

Efficiency of gas extraction in headspace analysis

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(Received November 12th, 1991)

ABSTRACT

A study of the variation of volatile concentrations in static and dynamic versions of headspace analysis was carried out to compare the efficiencies of single- and multistep gas extraction procedures with a stationary liquid or gas phase, and with two moving phases.

INTRODUCTION

Gas chromatographic headspace analysis (GCHSA) is based on gas extraction procedures performed under static and dynamic conditions [1]. The efficiency is a major characteristic of the extraction and is determined by the amount of analyte stripped by a fixed volume of the extracting phase. It is affected by various parameters of the heterogeneous system such as the partition coefficient, temperature, pressure and phase volume ratio. The influence of these parameters on the principal metrological characteristics of GCHSA has been extensively studied [1–3]. The actual conditions under which the extraction and analytical process are performed can also noticeably affect the efficiency and performance of the system.

This paper reports a comparison of static and dynamic versions of GCHSA used analytically and characterized by different relationships.

SINGLE-STEP CONTINUOUS GAS EXTRACTION

The efficiencies of single-step static gas extraction (the simplest version of GCHSA) and continuous gas extraction (CGE) underlying the widely adopted dynamic GCHSA technique will be compared first. It can be shown that, other conditions being equal, CGE is always more efficient than the discontinuous extraction carried out under static conditions. The

so-called extraction coefficient (X) can be introduced

$$X = V_G C_G / (V_L C_L) = V_G / (K V_L) \quad (1)$$

where $K = C_L / C_G$ is the partition coefficient representing the concentration ratio of a volatile in the liquid (L) and gas (G) phases and V is the volume of gas or liquid. According to the above definition of efficiency (E_j), for the static conditions ($j = s$) we have [4]

$$E_s = C_L^0 / [K(1 + X)] \quad (2)$$

whereas for CGE ($j = d$) this equation can be written as

$$E_d = C_L^0 [1 - \exp(-X)] / (KX) \quad (3)$$

where C_L^0 is the analyte concentration in solution before extraction. The ratio of these quantities representing the relative coefficient of efficiency (h) is always greater than unity

$$h = E_d / E_s = (1 + X)[1 - \exp(-X)] / X \geq 1 \quad (3a)$$

which follows from the well known inequality $\exp(-X) < 1/(1 + X)$. The highest gain in the dynamic process is reached, however, under optimum or close to optimum conditions. An analysis of eqn. 3a shows that the function $h(x)$ is described by a curve with a maximum (Fig. 1) at $x = 1.79$, allowing the calculation of the most efficient extraction of a volatile analyte from the solution under study. For

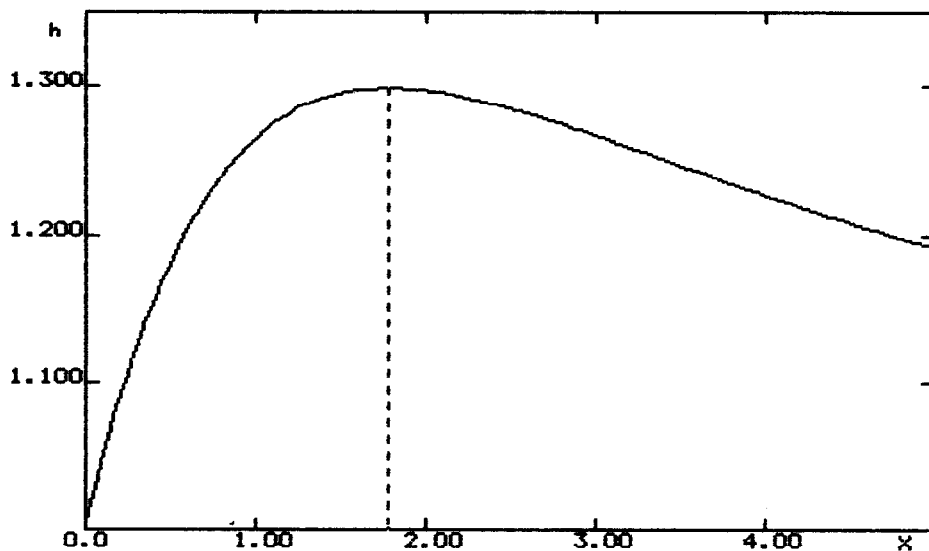


Fig. 1. Relative coefficient of efficiency (h) as a function of the extraction coefficient (X).

such a value of h , and other conditions being equal, the same volume of the stripping gas under dynamic conditions extracts 30% more of the volatile from the solution than the single extraction under static conditions.

