)
2	0.49	490	21	8.1 (1–19)
3	0.60	516	40	39.0 (2–72)
4	0.79	551	53	2.8 (0.3–11)
5	1.04	587	63	5.5 (2–9)
6	1.22	607	71	28.7 (3–73)
7	1.36	621	75	37.4 (1–74)
8	1.73	652	84	12.1 (0.1–32)
9	2.00	671	90	20.4 (3–60)
10	2.22	684	94	12.5 (0.6–49)
11	2.54	702	99	71.4 (35–174)
12	3.01	724	105	25.7 (3–88)
13	3.36	738	109	3.5 (0.1–13)
14	3.80	754	114	3.8 (1–9)
15	4.43	773	119	5.8 (1–10)
16	4.73	782	121	6.9 (2–16)
17	5.17	793	124	30.0 (1–43)
18	5.87	810	128	115.1 (25–224)
19	6.78	828	133	28.3 (3–81)
20	7.51	841	136	4.4 (0.4–9)
21	8.48	857	140	6.6 (1–17)
22	9.52	872	144	5.8 (0.1–10)
23	10.40	883	147	9.2 (0.1–44)
24	11.79	900	151	22.7 (2–48)
25	13.34	915	155	103.6 (3–180)
26	14.70	928	158	42.3 (4–80)
27	16.17	940	161	15.9 (2–37)
28	18.05	954	164	6.2 (0.1–13)
29	20.06	968	167	4.9 (0.1–20)
30	23.72	990	172	12.7 (0.1–28)
31	26.05	1002	175	7.2 (0.1–16)
32	28.98	1015	178	43.8 (0.1–100)
33	33.20	1033	182	36.7 (0.1–45)
34	38.12	1051	185	11.5 (0.1–15)
35	47.97	1080	191	24.3 (0.1–44)
36	58.70	1106	197	66.7 (0.1–133)
37	70.00	1130	200	0.1 (0–0.1)
38	82.20	1150	206	16.0 (0.1–16)

mass of analyte i, m_i, corresponding to a given peak in the chromatogram of the concentrate, is given by[26]

$$m_i = \frac{aA_i}{b} \frac{k_U k_D}{\beta} \frac{M_i}{(\sum C_{\text{eff}})_i} \tag{1}$$

where the individual symbols are: a = factor of sensitivity attenuation, A_i = peak area of analyte i, b = recorder chart speed, k_U = ratio of the ionization current and the electrometer output voltage at the full electrometer sensitivity, k_D = ratio of the voltage span and the scale width of the recorder, β = ionization efficiency, M_i = molar mass of analyte i, $(\sum C_{\text{eff}})_i$ = sum of the effective carbons[24] in the molecule of analyte i. With A_i in mm^2, b in mm/min, $k_U = 10^{-9}$ A/V, $k_D = 1.786 \times 10^{-5}$ V/mm, $\beta = 0.05$ Coulomb per gram-atom of paraffinic carbon, and $M_i/(\sum C_{\text{eff}})_i = 14.25$ g(g-atom C)$^{-1}$, Eq. 1 can be rewritten as

$$m_i[ng] = 0.03054 aA_i/b. \tag{2}$$

Clearly, whereas the relationship described by Eq. 1 applies generally (with a FID), Eq. 2 is valid only for alkanes and the given experimental conditions (k_U, k_D, β).

2. Calculation of the concentrations of the analytes in the air analysed To calculate the analyte concentration, c_i, in the sample analysed, it is necessary to know the volume, V, of the air that has been drawn through the trapping column and decide which analytes have been trapped under conservation conditions. The concentration c_i is then

$$c_i = m_i/V. \tag{3}$$

The following conditions must be fulfilled in this case

$$V \leqq V^x_{R_i} - 2\sigma^x_{V_i} = V_{R_i}(1 - 2/\sqrt{n^x}) \tag{4}$$

where $V^x_{R_i}$ and $\sigma^x_{V_i}$ denote the retention volume and the volumetric standard deviation of analyte i on the trapping column, and n^x is the

plate number of the trapping column under the conditions of sampling (temperature and sampling rate). With equilibrium trapping there holds

$$c_i = m_i / V^x_{R_i} \tag{5}$$

and V is controlled by the condition

$$V \geqq V^x_{R_i} + 2\sigma^x_{V_i} = V^x_{R_i}(1 + 2/\sqrt{n^x}). \tag{6}$$

The $V^x_{R_i}$ values were estimated by the equation[27]

$$log_{10} V^x_g = 340.4\frac{N-2}{T} + \frac{2052.7}{T} - 0.430(N-2) - 5.445 \tag{7}$$

