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GAS CHROMATOGRAPHIC HEADSPACE ANALYSIS WITH PNEUMATIC SAMPLING

A. G. VITENBERG* and T. L. REZNIK
Chemistry Department, Leningrad State University, 199164 Leningrad (U.S.S.R.)
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SUMMARY

A derivation is given of the major equations describing the multiple headspace extraction process involving partial replacement of the gas phase by pneumatic sampling from pressurized heterogeneous systems. New modifications of the quantitative headspace analysis and concentration of compounds present in liquid and solid states, as well as new methods of chromatographic detector calibration based on the specific features of pneumatic gas sampling from vials pressurized with inert gas, are proposed.

INTRODUCTION

In the past decade, gas chromatographic headspace analysis (HSA)[1] has been widely used in the determination of volatile compounds in water solutions, foods, biological objects, polymer materials and gases[2,3]. HSA competes successfully with the methods of analysis of volatiles based on liquid extraction while surpassing them in some cases in sensitivity, accuracy and time required for an analysis. The various modifications of quantitative HSA based on multiple headspace extraction (MHE) offer particular promise in this respect. They can be employed in the characterization of substances in any state of aggregation and do not require knowledge of the partition coefficients[4] or introduction of the compound of interest into the sample under study[5].

This procedure usually envisages total replacement of the gas equilibrated by pure gas. It is, however, very difficult, and in some cases impossible, to achieve total removal of the gas phase from the sample vial[6]. Apart from this, the design of modern MHE chromatographic equipment does not provide for automation of the analytical procedure. A more reasonable alternative in MHE analysis consists of an incomplete replacement of the equilibrated by pure gas. This operation can be readily carried out with a high accuracy by sampling from the vial a part of the gas kept at an elevated pressure and can be combined with pneumatic injection of the gas from the sample vial into the chromatograph[6,7].

The existing devices for pneumatic gas injection into the chromatograph have been discussed in detail[3,8] and are conventionally divided into two groups. The first

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group includes devices in which the pressure difference between the sample vial and the chromatographic column is produced only at the moment of injection by stopping the carrier gas flow. This principle is made use of in the Perkin-Elmer headspace analyzer[3,8,9]. The second group combines devices in which the pressure difference between the column and the headspace is produced in advance by pressurizing the sample vial. This technique of pneumatic gas injection into the chromatograph is preferrable for the MHE procedure since it provides for a wider range adjustment of the gas sample volume. Special attachments to all-purpose gas chromatographs based on this principle have been proposed[10–12]. They have not, however, enjoyed wide use in analytical practice because of the various shortcomings in their design. Among inherent drawbacks is the long sampling time associated with the exponential decrease of the preset pressure difference, as well as the diffusion of the gas under study from the tube connecting the sample vial with the chromatograph evaporator. The second factor affects the chromatographic column efficiency particularly strongly, sometimes producing asymmetric peaks (tails). Still another shortcoming is the essentially empirical choice of the sampling conditions, which should be attributed to the lack of a theory which would treat pneumatic injection into the chromatograph of a headspace gas and of methods to calculate the amount of the substance under study removed from the sample vial.

In this paper we propose a device for pneumatic gas sampling free from the drawbacks of the existing designs, together with methods of calculating the mass of the substance removed from the sample vial, and consider some analytical applications of HSA with pneumatic sampling.

EXPERIMENTAL

The sampler for pneumatic gas injection into the chromatograph is designed as an attachment to an all-purpose dual-column gas chromatograph and provides the possibility of adjusting the gas volume removed from the sample vial over a wide range and with good reproducibility.

The pneumatic sampler is shown schematically in Fig. 1*. Equilibration is carried out in a standard pharmaceutical glass vial (1) plugged with an elastic rubber septum (2). To exclude sorption losses or release of volatiles, the septum is protected on the inside by a PTFE or polyethylene film. The air-tightness of the sample vial at an elevated pressure is provided by a special cartridge (3) with a cap that can be screwed on to seal the rubber septum against the neck of the vial. The vial can be thermostatted at up to 95°C by passing a heated liquid through the cartridge. For higher temperatures, a special heated metal block with wells to accommodate the vials is used.

