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Dynamic modification of the stationary phase in capillary gas chromatography
II. Continuous introduction of water vapour

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Abstract

Water vapour was added to the carrier gas, at levels approaching saturation, to study its effect on the retention properties of a polyethylene glycol-coated capillary GC column. A dramatic increase in hydrogen bonding interactions was observed towards alcohols and carboxylic acids. The Kovats index of methanol was found to increase by 351 units. The application of the dynamically modified stationary phase to the analysis of alcohol additives in petrol is investigated.

Keywords: Stationary phases, GC; Carrier gas; Retention indices; Alcohols; Alkanes

1. Introduction

The aim of the wider project is to reversibly introduce special selectivity in conventional capillary GC columns. Part I of this paper [11] describes the procedure for batch vapour phase introduction of low volatility modifiers at high temperature, significantly altering the retention behaviour of the column at subsequently lower analysis temperatures. The modifier is effectively immobilized at the analytical temperature, preventing column bleed from interfering with detection and providing stable retention for an extended period of time. A less complicated method of dynamic modification involves the continuous introduction (during analysis) of a modifier that does not give a detector response. In this case even volatile modifiers can be used.

Volatile modifiers have indeed been studied extensively in packed column gas chromatography (GC) [1–3], where the procedure was termed vapour chromatography, if the modifier was undiluted with another carrier gas. Saturated water vapour was even used in one case to provide both the stationary and mobile phase in a packed column, resulting in such a high polarity stationary phase as to elute the heavier alcohols before the lighter ones [3]. An important feature of all these systems is the use of a detector that does not respond to the modifier used, as for example, an electron capture detector, when alkanes or alcohols are used in the carrier gas [4,5] or a UV detector when organic modifiers, without chromophore, are studied [6]. Water and formic acid [4] vapours have frequently been studied as modifiers in packed column GC due to their lack of response to FID. In packed columns the effect of vapours in the carrier gas stationary phase selectivity is complicated by the simultaneous deactivation effect normally observed due to the covering of the active sites on the solid support.

With the exception of the studies by Berezkin and

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Korolev [7], the deliberate modification of capillary column selectivity by water in the carrier gas could not be found in the literature. Even in this work, the aim was rather to study the effect of smaller amounts of water vapour on the retention time reproducibility in capillary GC systems. Carrier gas saturated with water at room temperature was the maximum concentration of modifier investigated. At a column temperature of 70°C the maximum Kovats retention index change of 13.74 units was reported for *n*-propanol on polyethylene glycol (PEG) 20M. However, even split injection of different volumes of aqueous samples on Carbowax capillary columns [8] seemed to indicate more drastic effects on the retention behaviour of some analytes.

It was thus decided to study even higher concentrations of water vapour in a capillary GC column coated with Carbowax 20M. This would also serve as an example of the general case of controlling capillary GC selectivity by continuous dynamic modification, without interference from the detector. The choice of this modifier would furthermore enable a comparison with the hydrogen bonding behaviour introduced by glycerol in the Carbowax column, as presented in the accompanying paper.

For the continuous introduction of various concentrations of water vapour, a simple, non-permanent, modification was made to the GC carrier gas system.

2. Experimental

2.1. Gas chromatographic equipment

A Carlo Erba Fractovap Series 4200 equipped with a FID system, split/splitless injector and a Carbowax 20M column, 25 m×0.32 mm I.D., 0.25 μm film thickness, was used for all the experiments. The column was prepared from borosilicate glass in our own laboratory according to the method by Grob [9]. Hydrogen was used as carrier gas at 50 cm s^{-1} linear flow-rate, for all experiments. The splitter flow was permanently set to a value of 50 cm^3 min^{-1}. The only non-standard device used is the vapour generator, described below.

All polarity tests were done isothermally at 50°C with injector and detector at 200°C. The column activity (Grob) test was done at the same detector and injector temperatures with a column oven temperature programme from 50°C to 200°C at a rate of 5°C min^{-1}.

2.2. Continuous introduction of water vapour

The system designed for the controlled addition of water vapour to the carrier gas can be explained with reference to Fig. 1. The basic principle is to provide a controlled flow-rate of carrier gas saturated with water vapour at the same isothermal temperature as the column oven. This stream is then mixed with the conventional, dry carrier gas stream coming from the column head pressure regulator. The water vapour concentration is controlled by setting the secondary hydrogen flow through the flow controller, FC, to any value lower than the splitter flow. As long as this condition is met, no re-condensation of water can take place in the column and no back diffusion of the water into the primary hydrogen supply line will occur. The closer the secondary flow-rate is to the