where V^x_g is the specific retention volume[28] (ml/g) of n-alkane with carbon number N at the absolute temperature T on Tenax GC. V^x_R is related to V^x_g by

$$V^x_R = V^x_g \frac{T w_s}{273} + V^x_M \tag{8}$$

where w_s is the mass of Tenax GC in the trapping column and V^x_M is the dead volume (usually negligible) of the trapping column. The $V^x_{g_i}$ values of the individual analytes were calculated by substituting the respective values of $I_i/100$, as measured on the Apiezon L column, in Eq. (7). Although the V^x_g so obtained were merely very rough estimates, they were sufficient to serve the purpose. To facilitate the estimation of the $V^x_{R_i}$ values, the $V^x_{R_i}$ for C_3—C_{15} n-alkanes on a column with 0.09 g of Tenax GC at temperatures of within 273–303 K were calculated by Eqs. (7) and (8) and presented graphically in Figure 3. Again, these data must be taken with reservation, as they have been obtained by extrapolation rather far beyond the region of experimental conditions under which the data used to derive Eq. (7) have been measured. A value of $n^x = 50$ mm was supposed for the estimation of $\sigma^x_{V_i}$. It follows from the plots in Figure 3 that with $N \geqq 7$ and $V \leqq 20$ litres the trapping of the analytes proceeds in the conservation regime.

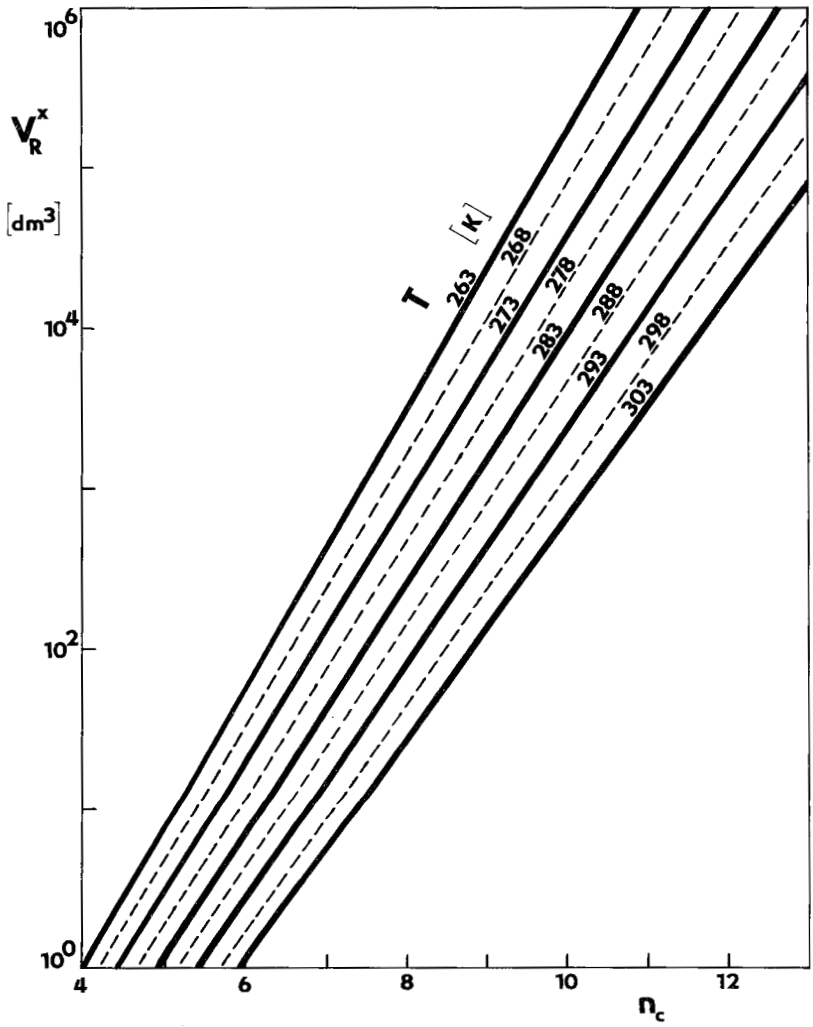

FIGURE 3 Plots of the carbon number (n_c) of *n*-alkanes against their retention volume (V_R^x) on a column with 0.09 g of Tenax GC at different temperatures (T).