It is well known that if the volume of the stripping agent is divided into q portions, then the total amount of the extracted analyte under static conditions will increase compared with a single-step use of this volume. For $q \rightarrow \infty$ the fractions of the extracted analyte under static and dynamic conditions will be equal.

Dynamic GCHSA is also preferable from the standpoint of the volume of the stripping gas required to extract a given fraction of the analyte. Indeed, for 95% extraction under dynamic conditions 7 times, and for 99% extraction 22 times, less gas is used than is needed in the single-step procedure under static conditions. However, for small fractions of extracted analyte dynamic GCHSA practically loses its advantages over the static version. It should also be pointed out that despite the higher efficiency of CGE, its application is useful only when used together with headspace cryogenic or adsorption trapping, or for the characterization of compounds with large partition coefficients (K). For small K values, although the total stripping gas volume decreases very little, the analyt-

ical techniques become more complicated and the accuracy is poorer because of the difficulties involved in maintaining a constant K value under dynamic conditions.

Expressing the efficiency in the form of a dimensionless quantity (Z), the fraction of extracted analyte [4]

$$Z = (C_L^0 - C_L)/C_L^0 \quad (4)$$

It can be seen that for the cases considered here this quantity will depend only on the extraction coefficient X .

MULTISTEP CGE

The efficiency of CGE can be increased by using a multistep procedure [4] which consists in dividing the analyte solution into N portions and passing the gas stream sequentially through them. A version of multistep CGE using a clean carrier gas was studied by Marinichev and Vitenberg [4]. Consider now a more general case of this process, when through a solution with an initial (mass/volume) concentration of the volatile C_L^0 a gas is passed containing the vapour of the same compound at a concentration C_G^0 . After the exchange of the analyte between the solution of volume V_L and the carrier gas stream of volume V_G (resulting in an enrichment or depletion

of the solution in the volatile analyte) its initial concentration in the solution will change to C_L^1 , related to C_L^0 by

$$C_L^0 = C_L^1 + m_G^1/V_L \quad (5)$$

Here $m_G^1 = V_G(C_G^{-1} - C_G^{\#})$ is the mass of the volatile exchanged between the condensed and gas phases, C^{-1} is the mean concentration in the volume V_G . Taking into account the fact that in CGE the analyte distribution reaches equilibrium in the limit of the volume V_G being brought in contact with the solution in infinitely small amounts, eqn. 5 can be rewritten in the form of a differential equation

$$dC_L^1/dx = -C_L^1 + KC_G^{\#} \quad (6)$$

with the solution

$$C_L^1 = C_L^0 \exp(-X) + KC_G^{\#}[1 - \exp(-X)] \quad (7)$$

In the second step, the gas volume V_G after the interaction in the first step is again brought into contact with another amount of the solution with the same initial concentration C_L . In place of eqn. 5, the equation can now be written as

$$(V_G/V_L)C_G^{-1} + C_L^0 = C_L^{\text{II}} + (V_G/V_L)C_G^{-\text{II}} \quad (8)$$

where C_L^{II} is the volatile concentration after the completion of extraction from the second portion of the solution, and $V_G C_G^{-\text{II}}$ is the mass of the analyte extracted in contact with this portion. The solution of the corresponding differential equation, which is similar to eqn. 7, can be written as

$$C_L^{\text{II}} = KC_G^{\#} + (C_L^0 - KC_G^{\#})(1 + X)\exp(-X) \quad (9)$$

If a sequence of N vials is made up with solutions of the same initial concentration C_L^0 , and these are passed consecutively through a stream of the stripping gas with the initial analyte concentration $C_G^{\#}$, the concentration in the solution at the N th stage will be described, as shown by Marinichev and Vitenberg [4], by the equation

$$C_L^N = KC_G^{\#} + (C_L^0 - KC_G^{\#})\exp(-X) \sum_{s=0}^{N-1} (X^s/s!) \quad (10)$$

