CHROMSYMP. 248

NEW APPLICATIONS OF GAS CHROMATOGRAPHIC HEADSPACE ANALYSIS

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SUMMARY

The problems of the concentration dependence of liquid–gas distribution coefficients and the matrix effects in complex systems with non-volatile components have been considered. On the basis of the relationships established, methods of headspace analysis of aqueous alcohol solutions of non-volatile substances in medium and high concentrations are proposed. The concept of the buffer properties of heterogeneous systems is introduced. Systems with high buffer coefficients can be used as standard mixtures for the calibration of gas chromatographic systems and components. Weakly buffered heterogeneous systems can easily be analysed by the method of discrete gas extraction and can serve for the preparation of standard mixtures with very low contents of volatile compounds. The application of headspace analysis to non-equilibrium systems is illustrated by an investigation of the volatile emissions from living plants. Data were obtained on the dynamics of emission of isoprene and terpenes by arboreous plants, and a number of compounds were detected the presence of which in plant emissions was previously unknown.

INTRODUCTION

This paper briefly presents some new concepts and applications of headspace analysis (HSA) developed in recent years in the Laboratory of Gas Chromatography of Leningrad University and only partially published in Russian. The new viewpoints concern the term "headspace analysis" itself, the dependence of partition coefficients in liquid–vapour systems on sample concentration and the concept of buffer properties of heterogeneous systems. These concepts make it possible to extend the range of applications of HSA to non-equilibrium systems (volatile emissions from plants), to determine the composition of complex mixtures of non-volatile substances present in high and low concentrations and to metrologic purposes and the preparation of standard mixtures with known contents of volatile components.

SOME CONSIDERATIONS ON THE TERM "HEADSPACE ANALYSIS" AND ITS FIELDS OF APPLICATION

We define headspace analysis as a combination of methods and technological

procedures used for obtaining information about the composition, nature or state of liquid and solid bodies by analysis of the gas phase with which they come into contact[1,2]. This definition does not limit the range of application of HSA to equilibrium systems alone and makes it possible to include very important problems of the characterization and identification of various objects emitting volatile substances into the environment. Hence, the range of interest of specialists on HSA should be extended to such subjects as microbiology (problems of taxonomy and biochemistry of microorganisms), the investigations of pheromones and allelopathy (chemical means of imparting information and interaction between living organisms), medicine (diagnosis of infectious diseases and metabolic disorders) and forensic science (proof of identity, determination of ownership of objects, identification of volatile poisons, combustibles, etc.).

It should be noted that at present this broad interpretation of the principles, methods and aims of HSA is not generally accepted. Some researchers prefer to apply this term only to the direct analysis of closed equilibrium systems. However, it seems to us that the exclusion of dynamic methods, methods using preliminary concentration and the exclusion of samples which are not in a state of thermodynamic equilibrium is unfounded and does not meet modern requirements. Restrictions of this type are inadvisable; they prevent further development of HSA and the extension of its range of application.

CONCENTRATION DEPENDENCE OF LIQUID–VAPOUR PARTITION COEFFICIENTS

At present the main field of application of HSA is the trace determination of volatile impurities in various materials. When the content of volatile components is low, the liquid–vapour partition coefficient may be considered to be constant. Most direct methods of determination of the content of these components are based on simple linear relationships between the concentrations of impurities in equilibrium phases. The restriction of the application of HSA to dilute solutions is not reasonable. However, its extension to medium and high concentrations requires that the composition dependence of partition coefficients be taken into account. This problem has not been studied extensively. In fact, only particular cases of maximum dilution of solutions of a volatile component in a binary solvent and the molar ratios of the component in the liquid and vapour phases of binary systems have been considered. The constancy of the liquid–vapour partition coefficient over the entire concentration range of ideal systems reported[2] is observed only when the components exhibit equal volatilities. The following simple relationships may be established for the general case of multicomponent systems and various methods of expressing concentration.

