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BASIC EQUATIONS IN CONTINUOUS GAS EXTRACTION AND THEIR APPLICATION TO HEADSPACE ANALYSIS

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SUMMARY

The evolution of ideas on the rules of continuous gas extraction based on dynamic headspace analysis is outlined. The application of a simpler exponential equation that describes well the course of gas extraction under the conditions of a sufficiently small volume of the vapour phase is recommended for practical purposes. The possibility of performing under non-equilibrium conditions not only stripping but also variants of the analysis that do not require full extraction of the sample components is considered. The expediency of the application of continuous gas extraction is demonstrated by the determination of volatile substances with low liquid-gas partition coefficients, where high sensitivity can be achieved by direct headspace analysis under static conditions.

INTRODUCTION

Dynamic variants of headspace analysis, allowing the limit of determination of comparatively low-volatile substances to be decreased, are finding widespread application. These methods are based on continuous gas extraction, *i.e.*, on the transfer of vapours of components from the condensed phase by a stream of gas passing through the bulk of a liquid or above the surface of a solid compound. Dynamic variants were not discussed in the first book on headspace analysis¹ and the usability of the method itself was limited to closed systems in thermodynamic equilibria. However, already in the early 1960s, at the outset of headspace analysis, work was reported in which continuous gas extraction of solutions was studied in order to determine and concentrate volatile admixtures, to measure partition coefficients and to calibrate gas chromatographic detectors. Such studies were performed independently and have remained little known for years. Information on this subject, collected together about 5 years ago², now requires the addition of the results of more recent studies. This paper is aimed at the generalization and classification of the rules based on dynamic headspace analysis. The use of headspace analysis for non-equilibrium systems, from which full extraction of sample component is difficult or impossible, is considered.

BASIC EQUATIONS OF CONTINUOUS GAS EXTRACTION UNDER EQUILIBRIUM CONDITIONS

In 1961, for the measurement of liquid-gas partition coefficients and hence also for analytical purposes, Wahlroos^{3,4} proposed the equation

$$C_G = C_G^0 \exp \left(- \frac{V_g}{KV_L + V_G} \right) \quad (1)$$

describing the changes in the concentrations, C_G , of vapours at the outlet from the vessel with an initial value C_G^0 as a function of the volume of the extracting gas passed, V_g ; V_L and V_G are the volumes of the liquid and the gas in the saturator, respectively, and K is the partition coefficient, $K = C_L/C_G$, where C_L is the concentration of the volatile compound in the liquid phase.

In 1963 the same equation was derived by Fowles and Scott⁵ in connection with the development of a new procedure for the calibration of chromatographic detectors. At the same time, in order to describe a similar gas extraction process, Burnett⁶ published another equation, used for the determination of partition coefficients. With our system of symbols it has the following form:

$$C_G = \frac{C_L^0}{K[1 - (V_g/KV_L)]} \cdot \exp(-V_g/V_L K) - \exp(-V_g/V_G) \quad (2)$$

where C_L^0 is the initial concentration of the volatile compound in the solution.

The above work preceded the development of headspace analysis, as continuous gas extraction gained widespread use in the 1970s. The reasons for the differences between eqns. 1 and 2 were then clarified. It was demonstrated⁷ that eqn. 1 concerns the situation where thermodynamic equilibrium between the liquid and the gas is established virtually instantly in all stages of the process, i.e., among gas bubbles passing through the solution and also between the solution and the gas enclosed above this solution. Under these conditions, a bubble of the gas leaving the solution and the gas leaving the vessel have the same composition. Eqn. 2 corresponds to a model in which the exchange between the liquid and the gas proceeds only during the passage of the bubble through the bulk of the liquid. In such a situation, the concentration of the compound in the stream of gas at the outlet from the vessel differs markedly from that in the gas bubble leaving the solution. Hence eqns. 1 and 2 describe two different models of the process; one of them assumes equilibrated exchange between the liquid and the gas in the volume V_G above the liquid layer in a closed vessel and the other one excludes it entirely.

The situation in which the exchange between the liquid and the gaseous phases in the vessel proceeds under static conditions only until the beginning of the flow of the gas through the solution is also possible. This is described by the equation

$$C_G = \frac{C_L^0}{K[1 - (V_g/KV_L)^2]} \left[\exp \left(- \frac{V_g}{KV_L} \right) - \frac{V_g}{KV_L} \exp(-V_g/V_G) \right] \quad (3)$$