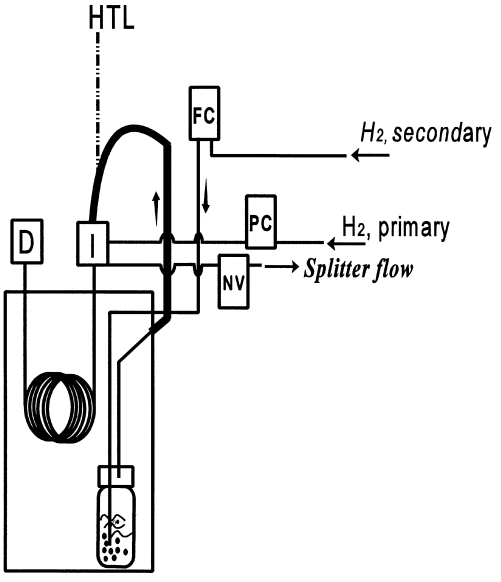

Fig. 1. The water vapour concentration is controlled by setting the secondary hydrogen flow through flow controller (FC) to any value lower than the splitter flow. As long as this condition is met, no back diffusion of the water into the primary hydrogen supply line will occur. PC=Pressure controller; NV=needle valve, D=detector, I=inlet, HTL=heated transfer line.

splitter (+column) flow-rate, the higher the water vapour concentration.

The secondary flow reaches the injector via a heated transfer line kept at 100°C that pierces the septum by means of a needle. This is removed briefly during injection of the sample.

SAFETY WARNING: **The use of hydrogen inside the GC oven is an explosive hazard, especially when using modified systems as described here; a hydrogen leak warning system is essential and special care must be taken to prevent leaks.**

2.3. Monitoring selectivity changes

Our first interest was to observe the changes in the retention times of alcohols relative to that of alkanes and aromatics. Brief tests were, however, also done with acetic acid and some ketones and ethers. Initial non-reproducible results prompted us to check whether the shifts in retention time were also a function of the contact time of the vapour with the stationary phase.

2.3.1. Changes of selectivity over time

This test was done with a secondary hydrogen flow-rate of 42.5 cm^3 min^{-1}, providing a carrier gas almost saturated with water. The test mixture containing methanol, ethanol, propanol, benzene, toluene, xylene (*o*-, *m*- and *p*-isomers), *n*-octane, *n*-nonane, *n*-decane and *n*-undecane, dissolved in hexane was injected at fixed time intervals (see Fig. 2). As it was first suspected the water temperature was not in equilibrium with the oven temperature and that slowly changing vapour concentration was responsible for the shifting of the retention time, care was taken to allow the water temperature to stabilize overnight at an oven temperature of 50°C.

To compare the polarity change with that obtained with glycerol, in the accompanying paper, a mixture consisting of 1-hexanol, *n*-undecane, *n*-dodecane, *n*-tridecane and *n*-tetradecane was injected with dry carrier gas and with the above concentration of water vapour, allowing time for the retention behaviour to stabilize.

Acetone, methyl ethyl ketone, diethyl ether, *tert*.-butyl methyl ether (MTBE), *tert*.-amyl methyl ether (TAME) and acetic acid were also injected with dry carrier gas and with the above concentration of water vapour, allowing time for the retention behaviour to stabilize.

2.3.2. Changes in selectivity with different vapour concentrations

A test mixture of methanol, ethanol, *n*-octane, *n*-nonane, *n*-decane and *n*-undecane in hexane was injected at different volume flow-rates of secondary, moist hydrogen, corresponding to different final vapour concentrations in the carrier gas. Sufficient time was given between settings for the elution profiles to stabilize.

2.3.3. Application to the analysis of alcohol in petrol

As an example of a possible application, petrol samples were analysed. A sample of commercial 91 octane petrol was analysed under dry and moist conditions, as was a sample of the same petrol spiked with 5% (m/m) each of methanol and ethanol. The concentration of alcohols was chosen to be in the range typically sold in blends in the times of local oversupply of alcohols.

2.4. Monitoring the stability of the Carbowax column

The stability of the Carbowax column was monitored using the standard Grob test [10] at regular intervals, after carefully drying the column at 50°C. This is a stringent test for monitoring column efficiency, surface activity and possible loss of stationary phase.

3. Results and discussion

3.1. Changes in selectivity over time and maximum shifts obtained

Fig. 2 shows the chromatograms obtained at 15 min, 1 h and 3 h after changing to the moist carrier gas. No change was observed after about 3 h carrier flow. It is clear that more than an hour is required to completely stabilize the system.