At any fraction units y_j of the expression for vapour composition the sum of the contents of all components is unity: $\sum_j y_j = 1$. Denoting the fraction in the liquid phase of the ith component of interest by x_i, its partition coefficient, $K_i = x_i/y_i$, can be expressed as:

$$K_i = K_i \sum_j y_j \equiv \sum_j \frac{x_i}{y_i} \cdot y_j \equiv \sum \frac{x_i y_j}{y_i x_j} \cdot x_j \tag{1}$$

The value of $x_i y_j / y_i x_j$ in equilibrium systems is actually the relative volatility, α_{ij}, of components i and j. In ideal systems it is equal to the ratio of the vapour pressures of the pure components, $\alpha_{ij} = P_j^0 / P_i^0$, and is independent of concentration. Hence, in ideal systems we have:

$$K_i = \sum_j \alpha_{ij} x_j \tag{2}$$

Consequently, the partition coefficient of each component is a sum of the contributions of all components and is a linear function of the composition of the liquid phase over the entire concentration range (expressed in molar, mass or volume fractions depending on the units used in calculating K).

The treatment of experimental data on the liquid–vapour equilibrium shows that a similar linear concentration dependence is also observed in non-ideal systems over very wide concentration ranges with some empirical constants a_{ij} which can markedly differ from the relative volatilities α_{ij}:

$$K_i = \sum_j a_{ij} x_j \tag{3}$$

For binary systems eqn. 3 becomes:

$$K = A + Bx \tag{4}$$

Table I shows that the linear relationship in eqn. 4 is observed with very high correlation coefficients over almost all the concentration range of binary organic systems. Eqn. 4 is also observed in azeotropic systems exhibiting considerable deviations from additivity such as aqueous alcohol solutions. According to the experimental data presented in Table II, in a water–ethanol system the average divergence of the partition coefficients calculated by using eqn. 4 from their experimental values does not exceed 1% at ethanol contents up to 66%. In a similar system with isopropanol the divergences are slightly greater, averaging 3%, but it should be borne in mind that when the alcohol concentration is increased to 60% the partition coefficients themselves increase by a factor of 10 (from 0.07 to 0.7).

The additivity of K (eqn. 3) may serve as a basis for evaluating "matrix effects": the effect of additives and the composition of a complex solvent on the partition coefficient of a given component. Among other applications of these relationships, the possibility of determining partition (and activity) coefficients at limiting dilutions should be mentioned. In fact, the constant A (eqn. 4) is the limiting value of K as $x \to 0$. A linear extrapolation of experimental data to $x = 0$ for concentrated solutions can be very useful at high K values when a direct determination of these data in dilute solutions leads to great errors.

HSA OF SOLUTIONS OF NON-VOLATILE SUBSTANCES

An important feature of eqns. 2 and 3 is the fact that they continue to be valid even when non-volatile components and virtually insoluble gases are present in a heterogeneous system. In ideal systems the terms $\alpha_{ij} x_j$ corresponding to these com-

TABLE I

CONSTANTS OF THE LINEAR EQUATION $K = A + Bx$ AND THE LIMITS OF ITS APPLIC-
ABILITY IN BINARY MIXTURES WITH ORGANIC COMPONENTS

Calculated according to data in ref. 15.

