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EFFECT OF WATER VAPOUR IN THE QUANTITATION OF TRACE COMPONENTS CONCENTRATED BY FRONTAL GAS CHROMATOGRAPHY ON TENAX-GC®

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SUMMARY

Specific gas chromatographic retention volumes (V_g) of model compounds (methanol, ethanol, propanol, ethyl acetate, acetone and benzene) on Tenax-GC® were measured with the use of a carrier gas (nitrogen) saturated with water vapour. The differences between the V_g values measured with and without water in the carrier gas varied approximately in the range $\pm 10\%$ of the values measured. The effects of the adsorbed water on the sorption properties of Tenax-GC are discussed with a view to using it as a packing for concentration tubes in the analysis of trace components of expired air and headspace samples by the method of chromatographic equilibration. From this viewpoint, the effect of water can be considered to be insignificant. Examples are given of the determination of trace amounts of acetone in air by the above method.

INTRODUCTION

Biomedical applications of gas chromatography are becoming increasingly significant[1]. Recently, the so-called metabolic profiles of volatile substances present in biological materials have been intensively studied, and it appears that these profiles may serve for diagnostic purposes[2–4]. Basically, the objective is the assay of trace amounts of volatile organic substances by means of the headspace method, *i.e.*, the analysis of the gaseous phase above samples of urine[2,3,5–7], blood, serum or plasma[5,8], or of expired air[4,6,7]. In a broader sense, the expired air may be supposed to be equilibrated with the blood in lung tissue[4,9]. A characteristic feature of the headspace method is that the substances analysed are present in very low concentrations in a gas (usually air) saturated with water vapour. The contents of the components of most interest for diagnostic purposes vary within the range from parts per million down to parts per billion and even less[4]. Another feature of the method is that the trace components have to be accumulated, under the above conditions (large excess of water), by sorption on a suitable sorbent[3,4] or by freezing out[2]. The concentrate is liberated from the sorbent by thermal desorption, whereupon the components are separated by gas chromatography.

A number of concentration methods have been evaluated from the above point of view[10,11]. There are essentially two basic procedures suitable for the accumulation

of substances by sorption[12,13]. In the first version[12], simple trapping of the components to be determined is carried out without changing their original proportions. In the second version[13], the accumulation is achieved by frontal chromatography, which enriches the components proportionately to their partition coefficients on the given sorbent. It is evident that when a sorbent material on which water vapour is not appreciably sorbed is used (the partition coefficient approaching zero), water can largely be eliminated from the headspace sample. This method has been applied successfully in air pollution studies[14–16].

In the investigation of metabolic profiles[7], porous polymers based on 2,6-biphenyl-*p*-phenylene oxide[17], known under the commercial name Tenax-GC®, proved to be the most suitable sorbents with both of the above concentration methods. The most advantageous property of this material is its thermal stability.

Whereas a number of the substances of the metabolic profiles have been identified, mostly by combined gas chromatography–mass spectrometry (see, *e.g.*, refs. 2 and 3), their quantitation, so far as it has been attempted at all, has been only approximate. Special advantages afforded in this respect by chromatographic equilibration[13] were checked in instances where a stationary liquid of low volatility was used as the sorbent; in these instances, the requirement of the mutual independence of the chemical potentials of the components of the sorption system is fulfilled almost perfectly. However, when employing an adsorbent, such as the organic porous polymer, the limits of the permissible approximation regarding the above thermodynamic qualification, the fulfilment of which is necessary for calculating accurately the composition of the gaseous mixture being analysed, are not clear, especially as even porous polystyrene polymers show some adsorption of water[18].

In this work, we have investigated the effect of water vapour on the quantitation of trace amounts of volatile organic substances by chromatographic equilibration, with respect to some typical components of expired air, urine and blood, and to the properties of Tenax-GC® as the adsorbent. As it is the specific retention volume, measured by elution chromatography on the packing used in the concentration tube, that represents the basic parameter of quantitation in the method of chromatographic equilibration, the actual subject of the study was the measurement of specific retention volumes of model substances of different polarity on Tenax at a defined content of water vapour in the carrier gas. The suitability of Tenax as the packing in the concentration tube was demonstrated in the determination of trace amounts of acetone in model acetone–air mixtures.

