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QUANTITATIVE HEADSPACE ANALYSIS UNDER NON-EQUILIBRIUM CONDITIONS

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SUMMARY

The concept of the degree of approach to equilibrium is introduced and used to consider problems associated with the need for and expediency of reaching phase equilibrium in headspace gas chromatographic analysis. In cases where thermodynamic equilibrium is impeded, attempts to attain equilibrium partition of the analyte between the two phases may not be necessary. It turns out to be sufficient to attain the close-to-equilibrium analyte concentration only in the phase to be analyzed. If the degree of approach to equilibrium in a system with unknown partition coefficients is reproducible, headspace analysis can be performed with a good accuracy also in cases where the analyte concentration in the phase being analyzed is far from the equilibrium value.

INTRODUCTION

In many studies dealing with headspace analysis (HSA) the onset of phase equilibrium is not considered a necessary prerequisite for obtaining reliable measurements[1–4]. The problems associated with quantitative HSA under non-equilibrium conditions are touched on in only two publications[5,6], where only particular cases of non-equilibrium vapour analysis have been investigated, namely single and multiple headspace extraction. In HSA, however, other variants of gas extraction are also employed. Among these are dynamic techniques involving partial replacement of the headspace gas, concentration of impurities, etc., which may differ also in the state of aggregation of the phase from which the system approaches equilibrium. The last factor turns out to be particularly important. Differentiation of HSA methods by this principle permits one to reveal their common features and to recommend for them the same methods of analysis.

The aim of this paper is to consider the problems associated with the need for and expediency of reaching phase equilibrium in HSA, as well as to reveal systematic errors of the method due to deviations of the analyte partition from equilibrium.

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THEORETICAL

HSA is carried out predominantly under non-equilibrium conditions with different degrees of approach to thermodynamic equilibrium. Therefore by equilibrium we should understand such a state of the system where the difference between the current and equilibrium values of the analyte concentration in each phase lies within the measurement error.

As a measure of the deviation from equilibrium one can take a quantity characterizing the degree of approach of the system to the phase equilibrium, *n*, which is equal to the ratio of the current to the equilibrium concentrations, C_L in the liquid and C_G in the gas phase. In cases where equilibrium is approached from the liquid phase, *i.e.*, initially all of the analyte is contained in the liquid phase, one can write for each of the phases:

$$n_G^L = C_G^L/C_G \tag{1}$$

$$n_L^L = C_L^L/C_L \tag{1a}$$

The presence of a superscript to a parameter means that the latter is non-equilibrium, and the symbols G or L represent the gas or liquid phase from which the system approaches equilibrium. A subscript denotes the phase to which the parameter refers. If equilibrium is approached from the gas phase:

$$n_L^G = C_L^G/C_L \tag{2}$$

$$n_G^G = C_G^G/C_G \tag{2a}$$

The degrees of approach to equilibrium in coexisting phases, n_G^L and n_L^L as well as n_L^G and n_G^G, vary within different ranges and are related to one another. This relationship can be derived from the equation describing the partition of the analyte between the liquid and gas phases in terms of the partition coefficient

$$K = C_L/C_G \tag{3}$$

and of the volumes of the liquid, V_L, and gaseous, V_G, phases in a vessel:

$$r = V_G/V_L \tag{4}$$

At equilibrium, the fraction of the analyte present in the liquid phase is[7]

$$\frac{M_L}{M_0} = \frac{K}{K + r} \tag{5}$$

and in the gas phase:

$$\frac{M_G}{M_0} = \frac{r}{K + r} \tag{6}$$

Similarly, under non-equilibrium conditions, when the system approaches equilibrium from the liquid phase, one can write for each of the phases brought into contact:

$$\frac{M_L^L}{M_0} = n_L^L \cdot \frac{K}{K + r} \tag{7}$$

$$\frac{M_G^L}{M_0} = n_G^L \cdot \frac{r}{K + r} \tag{7a}$$

The ranges in which the degrees of approach to equilibrium in each phase vary turn out to be $1 \leqslant n_L^L \leqslant M_0/M_L = (K + r)/K$ and $0 \leqslant n_G^L \leqslant 1$.