Experimental testing showed that real continuous gas extraction process is accomplished under intermediate conditions. Calculations based on eqns. 1–3 can be derived if the conditions for the realization of the corresponding models are provided. For the use of eqn. 1 it is essential to ensure intense mixing of the gaseous phase. Eqn. 2 can be used with sufficiently high (but compatible with the demands on equilibrium mass transfer) flow-rates of the gas, provided that the mass transfer above the solution with the solution itself is minimized or excluded. All of the above require the construction of complicated devices, which is not always feasible. It is much simpler to select for the performance of the experiment conditions under which the role of the gas in the vessel can be neglected. This can easily be achieved if considerable “dead” volumes of the gas above the solutions are eliminated, *i.e.*, if vessels having negligibly small values of V_G are used. Inserting $V_G/KV_L = 0$, eqns. 1–3 are simplified to

$$C_G = \frac{C_L^0}{K} \cdot \exp(-V_g/KV_L) \quad (4)$$

A criterion for the usability of eqn. 4 is the condition that the differences in the results obtained by calculations with eqns. 1–3 must not exceed the error of the setting or the determination of the concentration of the compound in the gaseous stream. Substantially it is controlled by the value of V_G/KV . For instance, with $V_G/KV_L = 0.02$ and $V_g = 350$ ml, the differences between the values of C_G calculated according to eqn. 4 and eqns. 1–3 are 7.6, 0.1 and 2.1%, respectively, and with an increase in V_G/KV to 0.45, the differences become intolerable (344, 80 and 83%, respectively).

Even though the relationships among the different models of continuous gas extraction had been explained in 1979, we can still come across applications of eqn. 1 under conditions that do not guarantee its validity. In a paper on the enrichment of volatile admixtures⁸, the theory of the method is presented on the basis of eqn. 1 without any comments concerning the constraints on its application. In a review⁹ the description of dynamic variants of headspace analysis is also based only on eqn. 1.

Eqns. 1–4 characterize the process of continuous gas extraction of volatile compounds from a non-volatile solvent under experimental conditions. The extension of gas extraction to solutions in volatile solvents can make the scope of practical applications considerably wider. In 1978, we investigated the general case of the continuous gas extraction of binary systems without restrictions on the volatility of their components, which can be described by the equation

$$C_L = C_L^0 \left(\frac{V_L^0 - FV_g}{V_L^0} \right)^{(1-FK)/FK} \quad (5)$$

where F is a measure of the volatility of the solvent at a vapour pressure P_L , density δ_L and molecular mass M at temperature T ($F = P_L M / RT \delta_L$). The physical meaning F is the volume of the solvent in unit volume saturated with it.

The assumptions of ideality of phases, distribution of linear isotherms and character of the extraction process equilibrium are common to all the above cases. For solutions of finite dilution the first two assumptions are sufficiently justified (in the determination of admixtures), but the last factor mostly depends on the conditions under which the extraction is performed and needs particular investigation.

DYNAMIC HEADSPACE ANALYSIS UNDER NON-EQUILIBRIUM CONDITIONS

For aqueous solutions and solutions in organic liquids of low viscosity, thermodynamic equilibrium is virtually achieved by bubbling with small gas bubbles at a speed of the order of tens of ml/min. This can be partially verified by the correspondence of the results of measurements of partition coefficients by static and dynamic methods (see ref. 2, Tables 1.1 and 1.2). However, in viscous liquids and in elastic and solid particles, the mass transfer is difficult and establishment of the equilibrium is slowed and restricted by diffusion processes. In stripping gas extraction it is obviously not important whether or not the process is an equilibrium one, as only the components to be determined need to be extracted completely. In any variants of dynamic headspace analysis with incomplete extraction of components it is necessary that non-equilibrium of the processes be taken into consideration.

As already observed in the evaluation of discrete gas extraction under non-equilibrium conditions¹⁰, the amount of the volatile component, m_τ , that has diffused into the gas phase within a time τ comprises a portion of this quantity, m_∞ , which would evaporate within the infinite time required for the establishment of true equilibrium. The ratio m_τ/m_∞ characterizes the degree of the approximation towards equilibrium so that under stable conditions of mass transfer (form and surface area of the interphase, particle size, values of the diffusion coefficients and concentration gradients) the degree of approximation to an equilibrium separation will be determined by the duration of contact of the gas with the condensed phase. With a fixed time τ , the gas extraction process under non-equilibrium conditions can be described by equations of the same form as for equilibrium conditions. The only difference is that in place of the partition coefficients K the equations will involve parameters k that depend on τ and conditions of the mass transfer that characterize non-equilibrium ratios of the concentrations of the sample components in co-existing phases.

It follows from the above considerations that in continuous gas extraction with instantaneous concentration under non-equilibrium conditions, which is based on the analysis of concentrates or condensates of the components of the gaseous phase that was blown through the sample for identical time interval, the same equations can be used for the calculation as in discrete gas extraction, provided that the conditions of the process and the time of the collection of fractions are strictly controlled.

