Review

Methods of equilibrium concentration for the gas chromatographic determination of trace volatiles

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ABSTRACT

This review deals with a gas chromatographic technique based on the use of equilibria in the condensed phase–gas system, which is currently in the stage of intense development. Problems bearing on the usefulness of different variants of headspace analysis and of related methods in reducing the threshold of the gas chromatographic determination of volatile impurities in objects taken in any aggregate state are considered. When analysing impurities in solid and liquid objects, major attention is focused on the specific features of headspace analysis and methods of improving its sensitivity. For gas objects the same problems are treated in the context of the reverse technique, *i.e.*, equilibrium saturation of a condensed phase with the gas to be analysed.

The theory and practice of equilibrium concentration, including headspace analysis techniques, are developing so fast that even fairly recent reviews and monographs no longer reflect the state of the art of this area in organic analysis. The methods of headspace analysis and its new modifications provide fairly accurate and selective determinations of a variety of impurities present in complex mixtures at the μg/l level or lower, and find broad application in the analysis of environmental samples and in biology, medicine, geochemistry, oceanology, power engineering, etc.

The review covers studies made in the field of headspace concentration and related methods in the last 10–12 years. Attention is focused primarily on the description of the fundamentals of these methods and the areas of their applicability.

CONTENTS

1. INTRODUCTION

The present-day requirements concerning the sensitivity of methods used to measure the content of harmful volatile impurities are so stringent that direct injection of a sample into the chromatograph may not ensure the desired detection limit. Indeed, transfer of liquid or gaseous samples to a chromatograph equipped with a flame ionization detector permits the determination of impurities at a level of a few milligrams per litre of liquid or per cubic metre of gas. The allowable concentrations in such essential objects as natural or tap water and atmospheric air are one to five orders of magnitude lower. Therefore, in common analytical practice one frequently uses various adsorption, absorption and cryogenic methods of concentration. While these traditional methods based on complete extraction of an impurity from an object under study are employed widely in trace analysis (see, *e.g.*, ref. 1), they possess a number of drawbacks associated with the need to remove water, or exclude its adverse action, to prevent or take into proper account the breakthrough of the analyte, etc. Some shortcomings of the traditional methods of concentration can be eliminated by using, in place of complete absorption, the principle of equilibrium concentration[a] [2,3] where the impurity to be trapped distributes in a trap between the condensed phase and the gas in accordance with a simple law governing the partitioning of a compound in a heterogeneous system:

$$K = C_L/C_G \tag{1}$$

where K is the partition coefficient and C_L and C_G are the equilibrium concentrations of the compound in the condensed and gas phases, respectively.

In contrast to complete trapping, the equilibrium mode tolerates breakthrough of the analyte and is used in most instances under conditions which do not require measuring the gas volume. The methods of equilibrium concentration are based on the laws governing gas extraction and headspace analysis (HSA) [4–9]. The latter occupies a key place among modern techniques for the determinations of volatile organic impurities.

The concentration methods currently in use can be classified according to the aggregate state of the object under study and to the actual approach used for the adsorption and absorption trapping of impurities in gas objects, frontal (sorption) and absorption concentration of volatile impurities present in liquids and solids.

The equilibrium concentration of impurities present initially in gas objects

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[a] The term "equilibrium concentration" was introduced by Ioffe *et al.* [9] and applied for the first time to the absorption concentration of atmospheric air impurities with their subsequent gas chromatographic characterization.

differs from the concentration of compounds extracted from liquids and solids in the absence of the gas extraction stage and may be considered as an inverse method to headspace analysis. In the course of trapping, the compound likewise distributes between the condensed and gas phases, but in the direction opposite to that typical of HSA, namely, the condensed phase extracts impurities out of the gas. This imparts certain features to the concentration methods based on sorption, the most essential being the constancy of the analyte content in the gas under study and predominant use of dynamic conditions in the concentration process.

Combining HSA with preconcentration before injecting the enriched sample into the chromatographic column can be done in several ways, namely, when the equilibrium gas extraction of compounds from a solution or a solid object occur under static or dynamic conditions, and the concentration in an adsorption or absorption trap is carried out in the complete or equilibrium trapping mode. Cryogenic concentration can be used only under the complete trapping conditions.

The above methods of concentration differ in technical detail, are described by radically different relationships and are characterized by different possibilities of sensitivity and selectivity improvement.

2. EQUILIBRIUM CONCENTRATION OF IMPURITIES PRESENT IN GAS OBJECTS

Outwardly, the process of equilibrium concentration differs little from methods involving complete trapping of analytes from gases. There is, however, a radical distinction between these methods in that under the complete trapping conditions the gas under study can be passed only before the breakthrough of the analyte. Further saturation of the concentrator with the gas results in a loss of the accumulating compound and, eventually, in large analytical errors. Equilibrium concentration is achieved by passing the gas through the absorber until the impurity concentrations in the gas flow at the entrance to and exit from the trap become equal, *i.e.*, until the absorption capacity of the trap has become exhausted. As a result of this difference in the concentrator saturation regime, in order to calculate the initial impurity concentration under total trapping one has to measure the gas volume passed and to avoid exceeding a certain maximum volume (V_g^{max}) for which the breakthrough volume just reaches the allowable limit (δ). In equilibrium concentration, however, one has to pass a minimum volume of gas (V_g^{min}) at which the impurity concentration throughout the absorber volume reaches the equilibrium value. Further streaming of the gas will no longer change the analyte concentration (mass) in the trap, the analytical result being calculated based on the parameters of the analyte partitioning between the two phases. Thus the equilibrium concentration, in contrast to complete trapping, ensures more efficient use of the sorbent and does not require measurement of the gas flow volume.

Two variants of equilibrium concentration in non-volatile and volatile liquids have been developed, experimentally verified and put into service. They are technically different and possess different possibilities and limitations.

Equilibrium concentration in non-volatile liquids (stationary phases for gas chromatography) was proposed in 1965 [10] and was used subsequently by Novák, Janak and co-workers [11,12], Dravnieks, Krotoszynski and co-workers [13–16] and others [17–19] in the 1970s and 1980s for the concentration of multi-component

mixtures of volatiles of complex composition [19] and of compounds emitted from polymer materials into the atmosphere [17]. The theory of the method proposed by Novák *et al.* [10] was subsequently developed and refined [17,20–22].

Equilibrium concentration in volatile liquids (allowing the use of low-volatility liquids) was proposed by Ioffe, Vitenberg and co-workers [9,23–26] for the determination of toxic microimpurities in gases, the method having been applied also to the determination of alcohols in air [27].

There is an essential difference between these two variants of the equilibrium concentration. Direct injection into the chromatograph of a solution in a non-volatile solvent is undesirable. Accumulation of a non-volatile liquid in a chromatographic column may result in a substantial change in the retention parameters and a sharp drop in the separation efficiency, as it is difficult to realize the instantaneous release of volatiles from a non-evaporating solvent. Therefore, equilibrium concentration in non-volatile solvents is achieved in the form of frontal saturation of a thin liquid film deposited on a solid support [10–13,15–17] (*i.e.*, chromatographic packing) or directly on the tube walls [14]. The concentrate obtained in this way in the non-volatile liquid is subsequently subjected to thermal desorption in a carrier gas flow, with the total amount (rather than a fraction) of the volatile components absorbed in the trap being determined in a single measurement.