If the system approaches equilibrium from the gas phase

$$\frac{M_L^G}{M_0} = n_L^G \cdot \frac{K}{K + r} \tag{8}$$

$$\frac{M_G^G}{M_0} = n_G^G \cdot \frac{r}{K + r} \tag{8a}$$

with the quantities n_G^G and n_L^G varying within $1 \leqslant n_G^G \leqslant M_0/M_G = (K + r)/r$ and $0 \leqslant n_L^G \leqslant 1$.

Combining eqns. 7 and 7a with eqns. 8 and 8a and recalling that the sum of the fractions of a volatile substance distributed in different phases is unity we obtain an equation relating the degrees of approach to equilibrium with the parameters K and r:

$$\frac{1 - n_G^L}{n_L^L - 1} = \frac{K}{r} = \frac{n_G^G - 1}{1 - n_L^G} \tag{9}$$

This equation can be used to calculate the interval of the degrees of approach to equilibrium within which the error introduced by a deviation of the system with given K and r from equilibrium will not exceed the prescribed level.

The absolute quantities n_L^L and n_G^G, whose numerical values do not exceed unity and whose variation depends on K and r, are not as informative and convenient for use as n_G^L and n_L^C which vary from 0 to 1. Therefore in some cases it may be profitable to use in place of n_L^L and n_G^G the quantities $(n_L^L)_R$ and $(n_G^G)_R$ which are related to the former by the expressions

$$(n_L^L)_R = (n_L^L - 1) \cdot \frac{K}{r} \tag{10}$$

$$(n_G^G)_R = (n_G^G - 1) \cdot \frac{r}{K} \tag{10a}$$

and vary from 1 to 0 but, in contrast to n_G^L and n_L^G, vanish at equilibrium rather than becoming unity. These quantities actually represent the difference between the current and equilibrium analyte concentrations referred not only to the equilibrium concentration, *e.g.*, for liquids $(C^L_L - C_L)/C_L = n^L_L - 1$, but also to the interval within which the degree of approach to equilibrium in the given phase varies from the moment of contact of the phases until the onset of equilibrium [for a condensed phase this interval is $(K + r)/K - 1 = r/K$].

Substituting $(n^L_L)_R$ and $(n^G_G)_R$ for n^L_L and n^G_G in eqn. 9, we obtain simple expressions relating the degrees of approach to equilibrium in both phases which vary within the same ranges:

$$n^L_G = 1 - (n^L_L)_R \tag{11}$$

$$n^G_L = 1 - (n^G_G)_R \tag{11a}$$

We have studied experimentally the effect on the accuracy of HSA due to a deviation from equilibrium in systems with different K and r by determining low concentrations of methane, ethylene and ethane in transformer oil whose relatively high viscosity makes the achievement of equilibrium a difficult task. This is of considerable practical interest in connection with the problem of monitoring the state of the insulation in power transformers by analyzing the gases dissolved in the oil[8].

EXPERIMENTAL

The measurements were carried out on a Tsvet-102 chromatograph with a flame ionization detector and a 2 m × 3 mm steel column containing Porapak N (50–80 mesh) at 70°C, and gas flow-rates of 30, 30 and 300 cm^3/min for argon, hydrogen and air, respectively. The electrometric amplifier sensitivity was set within the range $(2\text{–}20) \cdot 10^{-10}$ A and adjusted so as to obtain peak heights of not less than 20 mm for the weakest signals.

Equilibration was carried out in a 100-ml glass syringe with a thermostatting jacket[9]. The transformer oil was introduced into this syringe by means of graduated hypodermic syringes of capacity 20 and 100 ml together with a precise amount of pure gas, using a gas sampling valve provided with a 0.127-ml loop. Argon was used for the gas phase. The working volume of the syringe was fixed with a special limiter and calibrated by weight using distilled water. The volume of the gas phase was calculated from the difference between the inner volume of the syringe and the volume of the oil introduced. In all cases, equilibration at 20°C was achieved by continuously rotating the horizontal syringe for 10 min at 30 rpm.

