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Introduction of large volumes of water-containing samples into a gas chromatograph
Improved retention of volatile solutes through the swing system

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Abstract

The swing system is designed for introducing large volumes of water-containing samples into a gas chromatograph. Sample evaporation and solvent–solute separation are performed in separate compartments. This widens the application range to compounds of higher volatility. Sample evaporation takes place in a hot chamber packed with Carbofrit. Solvent–solute separation is performed in a cascade of increasing powers of retention. While high boiling solutes are retained in an oven-thermostatted retaining precolumn, the more volatile components are retained by a packed bed of sorbents of increasing powers of retention situated in a programmed temperature vaporiser. For elution, the gas flow is reversed and the solutes are discharged from the heated packed bed through the retaining precolumn into the separation column.

Keywords: Injection methods; Swing injection system; Programmed-temperature vaporizer; Instrumentation; Fatty acid methyl esters

1. Introduction

The introduction of large volumes of sample in capillary gas chromatography (cGC) has been widely investigated in the last few decades and numerous techniques have been developed. Most are restricted to organic solvents. In the first part of this paper, we summarise previous work on water-containing phases to explain why the swing system was developed.

1.1. Problems with water

The introduction of water-containing samples, e.g. reversed-phase liquid chromatography (RPLC) fractions, is difficult for a number of reasons. Water does not wet surfaces that are suitable for GC, such as uncoated precolumns [1]. This hinders the application of the most efficient reconcentration technique for volatile solutes, i.e. solvent effects. Cold trapping, the only readily available alternative, is hampered by unfavourable conditions; the relatively high boiling point of water requires rather high column temperatures during introduction, and the large volume of vapour per unit volume of liquid means that

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particularly strong band broadening has to be overcome.

1.2. On-column injection

If mixed with an organic solvent, water wets surfaces provided it evaporates at least as rapidly as the organic solvent (water left behind forms an unstable film [2]). On-column injection is therefore possible provided that water concentration does not exceed the azeotropic mixture [3–5] e.g. 28% water in 1-propanol or 16% in acetonitrile. A further problem is the aggressiveness of condensed water, which attacks silica and removes silylation [6,7].

1.2.1. Concurrent evaporation

Concurrent solvent evaporation occurs without the formation of a layer of the sample liquid on a capillary surface. In fact, LC–GC transfer of a 150-μl fraction through the loop-type interface is possible, but the first well-shaped peaks are only eluted at about 240°C, as the consequence of lacking phase soaking supporting the retention of more volatile solutes [8].

An attempt was made to reduce the loss of volatile components by co-solvent trapping. Up to 1 ml of water containing some butoxyethanol was introduced to the GC system [9]. For a volume of 250 μl with 22% butoxyethanol, methyl laurate (E12) was completely retained in the precolumn [10]. A problem which remained unresolved was that the precolumn eventually became adsorptive after attack by water.

1.3. Packed vaporising chambers

Packed vaporising chambers also retain non-wetting liquids. Other materials, such as Tenax and Carbofrit, also resist water. Packings are characterised by higher powers of retention than uncoated precolumns, which require higher desorption temperatures. This strong power of retention may also be an advantage as more volatile components are extracted from the vapours which are discharged through the exit when the sample is introduced.

1.3.1. Programmed-temperature vaporiser solvent split injection

The injection of large volumes of aqueous samples into a programmed-temperature vaporiser (PTV) by the solvent split mode was described by Mol et al. [11]. At 70°C (nominal) injector temperature, an evaporation rate of up to 70 μl min^{-1} was achieved with a carrier gas flow-rate of 600 ml min^{-1}. Engewald and co-workers [12–14] injected water at 10 μl min^{-1} using an injector temperature of 50°C and a gas flow-rate of 600 μl min^{-1}. A 500-μl volume was introduced to analyse triazines in distilled water. The low evaporation rate is due to the large vapour volume and the relatively low vapour pressure, but primarily to the strong cooling of the chamber by the large consumption of heat.

1.3.2. Overflow techniques

The PTV overflow technique was investigated because it self-regulates the effluent flow [15]. With vacuum at the outlet and a temperature of 85°C, an evaporation rate of 80 μl min^{-1} was reached.

Evaporation rates were far higher when classical splitless injection was used with the overflow technique. For the analysis of triazines in water, 400 μl was injected in 2–3 s into a bed of Tenax in an injector thermostatted at 310°C. Evaporation took <10 s, i.e. a rate of more than 2500 μl min^{-1} was reached [16,17]. With 400-μl injections, methyl palmitate was recovered almost quantitatively.

1.4. Vaporisation and solute retention in separate chambers

Up to now, sample (solvent) evaporation and solvent–solute separation (retention of the solutes from the discharged solvent vapours) have been performed in the same chamber. In PTV solvent split injection, solvent evaporation occurs in the same packed bed in which the solutes are retained. This forces a compromise: on one hand, the temperature should be low enough to achieve a high retention power for the solutes; on the other hand, heat consumption for the evaporation of water presupposes a higher temperature. The two functions, can be optimised individually when they are separated [18].

1.4.1. Vaporiser/precolumn solvent splitting

If the vaporising chamber is thermostatted at

temperatures well above the solvent boiling point, evaporation rates can be far higher, since the steep temperature gradient enables a more efficient transport of heat. Boderius et al. [19] showed that with a PTV injector at 300°C, up to 200 μl min^{-1} of water and 300 μl min^{-1} of methanol–water (1:1) can be evaporated.