Chromatograms in Fig. 3 are presented to emphasize the extent of the change in polarity between dry (a) and moist (b) carrier gas after 1 h stabilizing

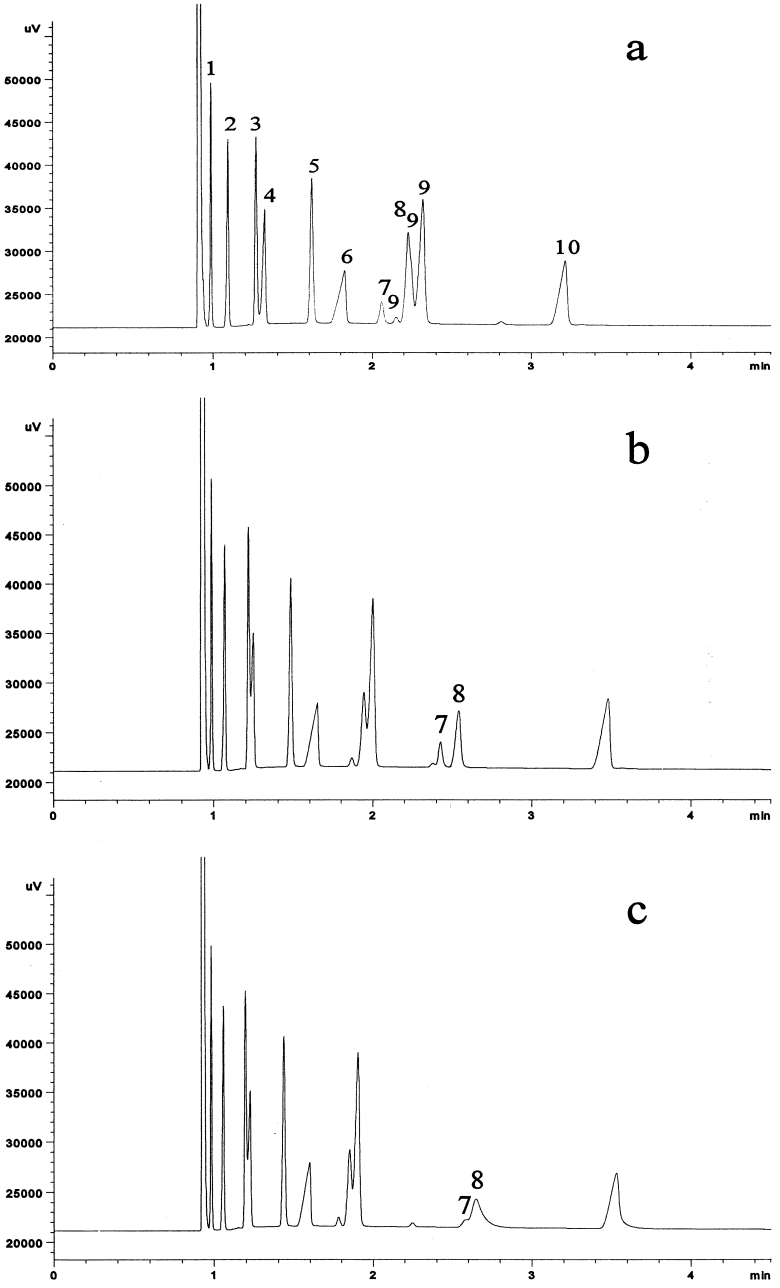

Fig. 2. Isothermal (50°C) chromatograms obtained (a) 15 min, (b) 1 h and (c) 3 h after continuous introduction of 42.5 cm^3 min^{-1} of secondary, moist carrier to the GC inlet with splitter set at 50 cm^3 min^{-1}. Peaks: 1=Octane, 2=nonane, 3=benzene, 4=decane 5=toluene, 6=undecane, 7=methanol, 8=ethanol, 9=xylene (*o*-, *m*- and *p*-isomers), 10=propanol.

time. Both alkanes and aromatics are eluted far quicker under moist conditions whereas there is strong additional retention for the alcohols. Based on this figure, the change in Kovats retention index, ΔI, when going from dry to wet carrier gas, was calculated for the following compounds (ΔI is given