The coefficients n^L_G and n^G_G defining the degree of approach to equilibrium in the gas phase were calculated by eqns. 1 and 2a basing on the measured detector signals which are proportional to C_G, C^L_G and C^G_G in the course of equilibration (the dynamic method of measuring n), and n^G_L and n^L_L were calculated by eqn. 9 using the numerical values of the partition coefficients at 20°C[10] (Table I) and the volume ratios of gas to liquid phases.

RESULTS AND DISCUSSION

The effect of non-equilibrium conditions on the accuracy of HSA manifests itself differently in systems with known and unknown partition coefficients.

TABLE I

EFFECT OF PARAMETERS OF AN HETEROGENEOUS SYSTEM IN SINGLE HEADSPACE EXTRACTION ON THE DEGREE OF APPROACH TO EQUILIBRIUM IN THE GAS PHASE

Gas	*Conditions of phase contact*	*K*	*Degree of approach to equilibrium, n_G^L*				
			V_L = 20 ml			*r = 4*	
			r = 1	*r = 2*	*r = 4*	*V_L = 10 ml*	*V_L = 5 ml*
Methane	10 min without mixing	0.43	0.17	0.19	0.24	0.32	0.36
	1 min with mixing		0.54	0.55	0.57	0.70	0.77
	3 min with mixing		0.73	0.77	0.81	0.93	0.98
Ethylene	10 min without mixing	1.70	0.27	0.28	0.29	0.35	0.38
	1 min with mixing		0.61	0.63	0.65	0.77	0.81
	3 min with mixing		0.75	0.80	0.87	0.98	1.0
Ethane	10 min without mixing	2.40	0.28	0.29	0.30	0.36	0.39
	1 min with mixing		0.64	0.66	0.71	0.77	0.81
	3 min with mixing		0.79	0.80	0.91	0.98	1.0

When analyzing systems with unknown partition coefficients, one introduces additional operations permitting direct or indirect determination of the partition coefficient[1]. In such cases it is essential that the degrees of approach to equilibrium at different stages of the analysis are the same. This largely determines the measurement error of the partition coefficient for the given system and the chosen conditions of analysis (including the equilibration time). For instance, in the method involving addition of analyte to the subject under study[1] under equilibrium conditions, the concentration in question can be expressed[2] as

$$C_L^0 = \frac{m_s - m_v}{V_L} \cdot \frac{C_G}{C'_G - C_G} \tag{12}$$

where m_s and m_v are the analyte masses added to the solution under study and removed from it for injection into the chromatograph; C_G and C'_G are the equilibrium concentrations of the analyte in the gas phase before and after its addition. Under non-equilibrium conditions, using eqn. 1 one can reduce eqn. 12 to

$$C_L^0 = \frac{m_s - m_v}{V_L} \cdot \frac{n_G^L C_G}{(n_G^L)' \, C'_G - n_G^L C_G} \tag{13}$$

where n_G^L and $(n_G^L)'$ are coefficients accounting for the degree of approach to equilibrium of the analyte concentration in the gas phase before and after analyte addition. If, however, equilibrium is not achieved but the same degree of approach to it occurs in both stages, *i.e.*, $n_G^L = (n_G^L)'$, then the deviation from equilibrium may be disregarded in calculations. A similar situation occurs in multiple headspace extraction carried out on systems with unknown partition coefficients.

In systems with known *K* one uses in the calculations their numerical values.

A deviation from equilibrium results in a change in the partition coefficients, and it is this effect that primarily determines the systematic component of the error in HSA, δ, due to the non-equilibrium conditions in an heterogeneous system.

Let us consider several examples of HSA error determinations involving the approach of a system to equilibrium from the liquid and from the gas phase. In the most widely used variant, namely, single headspace extraction, the system approaches equilibrium from the condensed phase. The concentration of a volatile analyte in the sample studied is calculated by the expression[2]:

$$C_{\mathrm{L}}^{0} = C_{\mathrm{G}}\,(K + r) \tag{14}$$

Under non-equilibrium conditions, one measures the analyte concentration in the gas above the solution, $C_{\mathrm{G}}^{\mathrm{L}}$, which corresponds to the actual non-equilibrium partition coefficient, K^{L}. Therefore the expression to use in calculations is:

$$C_{\mathrm{L}}^{0} = C_{\mathrm{G}}^{\mathrm{L}}\,(K^{\mathrm{L}} + r) \tag{14a}$$