RESULTS AND DISCUSSION

The overall concentration of the mixture of volatile substances estimated by our measurements approximated the lower limit of a very wide range of concentrations quoted in the literature. Especially high values have been published by the authors who employed the "wet burning" method or captured the volatile substances in liquid absorbents. For example Lachno and Kozlova[29] found concentration of about 0.5 mg/m^3 within the tree-crown space of pine or larch, 1.5 mg/m^3 in a mixed forest, and 27 to 420 mg/m^3 below the crowns of Ailanthus and Juniperus. Beriashvili[30] found 1 to 3 milligrams per cubic metre in pine or eucalypt forest and up to 1 mg/m^3 in oak forest. Spakhov[31] and Spakhova[32] found about 15 to 30 mg/m^3 in the tree-crown space of some broadleaf species and pine.

The concentrations found by the authors who employed gas chromatographic methods were substantially lower. Thus, Rasmussen and Went[33] have reported the mean concentration of volatiles in the atmosphere to be about 1:10^9 (1 microgram per cubic metre), Hedin[34] found about 0.2 to 0.7 ng/m^3 in a stand of cotton during the vegetation season. Yokouchi *et al.*[35] found about 0.1 to 3.0 micrograms per cubic metre (p.p.b.) in stands of Pinus, Cupressus and Cryptomeria. Holdren *et al.*,[36] when studying the same substances in the atmosphere of mountainous regions, found concentrations of within 10 to 730 p.p.t. (1:10^{12}, i.e. nanograms per cubic metre).

Apparently, the differences in the concentrations reported reflect differences in the plant species stands studied as well as differences in the meteorological conditions during sampling. Nevertheless, the exceedingly high concentrations reported in some earlier papers can be due to artifacts admixed during the manipulation with samples, e.g. if the air sampled was passed through a rubber tube, etc.

Our measurements revealed that the concentration of the mixture of volatile substances in the atmosphere of our laboratory was about three orders of magnitude higher than that of the mixture found in the atmosphere of the nearby forest. The ordinary laboratory air was concerned in the study, not particularly polluted by any significant additional source of impurities. When no special provisions were made to prevent the contamination of samples (i.e. trapping

columns) taken in the forest, the samples were deteriorated very quickly. The original signal was completely overlapped by artifact peaks within hours and/or even minutes if the samples (trapping columns without cover) were left unprotected in the laboratory. The course of sample contamination under various preservation conditions is shown in Figure 4. Closing the trapping column with silicone rubber plugs was found quite unsatisfactory, as the plugs themselves appeared to be a substantial source of pollutants. The brass casing with screw closure and aluminium sealing ring was found suitable, but even in this case it was so only if the casing with the trapping column was not left longer than about 100 hours in the laboratory. The time of manipulation with an open trapping column in the laboratory (from the moment of unscrewing the casing closure to that of installing the trapping column in the sampling port of the gas chromatograph) had to be as short as possible. This time did not exceed 10 seconds in our measurements, which was found satisfactory. The importance of artifacts in a similar situation has already been recognized and pointed out by Mattsson and Petersson.[20]

The extent of spontaneous absorption of volatile substances, i.e. the spontaneous "contamination" of the trapping column that took place when the latter was left exposed (being protected against water precipitation) in the forest atmosphere, showed that this could be used as an alternative sampling method, especially when information on the average composition of the volatiles over a longer period (about weeks to months) was to be obtained. Within certain limits, the composition of the samples obtained in this way was commensurate with that of the samples obtained by short-term sampling (several hours), i.e. by drawing the air through the trapping column.

An example of the spectrum of volatile substances from the atmosphere of a mixed forest (mostly coniferous) in the area of Carpineto-quercetum is shown in Figure 5. Under the conditions described, about 50 substances were found with concentrations ranging from tens to units of nanogram per cubic metre (p.p.t. range). The retention indices and boiling points of the substances ranged within 400 to 1200 and about 30 to 230°C, respectively (see Table I).

The air samples were taken in the course of the whole year, during the winter as well as summer seasons under various weather conditions, including cold days with light snow cover, days with high

