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HEADSPACE GAS ANALYSIS BY GAS CHROMATOGRAPHY

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1. INTRODUCTION

Modern gas chromatography is a powerful tool for solving difficult problems of trace analysis and has therefore found extensive use, particularly in the biological and medical sciences, forensic chemistry, the protection of the environment, food and agricultural sciences and space research. In this wide variety of applications the chromatographer meets with a large range of very diverse materials to be analysed and is confronted with a number of methodological problems the solution of which usually requires special approaches.

In most of the above-mentioned applications special sampling procedures are used in which the components to be determined are concentrated either directly on the chromatographic column proper or in a trap from which the concentrate is subsequently transferred into the chromatographic column and analysed in the usual way. Although there is some isolation of the components of interest from the matrix in these procedures, the latter essentially constitute direct analyses of the material studied, and it is possible to manage with conventional methods of calibration if quantitation is to be carried out. Exceptions in this respect are methods involving the equilibration trapping[1,2] of the components to be determined, which render it neces-

sary to take into account also the distribution of the components between the trapping sorbent and the parent material. However, it often happens that methods of direct analysis either cannot be used at all or do not provide for the desired analytical effect to be attained, and it is therefore necessary to carry out a preliminary isolation of the components of interest from their matrix. Liquid extraction and extraction with a gas are the most frequently employed techniques. Hence, contrary to methods of direct analysis, an extract of the material being studied rather than the material as such is introduced into the analytical instrument. Analytical procedures consisting in the extraction of the material with a gas and subsequent gas chromatographic analysis of the gaseous extract have been given the name "headspace gas analysis".

So far as qualitative analysis alone is concerned, the application of procedures of indirect analysis does not cause any unusual problems. However, from the viewpoint of quantitative analysis these procedures constitute a special category of methods the application of which requires that the properties of the entire system being processed, together with the rules implicit to the technique of quantitative chromatographic analysis employed, must be considered in order to obtain correct results. The properties typical of two-phase (gas–liquid, gas–solid) and/or even more complicated multicomponent systems are involved.

This review surveys the physicochemical aspects, methodology and applications of headspace gas analysis by gas chromatography, with special emphasis on quantitation.

2. GENERAL ASPECTS OF HEADSPACE GAS ANALYSIS

2.1. Distribution of the solute in the gas-condensed phase system

According to the method of carrying out the extraction with a gas, the techniques of headspace gas analysis can be classified into two groups: (i) techniques in which a sample of the gas taken from over the condensed phase in a closed static equilibrated system is analysed and (ii) techniques in which a stream of gas is passed through the condensed material and the gaseous effluent is analysed for the components stripped out from the material.

In the first instance the concentrations of the solute in the coexisting phases do not change with time after the system has reached a state of equilibrium. However, the equilibrium is disturbed temporarily upon sampling the headspace gas, the degree of the disturbance being dependent on the method of withdrawing the sample and on the properties of the system being analysed. The non-equilibrium associated with sampling introduces some uncertainty into the results; the role that the non-equilibrium plays in this respect is the more important the larger are the sample volumes withdrawn from the system. In the second instance the solute concentrations decrease continuously with time in both phases, approaching zero asymptotically. As the whole system is non-stationary, it deviates more or less permanently from equilibrium. However, it can be assumed that even under these non-stationary conditions the gaseous phase in the bubbles leaving the condensed phase is practically equilibrated with the latter.

2.1.1. Definition of the distribution constant

From the point of view of quantitative headspace gas analysis, the problem of equilibrium in the system being analysed is a matter of basic importance. According to the general definition of thermodynamic equilibrium, the system is equilibrated if the chemical potentials of all components in all phases are identical. The following holds[3] for a component (solute) i in such a system at a given temperature (T) and the overall pressure P:

$$(\nu_i)_P P y_i = \gamma_i (\nu_i^0)_{p_i^0} (p_i^0)_P x_i \tag{1}$$

where $(\nu_i)_P$ is the fugacity coefficient of component i in the headspace gas at the pressure P, $(\nu_i^0)_{p_i^0}$ is the fugacity coefficient of pure substance i at its saturation vapour pressure, p_i^0, $(p_i^0)_P$ is the saturation vapour pressure of substance i at the overall external pressure P, γ_i is the Raoult-law activity coefficient of component i and y_i and x_i are the molar fractions of component i in the gaseous and condensed phases, respectively. It holds[4] for the quantity $(p_i^0)_P$:

$$(p_i^0)_P = p_i^0 \left[\exp \int_{p_i^0}^{P} (V_i^L/RT)\mathrm{d}P\right] \tag{2}$$

where p_i^0 is the saturation vapour pressure of component i (at its own pressure), V_i^L is the molar volume of liquid substance i and R is the perfect-gas constant; all of the above quantities refer to the temperature of the system, T. By means of eqns. 1 and 2 it is possible to define the thermodynamic distribution constant of component i, K^*:

$$K_i^* = \frac{x_i}{P y_i} = \frac{(\nu_i)_P}{(\nu_i^0)_{p_i^0}} \cdot \frac{\exp\left[-\int_{p_i^0}^{P} (V_i^L/RT)\mathrm{d}P\right]}{\gamma_i p_i^0} \tag{3}$$

The distribution constant defined in the above manner (the inverse of the Henry-law constant) provides for an exact interpretation of the equilibrium distribution of the solute between the gaseous and condensed phases in terms of the thermodynamic properties of the system. However, as concerns the mass balance of the solute in the system it is more convenient to define the distribution constant of the solute as the ratio of the equilibrium concentrations of the latter in the condensed and gaseous phases, K_i:

$$K_i = \frac{W_{iL}/V_L}{W_{iG}/V_G} \tag{4}$$

where W_{iL} and W_{iG} are the masses of component i in the condensed and in the gaseous phase and V_L and V_G are the volumes of those phases, respectively. As

$$x_i = M_L W_{iL}/M_i V_L d_L \tag{5}$$

and

$$y_i = W_{iG} z_G RT/M_i P V_G \tag{6}$$

where M_L and M_i are the molar masses of the condensed phase and of component i, d_L is the density of the condensed phase and z_G is the compressibility factor of the gaseous phase, we can write

$$K_i = (z_G RT d_L / M_L) K_i^* \tag{7}$$

Combining eqns. 3 and 7 we obtain the following thermodynamically rigorous relation for K_i:

$$K_i = \frac{(\nu_i)_P}{(\nu_i^0)_{p_i^0}} \cdot \frac{z_G RT d_L}{\gamma_i p_i^0 M_L} \exp\left(-\int_{p_i^0}^{P} \frac{V_i^L}{RT} \cdot dP\right) \tag{8}$$

By neglecting the quantities accounting for the effects of non-ideality of the gaseous phase and compressibility of the condensed phase, we arrive at the equation used to express the distribution constant of a solute in gas–liquid chromatographic (GLC) systems:

$$K_i = RT d_L / \gamma_i p_i^0 M_L \tag{9}$$

2.1.2. Dependence of the distribution constant on the state conditions and the composition of the system

It is evident from eqns. 8 and 9 that the distribution constant is a function of the temperature, pressure and composition of the phases. For an n-component system

$$dK_i = \left(\frac{\partial K_i}{\partial T}\right)_{P,x_k} dT + \left(\frac{\partial K_i}{\partial P}\right)_{T,x_k} dP + \sum_k \left(\frac{\partial K_i}{\partial x_j}\right)_{T,P,x_{k \neq j}} dx_j \tag{10}$$

where $k = 1,2,\ldots,n$ denotes the individual components of the system, j denotes any component (including i) of the system and x is the molar fraction of the given component in the condensed phase. The following can be derived for the temperature and pressure dependence of the distribution constant described by eqn. 9:

$$\left(\frac{\partial \ln K_i}{\partial T}\right)_{P,x_k} = -\frac{\Delta H_i^v - \Delta \bar{H}_i^E}{RT^2} + \frac{1}{T} - \alpha_L \tag{11}$$

$$\left(\frac{\partial \ln K_i}{\partial P}\right)_{T,x_k} = -\frac{\bar{V}_i^L}{RT} + \beta_L \tag{12}$$

where ΔH_i^v is the molar enthalpy of vaporization of pure component i, $\Delta \bar{H}_i^E$ is the partial molar excess enthalpy of component i, $\bar{V}_i^L$ is the partial molar volume of component i in the condensed phase and α_L and β_L are the coefficient of thermal expansion and the coefficient of compressibility of the condensed phase[5], respectively.