The vial is connected with the gas stopcock through a steel needle (4), 4 cm × 0.5 mm I.D., the venting line (5) with a fine adjustment valve (6) soldered to its base. The gas stopcock connects to the main (10) and auxiliary (12) chromatograph evaporators via 1 mm I.D. steel tubes reaching into the evaporator inserts almost

* Pneumatic samplers functioning in accordance with such a method require regulation of the gas flow-rate by a pressure controller only and prohibit the use of a flow controller.

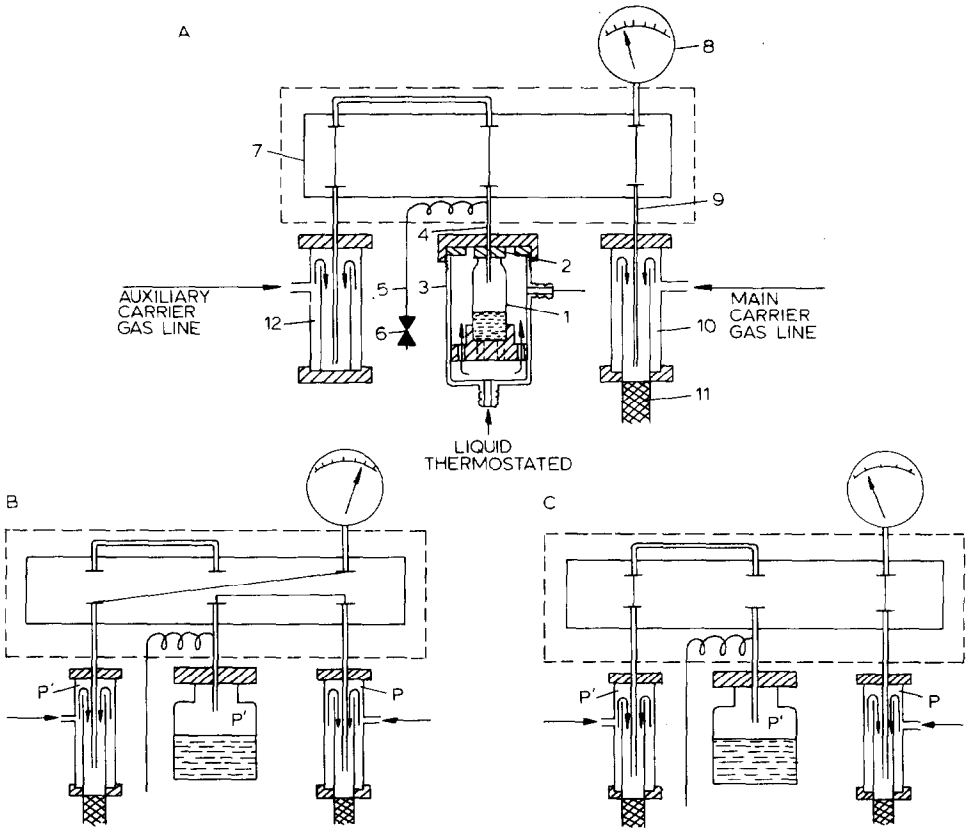

Fig. 1. Diagram of the pneumatic gas sampler. 1 = Glass vial; 2 = elastic rubber septum; 3 = cartridge for sealing and thermostatting the sample vial; 4 = steel needle with a side hole; 5 = gas venting line; 6 = fine adjustment valve; 7 = three-position, six-way gas stopcock; 8 = standard pressure gauge; 9 = sampling capillary; 10 = main evaporator; 11 = chromatographic column; 12 = auxiliary evaporator. The dashed line contour encloses parts heated to 150°C. (A) Pressurization of the vial to the level (p') above the pressure at column input; (B) gas transfer from the vial to the main evaporator; (C) vial replacement or reduction of gas pressure in the vial to atmospheric level.

down to their base. The lower sleeve of the auxiliary evaporator (12) is plugged*. The pressure in the main evaporator (10) depends on the required gas flow-rate through the chromatographic column, the auxiliary evaporator (12) being maintained at a higher pressure. A standard gauge (8) is provided for gas pressure measurements in the main and auxiliary chromatograph lines.