Components	Temp. (°C)	Limiting value of x^*	A	$B \cdot 10^2$
Ethane–pentane	37.8	95 (0.9998)	0.0351	0.9984
Propane–benzene	71	75 (0.9998)	0.0501	1.0072
Hexane–cyclohexane	70	90 (0.997)	0.6597	0.3582
Benzene–cyclohexane	60	50 (0.994)	0.7088	0.6049
Benzene–chlorobenzene	70	100 (0.9997)	0.2186	0.7814
Benzene–aniline	70	100 (0.99999)	0.0157	0.9843
Heptane–butanol	50	80 (0.99994)	0.0529	1.0694
Benzene–ethanol	50	70 (0.9996)	0.1910	1.1486
Perfluorohexane–hexane	25	85 (0.99994)	0.0176	1.1779
Carbon tetrachloride–benzene	50	75 (0.9993)	0.8195	0.2107
Ethyl bromide–ethanol	30	95 (0.99999)	0.0351	0.9984
Acetone–hexane	45	50 (0.9997)	0.1445	1.6130
Acetone–benzene	35	45 (0.998)	0.2432	1.0780
Acetone–methanol	20	55 (0.9995)	0.3139	0.8993
Acetone–ethanol	32	50 (0.9997)	0.1342	1.1980
Acetone–water	25	95 (0.99997)	0.0150	1.0072
Methanol–1,2-dichloroethane	40	90 (0.9998)	0.0453	2.8070
Cyclohexane–ethanol	25	90 (0.9999)	0.1910	1.2210

* Weight percentages with correlation coefficients indicated in parentheses.

TABLE II

LINEAR DEPENDENCE OF LIQUID–VAPOUR PARTITION COEFFICIENTS ON COMPOSI-
TION IN ETHANOL–WATER (30°C)

Alcohol concentration, weight %		$K = x/y$		Divergence	
x	y	Exptl. I	Calc.* II	Absolute $II-I$	Relative $(II-I)/I$ (%)
1.985	16.3	0.1218	0.1197	−0.0021	−1.7
4.11	28.8	0.1427	0.1422	−0.0005	−0.35
6.734	38.7	0.1740	0.1700	−0.0040	−2.3
9.41	47.0	0.2002	0.1983	−0.0015	−0.75
14.65	57.3	0.2557	0.2538	−0.0019	−0.74
21.03	66.3	0.3172	0.3214	+0.0042	+1.32
28.74	73.0	0.3937	0.4030	+0.0093	+2.36
30.22	72.6	0.4163	0.4187	+0.0024	+0.58
41.57	77.5	0.5364	0.5389	+0.0025	+0.47
48.80	78.9	0.6185	0.6154	−0.0031	−0.50
59.92	81.3	0.7370	0.7332	−0.0038	−0.52
66.39	82.7	0.8028	0.8017	−0.0011	−0.14
			Average divergence		0.98

* According to the equation $K = 0.09868 + 0.01059x$ ($r = 0.9999$).

ponents simply become equal to zero and the composition may be calculated for the sum of the volatiles. This allows the derivation of simple equations for the HSA of solutions of non-volatile substances. In the simplest case of a ternary system with one (the third) non-volatile component, eqn. 4 becomes:

$$K_2 = \alpha_{21}(1 - x_3) + (1 - \alpha_{21})x_2$$

Moving on to the expression for the concentration of the liquid phase in fractions of the sum of the volatile components, we obtain the equation for the partition coefficient in a ternary system, $K'_2 = x'_2/y_2$,

$$K'_2 = \alpha_{21} + (1 - \alpha_{21})x'_2 \tag{5}$$

which is analogous in form to the equation for binary systems.

The non-ideality of ternary systems may be taken into account by introducing additional terms into eqns. 4 or 5. These terms represent the effect of the non-volatile component on the partition coefficients of volatile components, *i.e.*, the salting-out effect. For example, the data for aqueous alcohol solutions of saccharose are adequately described by the empirical equation[3]:

$$K'_2 = 0.1014 + 1.052 \cdot 10^{-2}x'_2 - 6.474 \cdot 10^{-4}x_3 \tag{6}$$

This equation makes it possible to calculate the partition coefficient of ethanol in solutions containing up to 50% of saccharose with a relative error of about 0.9% at 30°C.

The analogous empirical equation

$$K'_2 = 0.05647 + 1.139 \cdot 10^{-2}x'_2 - 1.721 \cdot 10^{-5}x'_2x_3 \tag{7}$$

may be derived for carbamide solutions in isopropanol–water mixtures[4] (temperature 30°C).