Since the partition coefficients K and K^{L} are related by

$$K^{\mathrm{L}} = \frac{C_{\mathrm{L}}^{\mathrm{L}}}{C_{\mathrm{G}}^{\mathrm{L}}} = \frac{n_{\mathrm{L}}^{\mathrm{L}} C_{\mathrm{L}}}{n_{\mathrm{G}}^{\mathrm{L}} C_{\mathrm{G}}} = \frac{n_{\mathrm{L}}^{\mathrm{L}}}{n_{\mathrm{G}}^{\mathrm{L}}} \cdot K \tag{15}$$

we can, by solving eqn. 9 for $n_{\mathrm{L}}^{\mathrm{L}}$ and substituting in eqn. 15, obtain an equation containing only the degree of approach to equilibrium in the gas phase:

$$K^{\mathrm{L}} = \frac{K + r\,(1 - n_{\mathrm{G}}^{\mathrm{L}})}{n_{\mathrm{G}}^{\mathrm{L}}} \tag{15a}$$

If equilibrium conditions have not been reached, the use of K in place of K^{L} in calculations will entail a systematic error

$$\frac{\Delta K^{\mathrm{L}}}{K^{\mathrm{L}}} = \frac{K_{\mathrm{L}} - K}{K} \tag{16}$$

which will affect the final result, in accordance with the expression obtained by differentiating eqn. 14a:

$$\delta^{\mathrm{L}}{}_{0} = \frac{\Delta K^{\mathrm{L}}}{K^{\mathrm{L}}} \cdot \frac{K^{\mathrm{L}}}{K^{\mathrm{L}} + r} = \frac{K^{\mathrm{L}} - K}{K^{\mathrm{L}} + r} \tag{17}$$

It follows from this equation that the value of the systematic error, $\delta^{\mathrm{L}}{}_{0}$, is determined not only by the difference between the equilibrium and non-equilibrium partition coefficients, but also by the phase-volume ratio in the equilibration vial. The magnitude of $\delta^{\mathrm{L}}{}_{0}$ is least when $r \gg K^{\mathrm{L}}$. Substitution of K^{L} from eqn. 15a into eqn. 17 yields a simple expression for the systematic component of the error of single headspace extraction associated with the deviation of the analyte concentration in the gas phase from its equilibrium value, which is numerically equal to the relative degree of approach to equilibrium in the liquid phase:

$$\delta^{\mathrm{L}_0} = 1 - n_{\mathrm{G}}^{\mathrm{L}} = (n_{\mathrm{L}}^{\mathrm{L}})_{\mathrm{R}} \tag{18}$$

Table I illustrates the results of a determination of $n_{\mathrm{G}}^{\mathrm{L}}$ for three lower hydrocarbons carried out under different conditions of equilibration and for different phase-volume ratios. Increasing the gas phase volume at constant V_{L} results, other conditions being equal, in an increase in the degree of approach to equilibrium and a reduction in the systematic component of the error due to the deviation of the system from equilibrium. A similar effect is also observed under equilibrium conditions.

The results of a transformer oil analysis carried out at a constant $r = 4$ but with the liquid phase volume reduced four times (from 20 to 5 ml) indicate a substantial increase (by a factor of 1.25–1.5) in the numerical value of $n_{\mathrm{G}}^{\mathrm{L}}$, apparently due to the different thickness of the viscous liquid layer and the reduced concentration gradient in the condensed phase.

Thus the data of Table I suggest that the error of single headspace extraction analysis decreases with increasing phase-volume ratio, r, the decrease in the liquid layer thickness playing a major rôle.

The case of a system approaching equilibrium from the gas phase was considered by us in an example where the concentration of volatiles in a liquid was set by the technique[11] based on introducing a certain amount of pure gas into a closed heterogeneous system with a known phase-volume ratio.