In order to describe the dependence of K_i on the composition of the condensed

phase, it is expedient to consider that M_L/d_L is the molar volume of the condensed phase, V_L^m. Hence, with regard to eqn. 9 it is possible to write

$$\frac{\partial \ln K_i}{\partial x_j} = -\frac{\partial \ln \gamma_i}{\partial x_j} - \frac{\partial \ln V_L^m}{\partial x_j} \tag{13}$$

As $V_L^m = \bar{V}_1^L x_1 + \bar{V}_2^L x_2 + \ldots + \bar{V}_n^L x_n$ where $\bar{V}_1^L$, $\bar{V}_2^L$, etc. are the partial molar volumes of the individual components in the condensed phase, we can also write

$$\left(\frac{\partial \ln V_L^m}{\partial x_j}\right)_{T,P,x_{k \neq j}} = \frac{\bar{V}_j^L}{V_L^m} = \frac{\bar{d}_j M_L^L}{d_L M_j} \tag{14}$$

where $\bar{d}_j$ is the partial density of component j ($\bar{d}_j = M_j/\bar{V}_j^L$) and M_j is the molar mass of component j. The dependence of γ_i on x_j is given by the Gibbs–Duhem equation[6]:

$$\left(\frac{\partial \ln \gamma_i}{\partial x_j}\right)_{T,P,x_{k \neq j}} = -\Sigma\left[\frac{x_k}{x_j}\left(\frac{\partial \ln \gamma_i}{\partial x_k}\right)_{T,P,x_{k \neq j}}\right] \tag{15}$$

so that

$$\left(\frac{\partial \ln K_i}{\partial x_j}\right)_{T,P,x_{k \neq j}} = -\frac{\bar{d}_j M_L}{d_L M_j} + \Sigma\left[\frac{x_k}{x_j}\left(\frac{\partial \ln \gamma_i}{\partial x_k}\right)_{T,P,x_{k \neq j}}\right] \tag{16}$$

2.2. Stripping with a stream of gas

The rate of stripping, expressed as the time change of the total mass of component i in the system, $\mathrm{d}W_i/\mathrm{d}t$, can be described by

$$\frac{\mathrm{d}W_i}{\mathrm{d}t} = -W_i \cdot \frac{F}{V_G + K_i V_L} \tag{17}$$

where F is the volume flow-rate of the stripping gas, W_i is the instantaneous total mass of component i in the system and the meanings of the other symbols are the same as in the definition (eqn. 4) of the distribution constant K_i. Solving eqn. 17 for the initial conditions $t = 0$, $W_i = W_i^0$ we obtain

$$\frac{W_i}{W_i^0} = \exp\left(-\frac{Ft}{V_G + K_i V_L}\right) \tag{18}$$

where W_i^0 is the initial total mass of solute i in the system. The half-time of the stripping process, $t_{1/2}$, is given by

$$t_{\frac{1}{2}} = \ln 2 \cdot \frac{V_G + K_i V_L}{F} \tag{19}$$

The time necessary to strip 95% of the solute out of the system is $t_{0.05} = 3(V_G + K_i V_L)/F$.

Eqns. 17–19 involve the assumption that the concentration of component i in the stripping gas leaving the condensed phase is in equilibrium with the concentration of this component in the condensed phase.

2.3. Quantitation procedures in headspace gas analysis

A particular difference between quantitative analysis of one-phase systems and quantitative headspace gas analysis is that in the latter instance it is necessary to consider the distribution of the component under determination between the phases of the system. This is why the definitions of all of the methods of quantitative chromatographic headspace gas analysis involve in some manner, either explicitly or implicitly, the mass balance of the component to be determined in the system, except for a trivial case where it is possible to assume that the entire amount of the component has been transferred into the gaseous phase. The chromatographic aspects proper of the procedures of headspace gas analysis are the same as in the analysis of one-phase systems.

Considering the problem of quantitative headspace gas analysis, it is expedient to express the mass balance of component i in the gas–condensed phase (liquid) system by the relationship between the total amount of component i in the system and the equilibrium concentration of the component in the gaseous phase, *i.e.*,

$$W_i = c_{iG}(K_i V_L + V_G) \tag{20}$$

where $c_{iG} = W_{iG}/V_G$. It is evident from eqn. 20 that if the distribution constant and the volumes of the phases are known, the value of W_i can be calculated from c_{iG} determined by any of the usual methods of quantitative chromatographic analysis. However, the value of K_i is usually unknown and, therefore, particularly those procedures in which the necessity to know K_i and/or the whole factor $K_i V_L + V_G$ is obviated in some way are important. This can be done by using either of the following three principles:

(i) Real elimination of the distribution constant. The temperature of the system is raised to a value at which $K_i = 0$. In this case the value of W_i is given simply by $W_i = c_{iG} V_G$ where c_{iG} is determined by one of the usual methods of quantitative gas chromatographic analysis. The applicability of this principle is very limited.

(ii) Use of a reference model system. A model system with a known amount of the substance to be determined and with the composition of the matrix material being the same as that of the matrix in the system being analysed is prepared. Under these circumstances the values of K_i in both systems are the same, and if also the volumes of the individual phases in the systems are the same the effect of the factor $K_i V_L + V_G$ can be eliminated. Thus, if W_i and W_i^* are the overall masses of component i in the analysed and in the reference system, respectively, and c_{iG} and c_{iG}^* are the corresponding concentrations of component i in the gaseous phases of the systems, there holds under the above presuppositions

$$W_i = W_i^* c_{iG}/c_{iG}^* \tag{21}$$

Hence, in order to determine W_i it is sufficient in this instance to determine c_{iG} and

c^*_{iG} under identical conditions by any technique of quantitative gas chromatographic analysis. The use of this principle has serious limitations in that it is often impossible to simulate the composition of the matrix material.

(iii) Use of the standard-additions method. This procedure is based on the assumption that the addition of a small amount of component i, which already is present in the system, will not alter significantly the thermodynamic properties of the phases, and the distribution constant K_i will remain practically unchanged. If also the V_L/V_G ratio is not changed significantly, then it is sufficient to determine, under identical conditions, just the concentrations of component i in the gaseous phases of the system being analysed before and after the addition of a defined amount of component i in order to determine W_i. The value of the factor $K_iV_L + V_G$ is eliminated in the calculation of W_i. This method is universal; it can be shown[7] that, under certain circumstances, it can also be employed for the quantitative headspace gas analysis of non-stationary systems.

When using the standard-additions method the calculation of results is carried out with the equation

$$W_i = \frac{W_s - w_i}{(c'_{iG}/c_{iG}) - 1} \quad (22)$$

where W_s is the mass of standard (substance i) added after having withdrawn and analysed a sample of the gaseous phase of the original system, w_i is the mass of substance i contained in the above sample (w_i is determined by direct calibration; usually $w_i \ll W_s$) and c_{iG} and c'_{iG} are the concentrations of substance i in the gaseous phase of the original system before and after the addition of the standard, respectively.

This principle can also be applied in a reversed manner, *i.e.*, the value of W_i can be determined by measuring the decrease in c_{iG} brought about by repeatedly withdrawing and analysing defined samples of the gaseous phase[8]. The value of W_i is then calculated by applying the equation[9]

$$W_i = \frac{W_{iG0}}{1 - (c_{iG1}/c_{iG0})} \quad (23)$$

where W_{iG0} is the total mass of component i in the gaseous phase of the original system and c_{iG0} and c_{iG1} are the concentrations of component i in the gaseous phase of the original system before and after the withdrawal of the first sample of the gaseous phase, respectively.