Equilibrium concentration in volatile liquids is achieved through absorption of the impurities present in a gas by bubbling it through a layer of a well mixed trapping liquid. Therefore, it differs from the frontal adsorption variant primarily in that the impurity concentration in the liquid increases uniformly throughout the volume in the course of saturation. Apart from this, the concentrate in a volatile liquid can be injected directly into the chromatograph, with the analysis being repeated as many times as needed.

As a result of these specific features of the adsorption and absorption variants of the equilibrium concentration method developed for impurities in gaseous objects, these processes are described by radically different relationships.

2.1. Equilibrium frontal concentration

This is based not only on the solution of the impurity vapours in a thin layer of a non-volatile liquid but also on adsorption on the surface of the liquid and the solid support [28–30]. The actual contributions of each of these effects to the trapping of a compound in the absorption column (or to retention in the case of chromatography) are determined by the nature and properties of the packing and of the liquid phase, and by their relative amounts. Therefore, the theory of frontal concentration is based on the retention parameters of a chromatographic column which has the same size and packing as the concentrator, *i.e.*, the same retention volume V_R^0. The quantity V_R^0 takes into account automatically the adsorption and absorption effects affecting the amount of the trapped compound.

Having determined gas chromatographically (usually by means of thermal desorption) the mass of the concentrated compound (m_c), one can calculate the analyte concentration (C_G^0) by a simple relationship:

$$C_G^0 = m_c/V_R^0 \qquad (2)$$

The minimum gas volume (V_g^{min}) required to ensure equilibrium concentration along the trap can best be determined from the retention parameters (see p. 180 in ref. 7):

$$V_g^{min} = V_R^0 + \Delta V_R^0 \tag{3}$$

where ΔV_R^0 is the gas volume required for elution of half of the chromatographic band out of the column.

The sensitivity (S) of frontal concentration can likewise be expressed in terms of the retention parameters [7,8]:

$$S = fV_R^0 \tag{4}$$

where f is a coefficient accounting for the sensitivity of the chromatographic detector used to the analyte in question.

The possibilities of the method can be illustrated more graphically than is revealed by eqn. 4 by introducing the relative sensitivity (α) of the frontal equilibrium concentration, *i.e.*, the degree of reduction of its detection threshold compared with direct injection of the analyte gas into the chromatograph:

$$\alpha = V_R^0/v_g \tag{5}$$

where v_g is the volume of the gas sample pulse-injected into the chromatograph. This relationship may serve as a criterion in evaluating the usefulness of frontal equilibrium concentration to reduce the gas chromatographic detection threshold for volatile impurities in gaseous objects.

Eqns. 4 and 5 show that in order to improve the sensitivity of frontal concentration one has to increase V_R^0. For large V_R^0, however, the time required to remove an analyte from the concentration column in the cours of thermal desorption becomes substantially longer, which results in a reduced efficiency of chromatographic separation and puts a limit on the possibilities of the method in the variant of direct and complete desorption proposed by Novák *et al.* [10]. The ultimate possibilities of the method as related to reducing the impurity detection limit are usually limited by the value $\alpha = 100$.

The analytical aspects of equilibrium frontal concentration on polymer sorbents with subsequent capillary column gas chromatographic analysis were studied by Novotny *et al.* [19]. As a sorbent for mixtures of complex composition (food odours, volatile components of biological samples or atmospheric pollutants), one can recommend Tenax GC, which is capable of concentrating both polar and non-polar compounds. However, the chromatogram quality and also the possibility of quantitative analysis and of the identification of individual components depend to a considerable extent on the actual conditions of sample injection into the capillary column.

Pulsed injection of a thermally desorbed compound into the chromatographic column can be obtained by incomplete removal of the impurity from the concentrator [7,8]. The sensitivity of frontal concentration can also be improved by accumulating the impurities in a cryogenic trap prior to their transfer to the chromatographic column [13,14].

Equilibrium frontal concentration was tested on model vapour–gas mixtures of lower aromatic hydrocarbons, acetone and methanol in air over the concentration range 0.3 mg/l–0.3 μg/l [10]. Direct injection of the analyte gas into the chromatograph was used as a reference method. This technique was employed to analyze the air in factory shops polluted by benzene, chlorobenzene and nitrobenzene [11] and the air in surgery rooms for the presence of halothane [12] and to study the composition of the volatiles evolving from polymer materials [17]. The equilibrium and chromato-distributive [31] concentrations were combined [18] to identify the impurities present in air.

2.2. Equilibrium absorption concentration

This removes the complications arising from the need for thermal elution of the trapped impurities from non-volatile liquids or adsorbents. This method consists in saturating a few millilitres of a pure volatile liquid with a finely dispersed analyte gas. A small sample (1–5 μl) of the concentrate thus obtained is then injected directly into the chromatograph.

The theory of the method [23,24,26] yields the following equation:

$$C_L = KC_G^0 \cdot \frac{f_s}{1 - FK} \left[1 - \left(1 - F \cdot \frac{V_g}{V_L^0} \right)^{\frac{1 - FK}{FK}} \right] \tag{6}$$

which describes the variation of the impurity concentration in the trapping liquid (C_L) as the gas under study is passed through it, as a function of the content in the former of the microimpurity of interest (C_G^0), its partition coefficient (K), initial volume (V_L^0) and volatility (F) of the absorbing liquid: $F = p_L M / RT d_L$ (here M is the molecular mass and p_L and d_L are the saturated vapour pressure and trapping liquid density at temperature T, R is the universal gas constant), as well as of a coefficient $f_s = (p_a - p_L)/p_a$, which accounts for the change in the volume of the gas after its passage through the solution of the volatile absorbing liquid (p_a is the atmospheric pressure).

An analysis of eqn. 6 shows the method to be useful only for $FK < 0.5$. In other words, for the equilibrium absorption concentration to be applicable in analytical practice, the volatility of the trapping liquid should be less than half that of the analyte which is characterized by $1/K$.

For a non-volatile trapping liquid $F \to 0$, and eqn. 6 transforms into an exponential function:

$$C_L = KC_G^0 \cdot \left[1 - \exp\left(- \frac{V_g}{KV_L^0} \right) \right] \tag{7}$$

One can refrain from measuring the volume of the gas passed through the absorber and calculate the analyte content in the gas by the equation

$$C_G^0 = \frac{C_L^{lim}}{K} \cdot \frac{1 - FK}{f_s} \tag{8}$$

if the gas volume passed has become larger than

$$V_g^{min} = \frac{V_L^0}{F}\left(1 - \delta^{\frac{FK}{1-FK}}\right) \tag{9}$$

where C_L^{lim} is the limiting impurity concentration in the solution differing from the equilibrium value by not more than the error of its measurement δ.

The sensitivity of equilibrium absorption concentration depends primarily on the numerical value of K. This is clearly seen from the relationship

$$\alpha = \frac{m_L}{m_g} = \frac{v_L}{v_g} \cdot K \cdot \frac{f_s}{1-FK} = \frac{K}{10^3}\frac{f_s}{1-FK} \approx \frac{K}{10^3} \tag{10}$$

which characterizes the change in the analytical sensitivity compared with direct introduction of the gas under study into the chromatograph. Here m_L and m_g are the masses of the analyte introduced into the chromatograph in the form of a liquid concentrate of volume v_L or of a gas sample of volume v_g, respectively.