Under equilibrium conditions the gas concentration in a liquid can be calculated by[11]:

$$C_{\mathrm{L}} = \frac{M_0}{V_{\mathrm{L}}} \cdot \frac{K}{K + r} \tag{19}$$

If equilibrium has not been reached, the actual gas concentration in the liquid, $C_{\mathrm{L}}^{\mathrm{G}}$, will be less than the equilibrium value; according to eqn. 8 it will be

$$C_{\mathrm{L}}^{\mathrm{G}} = \frac{M_0}{V_{\mathrm{L}}} \cdot n_{\mathrm{L}}^{\mathrm{G}} \cdot \frac{K}{K + r} \tag{19a}$$

yielding for the error of non-equilibrium setting of the gas concentration in the liquid:

$$\delta^{\mathrm{G}} = \frac{C_{\mathrm{L}} - C_{\mathrm{L}}^{\mathrm{G}}}{C_{\mathrm{L}}} = 1 - n_{\mathrm{L}}^{\mathrm{G}} \tag{20}$$

Writing δ^{G} in terms of the degree of approach to equilibrium in the gas phase, we can transform eqn. 20, in accordance with eqn. 9, to:

$$\delta^{\mathrm{G}} = \frac{r}{K}(n_{\mathrm{G}}^{\mathrm{G}} - 1) = (n_{\mathrm{G}}^{\mathrm{G}})_{\mathrm{R}} \tag{20a}$$

TABLE II

EFFECT OF PARAMETERS OF AN HETEROGENEOUS SYSTEM ON THE DEGREE OF APPROACH TO EQUILIBRIUM IN THE LIQUID PHASE IN THE COURSE OF PREPARING GAS SOLUTIONS IN TRANSFORMER OIL

Gas	*Conditions of phase contact*	*Degree of approach to equilibrium for $r = 1$*		
		$V_L = 50$ *ml*	$V_L = 30$ *ml*	$V_L = 20$ *ml*
Methane	10 min without mixing	0.22	0.26	0.27
	1 min with mixing	0.52	0.62	0.65
	3 min with mixing	0.85	0.93	0.96
Ethylene	10 min without mixing	0.22	0.24	0.27
	1 min with mixing	0.60	0.64	0.75
	3 min with mixing	0.91	0.96	0.97
Ethane	10 min without mixing	0.26	0.30	0.38
	1 min with mixing	0.66	0.75	0.79
	3 min with mixing	0.95	0.97	1.0

Table II lists experimental data obtained by dissolving methane, ethylene and ethane in transformer oil at a constant $r = 1$ and different volumes, V_L. Other conditions being equal, reducing the oil layer thickness results in an increase in the degree of approach to equilibrium in the liquid phase, which eventually reduces the equilibration time in an heterogeneous system.

Experiments involving gas dissolution with a constant oil volume of 20 ml and r varied from 4 to 1 did not reveal any consistent effect of r on the magnitude of n_L^G, which can be accounted for by the comparatively narrow interval within which n_G^G varies under these conditions (with $r = 4$ for methane, $1 \leqslant n_G^G \leqslant 1.1$).

To summarize, if headspace extraction (as well as the reverse process, namely the transfer of a volatile from the gas to the liquid phase) cannot be carried out under equilibrium conditions, or when to reach equilibrium would entail considerable experimental difficulties, there may be several approaches to analyzing systems with a known K:

(1) One can use repeated or multiple headspace extraction, provided the degree of approach to equilibrium is maintained constant in all stages of the analysis.

(2) One should vary and, preferably, reduce the thickness of the liquid layer by adjusting r and K so as to increase the degree of approach to equilibrium and thus reduce the error of analysis.

(3) In cases where the degree of approach to equilibrium can be determined, one should use in calculations the current, or non-equilibrium, values of the partition coefficients.

CONCLUSIONS

It is appropriate to introduce as a measure of the deviation from equilibrium in the various HSA techniques, a quantity characterizing the degree of approach of an heterogeneous system to phase equilibrium which equals the ratio of the current concentration in one of the phases to its equilibrium value. This permits one not only to estimate the contribution of this deviation to the total error of analysis, but also to formulate the requirements to be placed on its conditions. In contrast to systems with known partition coefficients, headspace determination of compounds with unknown K allows considerable deviation from equilibrium concentrations without reducing the accuracy of analysis, provided the degrees of approach to equilibrium are constant. Increasing the ratio r/K, as well as reducing the volume of the condensed phase, reduces the equilibration time and the contribution to the total error of single headspace extraction analysis due to the system not being in equilibrium.

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