The aluminium body of the attachment is installed directly on the evaporator and heated by a heater to 150°C. The total length of the gas communications connecting the sample vial with the main evaporator does not exceed 10 cm.

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* Pressure regulators in the gas supply systems frequently do not provide for maintaining constant pressure in closed volumes from which the gas is not removed. In such cases, a throttle can be mounted on the lower sleeve of the auxiliary evaporator, with the gas flow-rate through it adjusted within 5–15 ml/min.

The sample preparation and gas injection into the chromatograph are carried out in the following way. A precisely measured volume or mass of the substance to be analysed (which may be a solid or liquid) is placed into an empty vial of known volume. The vial is plugged with the septum, inserted into the cartridge (3) and sealed, after which the septum is pierced by the needle (4) of the pneumatic sampler which should enter the gas space of the sample vial to a depth of 5–10 mm. Next the vial is thermostatted and the stopcock (7) is set in the position (Fig. 1A) in which the carrier gas from the auxiliary evaporator (12) will fill the sample vial to a pressure p'; the gauge (8) is connected to the main evaporator (10) so as to read the head pressure p at the entrance to the chromatographic column. After the equilibration in the sample vial is complete, the stopcock (7) is set to the position of Fig. 1B; now the vial will be connected with the main evaporator, the sample being forced in a short pulse into the column under the action of the pressure difference $p' - p$. The gauge (8) will now read the pressure p' in the auxiliary line of the chromatograph. With the stopcock in the position of Fig. 1C the needle (4) is disconnected from the gas supply lines. This position can be used when replacing vials or sampling without gas injection onto the column, as well as to reduce the pressure in the sample vial down to atmospheric level by venting the gas. The same position can be used to introduce into the vial through the venting line precisely measured volumes of gas or vapour samples.

The equipment permits sampling from the same vial to be carried out as many times as needed. For repeated sampling, the stopcock (7) is reset to position "A", a pressure difference $p' - p$ becoming restored between the sample vial and chromatographic column. Switching the stopcock over to "B" injects onto the column the same gas aliquot as before.

The reproducibility of the pneumatic sampling and the major relevant numerical relationships were checked by means of an attachment mounted on a Tsvet-102 chromatograph in an analysis of the headspace over a 0.01% water solution of acetone at 20°C and of hexane vapour in air at a concentration of 17 mg/l. The conditions of the acetone vapour determination were: 200 × 0.3 cm I.D. glass column packed with 80–100 mesh Chromosorb W with 10% Tween 20; column temperatures, 70°C; evaporator temperature, 160°C; sampler stopcock temperature, 140°C; carrier gas (nitrogen) flow-rate, 50 ml/min; main evaporator pressure* (p), 1.57 atm; auxiliary line pressure (p'), 1.79 atm. The volume of the gas sample used to obtain the dependence of detector signal on the amount of the gas sampled could be chosen by varying p' from 1.70 to 2.67 atm. The volume of the water solution of acetone was 10 ml, the volume of the equilibration vial 24 ml. The equilibration time was 15 min. The upper limit of the electrometer amplifier measurement was $2 \cdot 10^{-9}$ A.

The hexane–air mixture was prepared by injecting 0.5 μl of liquid hexane by a 1-μl microsyringe through the rubber septum into a 24-ml glass vial thermostatted at 60°C. The vapour–gas mixture was analysed with a 2-m long column packed with Chromosorb W containing 80% apiezone L. The conditions were: column temperature, 80°C; carrier gas (nitrogen) flow-rate, 20 ml/min; $p = 1.63$ atm; $p' = 2.0$ atm.

* Here and in what follows the numerical values correspond to the total pressure, *i.e.* the gauge plus atmospheric pressure.