The fraction of the extracted analyte in the case of N -step CGE (Z_{NL}) can be calculated by the relation

$$Z_{\text{NL}} = (V_L C_L^0 - V_L C_L^1)/NV_L C_L^0 + \dots + (V_L C_L^0 - V_L C_L^N)/NV_L C_L^0 \quad (11)$$

It is assumed here that the volumes of the solutions

involved in each step of the CGE are the same and equal to V_L/N . Bearing this in mind and substituting eqn. 10 into eqn. 11 gives

$$Z_{\text{NL}} = (1 - KC_G^{\#}/C_L^0) \{1 - \exp(-NX)\} \cdot$$

$$[1 + \sum_{s=1}^{N-1} (NX)^s(1 - s/N)/s!]$$

(12)

The coefficient of relative efficiency of MHE is defined by the relation $h_{\text{NL}} = Z_{\text{NL}}/Z_s$; from eqn. 2 the following equation for Z_s can be derived

$$Z_s = (1 - KC_G^{\#}/C_L^0)X/(1 + X) \quad (13)$$

Using these equations

$$h_{\text{NL}} = (1 + 1/X) \{1 - \exp(-NX)\} \cdot$$

$$[1 + \sum_{s=1}^{N-1} (NX)^s(1 - s/N)/s!]$$

(14)

Eqn. 14 describes the efficiency ratio for the N -step CGE and the static method—in other words, the relative efficiency.

The calculations made using eqn. 12 for the case $C_G^{\#} = 0$ and illustrated by Fig. 2 show that the efficiency of CGE increases with an increasing number of vials N containing the solution of the same total volume V_L . It is seen to grow noticeably up to N values of five or six. A further increase in N results only in an insignificant increase of Z_{NL} , and this is what places a limit on the required number of vials (steps) N .

An essential asset of multistep CGE lies in the possibility of stabilizing the volatile concentration in the gas stream at the outlet of the last vial (Fig. 3). An increase in the number of vials substantially increases the part of the curve with the almost constant analyte concentration in the last vial. This property can be used to advantage in producing gas flows with a given and practically constant trace concentration of a volatile.

CGE WITH STATIONARY GAS PHASE

The dynamic versions described in the preceding section have a common feature, namely, the liquid phase (or any other condensed phase) remains stationary while the gas phase is mobile. In practice, however, a reverse dynamic version used in characterization of gases dissolved in liquids is sometimes used [5,6]. This method is based on the outgassing of a liquid during filtration through a column filled