It has been shown [32] that in the case of a concentrate injected directly into the column, equilibrium absorption concentration permits the lowering of the gas chromatographic detection threshold by more than an order of magnitude while being slightly inferior to the variants involving impurity trapping on the column packing.

Thus, apart from different degrees of enrichment, the principal difference between the above two methods of equilibrium concentration of impurities present in gaseous objects is that using the absorption technique one determines the concentration of the trapped analyte rather than its total amount. In addition, it becomes possible to choose a suitable solvent from a large number of compounds, while the elimination of the thermal desorption stage permits the characterization of unstable compounds and improves the reliability of analysis.

One should also point out an essential distinction between the absorption and frontal concentration techniques connected directly with the specific features of impurity build-up in the concentrator. In frontal concentration, the mass of the trapped impurity (m_L) increases linearly (Fig. 1) with the volume of the gas passed through the concentrator, as long as $V_g^{max} \leqslant V_R^0 - \Delta V_R$. The first part of the concentration curve limited by the volume V_g^{max} corresponds to total trapping of the analyte (with no breakthrough). The calculation of the initial concentration C_G^0 within this section includes the gas volume passed. A further increase in V_g in the interval $V_R^0 - \Delta V_R \leqslant V_g \leqslant V_R^0 + \Delta V_R$ results in a non-linear increase of the mass of the concentrated impurity. The behaviour of the $m_L(V_g)$ relationship in the second part of the plot is determined by the shape of the analyte distribution isotherm in the concentrator, usually remains unknown, and is not used in analytical practice. In this part of the concentration curve, partial breakthrough of the impurity through the absorbent begins (Fig. 2). Equilibrium concentration occurs in the third part of the curve for $V_g > V_R^0 + \Delta V_R$. This regime is characterized by a constant content of the trapped impurity in the concentrator (Fig. 1), i.e., by a total breakthrough of the impurity or a linear increase in the mass of the impurity passing through the concentrator (Fig. 2).

The absorption concentration has a distinctive feature in that the impurity starts partially to break through the trap with the very first portions of the gas flow, the
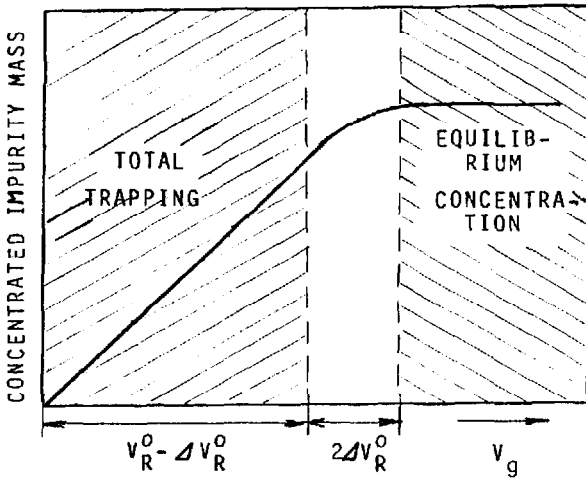
Fig. 1. Variation of the mass of the trapped analyte in the course of frontal sorption concentration.

build-up of the analyte in the concentrator up to the equilibrium state occurring exponentially. The regime of total trapping (Fig. 3) is limited by the allowable difference between the impurity concentrations achieved in the absence of breakthrough (curve I) and the absorption build-up (curve II). This difference should not usually exceed the error in the analyte concentration measurement in the absorbing solution (δ). The absorption equilibrium concentration regime sets in after the condition in eqn. 9 for V_g^{min} has been met.

The above equations describing the principal relationships which govern the absorption concentration not only permit one to calculate the equilibrium concentration parameters but can also be used to evaluate the optimum absorber volume and the allowed volume of the gas (V_g^{max}) passed under the total absorption conditions. The
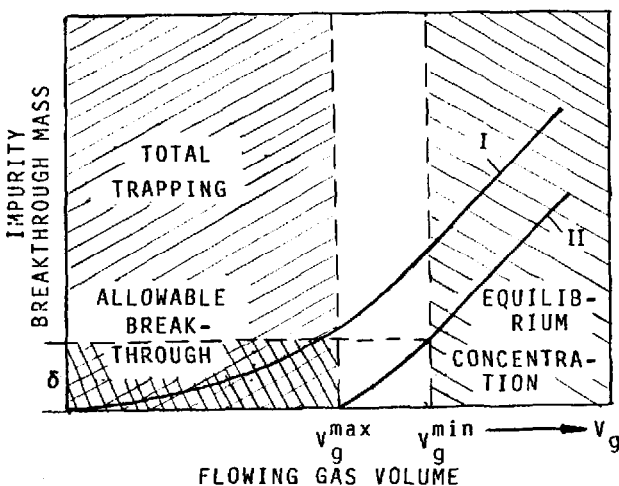

Fig. 2. Analyte breakthrough in (I) absorption and (II) frontal equilibrium concentration.
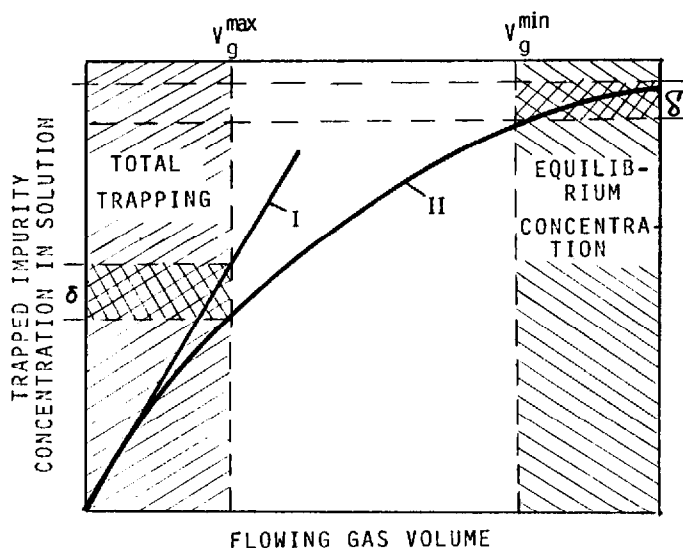
Fig. 3. Variation of analyte concentration in liquid absorber in the course of absorption concentration. (I) Total analyte absorption; (II) equilibrium concentration.

concentration parameters are still chosen arbitrarily without taking into proper account the absorbing capacity of the trapping liquid and the volatility of the analytes. As a result, the chosen volumes of the absorbent and of the analyte gas, and also the flow-rate of the latter, may turn out to be far from the optimum values. Apart from this, the combination of the total absorption and equilibrium concentration regimes in one sampling cycle eliminates errors in the analysis of the mixtures whose components differ substantially in the boiling temperature and solubility in the trapping liquid. High-volatility compounds can be trapped under the equilibrium concentration conditions, the less volatile being captured totally in the trap.