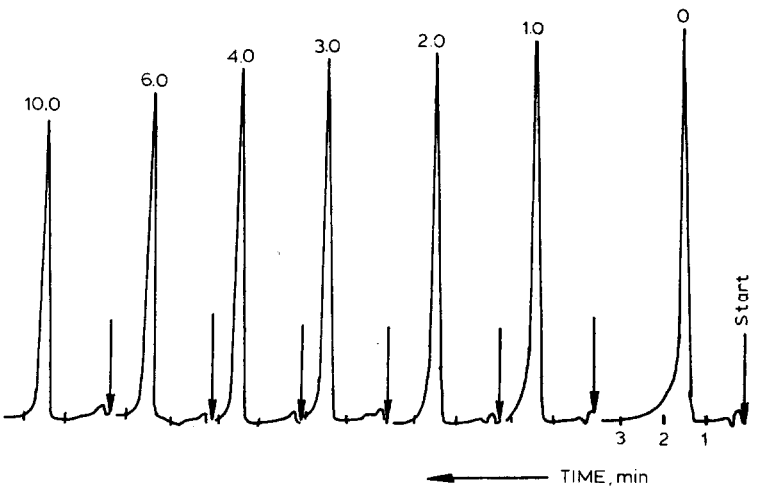

Fig. 2. Effect of gas flow-rate through the venting line on the shape of acetone peak in the chromatogram. The figure above each peak specifies gas flow-rate in ml/min. The conditions of analysis are given in the text.

RESULTS AND DISCUSSION

The time required to perform pneumatic gas injection into the chromatograph may be cut down by venting a fraction of the sample to the atmosphere through the venting line (5). Continuous transfer of the carrier gas through this line at a properly chosen flow-rate permits the expulsion of the gas under study from the sampling capillary (9), thus precluding diffusion from the latter of the vapour contained in the sample into the carrier gas flow and preventing the appearance of long tails on the chromatographic peaks. Fig. 2 shows the variation of the column efficiency as a function of venting flow-rate for the case of acetone vapour over its water solution. With the venting line closed (*i.e.* under the injection conditions in the existing devices[10–12]) the acetone peak in the chromatogram has a very long tail which decreases gradually as the venting line valve (6) is opened and the gas flow-rate is increased to 4–5 ml/min. A further increase of the gas flow-rate is inexpedient since it would result only in a reduced peak height without improving the column efficiency.

The reproducibility of pneumatic sampling of the vapours of hydrocarbons, the simplest carbonyl compounds (Fig. 3), alcohols and carboxylic acids over their water solutions within the concentration range 10^{-2}–10^{-4}% varies within 0.5–1.5% and does not depend on the venting gas flow-rate.

The good reproducibility typical for the pneumatic sampling of equilibrated gas offers the possibility of using any of the known methods of quantitative HSA, *i.e.* absolute calibration, addition of analyte, internal or external standard, depending on the actual object studied and its properties[3]. Precise measurement of the absolute pressures p' and p, however, permits calculation of the fraction and mass of the compound removed from the vial and thus opens additional possibilities for a quantitative determination of volatiles in systems with both known and unknown partition coefficients, and involving accumulation in an adsorption or cryogenic trap under

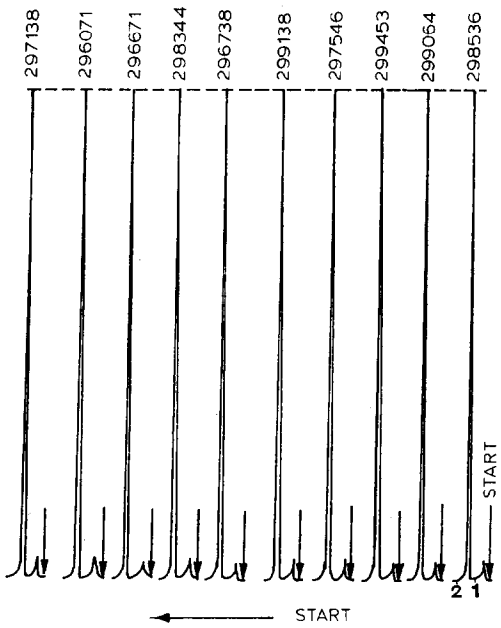

Fig. 3. Reproducibility of pneumatic injection into the chromatograph of acetone vapour above its water solution. The figure above each peak specifies its area computed by electronic integrator. Gas flow-rate through venting line, 5.5 ml/min; other conditions as in Fig. 2.

single or multiple extraction of equilibrated gas. Calibration of chromatographic detectors by the compounds to be analysed also becomes possible.