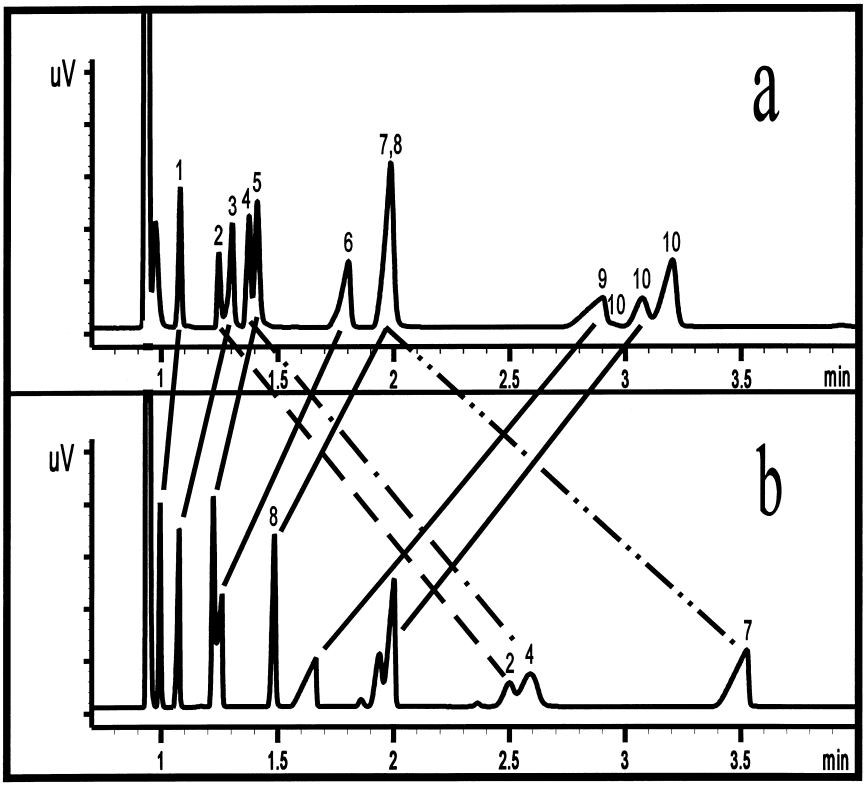

Fig. 3. Isothermal (50°C) chromatogram (a) obtained before and (b) after continuous vapour introduction at 42.5 cm^3 min^{-1} for 1 h. Peaks: 1=Octane, 2=methanol, 3=nonane, 4=ethanol, 5=benzene, 6=decane, 7=propanol, 8=toluene, 9=undecane, 10=xylene (*o*-, *m*- and *p*-isomers).

in parentheses): methanol (353), ethanol (314), benzene (55), toluene (39), *m*-xylene (27). Important to see is that methanol (I=1232) will elute after *n*-dodecane (by Kovats calculation) and far beyond the xylenes under the wet carrier gas conditions. This can be of practical importance to petrochemical analysis as no capillary column is available with this selectivity.

Chromatograms in Fig. 4 show the extent of shift for 1-hexanol from dry (a) to moist (b) carrier gas conditions. It is far more pronounced than that found for the glycerol modified Carbowax column.

With a dead time of 0.9 min the acetic acid eluted on the unchanged (''dry'') Carbowax column in 22 min, increasing to 85 min with water vapour close to saturation. This represents an increase in capacity factor, k, of about a factor 4. The equivalent increase in interaction strength with methanol is about a factor 5. This clearly indicates a strong additional interaction with OH containing compounds, the result of hydrogen bonding with quasi-stationary water in the column. Both alkanes and aromatics show reduced interaction strengths with the modified stationary phase. Acetone, methyl ethyl ketone, diethyl ether, MTBE and TAME showed only a very minor increase in k values (chromatograms not shown).

3.2. Changes in selectivity with different vapour concentrations

The chromatograms in Fig. 5 show the influence of the water vapour concentration on the stationary phase polarity of the Carbowax column. Values between 42 and 50 cm^3 min^{-1} (the latter giving 100% water saturation at the column temperature of 50°C) did not change the elution profiles considerably. Hence it was preferred to work at 42 cm^3