The basic points of the theory of equilibrium absorption concentration were checked for the absorption of aromatic hydrocarbon vapours with acetic acid, and also for some oxygen compounds and diethylamine with water [25,26]. Concentration of compounds with variable partition coefficients has also been considered [33,34].

In addition to these impurities, absorption equilibrium concentration has been used to develop gas chromatographic methods for the determination of gas moisture content [32,35] (with n-butanol as absorbent and $ca.$ 1 μg/l detection threshold), of aliphatic alcohols in atmospheric air (trapping in air with a detection threshold of $ca.$ 1 mg/m^3) [27] and of unstable lower thiols together with sulphides in natural gas and air [36] (benzene as absorbent, flame ionization detection, detection threshold at the $ca.$ 1 mg/m^3 level).

The possibility of determining unstable impurities is the most essential asset and a distinctive feature of equilibrium concentration. Whenever the analytes undergo chemical transformations in the course of sampling, any method based on the total absorption of impurities during concentration will result in large errors. The collection of gas samples containing unstable compounds without introducing substantial

distortions is made possible by the fact that the loss of the impurities trapped in the concentrator is compensated for by their inflow with the subsequent gas portions, the volume of the gas passed not entering into the calculations.

   Another feature of the equilibrium methods of concentrating impurities present in gaseous objects lies in the selectivity of impurity build-up in the absorber [7,8]. This opens up the possibility of separation from concomitant components in the concentration stage, which can be done only in the case of compounds with very different partition coefficients.

3. HEADSPACE CONCENTRATION OF VOLATILE IMPURITIES PRESENT IN LIQUID AND SOLID OBJECTS

   Headspace concentration (HSC) is employed to increase the sensitivity of HSA and to reduce the detection limit of the gas chromatographic detection of volatiles present in liquids and solids. In the literature, by headspace concentration one usually understands the modifications of analysis involving intermediate (cryogenic, adsorption or absorption) accumulation of the compounds present in the gas phase above the sample under study before their injection into the chromatographic column. The sensitivity of these variants of HSA is increased by increasing the single-injection dose of the equilibrium gas. This is seen readily from the equation [7,8,32] describing the sensitivity of the principal HSA variant, *i.e.*, single gas extraction:

$$S = f \cdot \frac{v_g}{K + r} \qquad (11)$$

whence it follows that, in addition to increasing the sample volume (v_g) injected into the chromatograph, the HSA sensitivity (S) can also be enhanced by reducing the partition coefficient (K), choosing an optimum ratio of the gas (V_g) to condensed phase (V_L) volumes ($r = V_G/V_L$) and by using selective detection (the factor f taking into account the sensitivity of the detector used to the analyte in question). Such modifications of HSA resulting in an improvement in its sensitivity and a reduction in the gas chromatographic detection limit should also be classified among HSC methods.

   The gain in the gas chromatographic sensitivity obtained in direct HSA compared with direct injection of a sample into the chromatograph can be written as [32]

$$\alpha = \frac{10^3}{K + r} \qquad (12)$$

and is reached at $\alpha > 1$, *i.e.*, when $K < (10^3 - r)$. The values of the partition coefficients between water and air for a number of compounds of interest for environmental monitoring range within 4–5 orders of magnitude (Table 1). The sensitivity and threshold of the HSA determination of these compounds also vary accordingly. Indeed, whereas gaseous hydrocarbons (methane, ethane, ethylene, etc.) present in water solutions can be detected in the most favorable cases at a level of 0.1–1 μg/l, for higly soluble compounds with $K > 10^3$ (alcohols, phenols, volatile fatty

TABLE 1

PARTITION COEFFICIENTS OF VOLATILES IN THE AIR–WATER SYSTEM AT 25°C

Compound	$K \pm \Delta K^a$	Ref.	Compound	$K \pm \Delta K^a$	Ref.
Methane	0.034	8	Acrolein	180	39
Ethane	0.045	8	Propionaldehyde	330	43
Propane	0.037	8	Dibutyl ether	5.3 ± 0.2	32
Ethylene	0.12	8	Methyl acetate	190 ± 5	32
Propylene	0.18	8		190	44
Acetylene	1.01	8	Ethyl acetate	150 ± 2	32
Methylacetylene	1.7	8		144	44
Benzene	4.0 ± 0.1	37	n-Butyl acetate	87 ± 2	32
Toluene	3.6 ± 0.2	37		87	44
m-Xylene	4.6 ± 0.3	37	Methyl propionate	130 ± 5	32
Chloroform	8.5 ± 1.4 (20°C)	38		141	43
Carbon tetrachloride	9.9 ± 1.9 (20°C)	38	Methyl butyrate	90 ± 5	32
Hydrogen sulphide	2.5	8		120	43
Ethanethiol	5.4 ± 0.3 (20°C)	45	Dioxane	5750 ± 450	32
Dimethyl sulphide	14.8 ± 1.4 (20°C)	45		5400	41
Dimethyl disulphide	20.2 ± 2.0 (20°C)	45	Methanol	5500	39, 40
Acetone	580 ± 45	32	Ethanol	5260 ± 610	32
	630	39		4800	40
	610	42		5700	41
Methyl ethyl ketone	380 ± 40	32	Propanol	4090 ± 390	32
	430	39		3600	40

^{a} $n = 5$-7.

acids) the detection limit exceeds 1 mg/l, which is usually unacceptably high for the determination of toxic compounds. In such instances one frequently resorts to the methods of enhancing HSA sensitivity which involve reducing K or r and are now well studied [4–8].

To reduce K, one frequently increases the equilibrium onset temperature or uses salting-out (when determining impurities in aqueous solutions). Each of these techniques permits one to reduce K from 5 to 10, so that by combining them the detection limit can be decreased by 1.5–2 orders of magnitude. One can facilitate the characterization of impurities in volatile solvents (alcohol, acetic acid, dioxane) by diluting them with water [32]. A promising approach for reducing the detection limit of gas chromatographic HSA of readily soluble and chemically reactive compounds (such as lower aliphatic alcohols, carboxylic acids and phenols in water) lies in their conversion into more volatile and less soluble derivatives (see, *e.g.*, ref. 46). However, the most widely recognized among the various HSC methods are currently those involving intermediate cryogenic or sorption concentration.

Intermediate headspace accumulation of compounds in a trap before their introduction into the chromatographic column is needed in cases where direct injection either does not provide a sufficiently high analytical sensitivity or reduces the separation efficiency, as this may occur when using a capillary column.

The actual magnitude of the sensitivity enhancement of HSA with intermediate impurity concentration depends on the volume of the gas passed through the trap and may be as high as 2 4 orders of magnitude. A correct choice of the concentrator parameters is of particular significance here. The search for the optimum regimes and

the potential and limitations of the HSA techniques involving concentration have been discussed [47–54]. In cryogenic accumulation these critical points are the trap design and the temperatures required for total absorption of the analytes, their separation from concomitant compounds (*e.g.*, water) and their subsequent quantitative removal from the concentrator. The factors essential for the adsorption accumulation are the nature and volume of the adsorbent in the trap and the adsorption and desorption temperatures. The conditions and relationships governing the build-up in the trap of a compound stripped by the gas from the object under study differ substantially, depending on the properties of the analyte and of the sorbent, and on the actual concentration technique chosen.