EXPERIMENTAL AND RESULTS

Measurement of the specific retention volumes

For these measurements, a Chrom-3 gas chromatograph with a flame ionization detector (Laboratory Equipment, Prague, Czechoslovakia) was modified, and a block diagram of the instrumental arrangement is shown in Fig. 1. In the column oven, a saturator containing about 100 ml of granular (particle size 0.3–0.4 mm) earthware support (Lachema, Brno, Czechoslovakia) wetted with water (about 20%, w/w) was inserted before the column inlet. The analytical column consisted of a 50 cm × 3 mm I.D. PTFE tube containing 0.7 g of Tenax-GC, 60–80 mesh (Enka, Arnhem, The Netherlands). The carrier gas was nitrogen. The sample was introduced at a posi-

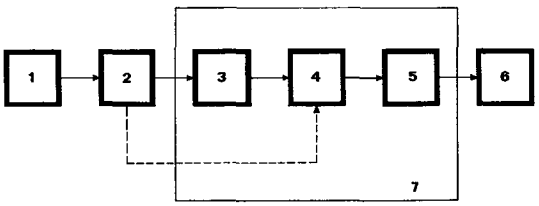

Fig. 1. Schematic diagram of the instrument used for the measurement of specific retention volumes with the carrier gas saturated with water vapour. 1 = Source of the flow of pure carrier gas; 2 = flow meter (measurement of the pressure drop across a capillary); 3 = water saturator; 4 = sample inlet port; 5 = chromatographic column; 6 = flame ionization detector; 7 = column oven.

tion between the outlet of the saturator and the column inlet, *i.e.*, into the stream of the mixture of the carrier gas and water vapour. With this arrangement (large surface area of the liquid water), it can be assumed that the carrier gas was completely saturated with water vapour at the temperature of the column oven.

The specific retention volumes of the substances studied (benzene, ethyl acetate, acetone, propanol, ethanol and methanol) were measured both in the presence and in the absence of water vapour in the temperature range 60–80 °C. As the flow-rate of the carrier gas was measured ahead of the saturator, it was necessary that the increase in flow-rate due to saturation with water vapour be taken into account in the calculation of the specific retention volume. At a given temperature and pressure, the flow-rate after and ahead of the saturator (F and F', respectively) are related to each other by the equation

$$F = F'(1 + y_w)$$

where y_w is the mole fraction of water vapour in the gaseous mixture leaving the saturator. The quantity y_w is given by the ratio of the partial molar volume of the water vapour and the molar volume of the mixture; when expressing these volumes at a temperature of 0 °C, for instance, we can write

$$F = F'\left(1 + \frac{p_w^0 \cdot 22.414}{R \cdot 273.16}\right)$$

where p_w^0 is the saturation vapour pressure (atm) of water at the temperature of the column oven and R is the perfect gas constant ($1 \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$).

In Figs. 2 and 3, the specific retention volumes measured both in the presence and absence of water are plotted against the reciprocal of the absolute temperature in the column oven. The plots were obtained by the least-squares linear regression of the data measured. Table I contains extrapolated V_g values at 25 °C (V_g^{25}) and the constants of the empirical equations $\log V_g = (A/T) - B$ for the compounds studied.

Determination of acetone by chromatographic equilibration

The analyses were carried out on a Hewlett-Packard Model 402 gas chromatograph (Palo Alto, Calif., U.S.A.) with a flame ionization detector. The detector response was integrated with an Infotronics CRS 101 integrator (Infotronics, Austin, Texas, U.S.A.).

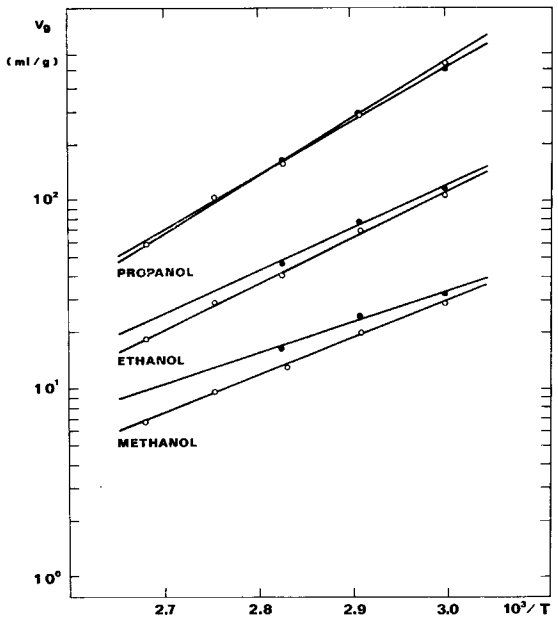

Fig. 2. Plots of log V_g *versus* $1000/T$ for lower alcohols on Tenax-GC, measured in the presence (●) and absence (○) of water vapour in the carrier gas.