A detailed elaboration of the theoretical aspects of quantitation in headspace gas analysis can be found in Novák's book on quantitative gas chromatographic analysis[9]. Practical procedures of headspace gas analysis and thermodynamic definitions of phase equilibria in gas–liquid systems are described in books by Berezkin *et al.*[10] and Hachenberg and Schmidt[11].

3. APPLICATIONS OF HEADSPACE GAS ANALYSIS

3.1. Direct analysis of headspace gas samples

Many of the papers published so far on headspace gas analysis describe quali-

tative and/or semiquantitative assays of given systems. Quantitative procedures have mostly been based on using a model reference system and processing the results by means of a calibration graph.

Nawar[12] investigated the factors that affect the concentration of volatiles in the headspace gas. By comparing the so-called headspace responses, *i.e.*, the peak areas of components in chromatograms of 3-ml headspace gas samples, he found that at a given concentration of a volatile in the condensed phase its concentration in the gaseous phase depends on the nature of both the volatile and the condensed phase and on the presence of other components in the condensed phase. For instance, the equilibrium concentration of *n*-heptane over a hydrocarbon oil was lower than that over a solution of the same compound in water, while with ethanol as the test volatile the situation was reversed. Weurman[13] studied the formation of volatile substances during enzymatic reactions taking place in a raspberry substrate. After the reaction had finished and the system equilibrated for 2–4 h at ambient temperature, 2-ml samples of the headspace gas were analysed by gas chromatography. Isopropanol, ethyl acetate, propanal, acetone and other volatiles with concentrations in the range 0.001–0.025% in the condensed phase were determined by means of model reference systems containing water as the liquid substrate, employing calibration graphs obtained from peak heights. However, the linearity of the calibration graphs was not very good, and the reference systems with water may have not corresponded with the systems being investigated. In order to increase the sensitivity of analysis, an all-glass distillation apparatus was developed, which provided for as much as a 10-fold increase in the concentration of the volatiles that could be measured in a single step[14].

Basette and co-workers[15,16] analysed dilute aqueous solutions of various volatile substances by chromatographing 1-ml samples of the gas taken from over the solutions after equilibration for 3 mins. Samples of 2 ml of the solutions being analysed, with 1.2 g of sodium sulphate being added in order to increase the concentration of the volatiles in the gaseous phase, were contained in 5-ml closed vessels kept at 60° in a water-bath. They determined lower aldehydes, ketones and esters at concentrations below 1 ppm in the liquid phase. The chromatograms were processed by correlating peak heights with solute concentrations. The calibration graphs, constructed from three points corresponding to 0.01, 0.1 and 1.0 ppm, were linear. The concentration of 0.01 ppm was indicated as a limit of the sensitivity of analysis by the above method, but no data were given on the reliability of the results obtained in this way. Alcohols up to C_4 could not be detected at concentrations lower than 0.1 ppm, and the calibration graph for methanol, as obtained for concentrations in the range 1–10 ppm, had a very small slope. A similar method was also employed for the determination of halogenated hydrocarbons in water[17]. The system being analysed, having a small headspace volume, was equilibrated under vacuum and at an elevated temperature, upon which the pressure in the system was equalized with the ambient pressure and a 5-μl sample of the headspace gas was withdrawn and chromatographed. The method of comparison with a model reference system by means of a calibration graph was used for quantitation. Employing a ^{63}Ni electron-capture detector, chloroform and other halogenated compounds were determined in concentrations of 0.1–10 μg/l in water.

Kepner *et al.*[18] described the headspace gas determination of volatile substances in multicomponent aqueous solutions by using the internal standard method

and applied the procedure to the determination of volatile components of rum and beer. Samples of 50 ml of the liquid material were thermostated in 120–360-ml flasks, and 6–20-ml volumes of the headspace gas were taken for analysis. The liquid phase was saturated with ammonium sulphate or sodium chloride in order to increase the concentration of the volatiles in the gaseous phase. The temperatures and times of equilibration were varied in the ranges 10–36° and 30–45 min in order to establish the optimal conditions for analysis. The quantitation proper was again carried out by means of model reference systems, employing a calibration graph constructed by plotting the ratio of the peak sizes (peak height × retention time) of the substance under determination and the standard in chromatograms of the headspace gas samples against the corrresponding concentration of the substance under determination in the condensed phase. The internal standard was heptanone. With concentrations in the range 1–100 ppm in the condensed phase the calibration graphs were virtually linear. However, it was demonstrated that the calibration graphs obtained in the above manner with water and with the material being analysed as the condensed phases had substantially different slopes (Fig. 1). Also, the presence of ethanol (7.5–75%) in the material being analysed influenced markedly the distribution of other components between the headspace gas and the condensed phase. The authors recommended that at higher contents of ethanol the system should be equilibrated at 10° in order to prevent the peaks of the substances of interest becoming overlapped by the peak of ethanol in the chromatogram.

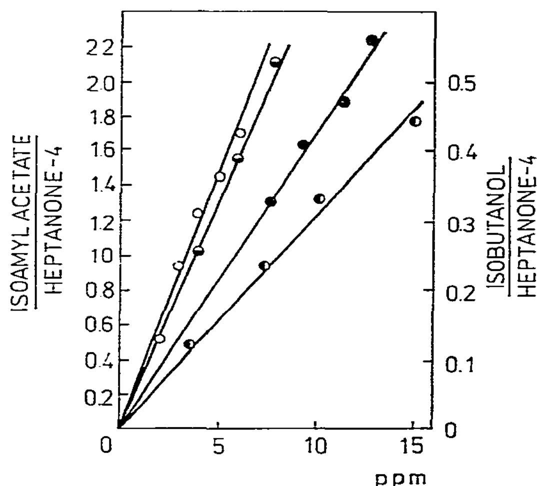

Fig. 1. Comparison of calibrations in 5% aqueous ethanol *versus* beer[18]. ○, Isoamyl acetate in beer; ⊖, isoamyl acetate in 5% aqueous ethanol; ●, isobutanol in beer; ◑, isobutanol in 5% aqueous ethanol. Internal standard, 4.5 ppm of heptanone-4. (Reprinted with permission of the authors.)

Cowen *et al.*[19] suggested that in experiments of the above type the septum of the gas chromatograph is insufficiently leakproof, so that the reliability of results may be impaired due to losses of samples. Therefore, they developed an arrangement for handling the headspace gas without using a septum (Fig. 2). The sample is sucked up by vacuum into a calibrated sampling loop and, upon turning over the eight-way

stopcock into the second operating position, the contents are purged into the gas chromatograph. Actually, this arrangement is a modified sampling loop commonly used in gas chromatography. Loper and Webster[20] equilibrated gas-condensed phase systems directly in a 100-ml syringe provided with a thermostating water-jacket. By using this arrangement they studied changes in the contents of volatile substances in alfalfa flowers. Owing to a relatively large volume of headspace gas available in this instance the analysis could be repeated several times. Larger samples were processed by condensing them in a trapping column.