Various modifications of HSC have been developed for use under static and dynamic conditions. The latter variant (frequently referred to as purge and trap) is more efficient, because by using a large volume of the extracting gas one can achieve a higher degree of enrichment. Apart from this, for the same gas volumes continuous gas extraction (CGE) ensures a more complete removal of the analyte from the sample [55]. Indeed, static HSA is employed much less frequently than that under dynamic conditions [7,8]. The method of CGE with subsequent accumulation of the impurities stripped by the carrier gas has found broad applications in the analysis of a wide variety of objects, ranging from the determination of volatile organic compounds in water and aqueous solutions to the characterization of complex aromas [7,8,51,56–67]. Dynamic HSA with intermediate concentration has also been applied to the analysis of foodstuffs [68–72], wine [73], cigarette filters [74], volatiles evolving from plants [75–77] and polymer materials [78–80], and to the chemotaxonomy of insects [81]. However, despite the high efficiency of CGE, the difficulties encountered in carrying out dynamic gas extraction under equilibrium conditions in the case of incomplete removal of an analyte from a sample, in addition to the high cost and long time taken up by an analysis, the artefacts related to thermal desorption and the presence of impurities in the extracting gas, make the static regime sometimes preferable in quantitative analysis [58,59,82–84]. From the technical standpoint this method is simpler, it provides gas extraction under equilibrium conditions and a high reproducibility of the degree to which one approaches phase equilibrium and, hence, of the fraction of the total amount of the analyte that enters the gas phase.

The equipment and techniques of headspace concentration which are based on dynamic and static HSA are described in reviews [56,57], monographs [4,5,7,8] and original papers [58,82–85]. One can find publications on commercial instrumentation and laboratory set-ups designed for routine analytical work in automatic and semi-automatic modes [82,83,86–89].

3.1. Cryogenic trapping of impurities

Cryogenic trapping of the impurities stripped with a gas from a solution or solid sample under study is employed only under conditions of complete trapping of the analyte, when the total mass of the impurity evolving from the object to be analysed into the gas phase is deposited in the trap and, after the latter has been heated, is injected into the chromatograph in a single step. A review [90] describes the various systems used to achieve cryogenic focusing.

For this analysis to be quantitative, the low-temperature traps have to be highly efficient. As traps one usually employs empty glass or quartz capillary tubes, and

sometimes the initial part of a capillary column or capillaries filled with glass beads. The latter are more efficient and are capable of retaining alkanes quantitatively. When using open capillaries, one should take into account not only the trapping temperature (which should be chosen as low as possible) but also the carrier gas flow-rate, trap geometry and the analyte concentration.

The enhancement of the analytical sensitivity depends on the amount of the analyte removed from the solution under study. In dynamic HSA, the fraction of the analyte extracted from a solution (Z_d) is dependent on the amount of the initial solution, its temperature and the volume of the gas passed, and for a system with a non-volatile solvent is described by the equation [91–93]

$$Z_d = 1 - \exp(-r/K) \tag{13}$$

For instance, in order to reach the detection threshold of a few fractions of a $\mu g/l$ when $K = 10^3$, one will have to extract the analyte nearly completely $(Z_d > 0.95)$ with a flow of a pure gas from 10 ml of solution. The required volume of the extracting gas should be about 30 l. If, however, the impurity is extracted from 100 ml of the solution, less than 10 l of pure gas will have to be passed to reach the same detection limit. A similar effect can be obtained by raising the solution temperature in CGE. A positive effect is given also by addition to aqueous solutions of large amounts of inorganic salts, because this usually results in a pronounced change of the vapour composition in favour of the analytes. To illustrate the potential of this technique, consider the detection of Freons in sea water [94]. Stripping of Freon 11 and 12 dissolved in 30 ml of water with their subsequent cryogenic focusing permits the determination of these compounds using a packed column with an electron-capture detector at levels down to a few hundredths of 1 pmol/kg in solution.

The appropriate regime of analyte extraction from solutions in a volatile solvent can be chosen based on the CGE relationships [95].

Under static conditions, the fraction of a volatile analyte (Z_s) removed from a system by passing through the trap the total volume of the gas phase is given by the expression

$$Z_s = \frac{r}{K + r} \tag{14}$$

When the analyte is accumulated in the concentrator under the conditions of partial sampling of equilibrated gas from a vial [96], e.g., as is done in the pneumatic headspace sampling technique [83,97–99], the amount of the analyte (m) collected in n samplings depends on, in addition to the numerical values of K and r and the total amount of the compound in the sample vial (M_0), also the pressure drop in the system $(\Delta P = p/p')$ before (p') and after (p) the sample collection. For known K and r, the corresponding calculations are carried out using the expression

$$\sum_1^n m_n = M_0 \left[1 - \left(\frac{K + rp/p'}{K + r} \right)^n \right] \tag{15}$$

If K and r are unknown, the mass of analyte removed is determined from the

measurement of the chromatographic peak areas (A_G^i) and (A_G^{i+1}) corresponding to the ith and $(i + 1)$th samplings:

$$\sum_1^n m_n = M_0[1 - (A_G^{i+1}/A_G^i)^n] \tag{16}$$

More precise results are usually obtained when characterizing systems with known K and r and using eqn. 15 for the calculations.

For illustration of the potential and specific features of static HSA with cryogenic concentration, compare the detection limits for halogenated hydrocarbons in water using flame ionization detection by direct injection of an equilibrium gas into the capillary column and with preliminary concentration in its initial part. Pneumatic sampling of equilibrium gas [84] was used for this purpose. Cryogenic headspace concentration was shown to reduce the detection limit of methylene chloride, chloroform, carbon tetrachloride and 1,2-dichloroethane by a factor of 12–20, and to allow the determination of halogenated hydrocarbons at the level of a few fractions of 1 μg/l.

The sensitivity of the determination of microimpurities in aqueous solutions can be further increased by removing moisture from the equilibrium gas by means of special condensers. For this purpose one employs quartz capillaries (30 cm × 0.32 mm I.D., sometimes coated with a thin film of liquid phase) [100], or Nafion desiccating membranes [100,101] (manufactured by DuPont).

Low detection limits with HSC and capillary column analysis can be achieved by using special techniques to narrow the initial chromatographic band, which may involve reducing the gas-to-liquid phase volume ratio in the trap, thermal focusing, etc. [102].

3.2. Adsorption headspace concentration

Adsorption headspace concentration with subsequent thermal desorption of the trapped analytes removes the principal drawback of the cryogenic concentration of impurities in aqueous solutions associated with the limited volume of the humid equilibrated gas passed through the trap. As adsorbers one employs [51] activated charcoal, Amberlite XAD, Chromosorbs or Tenax TA; however, the most widely recognized owing to its hydrophobic properties is Tenax GC, which has been proposed for the accumulation of organic impurities by Zlatkis and co-workers [103,104]. It should be pointed out that the use of Tenax materials meets with problems associated with the appearance of artefacts [105]. Thermal desorption brings about decomposition of Tenax GC with the formation of acetophenone, benzaldehyde, benzoic acid, ethylene oxide, phenol, etc. [106]. In addition, interaction with mineral acids (particularly those containing sulphur) may also result in the decomposition of Tenax GC and, eventually, in the formation of 2,6-diphenylbenzoquinone [107]. In addition to the oxidation products of Tenax GC, one observes unidentified high-molecular-weight products [108]. One may expect also the appearance of other artefacts, e.g., when analysing air containing chlorine, ozone or nitrogen oxides [109]. The adsorbent intended for trapping volatile impurities in HSC should meet certain requirements [110–112].