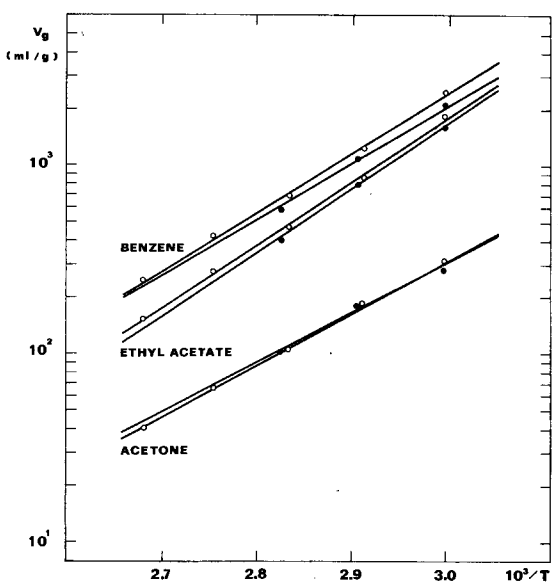

Fig. 3. Plots of log V_g *versus* $1000/T$ for acetone, ethyl acetate and benzene on Tenax-GC, measured in the presence (●) and absence (○) of water vapour in the carrier gas.

TABLE I

EXTRAPOLATED VALUES OF THE SPECIFIC RETENTION VOLUME (ml/g) AT 25 °C AND THE VALUES OF THE CONSTANTS IN THE EQUATIONS LOG $V_g = (A/T) - B$ FOR THE MODEL COMPOUNDS ON TENAX-GC IN THE PRESENCE AND ABSENCE OF WATER

Compound	*Without water*			*With water*		
	A	*B*	V_g^{25}	*A*	*B*	V_g^{25}
Methanol	1981	4.473	148	1629	3.362	126
Ethanol	2458	5.323	834	2244	4.655	742
Propanol	2940	4.654	5765	2778	5.616	5031
Benzene	3132	6.017	30,820	2997	5.667	24,220
Ethyl acetate	3358	6.821	27,650	3237	6.794	24,950
Acetone	2745	5.739	2928	2650	5.469	2631

A larger concentration tube, containing about 0.35 g of Tenax was employed for sampling the model acetone–air mixtures by the equilibration method. After its thermal desorption (180 °C), the concentrate was purged with a stream of nitrogen from this tube into a smaller tube (0.085 g of Tenax), which was cooled in solid carbon dioxide (*ca.* −70 °C). Under these conditions, it can be assumed that the components purged from the heated large tube were trapped completely in the cooled small tube. The small tube was constructed as a probe, providing for transfer of the sample into the gas chromatograph as described earlier[13,15]. This alternative affords a greater accumulation of the components to be determined (larger amount of the sorbent) and a sufficiently rapid transfer of the concentrate into the gas chromatograph (small void volume of the smaller tube). The results of replicate analyses of model mixtures with acetone concentrations at the parts per million level are summarized in Table II. The chromatograms were run at a sensitivity attenuation of 1/2000.

TABLE II

DETERMINATION OF ACETONE CONCENTRATION IN MODEL MIXTURES BY CHROMATOGRAPHIC EQUILIBRATION ON TENAX-GC

Acetone present in model mixture		*Acetone found*		*Relative error (%)*
μg/l	*ppm*	*μg/l*	*ppm*	
5.8	2.4	5.5	2.3	−5
8.4	3.5	8.0	3.4	−5
7.8	3.3	7.2	3.0	−8
4.8	2.0	5.0	2.1	+4

DISCUSSION

When the gaseous mixture is drawn through the sampling tube, the frontal chromatographic development takes place within the sorption bed at first, the velocity of the advancement of the front of a given component being determined by its parti-

tion coefficient in the system. After the front of the component breaks through the tube, the concentration of this component in the sorbent becomes equilibrated with the concentration in the gaseous sample and then remains constant. The ultimate equilibrium for all of the components is achieved as soon as the front of the most sorbed component has passed through, following which the composition of the gas leaving the tube is the same as that of the sampled gas. The degree of accumulation obviously depends on the temperature of the tube and the amount of the sorbent but, after equilibration, it is independent of both the amount and velocity of the gaseous sample drawn through the tube, so that the latter two quantities need not be measured. The concentrations of the components to be determined in the gas being analysed can be calculated from the absolute amounts of the components entrapped in the tube, the amount of the sorbent contained in the tube and the respective partition coefficients. It is inconvenient to measure the partition coefficient by frontal chromatography but, under certain circumstances, retention data measured by elution chromatography can be utilized for the above purpose[13]. In this context, it is expedient to refer to the Gibbs–Duhem equation, which, for systems corresponding to frontal and elution chromatography at constant temperature and pressure, can be written as