Similar equations may be used for the HSA of volatile solvents in solutions of non-volatile substances or substances decomposing upon injection into the chromatograph. In fact, since $K'_2 = x'_2/y_2$, the composition of the solvent, x'_2, may be established by the determination of y_2, *i.e.*, the gas chromatographic (GC) analysis of equilibrium vapour according to the equation

$$x'_2 = y_2(A + Bx'_2 + Cx_3)$$

or

$$x'_2 = y_2 \cdot \frac{A + Cx_3}{1 - By_2} \tag{8}$$

At low constants C or at low constants of the non-volatile component the term Cx_3 in the numerator of eqn. 8 may be neglected, and dilute solutions of non-volatile substances may be analysed by using the parameters A and B of the solvents. Table III lists the results of HSA of medicinal tinctures (aqueous alcohol solutions con-

TABLE III

DETERMINATION OF ALCOHOL CONCENTRATION (VOL. %) IN MEDICINAL TINCTURES

Tincture	Pharmaco-poeial analysis (I)	GC analysis of		Divergences	
		Liquid (II)	Vapour (III)	II−I	III−I
Calendula	67.6	67.5	67.9	−0.1	+0.3
Absinthium	70.4	69.7	70.6	−0.7	+0.2
Echinopanax	67.8	68.7	69.0	+0.9	+1.2
Labrador-tea	59.4	59.0	58.8	−0.4	−0.6
Valerian	68.7	68.6	69.3	−0.1	+0.6
Hawthorn	69.7	69.7	68.8	0.0	−0.9
Cimicifuga	69.3	68.8	68.2	−0.5	−1.1
Bilberry	69.5	69.0	69.4	−0.5	−0.1
Leonorus	68.2	68.2	67.7	0.0	−0.5
		Average divergence		0.4	0.6

taining a few per cent of non-volatile extractive substances). As can be seen, the precision of the analyses is almost the same as when the tinctures are injected directly into the chromatograph, and the difficulties caused by contamination of the columns with non-volatile substances are absent. Moreover, HSA may be carried out with the available automatic analyzers much faster than the standard pharmacopoeial method based on the distillation of the solvent and the determination of the distillate density.

At high concentrations of non-volatile components it is impossible to neglect their effect, and HSA should be combined with the measurement of a property of solution sensitive to the content of the non-volatile component. In many cases it is convenient for this purpose to use the refractive index. The determination of the
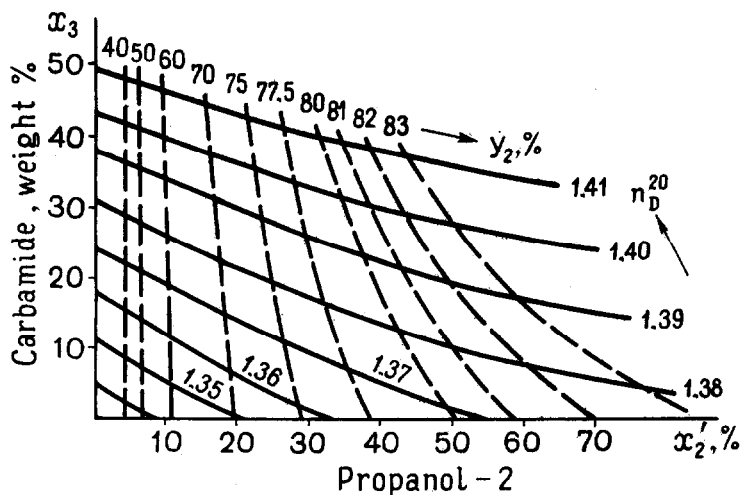

Fig. 1. Determination of the composition of solutions of carbamide in isopropanol–water mixtures fokm vapour phase GC analysis data and the refraction coefficient of the solutions.