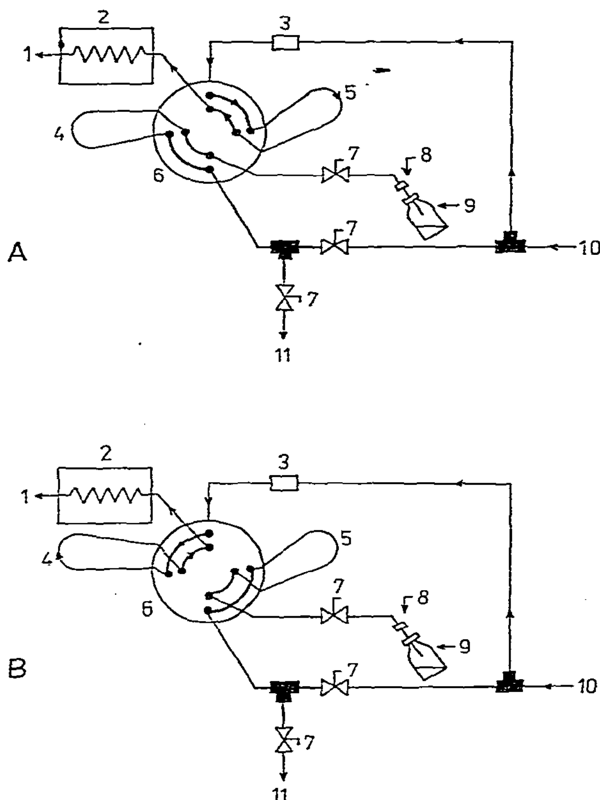

Fig. 2. Gas sampling device for headspace gas analysis[19]. 1 = To FID; 2 = GC column in oven; 3 = gas flow controller; 4, 5 = sampling loops; 6 = 8-port gas sampling valve; 7 = Whitey toggle valves; 8 = injection needle; 9 = serum bottle; 10 = carrier gas inlet; 11 = to vacuum. (Reprinted with permission of the authors and the American Chemical Society.)

Several methods have been developed for the determination of ethanol in blood by headspace gas analysis. Goldbaum *et al.*[21] simply analysed 1-ml samples of headspace gas (air) taken from over blood placed in a bottle thermostated at 25° and closed by a rubber stopper. Quantitation was carried out by using the method of model reference systems (0.01–015% of ethanol in the liquid phase) and a calibration graph. Other workers[22–24] improved the method by increasing the sensitivity of analysis by adding sodium fluoride and/or sodium chloride to the blood. Machata[25] increased the precision of analysis by applying the method of internal standards. A

0.5-ml sample of blood, serum or urine was pipetted into a 20-ml serum bottle and 0.1 ml of a 0.25% aqueous solution of acetone and/or a 0.20% aqueous solution of methyl ethyl ketone was added, then the bottle was closed with a rubber stopper and thermostated for 15 min at 60°. The relative standard deviation of a single determination was stated to be 5.6% and could be decreased to 4% by repeating the analysis. The application of the internal standard method combined with the addition of a salting-out agent was reported by Reed and Cravey[26]. A sample of 1 ml of blood is mixed with 1 ml of a 1% aqueous solution of 1,4-dioxane, 0.5 ml of the mixture is added to 0.75 g of sodium chloride in a 2-ml serum bottle, then the bottle is closed with a rubber stopper and the system is thermostated for 5 min at 85°. A 2-ml headspace gas sample is withdrawn with a 2-ml syringe and injected into the gas chromatograph, thus obtaining a chromatogram in which the peak heights of ethanol and dioxane are h_E and h_D. The same procedure is carried out with a calibration solution of a known concentration of ethanol, c_{SE}, the peak heights of ethanol and dioxane being h_{SE}, and h_{SD}, respectively, in this instance. The concentration of ethanol in the sample being analysed, c_E, is calculated by

$$c_E = (h_E h_{SD}/h_D h_{SE}) c_{SE}$$

However, this equation applies only if the distribution constants of ethanol and dioxane in the system with the blood being analysed do not differ from those in the reference system, *i.e.*, the composition of the condensed phase matrix and the equilibration conditions must be the same with both systems.

The effort to reduce the sample size necessary for analysis led to the development of a method that permits the analysis to be carried out with merely 20 μl of blood[27]. The sample of blood is deposited on a piece of filter-paper impregnated with a saturated solution of sodium fluoride and placed in a 25-ml flask, the system is equilibrated for 15 min at 35° and a 0.5-ml sample of the headspace gas is withdrawn and analysed by gas chromatography. The quantitation is carried out by direct calibration through use of model reference systems and a calibration graph. Wilkinson *et al.*[28] determined 0.003–1.2 mg/ml of ethanol in 20–50-μl samples of blood by the internal standard method, also employing model reference systems and a calibration graph, the latter being obtained by plotting the ratio of the areas of the peaks of ethanol and the standard (*n*-propanol) in chromatograms of headspace gas samples against the concentration of ethanol in the calibration solutions. The calibration graph obtained in this way was parabolic. The average relative error of the results was $\pm$ 4.6%. A good precision was attained by increasing the temperature of equilibration to 60°, thermostating the injection syringe and employing sodium nitrite, which exerts strong salting-out effects and prevents ethanol from being oxidized to acetaldehyde during equilibration.

With all of the methods in which injection syringes are used to sample the headspace gas the results may suffer from errors due to adsorption of sample components within the syringe. Although the adsorption of components in the syringe can be suppressed by keeping the latter at an elevated temperature, in some trace analyses it may lead to erroneous results. Further, if the matrix material of the condensed phase of the model reference systems used for constructing the calibration graph is not physically identical with that of the condensed phase of the system under analysis, the

applicability of the calibration graph is generally doubtful. This is probably the reason why neither the error nor the reproducibility of the results have been mentioned in many papers involving the use of the above method of quantitation.

A device has been developed for charging headspace gas samples into the gas chromatograph that obviates the necessity of using injection syringes. In addition to the already mentioned instrumentation[19], Pauschmann[29] and Göke[30] described a simple arrangement in which the excess pressure of the headspace gas within the equilibration container is utilized for the above purpose. Bodenseewerk Perkin-Elmer (Überlingen, G.F.R.) offers a fully automated headspace analyser, the Multifract F40, fitted with a special charging device in which spurious adsorption effects are suppressed to a minimum. This apparatus has been used in various applications of headspace gas analysis[31–35].

Surprisingly little attention has been paid to the design of the equilibration vessels. Vessels closed with rubber septa (*e.g.*, serum bottles) allow the vapour phase to be in contact with a relatively large area of the rubber surface, which may result in significant absorption of some components and adversely affect the results. Brief but significant studies of these problems were published by Davis[36] and Gilliver and Nursten[37], who measured the decrease in concentration of some headspace gas components with time when using either a rubber septum or a ground glass stopper (without grease) as closures for the equilibration vessel. Some of their results are given in Table 1. Of several test substances exposed to direct contact with the rubber surface for 30 min, only ethanol showed negligible losses due to absorption in the septum; with more lipophilic compounds the losses were significant.

TABLE 1

CHANGE OF THE CONCENTRATION OF SOME SUBSTANCES WITH TIME IN A FLASK CLOSED WITH A RUBBER SEPTUM (A) AND A GROUND-GLASS STOPPER (B)[37]

The concentrations (h) are given in terms of the corresponding chromatographic peak heights and the differences (Δh) are expressed as percentages; corrections have been made for the decrease in concentration due to the preceding samplings.

Time (min)	*Ethanol*		*Isopropanol*		*n-Butyl acetate*		*Isopropyl acetate*		*Isobutyl butyrate*		*n-Butyl butyrate*	
	h	Δh	h	Δh	h	Δh	h	Δh	h	Δh	h	Δh
(A)												
0	34.5		85		41.5		82		91.5		60.5	
30	32.5	−1.5	51.5	−37	21.5	−46.5	35	−55.5	29	−67	14.5	−75
60	30	−6.5	37.5	−52.5	15	−61	22.5	−70.5	16.5	−80.5	7.5	−87
90	27.5	−11.5	30.5	−60	11.5	−69	16.5	−77.5	11	−86.5	5	−91
120	26	−13.5	26.5	−64	10	−72	13.5	−81	8.5	−90	3.5	−93.5
150	24	−17	23	−67.5	8.5	−75	11	−84	7.5	−90	3	−94
(B)												
0	36.5		92.5		34		70		80.5		56.5	
60	34.5	−1.5	90.5	+1.5	33	0	68.5	+1.5	79.5	+2.5	56	+3
120	33	−3	88	+2.5	32	+1.5	66	+1.5	76.5	+2	54.5	+4
180	31	−4.5	83.5	+0.5	30.5	0	63	0	73	+1.5	51.5	+2
240	30	−5	80.3	+0.5	29	−1.5	60	−1	69	−0.5	49	0
300	29.5	−3.5	77.5	+0.5	28	−2	57.5	−1.5	65.5	−2	46	−2

The same conclusions were drawn by Maier[38]. Fig. 3 shows the time dependences of the amounts of substances absorbed in the rubber septum. The dependences were obtained by measuring the decrease in the concentration of the substances contained in a closed vessel. Similar results were also obtained when using a silicone-rubber septum.