$$N_s \cdot \frac{\partial \mu_s}{\partial N_j} + N_j \cdot \frac{\partial \mu_j}{\partial N_j} + \sum_{\substack{i=1 \\ i \neq s\, j}}^{k} N_i \cdot \frac{\partial \mu_i}{\partial N_j} = 0$$

and

$$N_s \cdot \frac{\partial \mu_s}{\partial N_j} + N_j \cdot \frac{\partial \mu_j}{\partial N_j} = 0$$

respectively, where N and μ are the number of moles and chemical potential of the given component and subscripts s and i,j,k denote the sorbent and the individual components, respectively, where j is the component under examination. The conditions under which the situation existing in a frontal chromatographic system can be described by virtue of the data measured by elution chromatography is characterized by the inequality

$$\frac{N_s}{N_j} \cdot \frac{\partial \mu_s}{\partial N_j} \gg \frac{\sum_{i=1}^{k} N_i}{N_j} \cdot \frac{\partial \mu_i}{\partial N_j}$$

In fact, this means that the concentrations of each of the components accumulated in the sorbent must be extremely low ($\Sigma N_i \ll N_s$).

When considering the sorption of a given component on an adsorbent in the presence of water, it is necessary to take into account the change in the sorption properties of the adsorbent brought about as a result of covering part of its surface by the adsorption of water on the one hand, and the interactions of the substance with the adsorbed water itself on the other. Fortunately, when a non-polar porous organic polymer is used as the adsorbent, the amount of the water adsorbed is relatively small, owing to the water-repellent properties of these materials, and it can be assumed that the adsorption of other substances will not be influenced appreciably by the adsorbed water. However, in instances where the substance in question also displays weak adsorption on the polymer, solute–water interactions in the gaseous phase may become

important as a factor affecting the solute retention. The results in Table I provide evidence that the effect of the adsorbed water is, in fact, insignificant. A more pronounced effect can be observed only with either slightly polar (benzene) or highly polar (methanol) compounds. This phenomenon is easy to explain. While with the strongly adsorbed benzene the presence of adsorbed water adversely affects the chemical similarity between the adsorbent and adsorbate (the presence of water decreases the sorption of benzene), with the weakly adsorbed methanol the presence of water enhances the chemical similarity (the adsorption of methanol increases in the presence of water). The differences between the V_g values measured with and without water in the carrier gas vary approximately in the range $\pm 10\%$. Hence, this would be the error that might be expected to arise if the effect of water is neglected when employing the method of chromatographic equilibration and analysing a gas saturated with water vapour. This error is insignificant and can be neglected in comparison with that normally accepted in trace analysis. However, it is necessary to stress that this applies only if the concentrations of all the components to be determined are low; in the analysis of the model acetone–air samples, an appreciable negative error was observed if the acetone concentrations exceeded 10 ppm. This error rose proportionately to the concentration and was apparently due to the onset of a non-linear course of the sorption isotherm in the region exceeding this concentration limit.

The calculation of the concentration of component j, c_j, in the gaseous sample is carried out by the relation[15]

$$c_j = [w_j\,(\mathrm{SG}) \cdot 273/w_s V_{gj} T]/[1 + (V_G \cdot 273/w_s V_{gj} T)]$$

where c_j has units of weight per unit volume (consistent with the dimensions of V_g), w_j (SG) is the weight of component j entrapped in the sampling tube (both within the sorbent and the void space of the tube), w_s is the weight of the sorbent in the tube, V_{gj} is the specific retention volume of component j at the temperature of sampling (T) and V_G is the void space of the entire tube. In most instances $V_G \ll V_{gj} w_s$, so that the effect of the void volume of the sampling tube can usually be neglected.

CONCLUSIONS

The effect of water vapour on the determination of trace components contained in expired air or headspace samples analysed by chromatographic equilibration with the use of Tenax-GC is insignificant. At concentrations of the component to be determined (acetone) at the parts per million level, the error incidental to the above effect usually varies by approximately $\pm 10\%$ of the value determined.

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