TABLE IV

RESULTS (wt.%) OF THE ANALYSIS OF CONTROL CARBAMIDE SOLUTIONS IN AQUEOUS
ISOPROPANOL

y_2 (%) at 30°C	Refr. index n_D^{20*}	Found (%)		Introduced (%)		Divergences	
		Carbamide, x_3 (I)	Alcohol, x_2 (II)	Carbamide, x_3 (III)	Alcohol, x_2 (IV)	I−III	II−IV
58.8	1.3490	5.30	9.90	5.33	9.77	−0.03	+0.13
77.7	1.3677	5.40	35.8	4.94	35.87	+0.46	−0.07
56.7	1.3571	11.75	8.62	11.62	8.92	+0.13	−0.10
83.0	1.3853	11.75	65.4	11.23	66.76	+0.52	−1.36
68.5	1.3679	15.85	15.95	16.20	14.94	−0.35	+1.01
82.5	1.3985	27.9	46.3	27.57	46.74	+0.33	−0.44
75.8	1.3893	27.95	24.8	28.21	22.61	−0.26	+2.19
36.1	1.4014	43.1	3.32	42.96	3.36	+0.14	−0.04
			Average divergence			0.28	0.67

* IRF-22 refractometer (Abbe type).

composition of ternary mixtures of carbamide, propanol-2 and water used in indus-
trial dewaxing of oil products may serve as an example of this type of analyses.
Further development and automation of the industrial control of large-scale pro-
duction at oil refining plants will be favoured by a combination of HSA with refrac-
tive index measurement carried out directly in pipelines with automatic flow refrac-
tometers.

The principle of this method is illustrated in Fig. 1 which shows a network of
vapour isoconcentrates (lines of constant y values) and isorefracts of the liquid in a
linear coordinate system of the composition (x_2', x_3) of carbamide solutions in
aqueous isopropanol. The composition of the solution is determined by the intersec-
tions of the corresponding isolines. The precision of analysis attained by this method
can be seen from the data presented in Table IV. When the refractive index is mea-
sured with a common Abbe-type refractometer and the peak areas for alcohol and
water are calculated with an electronic integrator of the Hewlett-Packard 7620A
chromatograph with a katharometer, the average error in the determination of car-
bamide concentration was about 0.3% and that for isopropanol was 0.6%. Naturally,
it is not necessary to plot nomograms similar to those shown in Fig. 1 because the
combined solution of eqn. 8 and the polynomials expressing the dependence of the
physical properties on solution composition can easily be carried out with common
programmed pocket calculators.

These examples show the possibility of application of HSA to medium and
high concentrations of non-volatile compounds.

APPLICATION OF HSA TO THE TESTING AND CALIBRATION OF GC INSTRUMENTS

One of urgent problems of modern analytical chemistry is further development
of methods for the preparation of control mixtures with very small but precisely
known (and stable) component contents. The use of gas extraction relationships[2]

opens up new prospects for the solution of this problem in the most complex case of solutions of volatile compounds.

The idea of calibrating GC detectors according to the principles of liquid–vapour equilibria is not new. The first publications on this problem appeared 20 years ago, and previous studies are briefly considered in our monograph[2]. The necessity of knowing the precise values of the partition coefficients and the vagueness and complexity of calculations of dynamic variants have long restricted the practical metrologic application of HSA. The main features of such methods and the possibilities of using them become very clear in the light of the concepts of the "buffer effect" of heterogeneous systems and the "buffer coefficient". The desirability of introducing these concepts for describing the processes of gas extraction under equilibrium conditions has already been pointed out in our work on the determination of volatile impurities in polymers[5].