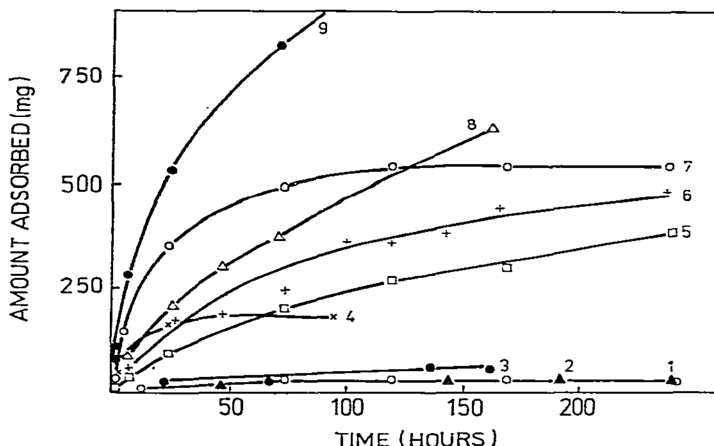

Fig. 3. Sorption of vapours in a rubber stopper at 23°[38]. 1 = Water; 2 = ethanol; 3 = methanol; 4 = acetone; 5 = acetic acid; 6 = pyridine; 7 = ethyl acetate; 8 = formic acid; 9 = butylamine. (Reprinted with permission of the author.)

In spite of its shortcomings, the method of using model reference systems and a calibration graph for quantitation has been applied to the determination of volatiles in oils[31], tea[32], various foodstuffs[39–42], biological materials[27] and to the determination of monomeric vinyl chloride in PVC[33] and of solvent or monomer residues in various plastics[33–35,43].

The method of direct analysis of headspace gas samples has also been used for studying non-ideal solutions[44] and chemical equilibria in solutions[45] and for measuring gas–liquid distribution constants[46,47].

McAuliffe[8] described a method of headspace gas analysis based on multiple extractions of a fixed sample of liquid with a gas. The method was applied to the determination of hydrocarbons in water. A 25-ml sample of water is equilibrated with 25 ml of pure gas (helium or nitrogen) in a 50-ml injection syringe at an elevated temperature, the entire volume of the gas is ejected from the syringe into the sampling loop of the gas chromatograph, in order to determine the contents of hydrocarbons in the gas, then another 25-ml volume of pure gas is drawn into the syringe and the whole procedure is repeated several times. The initial concentration of hydrocarbons in the original sample of water is calculated from the dependence of the concentration of hydrocarbons in the headspace gas samples on the serial number of the extraction step. It is claimed that alkanes and cycloalkanes at concentrations as low as 3 parts in 10^{12} in water can be determined in this way.

A similar method of discontinuous extraction with a gas was applied to the determination of solvent residues in plastic foils[48]. The extraction was carried out directly in the adapted injection port of the gas chromatograph. The method is

relatively complicated and time consuming, but if solid materials are to be analysed it is apparently one of few methods that can give reliable quantitative results.

The standard additions method was employed only recently as a means of quantitation in headspace gas analysis. The possibilities and advantages of this method were demonstrated[49–51] by the headspace determination of various solutes in gas–aqueous liquid model systems, employing the so-called single-sample procedure[9]. In this procedure, a volume v_G of the headspace gas is withdrawn from the equilibrated system and injected into the gas chromatograph, thereby obtaining a peak area A_i for the component to be determined. Then a defined mass, W_s, of the component being determined (i) is introduced into the system and, after the latter has been re-equilibrated, a volume v'_G of the headspace gas is again withdrawn and chromatographed, thus obtaining a peak area A'_i for component i. The total mass, W_i, of component i in the original gas-condensed phase system is calculated (*cf.*, eqn. 22) by

$$W_i = \frac{W_s - w_i}{(A'_i v_G / A_i v'_G) - 1}$$

In this way, hydrophilic solutes at concentrations in the range *ca.* 1–100 ppm and both aliphatic and aromatic hydrocarbons at concentrations in the range *ca.* 0.001–20 ppm in the aqueous phase were determined with relative errors of *ca.* 20–2 and 10–2%, respectively. The standard additions method was shown to make possible the elimination even of matrix effects such as those which occur in multicomponent three-phase systems[52].

3.2. Accumulation of headspace components and the analysis of the concentrate

3.2.1. Use of open cryogenic traps

The simplest means of accumulating trace amounts of volatile substances present in the headspace gas is to freeze them out by drawing the gas through a loop with a cryogenic trap. However, when analysing systems in which the major components of the condensed phase are also volatile, the analysis is usually complicated by excessive accumulation of major components together with the trace components. Loper and Webster[20] analysed volatile constituents of alfalfa flowers. An amount of fresh flowers was placed in a 100-ml injection syringe, the system was equilibrated for 30 min at 32°, then 70 ml of the headspace gas were introduced at a flow-rate of 25–30 ml/min into a short column which was cooled in acetone–dry-ice. The trapping column constituted part of a sampling port situated at the inlet of the chromatographic column; on warming the trap and switching over the sampling loop stopcock, the concentrate was purged by the carrier gas into the chromatographic column. The reproducibility of the data obtained was better than 8%. However, the authors did not discuss the quantitation of their results, but just measured so-called aromagrams, from which it was possible to follow changes in the contents of volatiles in the material being analysed.

The condensation trap is either a self-contained unit[53] or it is possible to utilize directly a cooled section of the chromatographic column itself at its inlet as a trap. A U-shaped and/or spiral trap is immersed in a cooling bath and connected to the

headspace gas sampling system. After having drawn the required amount of the headspace gas through the trap, the latter is connected by means of a system of valves to the gas chromatograph, the cooling bath is replaced with a heater and the vaporized concentrate is swept by the carrier gas into the gas chromatograph and analysed. When working with aqueous systems, a cooler is placed between the condensation trap and the system being analysed in order to suppress the transfer of water into the trap. Such a method was applied to the routine determination of volatile constituents of urine, the whole analytical procedure being controlled automatically[54]: the purge (carrier) gas (helium) is directed by means of two valves either via the headspace gas phase of the system being analysed and the condensation trap, which is cooled, into the atmosphere or via the condensation trap, which is heated, into the gas chromatograph (Fig. 4). The chromatograms obtained were used to determine diagnostic profiles. The quantitative processing of data obtained in this way is very difficult owing to a number of factors which are difficult to define.

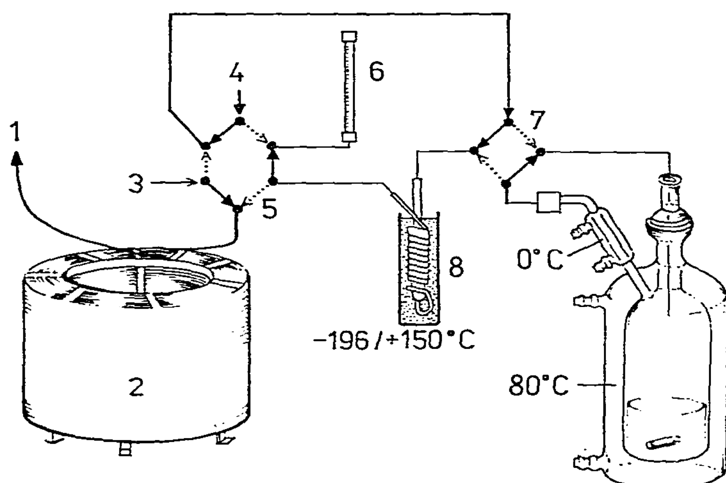

Fig. 4. Schematic diagram of an apparatus for the determination of volatile compounds in urine[54]. 1 = To FiD; 2 = 300-m capillary column; 3 = carrier gas (helium) inlet; 4 = helium collector; 5 = 6-way valve; 6 = flow meter; 7 = 4-way valve; 8 = collector. (Reprinted with permission of the authors.)