The adsorption variant provides a further reduction in the detection limit of

impurities by gas chromatographic headspace analysis and can be used under the conditions of complete trapping and equilibrium concentration, each of them imposing certain restrictions on the volume of gas passed through the tube with the sorbent.

As follows from the above description of the equilibrium frontal concentration method [10], the impurity trapping remains complete as long as the sweeping gas volume does not exceed $V_R - \Delta V_R$. This volume of the sweeping gas places a limit on the amount of the analyte extracted from the object under study that can be concentrated under the total trapping conditions. If the amount of the analyte adsorbed under these conditions turns out to be insufficient for achieving the desired detection limit, one will have to increase the packing mass and the sorbent layer length in the concentrator which, consequently, will increase V_R.

If the sweeping gas volume satisfies the condition $V_g \geqslant V_R + \Delta V_R$, we come to the equilibrium concentration regime, $i.e.$, a total breakthrough of the impurity. The headspace adsorption concentration differs radically from the frontal equilibrium concentration of impurities present in gases in that the content of the analytes in the gas passing through the concentrator gradually decreases. In the case of CGE it occurs by an exponential law, and in discontinuous extraction in steps. Therefore, if the gas volume passing through the trap is too large, $i.e.$, $V_g \geqslant V_R + \Delta V_R$, this may result in the removal of the analyte from the concentrator and, thus, in reduced analytical sensitivity. So far only the total trapping regime has been used in adsorption headspace concentration.

Thermal desorption is a process occurring in time and, hence, it frequently involves a decrease in the efficiency of the chromatographic column. This effect is removed by using the cryogenic focusing technique. Werhoff and Bretschneider [51] studied the possibility of quantitative measurements using dynamic HSA with concentration. Optimum HSC conditions were found, and quantitative data obtained, in an analysis of eleven volatile aromatic compounds (primarily terpenes). With Tenax GC used under optimum volatile trapping conditions (gas flow-rate 50 ml/min, trapping time 2 h at 80°C), subsequent desorption at 250°C and a carrier gas flow-rate of 30 ml/min for 30 min and a cryogenic trap temperature of $-130°$C, the analyte losses did not exceed 4%.

In analyses for the presence of halogenated hydrocarbons in water [84], a transition from cryogenic to adsorption concentration brings the detection limit down to a few hundredths of 1 mg/l, but the reproducibility of measurements on the same solutions decreases. The high sensitivity of HSA with intermediate adsorption concentration can be illustrated by the determination of the volatiles present in human blood (Fig. 4).

Despite the widespread recognition of dynamic HSC, data on the quantitative characterization of volatile impurities with headspace concentration are scarce (see, $e.g.$, refs. 84, 89 and 113–115). Most of the studies are either of an illustrative character or are aimed at finding qualitative characteristics of the objects of interest. The approach to choosing the analytical conditions is predominantly empirical. Inadequate attention is focused on the relationships governing the extraction of volatiles from liquid and, particularly, solid materials, $i.e.$, in the CGE stage. The various models of this process and their mathematical description have been discussed [93,116].
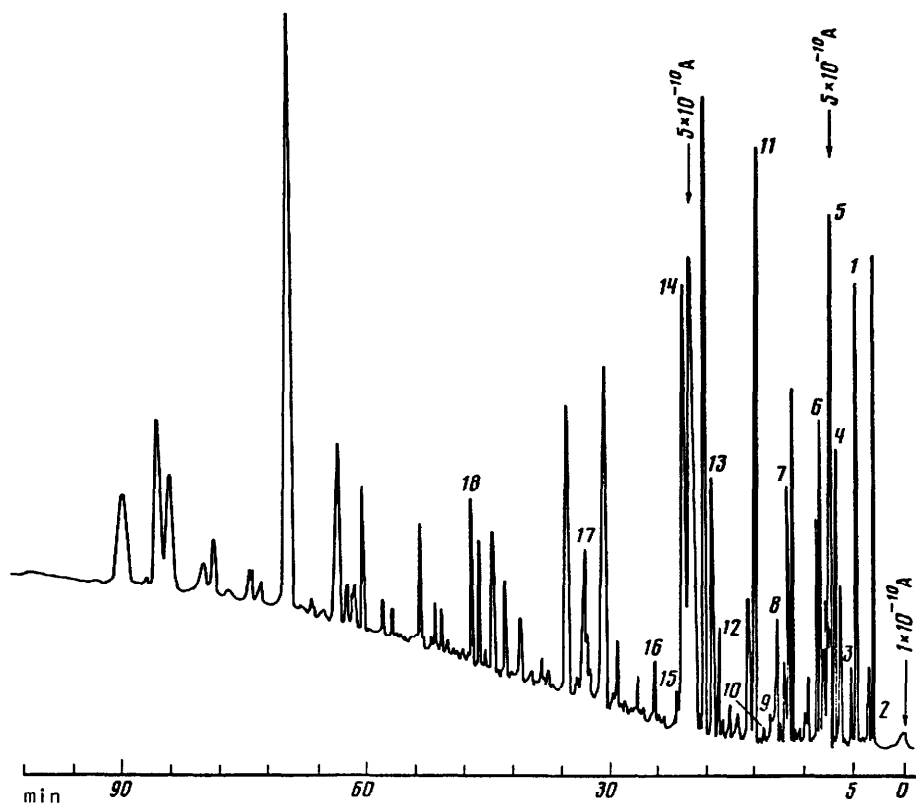
Fig. 4. Chromatogram of volatile organic impurities concentrated on Tenax GC from a sample collected
from the headspace above human blood [84]. Conditions: blood sample volume, 3 ml; gas-phase volume,
20 ml; temperature and equilibrium onset time, 60°C and 45 min; sampling, pneumatic under static
conditions; number of gas-phase samplings, 3, with pressure drop of 5 atm (507 MPa); capillary column with
dinonyl phthalate (45 × 0.25 mm I.D.); carrier gas (helium) flow-rate, 1 ml/min; column temperature, 50°C
for 5 min, increased to 130°C at 2°C/min. Peaks: 1 = acetaldehyde; 2 = methanol; 3 = isoprene;
4 = acetone; 5 = ethanol; 6 = dichloroethane; 7 = methyl ethyl ketone; 8 = heptane; 9 = carbon
tetrachloride; 10 = chloroform; 11 = benzene; 12 = methyl propyl ketone; 13 = dioxane; 14 = octane;
15 = butanol; 16 = toluene; 17 = nonane; 18 = n-decane.

3.3. Absorption headspace concentration

Absorption headspace concentration removes the limitations inherent in the
cryogenic and adsorption variants and stemming from the adverse effects of water and
the need for thermal desorption and for prevention of analyte breakthrough. In
addition, if the absorbing liquid has been chosen correctly, and proper techniques to
enhance the HSA sensitivity have been used, equilibrium absorption concentration not
only reduces the detection limit but also permits one to improve the selectivity of
discrimination between the various components in the mixture under analysis.