Mass of compound removed from the vial

If we remove from a closed volume V_G of air or inert gas maintained at a pressure p' and containing a mass M_G of the vapor of a compound (distributed uniformly over the volume) a fraction of this gas, then the pressure in the volume will drop to a value p. The sampled volume v_G will contain a fraction $(p' - p)/p'$ of the initial mass M_G, *i.e.* the mass m_1 of the removed compound will be

$$m_1 = M_G \frac{p' - p}{p'} \tag{1}$$

The mass M_1 of the compound remaining in the gas volume will be

$$M_1 = M_G - m_1 = M_G \frac{p}{p'} \tag{2}$$

Each subsequent sampling performed at the same pressure difference $(p' - p)$ will reduce the mass of the removed compound p/p' times bringing it after an n-th sampling to the value

$$m_n = M_G \left(\frac{p}{p'}\right)^{n-1} \left(\frac{p' - p}{p'}\right) \tag{3}$$

Consider now a closed heterogeneous system of a gas over a non-volatile liquid containing a mass M_0 of a volatile compound distributed between the liquid of volume V_L and the gas of volume V_G in accordance with the corresponding partition coefficient K. After thermodynamic equilibrium has been reached, the gas phase will contain a mass M_G of the compound, its fraction of the total content of the compound in the system being related to the partition coefficient and the phase ratio $r = V_G/V_L$ by

$$\frac{M_G}{M_0} = \frac{r}{K + r} \tag{4}$$

Solving this equation for M_G and substituting it into eqn. 1 we obtain an expression for the calculation of m_1 for the case of gas sampling from the gas-condensed phase heterogeneous system:

$$m_1 = M_0 \frac{r}{K + r} \frac{p' - p}{p'} \tag{5}$$

The remaining mass of the compound will be

$$M_1 = M_0 \frac{K + rp/p'}{K + r} \tag{6}$$

After an n-th sampling the removed mass will be

$$m_n = M_0 \left(\frac{K + rp/p'}{K + r}\right)^{n-1} \frac{r}{K + r} \frac{p' - p}{p'} \tag{7}$$

while the mass remaining in the vial is given by

$$M_n = M_0 \left(\frac{K + rp/p'}{K + r}\right)^{n} \tag{8}$$

For these expressions to be useful for quantitative calculations, the mass of the compound injected onto the column or the height of the chromatographic peak should be linearly related to the fraction of the compound removed from the headspace of the vial. This relationship was checked for the case of injection onto the chromatograph of acetone vapour present over its water solution. As seen from Fig. 4, the detector signal rises linearly with the fraction of removed gas up to 0.3, which in this particular case corresponds to a sample volume of *ca.* 9 ml (at NTP)*. The deviation from linearity at large sample volumes is probably associated with the overfilling of the standard evaporator of the Tsvet 100 and the spreading of the initial

* The sample volume was calculated by the expression $v_G = V_G(p' - p)/p^0$, where p^0 is the pressure in the system into which the sample is injected. If the sample is transferred into the main evaporator than $p^0 = p$, and if it is vented into the atmosphere, then $p^0 = 1$ atm.

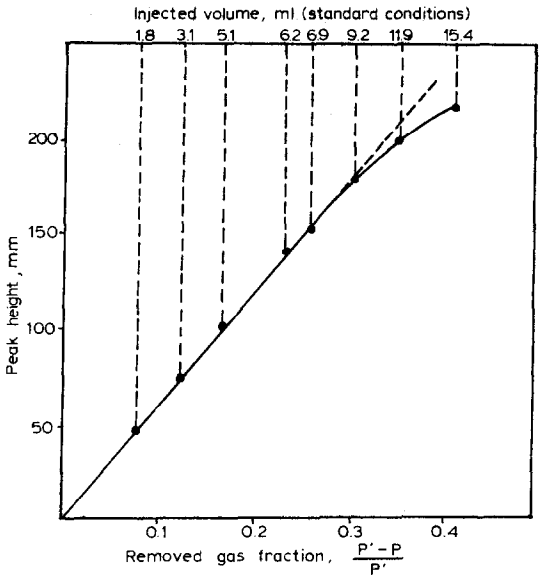

Fig. 4. Chromatographic peak height *vs.* volume of sampled gas equilibrated with an acetone–water solution. Venting line closed; other conditions given in the text.

chromatographic band. The fraction of the sampled compound can be increased to 0.7–0.8 without any loss in linearity of the detector signal by properly reducing the gas volume of the sample vial.