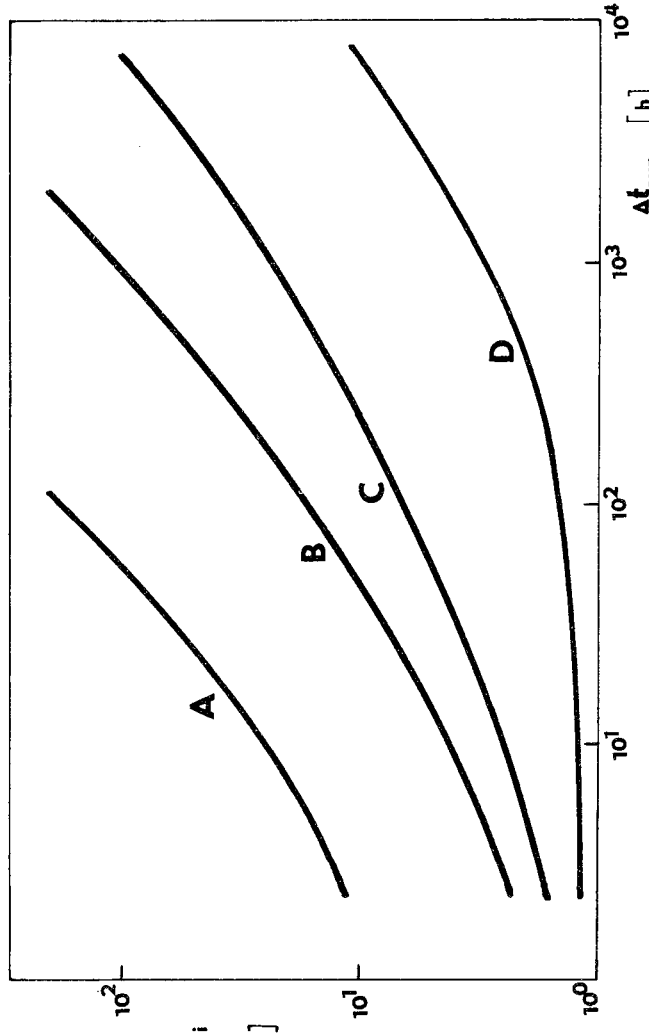

FIGURE 4 Representation of the course of sample contamination under different conditions. m_i, analyte mass determined in the sample concentrate; t_{exp}, time of the exposition of the trapping column with the sample concentrate. *A*, trap left unclosed in the laboratory; *B*, trap stoppered on both ends by silicone rubber plugs and left in the laboratory; *C*, trap left unclosed in the forest atmosphere (tree crown level); *D*, trap closed in the brass casing and left in the laboratory.

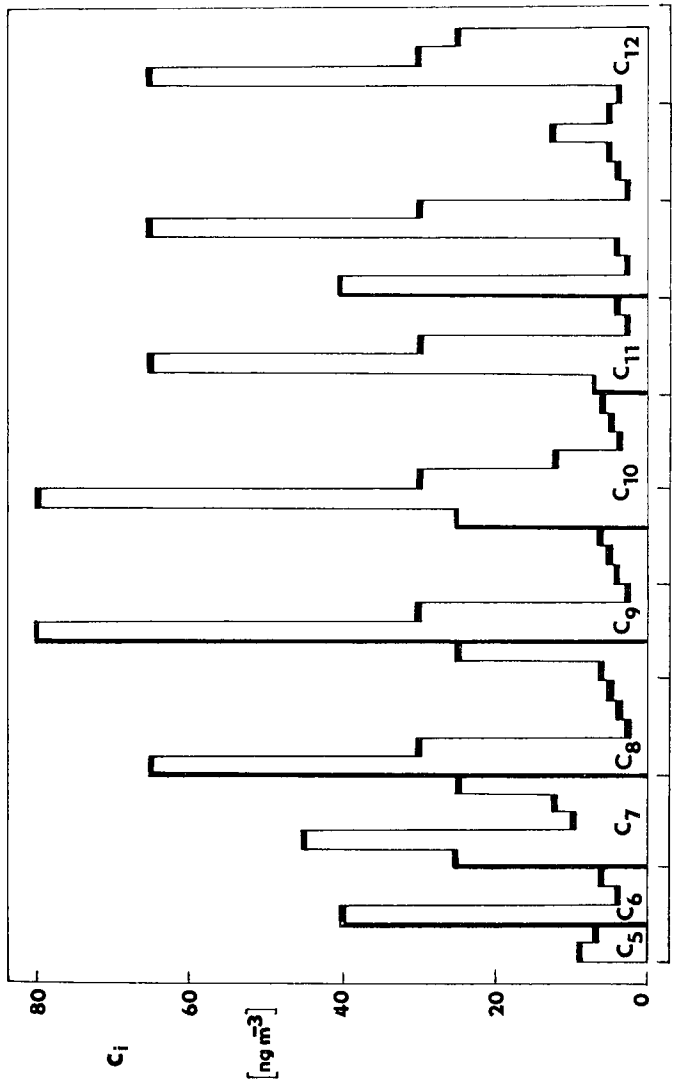

FIGURE 5 Schematic representation of the relationship between the peak number (n_i) and concentration (c_i) of the analytes determined in the atmosphere of a mixed (mostly coniferous) forest. The carbon numbers refer to the reference *n*-alkanes used to define the retention index scale.

air humidity, and hot summer days. No detailed analysis of the influence of weather conditions on the changes in the composition of the volatile substance was carried out in the present study. However, the range of the concentrations of the individual substances, shown in Table I, indicates the interval over which the influence of weather manifests itself.