Another method of concentrating volatiles from headspace gas was described by Hurst[55] and demonstrated by the analysis of flavour compounds in fruit preserves[56]. The headspace of a container with the sample is connected, via injection needles pierced through the septa of the container, with a 50-ml syringe and with a condensation tube of volume *ca.* 3 ml immersed in liquid nitrogen. While the volatiles condense in the tube the pressure in the system decreases and the piston of the syringe moves towards the empty-syringe position. On interruption of cooling the pressure increases and the piston is shifted back to its initial position. The process can be repeated several times; after the last step has been completed the cooled condensation trap is disconnected and, when its septum-holder screw nut has been tightened up, is transferred in an aluminium jacket, in which it is heated to 50°. Then both the septum of the trap and that of the gas chromatograph are pierced through by a

connecting injection needle and the vaporized concentrate is blown by its own excess pressure into the gas chromatograph. A comparison of the direct injection of 10 ml of the headspace gas and the analysis by the above procedure involving either one or four condensation steps (Fig. 5) showed that the accumulation of volatile components was substantial, but it did not correspond to the total volume sampled. Probably part of the condensate passes back into the headspace of the sytem being analysed during the periods when the trap is not cooled. Quantitative interpretation of the results is feasible only through the use of a standardized procedure employing a calibration graph.

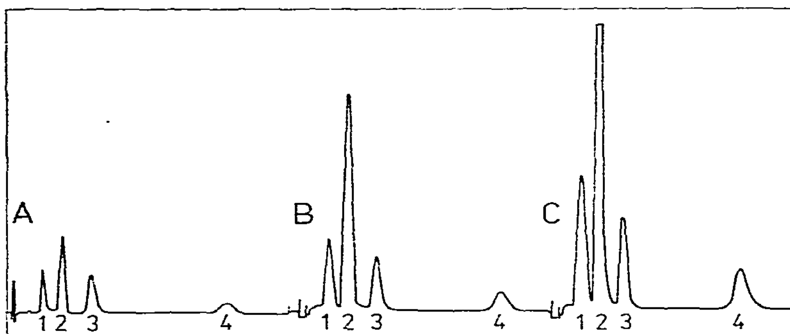

Fig. 5. Gas chromatograms of alcohols collected from the headspace above glycerol containing 40 ppm of each alcohol[55]. 1 = Methanol; 2 = ethanol; 3 = *n*-propanol; 4 = *n*-butanol. (A) Sampling of 50 ml of the gas with a gas-tight syringe; (B) one condensation of 50 ml of the gas; (C) four condensations of 50 ml of the gas. (Reprinted with permission of the author.)

3.2.2. Use of traps packed with sorbents

Trace amounts of volatile constituents of headspace gas can be concentrated by trapping them in a short column packed with a sorbent. The headspace of the system is purged by a stream of pure gas (helium) and the effluent gas is fed into a trap containing a chromatographic packing. The trap may either be cooled[57] or kept at room temperature[58]. In work with aqueous systems, especially if the trap is cooled, excessive amounts of water may accumulate in the trap. Therefore, a cooler is installed between the system being analysed and the trap[59] and/or the cooled trap is purged by a stream of dry gas[60] after having finished the trapping process proper, in order to reduce the amount of water in the trap. However, the second alternative may result in losses of the substances to be determined. The trap with the sorbates is placed in the adapted injection port[58] of the gas chromatograph and/or connected directly to the inlet of the chromatographic column[57], then the deposit is thermally desorbed and chromatographed. The mode in which the trap constitutes directly part of the column requires that the sorbates form a narrow initial band in the trap in order to prevent excessive zone broadening.

The method of concentrating volatiles in traps with sorbent provides for convenient storage and transportation of concentrated headspace gas samples. If a capillary chromatographic column[58] and/or a combination with a mass spectrometer[60] is to be employed for the separation and identification of the sorbates, the latter are first transferred by thermal desorption and a stream of gas into a short cooled capil-

lary from which the condensate is again thermally desorbed and swept by the carrier gas into the capillary column. The sorbates can also be recovered by liquid extraction[61]; the extract is condensed by evaporating part of the extrahent*, if necessary, and analysed. This technique is particularly suitable with traps containing very strong sorbents, requiring inadmissibly high temperatures to release the sorbates.

The trap containing a sorbent actually functions as a chromatographic column. Feeding into such a column a gas that contains substances that are subject to sorption results in the frontal chromatography of the substances in the column. The fronts of the individual components advance along the column at rates given by $u/(1 + k_i)$ where u is the forward velocity of the gas, as measured in the column, and k_i is the capacity factor of a given component (i). After a volume corresponding to the retention volume plus two volumetric standard deviations of the zone of component i has passed through the column, the front of the component breaks through and, provided that the concentration of the component in the entering gas is constant, the amount of the component entrapped does not change on further drawing the gas through the column. Under the above equilibration conditions the concentration of component i in the gas entering the trap, c_{iG}, is related to the mass of the component accumulated in the trap, W_{is}, by[1,9]

$$c_{iG} = \frac{W_{is}}{V_{gi} W_S (T/273) + V_G}$$

where V_{gi}, W_S, T and V_G are the specific retention volume of the component on the given sorbent at the temperature of the trap, mass of the sorbent in the trap, absolute temperature of the trap and the free (gaseous) volume within the trap, respectively. In most instances $V_G \ll V_{gi} W_S(T/273)$. The V_{gi} values can be determined from data measured in the usual way by elution gas chromatography on the given sorbent, and W_{is} is determined by direct calibration of the gas chromatograph. The above principle constitutes the basis of the so-called equilibration method of concentrating trace amounts of volatiles in gases[1]. Another useful technique utilizing the principle of phase equilibria for concentrating trace components of gases is to pass the gas being analysed through a vessel containing a volatile liquid and analysing by gas chromatography a sample of the liquid saturated with the substances trapped from the gas[2]. When applying the equilibration methods it is not necessary to know the volume of the gas being analysed in order to determine c_{iG}.

If the trapping of components in columns containing sorbents is to be carried out in the conservation manner, *i.e.*, if it is required that the total amount of a given component contained in the volume of gas passed through the trap be captured in the latter, the volume of the gas must not reach that which would cause the frontal zone of the component to start breaking through. In this instance the concentration c_{iG} is given simply by $c_{iG} = W_{is}/V$ where V is the volume of the gas drawn through the trap. Raymond and Guiochon[62] recommend that the volume of the gas being analysed should not exceed one third of the retention volume of the given component. When determining several substances covering a wide range of retentions in the given sorbent, the method of conservation trapping results in a relatively small accumulation of strongly sorbed components.

The sorbents for concentrating headspace gas components are essentially the

* Extrahent: the agent used to extract the sample.

same as those employed in traps for the determination of trace impurities in the atmosphere and other gases, as outlined below.

Activated carbon and various products of its treatment (carbon molecular sieves, graphitized carbon black, etc.)[61–63]. Most of these adsorbents have large specific surface areas and show high sorption capacities. The sorbates are retained very strongly on their surfaces, and high temperatures are necessary to recover the concentrate quantitatively. Therefore, these adsorbents are not suitable for the concentration and thermal desorption of thermally unstable compounds. On the other hand, they may be very advantageous when an extremely high concentration effect is required for the determination of ultratrace amounts of substances. The problems incidental to thermal desorption can be obviated by employing liquid extraction to recover the sorbates[61]; carbon disulphide is the most frequently used extrahent.