Quantitative analysis with known K and r

The initial mass M_0 of the compound may be calculated from eqn. 5. To do this, one sampling only of the headspace gas need be carried out and the mass m_1 of the compound removed can be determined from the area or height of the chromatographic peak by making use of the available detector calibration. Note, however, that the actual conditions of analysis and sampling (*i.e.* the phase volume and pressure ratios) affect markedly the error with which M_0 is determined. This relationship is given by the equation

$$\frac{\Delta M_0}{M_0} = \frac{\Delta m_1}{m_1} + \left(\frac{\Delta K}{K} + \frac{\Delta r}{r}\right)\frac{K}{K + r} + \left(\frac{\Delta p'}{p'} + \frac{\Delta p}{p}\right)\frac{p}{p' - p} \qquad (9)$$

obtained by differentiating eqn. 5. Eqn. 9 shows that in order to reduce the contribution of the pressure (p' and p) measurement error to the total error of an analysis, their difference ($p' - p$) should be as large as possible, and in order for this contribution not to exceed the total error of p' and p measurement (which is not more than 1–2% when a standard pressure gauge is employed), the condition $p' \geqslant 2p$ should be satisfied. Since the volume injected into the evaporator of a standard chromatograph should not exceed 9 ml (see Fig. 4), the condition $p' \geqslant 2p$ imposes certain limitations on the volume of the gas phase in the sample vial. If, for instance, the

head pressure in the evaporator before the chromatographic column is 1.5 atm, the headspace volume should not exceed 6 ml, otherwise the relationship $m_1 = f\left(\frac{p' - p}{p'}\right)$ will deviate from a straight line, and the calculation of M_0 from eqn. 5 will result in errors exceeding those that follow from eqn. 9.

Quantitative analysis with unknown K and r

In this case, in order to calculate M_0, not less than two samplings of the headspace must be carried out and the areas (or heights) of the peaks A_1 and A_2, which are proportional to the masses of the compound removed in the first (m_1) and second (m_2) sampling, must be measured.

By definition[6,13], the numerical values of the ratios

$$\frac{m_2}{m_1} = \frac{A_2}{A_1} = B_u \tag{10}$$

represent the fraction of unextracted compound or the buffer coefficient (B_u) which under the MHE conditions, according to eqns. 5 and 7, may be written as

$$B_u = \frac{K + rp/p'}{K + r} \tag{10a}$$

Then the fraction of the compound removed in each sampling will be

$$1 - B_u = \frac{r}{K + r}\frac{p' - p}{p'}$$

which permits us to rewrite eqn. 5 in a simpler way

$$M_0 = \frac{m_1}{1 - B_u} = \frac{m_1}{1 - A_2/A_1} \tag{11}$$

This equation, which was derived earlier by Novák[14] in a different way, makes it possible to calculate the original amount of the compound in the system using the detector calibration graph $A = f(m)$ and the peak areas measured in each headspace sampling. The accuracy of such measurement of M_0, similar to the case of MHE involving total replacement of the gas phase[4,13], depends substantially on the magnitude of the buffer coefficient. The error of an analysis increases as the value of B_u approaches unity. This is seen readily from the equation

$$\frac{\Delta M_0}{M_0} = \frac{\Delta m_1}{m_1} + \frac{\Delta B_u}{B_u}\frac{B_u}{1 - B_u} \tag{12}$$

obtained by differentiating eqn. 11. Therefore the conditions of measurement should be chosen such that the peak area obtained in each subsequent sampling from the same vial will decrease by not more than 15–20%. As follows from eqn. 10a, at $K \leqslant r$ the most efficient way to achieve this is to increase the pressure differential. If,

however, B_u is close to unity, *i.e.* $K \gg r$, even under the maximum possible pressure difference, then the temperature and the magnitude of r should be increased substantially.

Accumulation of volatiles

In cases where direct sampling either does not provide the desired sensitivity or reduces the separation efficiency, as may occur when using a capillary column, a problem may arise in a preliminary accumulation of the compounds present in the headspace before their injection onto the column. With capillary columns the accumulator is usually the entrance section of the column, cooled with liquid nitrogen or dry ice. If packed columns are used, a cryogenic or adsorption-type accumulator inserted in the gas supply line between the evaporator and the chromatographic column may be employed.