The total time of analysis is pretty long. Under the conditions used in this work, the drawing of 15 l of air through the trapping column, gas chromatographic analysis of the concentrate from the trapping column, and the manual (our case) processing of the chromatogram, i.e. the measurement of the retention times and peak areas together with the qualitative characterization and quantification as described above, took 150, 90, and about 60 min, respectively. The times necessary to manipulate with the trapping column when closing it in the casing, installing it in the arrangement for thermal desorption on the gas chromatograph, and carrying out the thermal desorption proper were negligible. Hence, one analysis lasted about 5 hours. However, if the fact is taken into account that the ultratrace quantitative analysis of a multicomponent mixture, providing absolute quantitative data is concerned, the time of analysis can be considered as fairly adequate to the information yield. The time of analysis can be substantially shortened by employing a capillary analytical column instead of the packed one and by the automatic processing of the chromatographic data according to a suitable program for the qualitative characterization and quantification of the individual analytes. In this case the time of the gas chromatography of the concentrate could be shortened, at about the same peak resolution, to about a tenth of that necessary with the packed column, and the time necessary for the chromatogram processing and data handling would be made virtually negligible. Thus, the total analysis would then be given practically by the time of sampling only, i.e., it would amount to about 1.5 hours. This time cannot be shortened very much any longer, as on increasing the rate of sucking the air sampled through the trapping column the separation efficiency of the latter decreases and the safe sampling volume for the conservation variant of analysis decreases accordingly (see Eq. (4)).

The use of a capillary column not only provides for a much faster chromatography of the concentrate, but it automatically makes the

analysis proper an order of magnitude more sensitive.[37] On the other hand, however, problems can arise with transferring the concentrate from the trapping column into the capillary analytical one. At the analyte concentrations determined in this work, it is inevitable to employ the splitless mode of sample introduction and the cold focusation of the concentrate zone at the capillary column inlet. As the concentrate contains an appreciable portion of very low-boiling compounds (see Table I), focusing the concentrate zone in the capillary column may be a problem. Programming the temperature of the analytical column can give a better resolution of the early eluted components and a more sensitive detection of the slowly eluted ones, but the possibility of speeding up the analysis in this way is very debatable.[38] Moreover, in programmed temperature gas chromatography the qualitative characterization of the eluates by virtue of their retention behaviour is not so straightforward and reliable as in isothermal gas chromatography.[39]

Owing to the long analysis time, no statistical evaluation of the quantitative results was carried out. Only the estimates of the relative standard deviations of the adjusted retention times were calculated, which amounted to 6.8% on an average. As the retention indices and boiling points have been calculated from the adjusted retention times by means of the plots in Figure 2, it can be supposed that the I_i and b.p. values suffer from roughly the same error as the t'_{R_i} values. As to the error of the determination of concentration c_i, it may amount to as much as 100% with minor components (low ng/m^3) and about 20% with major ones under the conditions of our measurements.

CONCLUSION

By gas chromatography with a flame ionization detector of defined ionization efficiency (Coulombs per gramatom of paraffinic carbon) it is possible to estimate the absolute masses of the individual solutes without direct calibration for these solutes and without their exact identification, provided the solutes are hydrocarbons. In combination with an efficient sample enrichment technique, this method provides for the convenient and relatively reliable estimation of trace and ultratrace concentrations of substances in various matrices directly

from the chromatogram of the concentrate and the known volume of the sample of the material analyzed. This makes it possible to completely obviate the very difficult step of calibration on a level of ultratrace concentrations. The method is especially suitable for monitoring slow changes in the concentrations of hydrocarbonaceous compounds in the atmosphere of various ecosystems. When taking a 15 l sample of air for analysis and employing a Tenax GC trapping column, it was possible to determine concentrations down to low ng/m^3 with out instrumentation (10^{-11} A f.s.d. electrometer sensitivity, packed analytical column). The use of a more sensitive electrometer (10^{-12} A f.s.d.) and a capillary analytical column theoretically renders the possibility of increasing the sensitivity of analysis still by about two orders of magnitude. A critical point of the procedure is the protection of the sample taken for analysis against its contamination by artifacts.

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