The buffer coefficient, B, characterizes the possibility of stabilizing the concentration of one phase at a given gas-to-liquid volume ratio, $r = V_G/V_L$, and a given partition coefficient, K:

$$B = K/(K + r) \tag{9}$$

The value of B is the fraction of the volatile component remaining in the liquid after the establishment of equilibrium with the gas. It can be measured directly from the ratio of areas, A, or heights under the peaks on the chromatograms of the gas phase when it is successively replaced

$$B = A_{n+1}/A_n \text{ or } B = \sqrt[n]{A_n/A_0} \tag{10}$$

where n is the number of replacements of the equilibrium gas phase with a pure gas and the subscript zero refers to the initial gas phase at $n = 0$.

In heterogeneous systems with high values of the buffer coefficient, B, the concentrations in the gas phase will remain constant even after a considerable proportion of the vapour of a component has been removed from this phase by sorption on the walls of the vessel, stoppers or gaskets or by slow decomposition, oxidation, polymerization and photo- or biochemical processes. Compensation for the change in the content of trace components and their constant concentration in the gas phase will be ensured by the restoration of the phase equilibrium and the passage of volatile components from the liquid phase which acts as a buffer reservoir of large capacity. A strongly buffered heterogeneous system can be used several times as a standard sample with a constant vapour concentration. In fact, if the required constancy in concentration, *i.e.*, the allowed relative decrease in component concentration in the gas phase, δ, does not exceed a few per cent, then the number of possible repeated gas extractions, n, is determined by the condition

$$n \leqslant -\delta/100 \ln B \tag{11}$$

Thus, when the concentration in the gas phase is constant to 1% of its value and the partition coefficient K is 1000, a standard solution may be used up to ten times for the preparation of a gas mixture of required concentration in portions of volume

equal to its own volume: $B = 1000/(1000 + 1) = 0.999$ and $n \leqslant -1/100 \ln B \approx 10$.

The gas phase of relatively weakly buffered heterogeneous systems with coefficients $B < 1$ may also be regarded as a concentration standard, but in this case the change in the concentration of the initial solution, C_L^0, caused by evaporation of the volatile component should be taken into account and the equilibrium concentration of the gas phase after n replacements with a pure gas should be calculated according to the equation:

$$C_G = C_L^0 B^{n+1}/K \tag{12}$$

The concentration of the liquid phase will decrease according to:

$$C_L = C_L^0 B^{n+1} \tag{13}$$

Hence, under equilibrium conditions, discontinuous gas extraction may be used to prepare solutions of volatile substances and gas mixtures of known concentration. At favourable (in this case at not very high) values of the buffer coefficient the degree of dilution may be very high. It should be borne in mind, however, that an excessive increase in the number of repeated extractions leads to a decrease in the precision of determination of the final concentration because the experimental errors are summed. The initial concentration, C_L^0, is fixed by the injection of a precise feed of a volatile liquid or a precise gas volume into the closed heterogeneous system with known phase volumes. It is essential that the values of the coefficients B and K required for the operation are obtained in the process of preparation of mixtures by chromatographic analysis of the equilibrium vapour phase and calculated according to eqns. 10 and 14:

$$K = rB/(1 - B) \tag{14}$$

This method of preparation of standard mixtures with low contents of volatile components proved to be very suitable for solutions of gaseous hydrocarbons in insulation oils. Such solutions are necessary for HSA diagnosis of defects in power transformers[7,8].

Table V lists the precision of the concentrations of acetone and benzene vapours over solutions in water and Carbowax. It is seen that the calculated concentrations and those determined by GC coincide within the experimental error. The stability and reproducibility of low concentrations of alcohols, simple ketones, esters, dioxane and hydrocarbons in gas mixtures prepared by the static method are characterized by a relative standard deviation of about 2% over a wide range from several tens of mg/l to a few μg/l.

The existing headspace analyzers and accessories are based on pneumatic dosing of the gas phase, the general principles of which have recently been considered[9]. Under these conditions the values of the buffer coefficients depend on the degree of replacement of the gas phase and are related to the values of B in eqn. 9 by[10]

$$B_n = B + (1 - B)\beta \tag{15}$$

TABLE V

RESULTS OF THE STATIC METHOD OF PREPARATION OF GAS MIXTURES WITH A PRE-DETERMINED CONCENTRATION

Data of M. I. Kostkina.