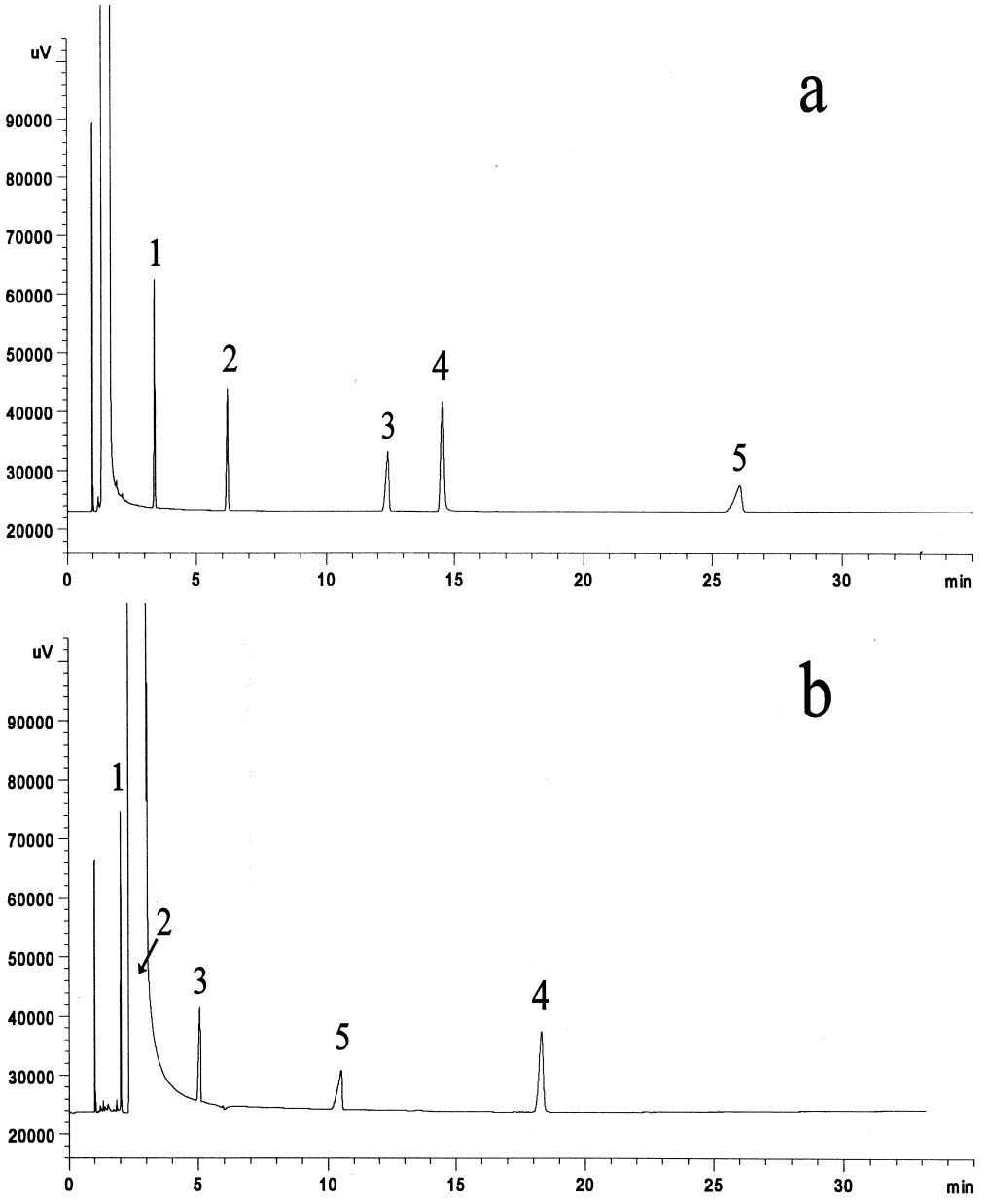

Fig. 4. Isothermal (50°C) chromatogram obtained with (a) dry an (b) moist carrier after stabilization. Peaks: 1=Undecane, 2=dodecane, 3=tridecane, 4=1-hexanol, 5=tetradecane.

min^{-1}, ensuring no water vapour enters the inlet system by back diffusion – a potential hazard to the Carbowax column when it is baked out under ''dry'' conditions and prepared for the Grob test at high temperatures. Traces of water in the carrier gas are known to shorten the lifetime of Carbowax columns at high temperature.

The hump in Fig. 5c corresponds to the returning water profile after brief interruption when the wet carrier line is removed for injection of the sample through the septum. The hump varies in size and could be the result of contaminants desorbed by the water near the FID system. For other possible explanations the reader is referred to the work of