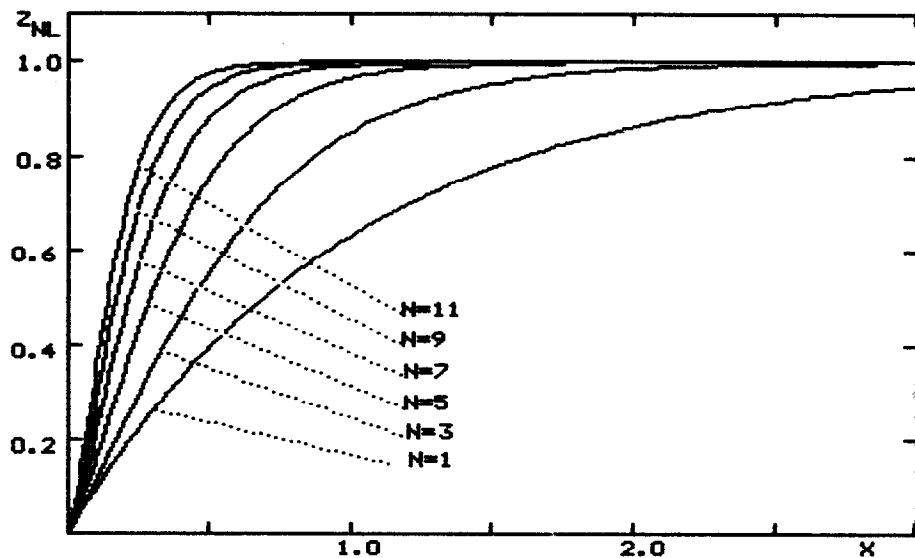


Fig. 2. Fraction of extracted analyte for N -step CGE (Z_{NL}) as a function of the extraction coefficient (X) for $N = 1, 3, 5, 7, 9$ and 11.

with a porous polymer which has a free gas volume acting as a "fixed" extracting gas. This method is actually a variant of the chromatographic technique, referred to as "liquid-gas distribution chromatography" [6], which is a reverse analogue of the frontal concentration of volatiles present in gases [7]. The calculations in these two methods are based on

the relations conventionally used in chromatography and assuming that the retention volume is proportional to the volume of the stationary phase.

Volatiles can be extracted by a stationary gas phase from a moving solution not only in the chromatographic regime but also, for instance, by passing a stream of liquid under a gas bubble or by

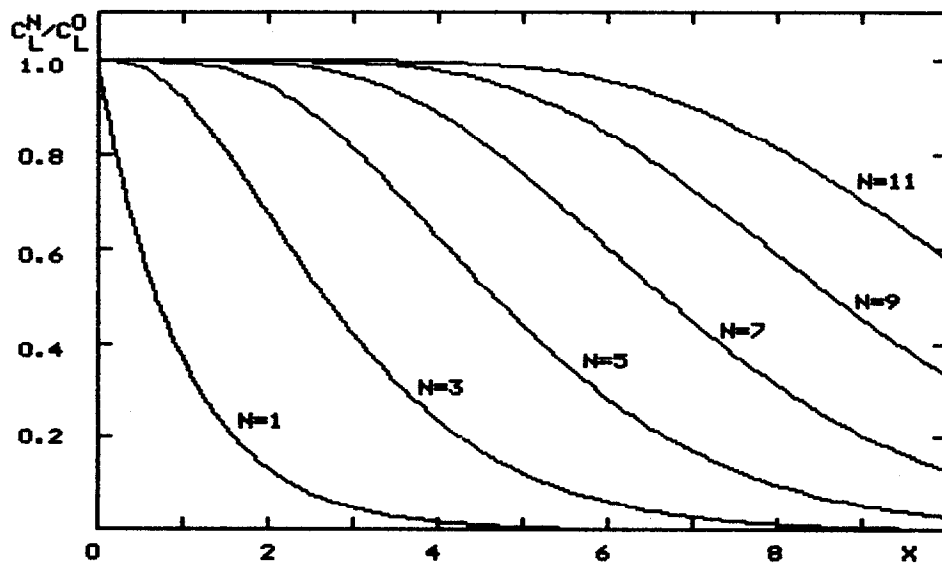


Fig. 3. Fraction of analyte in the liquid phase of the last vial for N -step CGE ($N = 1, 3, 5, 7, 9$ and 11).

spraying the liquid in a vial containing a volume of gas. This process is a reverse variant of the equilibrium absorption concentration proposed in the early 1970s and is used to trap volatiles present in a gas by volatile or non-volatile liquids [8]. The single-step variant of the gas extraction of volatiles from a moving liquid flow by a stationary gas phase is described by the equation [9]

$$C_G = C_L^\# [1 - \exp(-1/X)]/K$$

which is similar to the relations characterizing the absorption equilibrium concentration of volatiles present in a gas [10]. The multistep modification with a stationary extracting gas has not yet been considered and can be described by equations similar to those derived for CGE with a stationary liquid. If the gas phase is divided into N cells (portions) and $C_G^0 = 0$, while the liquid phase moves and comes into contact consecutively with each cell, with $C_L^\# > 0$ before extraction, then after replacing X and K in eqns. 10 and 12–14 by the corresponding reciprocal quantities, as well as G by L , and L by G