Porous organic polymers of the Porapak type. These sorbents have a lower sorption capacity in comparison with activated carbons and some of them display a certain selectivity towards some classes of compounds. The temperature limit of their stability does not exceed 200°; when exposed to higher temperatures they exhibit appreciable bleeding and may produce artifact peaks in the chromatograms of the concentrates. Krumperman[64] found that even well conditioned Porapak Q produced artifact peaks when operated at temperatures above 170°.

Porous organic polymer Tenax GC. This sorbent seems to be the best material for packing trapping columns. Despite its relatively low specific surface area (about 19 m^2/g)[65] it has a high sorption capacity towards most compounds[66] and its high thermal stability (375°) allows thermal desorption of substrates to be carried out at temperatures as high as 300° without any artifacts being produced. The retention of water on Tenax GC is very small, so that the competitive sorption of water is not significant even at a very high relative excess of water in the gas being analysed. Hence, it is possible with Tenax GC to trap efficiently components from water-saturated gases, which very often is the case in headspace gas analysis. It was found[66,67] that the presence of large amounts of water in the carrier gas did not alter the retention volumes of various solute compounds on Tenax GC by more than $\pm 10\%$. This is important with regard to the possibility of using the method of equilibration trapping. Some experience with other organic polymers and an interesting instrumentation for combined capillary column GC–MS were described recently[68].

Other materials. Generally it is possible to employ any suitable chromatographic packing as a sorbent of the trapping column. The main considerations in individual cases are the sorption capacity towards the components of interest, the temperature necessary to desorb the deposit and the thermal stability of both the sorbent and the sorbates; when using liquid extraction to recover the sorbates it is necessary to consider whether the sorbent may be soluble in the extrahent.

The methods of concentrating headspace gas components in traps packed with sorbents have been utilized, *e.g.*, for the determination of volatile substances in foodstuffs[57,69] and beverages[70,71] and of volatile metabolites in urine[72,73]. Usually the results of such analyses are interpreted merely as characteristic profiles of volatile constituents, the identification of the latter being carried out by GC–MS. No satisfactory method for the quantitative evaluation of such profiles has yet been presented.

All of the procedures based on concentrating headspace-gas components in traps and analysing the concentrates suffer from the uncertainty as to whether all the

volatiles have passed into the gaseous phase and were transferred into the trap. Hence, it is necessary to employ standardized procedures involving the use of model reference systems with the same matrix as in the system under analysis in order to obtain reliable quantitative results.

3.3. Stripping of the analysed material with a stream of gas

3.3.1. Direct analysis of the gaseous extract

During the process of stripping, the concentrations of the components in the gas leaving the system continuously decrease. Hence, the procedure must be carefully standardized if quantitative analysis is to be carried out in this way.

Wasik[74] has developed a special electrolytic stripping cell for the determination of hydrocarbons in sea water. In the main compartment of the cell, several litres in volume, bubbles of the hydrogen being developed on an electrode with a large area pass through the entire sample of water (1–3 l) and transport the hydrocarbons into the gradually increasing volume of the gaseous phase above the liquid. The amount of hydrogen evolved can be precisely controlled by the magnitude of the electrical charge having passed through. In Fig. 6, the upper and the lower chromatogram were obtained from 1-ml samples of the headspace gas after the total volume of the latter had reached 10 and 100 ml, respectively. The most volatile components are almost completely stripped out of the liquid by the early portions of hydrogen, so that the relative proportions of the peaks of these components in the second chromatogram should be substantially smaller than those in the first one. It is surprising that no peaks of the more volatile substances appeared in the second chromatogram. Direct analysis of a sample of the headspace gas permits the determination of a few parts per million of hydrocarbons in water. For the determination of lower concentrations Wasik[74] rec-

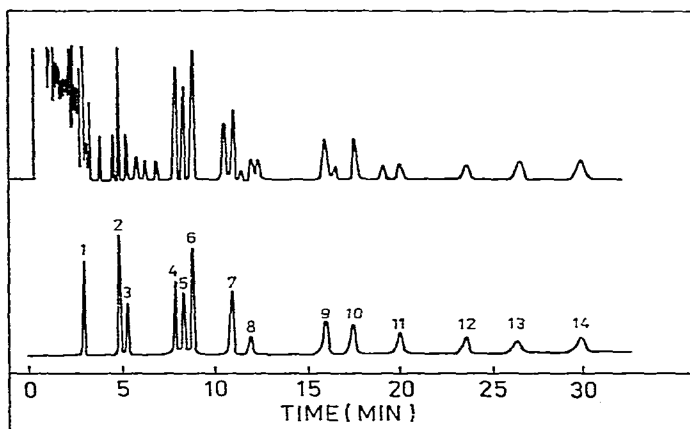

Fig. 6. Hydrocarbons stripped from artificial sea water[74]. 1 = Benzene; 2 = toluene; 3 = toluene-d_8; 4 = ethylbenzene; 5 = *p*-xylene; 6 = *m*-xylene; 7 = *o*-xylene; 8 = *n*-propylbenzene; 9 = 1-methyl-4-ethylbenzene; 10 = 1,3,5-trimethylbenzene; 11 = 1-methyl-2-ethylbenzene; 12 = 1,2,4-trimethylbenzene; 13 = *n*-butylbenzene; 14 = 1,2,3-trimethylbenzene. SCOT column (15 m × 0.5 mm I.D.) coated with *m*-bis(*m*-phenoxyphenoxy)benzene; helium carrier gas, 4 ml/min; column temperature, 80°. (Reprinted with permission of the author.)

ommends that the components stripped out of the liquid be concentrated by recycling in a closed circuit the entire volume of the gas through 2–3 mg of active carbon and subsequent extraction of the sorbates with carbon disulphide.

An advantage of the above method is that no artifacts are introduced into the system by the stripping gas. This method may be of great importance in ultratrace analysis, *e.g.*, at the parts per 10^{12} level. With substances that have higher solubilities in water (large K_i values), the concentrations in the gaseous phase may not reach levels sufficient for direct analysis, and a pre-concentration step is then necessary.

3.3.2. Accumulation of components stripped out and analysis of the concentrate

In addition to the problems that are basically the same as those encountered in concentrating samples of the headspace gas of a static equilibrated system, procedures that involve the process of stripping present some further problems. In work with aqueous materials, the use of larger volumes of stripping gas has associated with it larger amounts of water accumulated in cryogenic traps and, as the concentrations of the components to be determined in the gas leaving the material being analysed continuously decrease, it is impossible to use methods of equilibration trapping. On the other hand, in certain instances the sensitivity of analysis can be increased by using larger amounts of the stripping gas. The instrumental arrangement is similar to that used for trapping components of the headspace gas of static systems.

For the trap, use is made either of part of the GC column itself[70,75,76] or of various short columns packed with sorbents[77–79]. The stripping process proper is accomplished in a flask provided at the bottom with a frit through which the gas is fed into the system. When working with aqueous materials, a cooler and/or desiccator is installed between the outlet of the flask and the inlet of the trap in order to reduce the amount of water in the gas. The use of magnesium perchlorate as a drying agent was described in connection with the determination of organic compounds in drinking water by stripping a sample of the latter with a gas and condensing the volatiles in a cooled capillary[80]. However, the possibility must be considered of losses of the volatiles owing to their sorption in the desiccator, especially if they are present in very low concentrations.