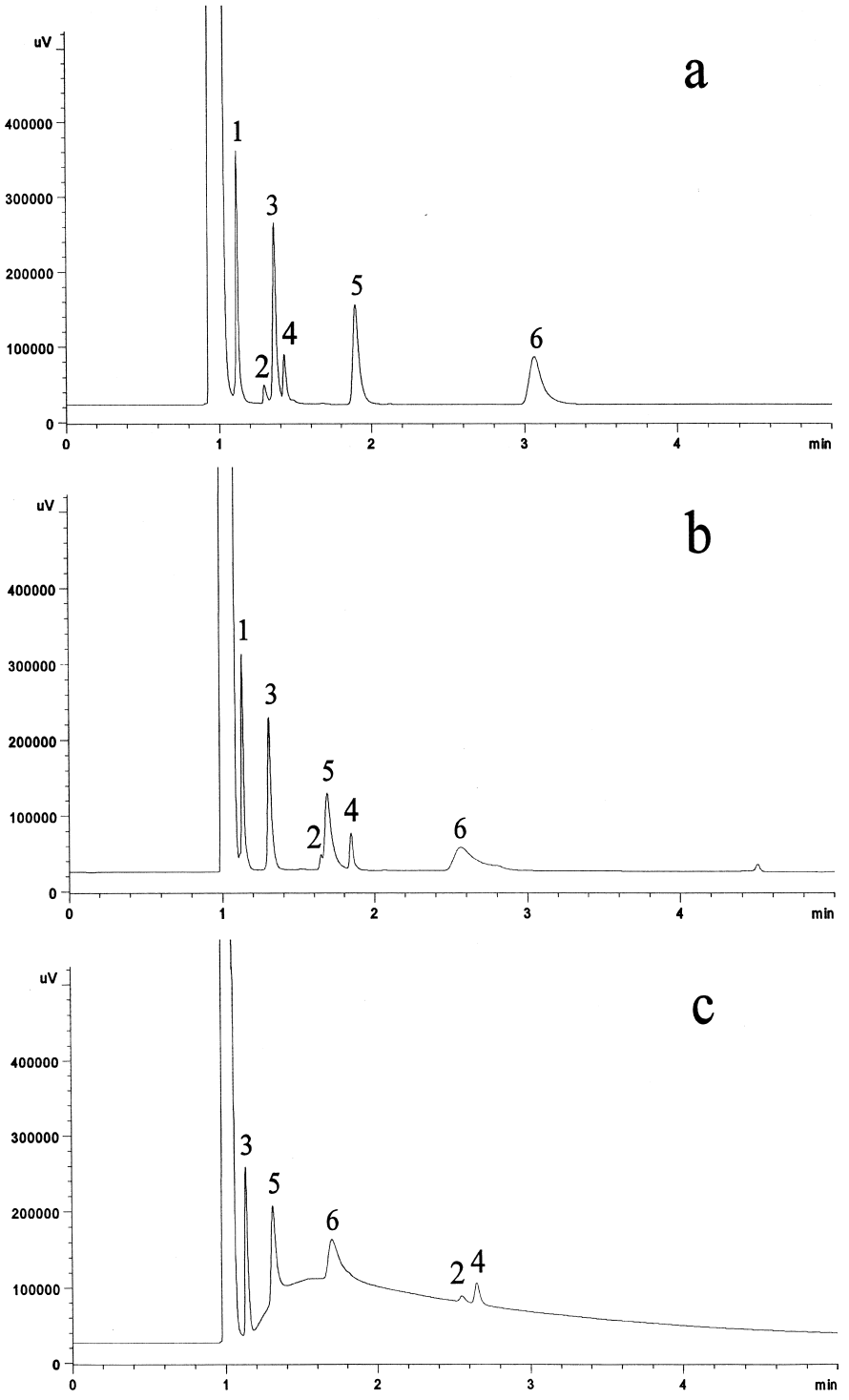

Fig. 5. Isothermal (50°C) chromatograms obtained after 1 h stabilization with (a) no flow, (b) 27 cm^3 min^{-1}, and (c) 42 cm^3 min^{-1}. Peaks: 1=Octane, 2=methanol, 3=nonane, 4=ethanol, 5=decane, 6=undecane.

Grob and Habich [8]. A minor modification to the system, eliminating the requirement for the brief interruption of the moist carrier during injection, should thus be beneficial.

3.3. Application to the analysis of alcohol in petrol

The chromatograms in Fig. 6 show petrol spiked with methanol and ethanol under dry (a) and moist (b) carrier gas conditions after 1 h stabilization. The peak allocation could be done reliably by recording some interim chromatograms during the first hour of stabilization. The gradual alteration of the elution profiles with time is in itself a powerful tool for peak identification. Peak allocation across two chromatograms obtained from different polarity columns cannot normally be done reliably. Note that a number of windows exist in the chromatogram into which the alcohol peaks can be positioned by appropriate choice of the vapour concentration of the carrier gas. This would allow reliable quantitation.

3.4. The stability of the Carbowax column

The chromatograms in Fig. 7 show analysis of the Grob test mixture, before (a) and after (b) the first series of experiments performed under moist conditions. Apart from a slight deterioration of the butanediol peak shape, the rest of the peaks elute without any additional peak tailing – an essential prerequisite for the dynamic modification with water to be used in practise. There is however a slight reduction in the phase film thickness as indicated by the peaks eluting about 2 min earlier. Grob tests done after subsequent experiments with moist carrier were however identical to the one in Fig. 7b, indicating a once-only initial loss of phase.