Wahlroos and Nikkila [117] were the first to strip volatile impurities from
solutions with a carrier gas with their subsequent accumulation in a non-volatile liquid
as far back as 1966. This study was not extended, however, because there was only
a small gain in sensitivity. Nearly 20 years later, Vitenberg and Kostkina [118]

considered a more general variant of headspace absorption concentration of impurities in volatile solvents, and found ways to improve the degree of concentration and to reduce further the detection limit of volatiles in solutions.

Headspace absorption concentration of volatile impurities by CGE actually represents a combination of extraction with a gas flow of analytes from the solution of interest with their subsequent equilibrium concentration in a volatile liquid. The fairly cumbersome equations describing this process have been validated experimentally [118] for the case of absorption concentration in glacial acetic acid of benzene, toluene and m-xylene present in aqueous solutions.

A major criterion for the practical use of headspace absorption concentration is the difference between the partition coefficient in the stage of stripping from the solution under study (K_1) and of the absorption coefficient in the trapping liquid (K_2), as the degree of concentration is $b = f(K_2/K_1)$. This difference should be as large as possible. The values of K_1 and K_2 and the calculated and experimentally confirmed values of b in Table 2 indicate that the gain in sensitivity observed on injecting acetate concentrate into the chromatographic column compared with direct introduction of the original aqueous solution is in excess of two orders of magnitude, the threshold of gas chromatographic detection of aromatic hydrocarbons in aqueous solutions being as low as 1–10 mg/l. The detection limit can be reduced by two more orders of magnitude down to a few hundredths of 1 mg/l if one uses headspace analysis of the concentrate after neutralization of the acetic acid with an alkali, similar to the technique proposed by Vitenberg and Tsibul'skaya [119].

The absorption concentration of volatile microimpurities present in solutions by CGE offers a substantial improvement in the selectivity of analyte discrimination against the background of concomitant components with strongly differing partition coefficients. For instance, in the above case the selectivity of characterization of aromatic hydrocarbons increases in all stages of the analysis. The CGE of the components of the aqueous solution and their equilibrium concentration in acetic acid is accompanied by depletion of the absorbing liquid in concomitant impurities with small partition coefficients (n-hexane, n-octane), which are removed almost completely not only from the aqueous solution but also from the absorber. The selectivity of discrimination against the concomitant impurities having large partition coefficients (alcohols, carbonyl compounds, carboxylic acids) stems from the fact that for them to be extracted nearly completely from the aqueous solution, one has to pass

TABLE 2

PARTITION COEFFICIENTS OF AROMATIC HYDROCARBONS IN WATER (K_1) AND GLACIAL ACETIC ACID (K_2) AT 20°C, AND THE DEGREE OF ENRICHMENT IN LIQUID ABSORBER (b) IN ABSORPTION CONCENTRATION OF HYDROCARBONS FROM AQUEOUS SOLUTIONS IN GLACIAL ACETIC ACID

Impurity to be concentrated	K_1	K_2	b
Benzene	4.0	900	115
Toluene	3.6	2480	242
m-Xylene	4.6	6370	287

much larger gas volumes. Therefore, the degree of concentration of such concomitants is considerably smaller than that of the analytes. Apart from this, after neutralization of the acetate concentrate, the equilibrium gas phase becomes depleted in the compounds that are more soluble in aqueous solutions.

3.4. Circulation concentration

This was proposed and used by Grob and co-workers [120–123] for the determination of hydrophobic compounds (*i.e.*, compounds with small K) in aqueous solutions. Later, Drozd and co-workers [124,125] employed the circulation arrangement in the analysis of hydrophilic (*i.e.*, with large K) compounds in aqueous solutions.

The essence of this method lies in the multiple use in a closed system of the same volume of extracting gas for the concentration of impurities present in solutions. In practice this is done by pumping the gas into the solution with a special pump [124].

The principal and essential advantage of this method over the conventional (direct-flow) variant of CGE is that when large volumes of the stripping gas are swept through a system, its own impurities do not build up in the concentrator. In addition, because the extracting gas volumes are small, the volatility of the main solvent may be neglected.

The calculations of HSA with circulation concentration made by Novák *et al.* [124] and, subsequently, by others [57,126] are based on the equation

$$C_L = C_L^0 \exp\left(-\frac{V_g}{KV_L + V_G}\right) \tag{17}$$

Other equations have also been proposed for CGE [116,127]. A comprehensive study of the CGE of volatiles from a non-volatile solvent [116] showed that the various expressions describing CGE are based on different models of the process. Realization of the conditions approximating each of these models would require the development of the corresponding experimental set-ups, and this could complicate substantially the analytical procedure.

Of particular importance for practical implementation of the process and the correct choice of the basic equation is the ratio of the phase volumes in the extraction vial. If the condition $KV_L \gg V_G$ is met, one can use for the calculations the approximate equation

$$C_L = C_L^0 \exp\left(-\frac{V_g}{KV_L}\right) \tag{18}$$

which describes with acceptable accuracy any CGE model and does not require additional complication of the analytical procedure. The stages of the adsorption and absorption trapping of impurities from the gas flow which represent an integral part of the calculation variant of CGE are described by the relationships given in preceding sections.

The possibilities and limitations of the calculation HSC were explored by Curvers *et al.* [126] in a study of the determination of hydrocarbons, halogenated hydrocarbons and ketones in water, stripping in closed systems having been used [128]

to detect bromoalkanes in aqueous solutions. The detection limit of non-polar impurities is a few thousandths of 1 mg/l. The reproducibility of the extracted fraction of the analyte is 10–15% over the concentration range 0.2–20 mg/l.

Circulation concentration can be used to advantage when determining impurities in solutions with high partition coefficients present in very low concentrations (less than 1 mg/l). Compounds with small K can be determined more simply and accurately under static conditions. This procedure provides virtually complete extraction of an impurity from a solution by simpler technical means.

Circulation concentration can be employed with any quantitative HSA technique [6,7,32]. Novák et al. [124] recommended the method of addition. We believe a more preferable approach to be absolute calibration, which does not require double chromatographic analysis of the concentrate. For systems with unknown K one can use the discontinuous technique [125] or the method involving complete extraction of the analyte from the solution under study.

3.5. Liquid–gas distributive chromatography (LGDC)

This technique, proposed in 1982 by Moskvin et al. [129] and subsequently developed [130,131], was used to analyse gases dissolved in liquids [131,132]. This method may be considered as a variant of HSC which differs from CGE only in that the mobile phase here is the solution under study, the extracting gas remaining fixed. LGDC is based on the degassing of a liquid as it is filtered through a column filled with a porous packing, which holds a volume of gas acting as a fixed gaseous extractant. LGDC actually represents a counterpart of the frontal concentration of impurities present in gas objects which, in contrast to the latter, has been implemented also in an elution-type procedure. The analytical calculations used in LGDC are based on relationships [132,133] assuming that the retention volume (mobile liquid phase) depends proportionally on the volume of the stationary gas phase. Whereas this method offers a considerable increase in the sensitivity of chromatographic determination of gases dissolved in water, the detection limits for oxygen, nitrogen and hydrogen in water [134] are comparable to those obtained with direct HSA under static conditions.