The identification of the individual components of the concentrate is carried out either by correlating their retention data with those of reference compounds or, with more complex mixtures, by means of GC–MS[79,80]. For quantitative analysis, it is necessary to consider the efficiencies of the processes of stripping and trapping and the efficiency of the recovery of the concentrate from the trap; a suitable means of obtaining an insight into this matter is to study the procedure by analysing model systems with known contents of the substances to be determined. For instance, it is possible to determine by this method hydrocarbons in water at concentrations as low as tenths of a microgram per litre, but, in most instances, neither the accuracy nor precision of the results was quoted. Hrivňák and co-workers[81,82] have developed a procedure for the determination of volatile substances in aqueous media, employing the arrangement shown schematically in Fig. 7. A stream of pure gas from a tank bottle is passed through the liquid being analysed, and the effluent gas is fed via a magnesium perchlorate desiccator into a short capillary cooled in a mixture of solid carbon dioxide and ethanol. After the process of stripping and trapping has been finished, the capillary with the condensate is introduced through a special adaptor into

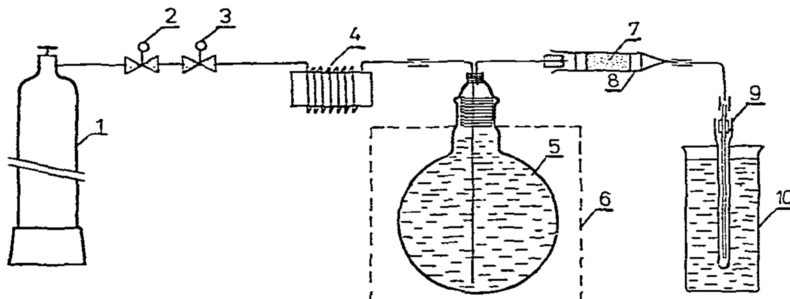

Fig. 7. Schematic diagram of an apparatus for the collection of volatiles from milk[81]. 1 = Gas cylinder; 2, 3 = regulation valves; 4 = capillary resistor; 5 = flask containing sample; 6 = thermostat; 7 = tube filled with 30 mg of magnesium perchlorate; 8 = glass-wool plug; 9 = collecting capillary; 10 = freezing bath (dry-ice–ethanol).

the inlet port of a capillary column gas chromatograph (Fig. 8), whereupon the condensate is vaporized and swept into the chromatographic column. As small streams of stripping gas were used, it was unlikely that the volatiles would be stripped out completely from the liquid. It can be estimated by virtue of eqn. 18 that in many instances (especially with strongly hydrophilic solutes) most of the components will remain in the liquid. Under these circumstances, quantitation is feasible only by calibration using a reference system with the same matrix material as in the system being analysed,

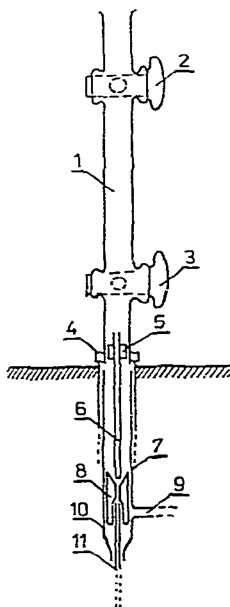

Fig. 8. Device for the introduction of a capillary trap with collected volatiles into the injection port of the gas chromatograph[82]. 1 = Glass liner with (2, 3) two valves; 4 = silicone-rubber gasket; 6 = capillary trap with (5) a steel collar; 7 = GC injection port; 8 = brass joint for connecting the trap with (11) the chromatographic column; 10 = splitter with (9) a valve.

keeping constant the rate and time of stripping and the temperature of the liquid being stripped.

3.3.3. Stripping and trapping components in a closed circuit

This elegant method was introduced by Grob and co-workers and applied to the determination of trace amounts of organic pollutants in water[83–86]. The head-space gas of the gas–liquid system being studied is recirculated by means of a pump via the liquid of the system and a trap connected in a closed circuit, as shown in Fig. 9. The components to be determined are gradually removed by the gas from the liquid and accumulated in the trap. Finally, the concentrate is recovered from the trap and analysed. Charcoal filters were used as traps; according to the contents of pollutants in the sample of water being analysed, the filters contained either 1.5 or 5 mg of charcoal. The concentrate was recovered by extracting the filter with 5–30 μl of carbon disulphide. If necessary the extract can be condensed by evaporating part of the extrahent. By optimizing the temperature of the system and the rate of recirculation of the gas, it was possible to decrease the sample size and the time of analysis from the earlier employed 5 l and 12 h to 1 l and 1–3 h. The possibility of obtaining quantitative results by using this method was demonstrated by the determination of trace amounts of oils and other organic substances in water at concentrations of 1–10 ng/l.

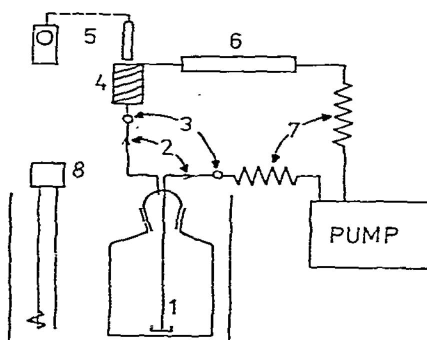

Fig. 9. Arrangement for stripping and trapping components in a closed circuit[86]. 1 = Glass frit; 2 = Rotulex bowl joints with PTFE seals (Sovirel); 3 = fused glass-metal connections; 4 = aluminium heating cylinder; 5 = soldering iron (15 W) with time relay; 6 = filter holder; 7 = stainless-steel tubing (1 m × 3.2 mm O.D. × 2 mm I.D.); 8 = thermostated water-bath. (Reprinted with permission of the authors.)

The reliability of the results depends on a number of factors, some of which may be unknown and/or very difficult to reproduce, *e.g.*, the efficiencies of stripping the components from the liquid, capturing them in the trap and recovering them from the latter, and the losses incidental to condensing the extract and due to spurious sorption of the components in various parts of the instrumental set-up. The authors tried to eliminate the effects of these factors by employing internal standards (1-chloroalkanes); the peak areas of the latter were used to correct the results to values corresponding more closely to reality. However, the use of model reference systems should permit more accurate analyses. Recently, the prospects of using the standard additions

method as a means of quantitation in trace analysis by the method of Grob and co-workers were discussed[7], considering both the conservation and equilibration modes of trapping the components to be determined.

The method of stripping and trapping components in a closed circuit appears to be a very powerful means of headspace gas trace and ultratrace analysis. It permits high concentration effects to be attained while covering a wide range of compounds which can be determined in this way. As the liquid being analysed is stripped by the headspace gas itself, the danger of introducing artifacts into the system is significantly reduced. The possibility of bringing the gas–liquid–sorbent (trap) system into equilibrium makes it feasible to apply methods of equilibration trapping.

4. CONCLUSIONS

From the physical point of view, headspace gas analysis can generally be characterized as a method of obtaining information on the contents of volatile components in a condensed material indirectly by analysing the coexisting gaseous phase. The same principle can obviously be applied in an analogous way with procedures that involve liquid extraction of the material, *i.e.*, to analysing the liquid extract rather than the headspace gas, thus making it possible to determine also components of low volatility; non-volatile extrahents can be analysed by liquid chromatography. Hence, the method is especially suitable when the material is not amenable to direct chromatographic analysis.

When applied merely to the identification of compounds, headspace gas analysis can be carried out without any special provisions. For fingerprint comparisons or the determination of characteristic profiles it is sufficient just to keep the system under constant conditions and to standardize the working procedure. However, in accurate quantitative analysis it is necessary to take into account all of the parameters determining the distribution of the components among the phases of the system and to proceed in compliance with the requirements normally made for physicochemical measurements of phase equilibria.

In headspace gas analysis of materials with matrices the nature of which renders it impossible to prepare adequate model reference systems, the only means of accurate quantitation is the standard additions method.

5. SUMMARY

General aspects of headspace gas analysis are discussed, involving topics such as: the distribution of the solute in the gas-condensed phase system, stripping of solute components with a stream of gas, and quantitation procedures in headspace gas analysis. A survey is given of the applications of headspace gas analysis, reviewing the techniques of direct analysis of headspace gas samples, accumulation of headspace components and analysis of the concentrate, and stripping of the analyzed material with a stream of gas. Emphasis is placed on the problems of quantitation. The standard-addition method is featured as a universal means of eliminating the matrix effects occurring in complex multiphase multicomponent systems.

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