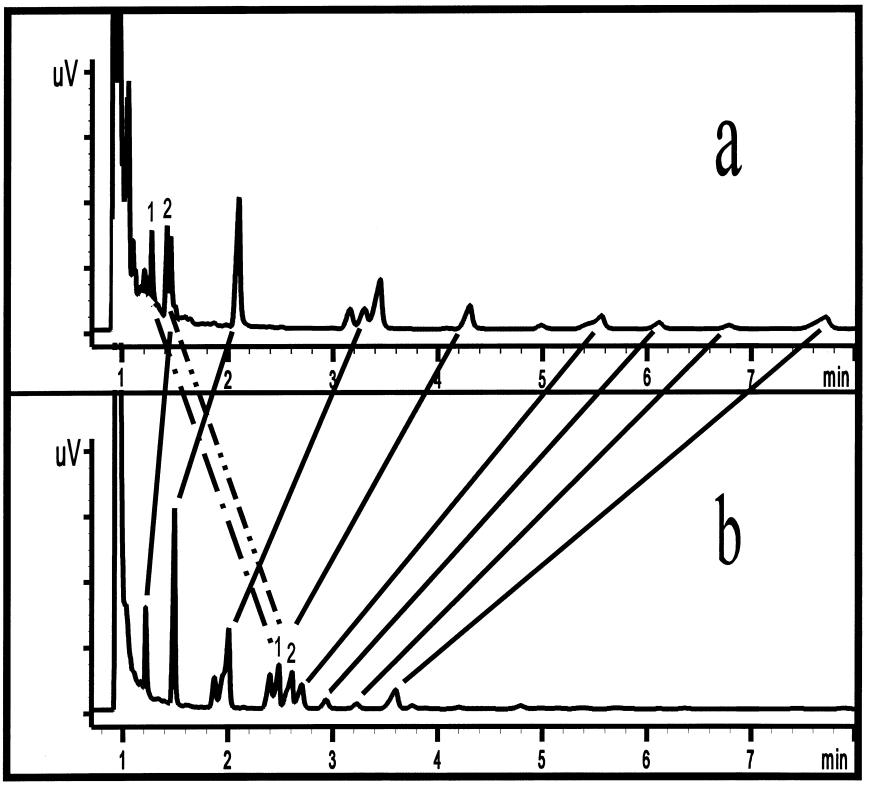

Fig. 6. The sample is a commercial petrol spiked with 5% (m/m) each of methanol (peak 1) and ethanol (peak 2). The isothermal (50°C) chromatogram (a) was recorded with dry carrier gas and (b) was obtained after 1 h stabilization with 42 cm^3 min^{-1} moist carrier. Peak correlation could be made through the gradual monitoring of shifts from chromatograms registered at interim times.