Solution concentra-tion, C_L^0 (mg/l)	Concentration of equilibrated vapour phase, C_G (mg/l)		
	Calculated according to eqn. 12 (n = 0)	Found from peak areas	Found from peak heights
Acetone (solvent: water, 20°C, B = 0.970, r = 18.5)			
1025	1.33	1.32 ± 0.7	1.37 ± 0.4*
97.0	0.125	0.123 ± 0.6	0.127 ± 0.6
51.5	0.0666	0.0656 ± 1.7	0.0645 ± 0.7
10.2	0.0133	0.0133 ± 1.5	0.0131 ± 2.9
Benzene (solvent: Carbowax 300, 25°C, B = 0.962, r = 23.5)			
6.2	0.0099	0.0100 ± 2.7	0.0101 ± 0.7

* Relative standard deviation at ten-fold dosing.

where β is the fraction of the gas phase remaining after its partial replacement. Using pneumatic injection this fraction is equal to the ratio of the pressure in the vessel after injection of the gas phase to the initial pressure.

When the coefficients B_n are substituted for B the main equations for gas extraction are still valid.

Beside the static methods, a dynamic method may also be convenient for detector calibration over a wide concentration range. If the dead volume of gas over
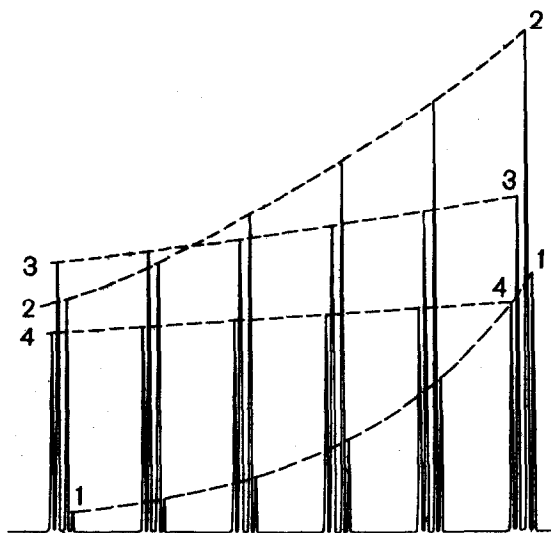

Fig. 2. Chromatograms of the vapour phase obtained on bubbling nitrogen through 3.9 ml of a solution of hydrocarbons in squalane at a rate of 55 ml/min at 30°C. Sampling interval: 15 min. Key: 1 = benzene; 2 = toluene; 3 = p-xylene; 4 = cumene.

the solution in the saturator is negligible, the concentration of volatile compounds in the inert gas after V ml of this gas are passed through V_L ml of solution at the initial concentration, C_L^0, may be calculated according to the simple exponential equation:

$$C_G = \frac{C_L^0}{K} \cdot \exp\left(-\frac{V}{KV_L}\right) \qquad (16)$$

Fig. 2 illustrates the shape of the chromatograms of the vapour phase obtained in this case. The first six chromatograms of a nitrogen flow passing through a solution of the four simplest aromatic hydrocarbons in squalane are shown. The apexes of the peaks of each component lie on exponents in eqn. 16 the slope of which is determined by the values of K. The precision of the gas phase concentration attained in this experiment was 4–5%.

After the experimental conditions have been established in detail and the equations for static and dynamic gas extraction methods of preparation of mixtures with low contents of volatile components have been simplified, these methods will find a much wider application.