4. COMBINATION OF EQUILIBRIUM ABSORPTION CONCENTRATION WITH HEADSPACE ANALYSIS

The possibilities inherent in the equilibrium absorption concentration of impurities present in gas and liquid objects can be broadened substantially if one measures the content of an analyte in the absorber by headspace analysis rather than by its direct injection into the chromatograph. This variant may include enrichment of the equilibrium gas with the impurity, or may be implemented without it.

4.1. Direct headspace analysis of the concentrate

Direct headspace analysis of the concentrate solution saturated preliminarily with the analyte gas under study is the simplest case. No enrichment occurs, as the content of impurities in the gas equilibrated with the concentrate hardly differs from the initial concentration C_G^0. This method may be considered only as a means of collecting samples which permit one to store the gas samples of interest for long

periods of time. The liquid phase acts as a certain buffer which stabilizes the microimpurity concentration in the collected gas sample as a result of suppression of sorption on the vial walls and of the possible analyte losses in the gas phase being compensated for by the impurity entering the gas from the solution.

The above principles underlie a technique for the determination of lower aromatic hydrocarbons in humid air [135], its remarkable feature consisting in the use of water as the trapping liquid. Direct introduction into the chromatograph of an aqueous solution saturated with the analyte gas is not reasonable here as this would reduce drastically the analytical sensitivity. Therefore, after equilibrium has been reached in the absorbing vial, it is recommended to analyse the headspace above the liquid concentrate.

The distinctive features of this technique are its simplicity and short operating time. The sample collection with the gas bubbled through 10–20 ml of water does not take more than 2–5 min, as V_g^{min} is only 100–130 ml. The use of such a small volume of air increases the sensitivity because the concomitant impurities with high partition coefficients ($K > 10^3$; alcohols, carbonyl compounds, amines, acids, etc.) do not have time to build up in the liquid, their equilibrium concentration in the gas phase therefore being extremely low. This technique permits the determination of aromatic hydrocarbons in humid air over the concentration range 1–50 mg/m^3 and can be employed to analyse the exhaust fumes from internal combustion engines, the air in industrial sites, garages, etc.

4.2. Headspace analysis of the concentrate with equilibrium gas enrichment of the analyte

This involves the inclusion in the procedure of an additional operation resulting in a dramatic reduction in the original impurity partition coefficient between the liquid concentrate and the air (such as raising the temperature, salting out or dilution of a solution in organic solvent with water). After such a treatment the analyte concentration in the gas above the solution (C_g') is related to C_L^0 through

$$C_G' = C_L^0 \cdot \frac{KV_L}{K'V_L' + V_G'} \cdot \frac{f_s}{1 - FK} \tag{19}$$

(the primes denoting the parameters obtained after the reduction of the partition coefficient). As shown by this equation, the degree of enrichment of the gas under study with an analyte (C_G'/C_G^0) depends primarily on the relative magnitude of K and K', as the factor $f_s(1 - FK)$ differs very little from unity, the volume ratio V_G'/V_L' usually varying from one to five. Recalling the possibility of improving the HSA sensitivity by reducing the partition coefficients, we see that the detection threshold can be decreased by 1–3 orders of magnitude.

The procedure combining absorption concentration with HSA and providing a substantial enrichment of an analyte in the gas phase can be illustrated by the determination of aromatic hydrocarbons in air by trapping them in acetic acid, a subsequent sharp reduction of the original value of K through neutralization of the acetic acid with a solution of potassium hydroxide and the analysis of the gas equilibrated with the aqueous salt solution thus obtained [119]. The partition coefficients of benzene, toluene and m-xylene in the aqueous solution of potassium

acetate are much lower than those in water (the salting-out effect), and 10^3–10^4 times lower than those in acetic acid [136]. Therefore, a transition from direct gas chromatographic analysis of the acetate concentrate to an investigation of the equilibrium vapour after the neutralization of the solution, a procedure carried out under the conditions proposed by Vitenberg and Tsibul'skaya [119], permits an increase in the sensitivity of determination of aromatic hydrocarbons in air by two orders of magnitude.

The technique for the determination of aromatic hydrocarbons in atmospheric air based on combining the absorption concentration with HSA has been approved by the USSR Ministry of Health for use in environmental monitoring stations [137].

This procedure is fairly simple and consists in saturation of 2 ml of 80% (at temperatures above $0°C$) or 65% (at temperatures from 0 to $-24°C$) acetic acid with atmospheric air, neutralization of the concentrate thus obtained with an alkaline solution in a closed volume and subsequent gas chromatographic analysis of the headspace above the aqueous salt solution. A calibration solution with a known content of aromatic hydrocarbons in acetic acid is also analysed under identical conditions. An essential asset of the technique is the capability of determining aromatic hydrocarbons at the level of a few hundredths of 1 mg/m^3 in air with a high absolute humidity (up to 23 mg/l).

Apart from stabilization of the impurity content in the gas under study, in addition to improved sensitivity and selectivity of analysis, the combination of absorption concentration with HSA has the following attractive features: a higher precision of measurement, as the reproducibility of injection into the chromatograph of gas samples is much better than that of liquids; and the possibility of automating the analytical procedure by employing headspace analysers and special attachments to the all-purpose gas chromatographs produced by various instrument manufacturers.

Selyutina and Vinnikov [138] used the combination of CGE with absorption trapping (under the total trapping conditions) for the headspace concentration and gas chromatographic determination of volatile amines in water. Aniline and ethyl-, diethyl- and triethylamines present in the aqueous solution were removed with a gas flow at 70–90°C, 0.1 M sulphuric acid being employed as the absorber. To increase the efficiency of CGE, potassium hydroxide was added before the analysis to the solution under study at a concentration of 40–50 g/l. At an elevated gas temperature and an air flow-rate of 1 l/h, such an alkali content ensures virtually complete extraction of primary amines from 1.6 l of aqueous solution in 90 min and of secondary and ternary amines in 60 and 30 min, respectively. Aniline is more difficult to remove from solution, so that even after 90 min only 70% of it is extracted. More complete removal can be achieved by increasing the alkali concentration in the solution to 120 g/l.

The amine content in the sulphate concentrate obtained in the first stage after its neutralization with solid potassium hydroxide is determined by static HSA. For this purpose the authors employed a laboratory set-up [139] based on the pneumatic arrangement which is used in Hewlett-Packard instrumentation [83]. The detection limit for amines in water with this set-up is about 0.5 μg/l.

5. CONCLUSIONS

Equilibrium concentration of volatile impurities based on the distribution of the

compounds under study between the condensed and gas phases broadens substantially the scope and potential of the traditional methods of concentration assuming total extraction of the analyte from the object in question, and represents not only a useful addition to the list but, in a number of instances (*e.g.*, characterization of unstable microcomponents in atmospheric air and water), the only reasonable approach. The use of the gas extraction and related methods permits the development of acceptably simple, partially or totally automated procedures for sample preparation based on the available commercial equipment.

Headspace analysis provides a reduction in the gas chromatographic detection thresholds for volatiles with partition coefficients below 10^3. Combining equilibrium concentration with the headspace techniques improves the sensitivity and selectivity of the gas chromatographic determination of volatile impurities and brings their detection threshold in liquid and gas objects down to a few ppb and lower.

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