Such an approach was applied to the determination of trace amounts of interfering admixtures in electrolytes of lithium galvanic elements¹¹. Propyl carbonate, serving as a solvent, can contain undesirable contamination with propylene oxide, propanal, acetone and chloropropanols, which possess extremely high partition coefficients. Total extraction of these contaminants is difficult and the use of stripping is expedient, but direct headspace analysis when their concentrations are less than 100 mg/l is impossible. By repeating bubbling of the electrolyte with nitrogen for 30 min and analysing the contents of the cryogenic trap on the chromatograph each time, it was possible to determine the content of contaminants (with a relative standard deviation of 10%) from the ratio of the areas A (or heights) of the corresponding peaks on the chromatograms:

$$S_i = f_i A_i / (1 - A_2/A_1) \quad (6)$$

where f_i is calibration factor for each component i .

Eqn. 6 is analogous to the equations for calculation in multiple gas extraction under static equilibrium conditions. Non-equilibrium of the process leads only to a slight increase in the ratio A_2/A_1 and to a corresponding decrease in the precision of the analysis.

As the ratio A_{n+1}/A_n remains constant with increasing number of multiple extractions n , it can serve as an objective criterion of the possible application of such an approach to the determination of volatile components. However it is necessary to consider that a substantial increase in the number of extractions or in the volume of gas bubbled through can lead to the appearance of apparatus memory effects¹², which will cause a deviation from linearity of the function $\log A(n)$. However, these comments are associated with the question of applicability limits and with the field of most expedient applications of continuous gas extraction.

APPLICATIONS OF DYNAMIC HEADSPACE ANALYSIS

Extraction of volatile components of solutions with a stream of inert gas has been widely used in analytical practice for the determination of contaminants. The most popular variant is the purge and trap technique, which makes it possible to set the limits of the determinations of volatile components in solutions at units of parts per 10^9 with enrichment of the determined contaminants in cryogenic, adsorption or absorption traps. The possibilities of the method were found to be so attractive that most of the companies manufacturing gas chromatographic instrumentation supply their products with equipment for dynamic headspace analysis. However, the use of dynamic headspace analysis for the enrichment and determination of volatile contaminants is not always justified. First, this is connected with the complexity of the technical performance of the analysis, with the possibility of forming fog and with mechanical delivery of the condensed phase in a gas stream. In a number of instances, particularly in the determination low-volatile and poorly soluble compounds, the use of direct static headspace analysis appears more appropriate as it makes it possible, without any concentration, to decrease the limit of determination of the components, with low partition coefficients ($K < 10$) by gas chromatography by 2–3 orders of magnitude² to the level of units of parts per 10^9 . An exception to this rule arises in instances where the concentrations of volatile compounds in the sample material are very low (parts per 10^9 and below) and the concentrations of the components to be determined in the extracting gas are at the same level as those of impurities present in the gas. In such instances it is appropriate to use the circular version of dynamic headspace analysis¹³, which avoids the accumulation of contaminants of the carrier gas in the concentrator.

When the sensitivities of static and dynamic headspace analyses are the same, the static variants, the reproducibility and accuracy of which are better, are to be preferred. Regardless of evidence for this aspect, descriptions can be found in the literature of applications of the purge and trap technique to situations where it need not have been used and where static headspace analysis could have readily provided the required sensitivity. The determination of halocarbons in water represents the best example. The importance of the solution of this problem, particularly for drinking water, stimulated a number of studies in which dynamic headspace analysis was mainly

used (e.g., refs. 14–17) and static variants for the same purposes were hardly mentioned. The required limit of determination of halocarbons, of the order of micrograms per litre, can also be achieved by direct headspace analysis under static conditions as the partition coefficients of the simplest halocarbons differ only slightly from unity¹⁸ at about room temperature.

The use of dynamic headspace analysis is suitable only in the determination of compounds with high partition coefficients ($k > 10^3$), where the volume of the gaseous phase must be increased considerably in order to extract an amount of the compound sufficient for the determination. Under static conditions the ratio of the volume of the extracting gas to that of the condensed phase usually seldom exceeds 10–20. In a dynamic version this ratio is limited by the volatility of the condensed phase only and values of 10^3 and higher can be achieved.

The higher efficiency of dynamic headspace analysis is an advantage over static variants as, with the use of the same volume of gas, continuous gas extraction extracts larger amounts of a compound. In addition, a higher degree of enrichment can be achieved by headspace concentration at the expense of using a larger volume of the extracting gas. However, regardless of the higher efficiency of continuous gas extraction, static conditions for the determination of compounds with high partition coefficients are sometimes preferred owing to difficulties with the reproducibility of the conditions of the dynamic versions.

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