HSA OF LIVING PLANTS

In the beginning of this paper we pointed out that the range of applications of HSA should not be limited to equilibrium systems and the problems of determination of the composition of the condensed phase. One of many examples of the use of HSA in obtaining important information on substances of unknown composition in contact with vapour phase in open and not necessarily equilibrium systems is the investigation of the emission of volatile organics by living organisms. The purpose of such studies may be the solution of not only biological (physiological and taxonomic) and medical (diagnostic) problems but also ecological problems. In this connection we should like to report some new data on the HSA of living branches of trees. This work was started in 1980 in connection with a detailed investigation of organics in the atmosphere[11], and the results have been published only in part[12,13]. They demonstrate the importance of the information which HSA of living leaves and needles may yield. It was found that arboreous plants emit not only the simplest saturated alcohols and carbonyl compounds but also unsaturated compounds. For example, one of the main components of volatile emissions of birch is 3-hexen-1-ol. Even the first experiments detected many compounds the existence of which in plants was previously unknown. Thus, it was found that the volatile emissions of deciduous trees widespread in our latitudes, e.g., willow, aspen, oak and birch, contain methyl-, ethyl- and vinylfuran. Furan itself was found in the volatile emissions from mountain ash.

Very interesting results on the isoprene emission rate by the foliage of oak, aspen and willow and the terpene emission rate by pine, spruce and larch were obtained last summer near Leningrad. Isoprene is the main component of the volatile emissions from oak and aspen. Table VI presents the results of measurements of the isoprene emission rate from one square metre of foliage referred to 1 hectare of oak wood (the area of oak foliage in 1 hectare of wood being taken to be equal to 47,000

TABLE VI

DEPENDENCE OF ISOPRENE EMISSION BY OAK (*QUERCUS ROBUR*) FOLIAGE UNDER NATURAL CONDITIONS (LENINGRAD SUBURB, 1982)

Date and time of day		Temp. (°C)	Cloudiness*	Emission rate	
				$mg/m^2 \cdot h$	$g/hectare\ of\ wood \cdot h$
June 19,	16 h 30 min	15	II	1.6	76
June 24,	15 h	19	I	3.2	149
	19 h	17	III	0.5	22
	23 h 30 min	12	III	0.2	8
June 26,	17 h	26.5	III	0.7	33
July 25,	12 h	25.5	I	4.7	221

* I = Sunny; II = variable; III = cloudy.

m^2). It is seen that isoprene emission varies greatly depending on the sweather conditions: on overcast evenings it is considerably decreased and on warm sunny days increases up to 150–220 g/hectare · h. Thus, on a summer day a section of oak or aspen wood 30 × 30 km in area emits about 90 ton of isoprene. This compares with the annual production capacity of a factory of 90,000 ton. Probably, isoprene emission by plants is much more widespread than might be expected on the basis of literature data. At any rate it was detected (as well as acetone) in the volatile emissions of all fourteen species of arboreous plants investigated. The total production of isoprene rubber does not attain even 1% of the annual amount of isoprene emitted into the atmosphere by vegetation (over 500 million ton[11]).

As to the emission rate of terpenes, in contrast to the opinion sometimes expressed in the literature, the data listed in Table VII indicate that there is a distinct dependence on air temperature. This does not mean, however, that the terpene concentration in air is at a maximum at the warmest time of the day because the decisive factors are the conditions of dispersion in the atmosphere.

The total emission of volatile organic substances by plants may be over 1500 million tons per year[14], which corresponds approximately to the world oil output at the beginning of the 1970s.

TABLE VII

DEPENDENCE OF TERPENE EMISSION BY SCOTCH PINE (*PINUS SILVESTRIS*) NEEDLES ON AIR TEMPERATURE

Temp. (°C)	Terpene emission rate	
	$g/t \cdot h$	$kg/km^2\ of\ wood \cdot h$*
14	1.6 ± 0.2	1.4
18	3.0 ± 0.3	2.7
20	4.1 ± 0.3	3.7
24	8.9 ± 0.9	8.0
28	18.8 ± 1.9	16.9

* Considering needle weight per hectare of wood as equal to 9 ton.

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