$$C_G^N = C_L^\#/K + (C_G^0 - C_L^\#/K) \exp(-1/X) \sum_{s=0}^{N-1} (X^{-s}/s!) \quad (15)$$

$$Z_{NG} = (1 - C_L^\#/KC_G^0) \{1 - \exp(-1/X) [1 + \sum_{s=1}^{N-1} (X/N)^{-s} (1 - s/N)/s!]\} \quad (16)$$

$$Z_s = (1 - C_L^\#/KC_G^0)/(1 + X) \quad (17)$$

$$h_{NG} = (1 + X) \{1 - \exp(-N/X) \cdot [1 + \sum_{s=1}^{N-1} (X/N)^{-s} (1 - s/N)/s!]\} \quad (18)$$

The relative efficiencies $h_{NL}(X)$ and $h_{NG}(X)$ calculated for several values of N and X are listed in Table I. It is readily seen that for $X > 1$ the highest efficiency is provided by the modification with a stationary liquid, and for $X < 1$ by the method using a stationary stripping gas. As the number of steps N increases for $X = \text{constant} = 1$, both quantities, h_{NL} and h_{NG} , grow monotonically and approach one another. In the particular case of $X = 1$ the gas extraction efficiencies are equal irrespective of the state of aggregation of the stationary phase.

CGE WITH MOVING PHASES

In analytical practice this process is used in the

characterization of organic volatiles (simple and halogenated hydrocarbons) present in water under counter-current conditions [12–14] and when analysing gases dissolved in water under the co-current regime [15]. The variation of the volatile concentration in the liquid phase is described by the relation [10]

$$C_L(t) = C_L^\# [(1 - a/b) + (a/b) \exp(-bt)] \quad (19)$$

where $a = w_G/(Kv_1)$, $b = a + w_L/v_1$ and t is time, w_L , w_G are, respectively, the flow-rates of the liquid and gas phases and v_1 is the volume of liquid from which the analyte is extracted—in other words, the volume of the liquid in the vial. Using eqn. 19 the following relation is obtained for the fraction of the extracted analyte

$$Z = X \{1 - \exp[-R(1 + X)]\}/(1 + X) \quad (20)$$

Here $R = V_L/v_1$ is the volume ratio of the liquid passed through the vial to that present in it, or, which is the same, the number of “fillings” of the volume v_1 during the extraction process. If $Y = RX$, then eqn. 20 takes the form

$$Z = Y \{1 - \exp[-(Y + R)]\}/(Y + R) \quad (21)$$

The parameter Y represents the extraction coefficient reduced to the volume v_1 , in contrast to X which relates to the total volume V . In the limit, as $R \rightarrow 0$, eqn. 21 degenerates to the relation for Z for single-step CGE.

The relative efficiency (h) for moving phases, as follows from eqns. 13 and 20, is described by

$$h = 1 - \exp[-R(1 + X)] \quad (22)$$

which shows that the efficiency of this modification

TABLE I
RELATIVE EXTRACTION EFFICIENCIES h_{NL}/h_{NG} FOR VARIOUS VALUES OF N AND X

N	X				
	0.5	1	1.5	2	3
1	1.18/1.30	1.26/1.26	1.29/1.22	1.30/1.18	1.28/1.15
3	1.41/1.46	1.55/1.55	1.53/1.48	1.46/1.41	1.33/1.30
5	1.46/1.49	1.65/1.65	1.59/1.56	1.49/1.46	1.33/1.32
10	1.49/1.50	1.75/1.75	1.64/1.63	1.50/1.49	1.33/1.33

of CGE is always lower than that of the static method for the same liquid and gas volumes, the two quantities closely approaching one another for a sufficiently small volume v_1 (i.e. when it can be assumed that $R \gg 0$). CGE with moving phases may be preferable when the purpose is to extract the largest possible amount of analyte.

CONCLUSIONS

The method chosen for gas extraction substantially affects the efficiency. This increases when dynamic rather than static modifications are used, and multi- in place of single-step head-space analysis techniques.

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