The calculations for the case of a single sampling from the vial followed by accumulation do not differ from the above situations with known and unknown K and r. When a compound is accumulated by MHE from the sample vial, the mass of the compound removed in n samplings, according to eqns. 8 and 10a, may be calculated in the following way:

$$\sum_{1}^{n} m = M_0 - M_n = M_0 [1 - (B_u)^n] \tag{13}$$

For known K and r, the magnitude of B_u is calculated from eqn. 10a, whereas if these parameters are unknown, B_u will have to be measured experimentally and calculated from eqn. 10.

HSA with pneumatic gas sampling can also be employed to advantage when analysing volatile compounds trapped on sorbents packed in small diameter (2–3 mm) tubes. The analytical procedure consists of high temperature (250–400°C) desorption in an inert gas flow until the volatiles are practically completely removed from the adsorbent surface. This results in a fairly long sample injection onto the column and a reduction of its efficiency, and does not exclude the possibility of losses associated with the high desorption temperature.

If the concentrate thus obtained is transferred from the tube into the sample vial and the headspace gas is pneumatically injected into the chromatograph, then the desorption temperature and the associated possibility of formation of artefacts may be reduced substantially owing to a drastic increase in the phase volume ratio. Apart from this, the pulsed pattern of sampling provides for a higher column efficiency and in this way compensates for the reduced sensitivity of the analysis resulting from its being carried out under incomplete desorption of the volatiles from the adsorbent surface.

The injection of partially described compounds onto a chromatographic column has already been considered for the case of the determination of trichloroethylene in air[15] and the equilibrium accumulation of volatiles present in gases[3]. When the concentrate is obtained by trapping on a sorbent all of the compound under study, then one may use for calculation the relationships derived for the case of the quantitative analysis of systems with unknown K and r.

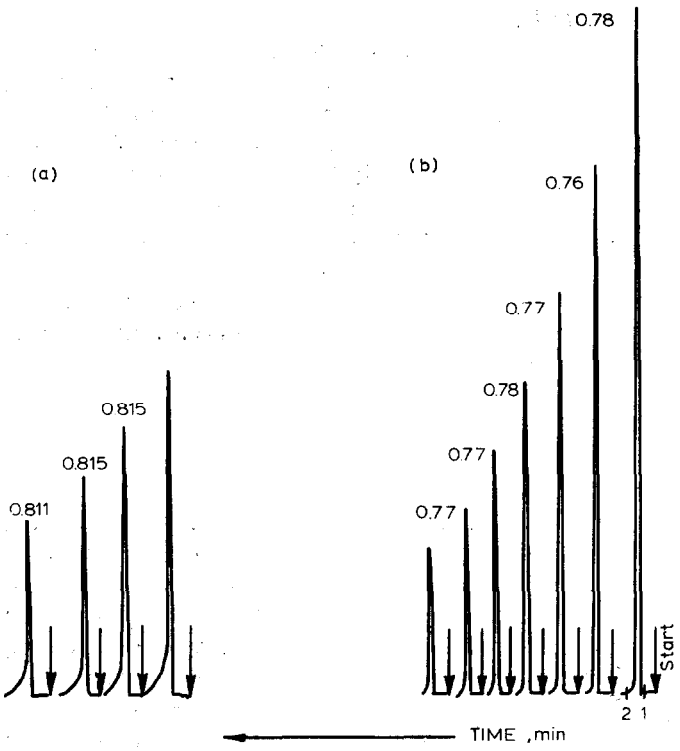

Fig. 5. Constancy of peak height ratio under multiple sampling of hexane vapour from the vial without liquid. The chromatograms were obtained by consecutive sampling from the same vial; series "b" with venting (gas flow-rate 5.5 ml/min), series "a" without venting; $p/p' = 0.815$. Upper limit of electrometric amplifier measurement: a = $1 \cdot 10^{-9}$ A; b = $2 \cdot 10^{-9}$ A.