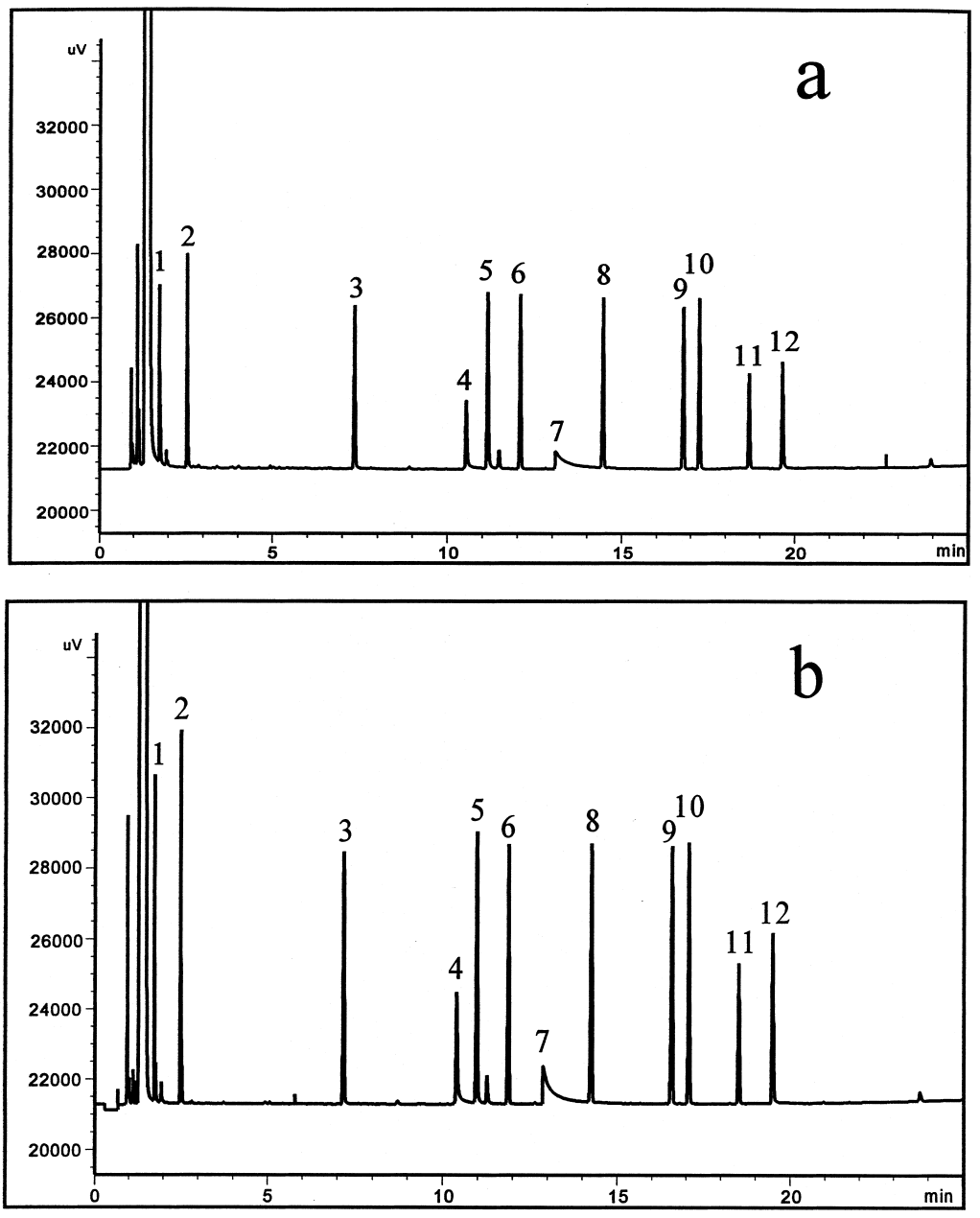

Fig. 7. The chromatograms show the analysis of the Grob test mixture, (a) before and (b) after the series of experiments were performed under moist conditions. Tests were performed after careful flushing of the column overnight with dry hydrogen carrier. Temperature programme: 50°C to 200°C at 5°C.min^{-1}. Peak identification: 1=decane, 2=undecane, 3=nonanal, 4=2,3-butanediol, 5=1-octanol, 6=methyl decanoate, 7=dicyclohexylamine, 8=methyl undecanoate, 9=methyl dodecanoate, 10=2,6-dimethylaniline, 11=2,6-dimethylphenol, 12=2-ethylhexanoic acid.

As all the moist carrier tests have been performed at 50°C (isothermal), no general statement can be made as to the upper temperature limit of the Carbowax column under these harsh conditions.

4. Conclusions

Dynamic modification of a Carbowax 20M capillary column has for the first time been studied with water vapour at concentration levels close to saturation. Drastic changes to the stationary phase characteristics could be shown with the addition of hydrogen-bonding properties not found in conventional columns. The process is reversible, allowing the testing of a multitude of volatile modifiers, provided these do not interfere with the mode of detection. Although itself not strongly retained by PEG phases, water has a remarkably strong effect on the retention of OH-containing compounds in comparison with the glycerol studied in the accompanying paper.

A shift of 351 Kovats retention units is achieved for methanol, which will elute after dodecane under moist carrier conditions. Hexanol can be eluted far beyond *n*-tetradecane – a feat difficult to achieve with conventional high polarity phases as these tend to pull into droplets, even during the manufacturing step. The strong retention of alcohols and organic acids may be of interest for the direct analysis of aqueous samples, for example, beverages containing organic acids and alcohols. Elution should be after the organic flavour compounds and there should be no shifting of retention times due to the water in the sample. The hydrogen-bonding selectivity may be of use in, amongst others, the analysis of alcohol additives in commercial petrol. Controlling the polarity in a continuous way rather than a stepwise manner is of great help with method development. Comparison with the high polarity TCEP column (Alltech) for petrochemical analysis shows that water modified PEG gives higher Kovats indices for alcohols and far lower ones for aromatics. Together, this produces a high selectivity for alcohols in the presence of aromatics. Unlike the TCEP phase which provides dipole interaction with polar and polarizable analytes, the PEG–water phase retains mainly OH-containing compounds by strong hydrogen bonding interactions. As a result, methanol elutes before benzene on TCEP, whereas it elutes far later than xylene on PEG–water.

An interesting aspect of the modification is that stable retention is only achieved after a couple of hours, indicating slow kinetics in the phase ''swelling'' process. This process allows the tentative identification of acids and alcohols in unknown samples, as their increasing retention over time clearly distinguishes them from other peaks. The slow kinetics also correlate with the observation by Grob and Habich [8], that not only the amount of aqueous sample injected but also the time interval between subsequent analyses influences the retention of analytes on Carbowax. With the relatively short ''conventional'' GC retention time of small amounts of water, this would normally not be expected.

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