pressure ratios for systems with known K, one should use eqn. 10a, with the mass of the compound removed from the vial calculated from eqn. 7. If the partition coefficients are unknown, the conditions should be chosen empirically, and the numerical values of B_u determined experimentally as a ratio of the peak areas obtained in a consecutive sampling of the headspace from the same vial (eqn. 10). The mass of the compound removed from the sample vial can be calculated in this case from the expression

$$m_n = M_0 (B_u)^{n-1} (1 - B_u) \tag{15}$$

A series of constant amplitude signals (*e.g.* for checking the sampler reproducibility) can be obtained by headspace sampling from systems with a value of B_u close to unity. The maximum number of samplings that can be made from one vial depends, besides the numerical value of B_u, on the acceptable error δ of detector signal measurement and can be calculated[16] by the expression

$$n^{max} = \frac{\ln (1 - \delta)}{\ln B_u} \tag{16}$$

Calibration of chromatographic detectors

The chromatographic detectors can be calibrated by injecting onto the column headspace gas from a vial with or without liquid phase. Sampling from a vial that does not contain condensed phase permits the injection onto the chromatographic column of equal volumes of gas with a progressively decreasing mass of the compound under study. The corresponding relationship is described by eqn. 3. Therefore if the initial mass M_G in the vial is known, then eqn. 3 will yield the mass of the compound removed from the vial in any of the consecutive samplings, provided the given absolute pressures p' and p are accurately reproduced*.

Eqn. 3 describes the reduction of the mass of a compound in consecutive sampling from the vial without condensed phase present, and it has been verified experimentally by checking the equality

$$\frac{A_{n+1}}{A_n} = \frac{p}{p'}$$

Fig. 5 shows the constancy of the peak height ratio under multiple sampling of hexane vapour in two cases, *i.e.* with a closed venting line and at a venting flow-rate of 5.5 ml/min. In both cases the reproducibility of the peak height ratio is not worse than 0.3–1.0%; however, with the venting line open the absolute magnitude of the ratio differs from the fixed pressure ratio p/p' by 5.5% while with no venting no difference between the peak height and pressure ratios is seen within experimental error. This effect should be taken into account when calibrating a detector by sampling from a vial without condensed phase present, and the measurements should be carried out with the venting line closed or only very slightly open.

The accuracy of measurement of the mass injected onto the column is governed not only by the accuracy of transfer of the original mass M_G, but also by the sampling conditions, *i.e.* by the magnitude of p' and p. This is clearly seen from the following expression derived from eqn. 3:

$$\frac{\Delta m_n}{m_n} = \frac{\Delta M_G}{M_G} + \left(\frac{\Delta p'}{p'} + \frac{\Delta p}{p}\right)\left(n - \frac{p'}{p' - p}\right) \qquad (14)$$

which should be consulted when choosing the sampling conditions, as well as when estimating the optimal and limiting number of samplings.

Pneumatic sampling from a vial containing a liquid provides the possibility of continuous injection onto the column of samples with a variable or practically constant mass of the compound under study. The major advantage of this version consists in the simplicity of introduction into the vial of a known mass of the compound to be analysed in the form of a solution in a suitable solvent.

If calibration of a detector over a wide concentration range requires obtaining a series of progressively decreasing signals, the conditions should be chosen such that the magnitude of B_u will not exceed 0.7–0.8. When choosing the phase volume and

* Consecutive sampling and detector calibration can be carried out also with varying p' and p, however this will entail a complication of the calculations and reduced accuracy of determination.

The possibility of performing multiple extraction of samples from the vial with a practically constant mass removed is indicated by Fig. 3, which shows the constancy of peak heights on the chromatograms obtained in a consecutive sampling of acetone vapour over its water solution. Since in this case $K = 750$ (ref. 3), and B_u is in excess of 0.999, the mass of the compound removed in the first and tenth samplings differ by less than 1%. Therefore the chromatogram will consist of a series of well reproducible peaks which will be equal in amplitude within the error of detector signal measurement.

Thus the method of detector calibration based on the specific features of pneumatic gas sampling permits the calibration of a detector over a broad concentration range with only one sample which offers obvious advantages over Lovelock's method of exponential dilution[17], since the possibility of high temperature (up to 150–200°C) sampling enables calibration by any volatile compound which can be analysed by the gas chromatographic technique.

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