Optimisation of the second function, retention of the solute material from the discharged solvent vapours, results in a capillary precolumn. The solvent vapour outlet is no longer the split line of the injector, but a vapour exit like that for large volume on-column injection or on-line LC–GC. Solvent trapping, which presupposes partial recondensation of the solvent in an uncoated precolumn, is the most efficient way of retaining the solute. This is also the best method for analysing high boiling sample components: the extremely high retention power built up by the sample (solvent) layer while the volatiles are retained disappears when the solvent has evaporated and no longer hinders volatilisation of high boilers. An uncoated precolumn and solvent trapping therefore provides a near-perfect analysis from the volatile to the high boiling compounds.

As no sample film can be formed with aqueous samples, solvent trapping cannot be applied. Only permanent retention power can be used, such as that from a coated ('retaining') precolumn. As long as thermostated in the same oven, the maximum retention power corresponds to that of the separation column. This is in fact rather modest: when 100 μl of fatty acid methyl esters and alcohols were injected in water at 100 μl min^{-1}, methyl stearate was only partially recovered [18]. This makes improvement desirable and this is why the swing system was developed.

2. Concept of the swing system

Permanent retention power is substantially higher from packed beds such as Tenax. These improve the retention of the volatiles, but also hinder desorption of the other compounds. High boiling solutes are lost, and the increased desorption temperatures cause unstable compounds (e.g. many pesticides) to decompose.

2.1. Cascade of retention power

The problem outlined above is avoided when the retention power is increased stepwise: the high boiling solutes are retained in a zone of rather low retention power. The more volatile compounds breakthrough this weak trap and are extracted into beds packed with materials of increasing retention power. Similar systems are used as traps for analysing air.

The first step in the cascade was a coated capillary column of 0.53 mm I.D., which, during solvent evaporation, allowed flow-rates of around 200 ml min^{-1}. Retention power was slightly lower than with the separation column because the broadening of the band, caused by the extremely high flow-rate when the sample was inserted, must be reconcentrated at the inlet of the separation column by a weak retention gap effect.

When the sample is introduced, solute retention increases as the temperature of the oven decreases. The lowest oven temperature is the dew point of the gas–vapour mixture: below this limit, water recondenses. Hot water may attack the stationary phase and remove the more water-soluble components. Tedious optimisation of this temperature is not critical, however, because the solute material breaking through the retaining precolumn is recovered by the next trap.

Solutes must be desorbed from traps with high retention power at temperatures above that of the oven. Packings of Tenax and Carbotrap were placed in a PTV injector. Minimum temperature requirements are the same as for the retaining capillary, i.e. the packed bed can be oven-thermostatted when the sample is introduced.

2.2. Desorption in reversed flow

Desorption from a cascade of retention elements requires that the flow direction be reversed: the high boilers trapped in the chamber with the lowest retention power must leave it backwards to avoid contact with the more strongly retaining chambers.

During sample introduction, the 'swing system' feeds the carrier gas from the vaporiser through the retaining precolumn into the packed PTV chamber (Fig. 1). For desorption and analysis, the system

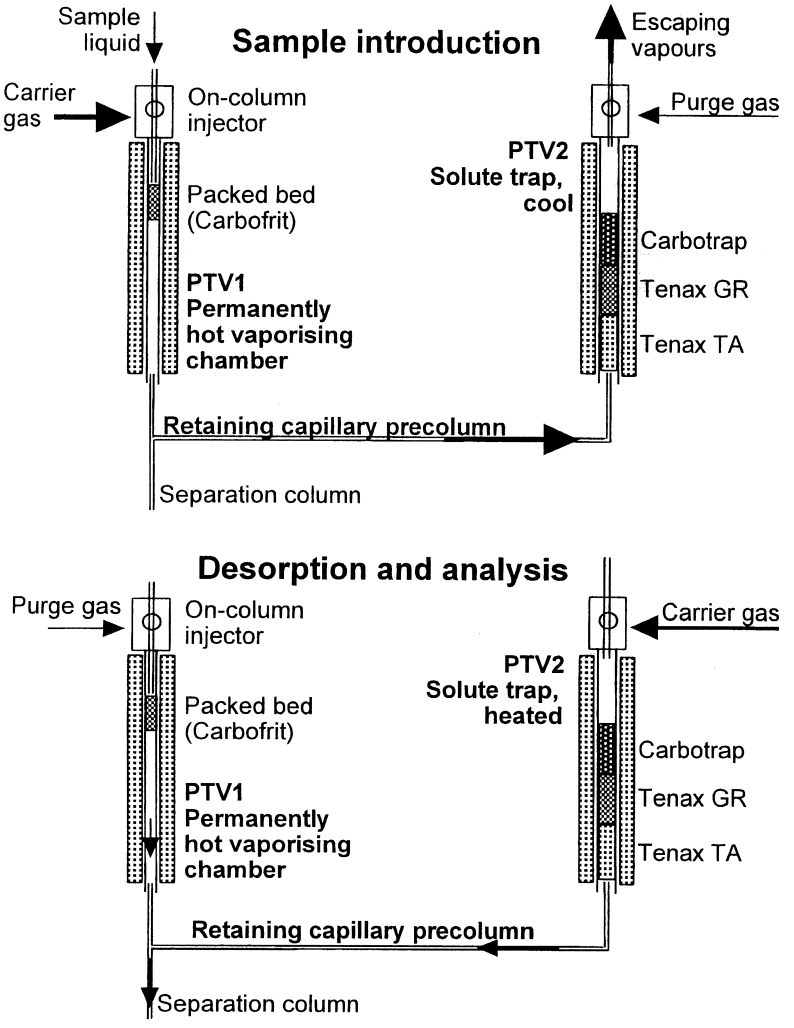

Fig. 1. Swing system in the injection and the desorption mode.

swings backwards: the carrier gas now drives the volatile solutes from the packing with the highest retention power through the weaker ones and the retaining precolumn into the separation column.

2.3. Supply of sample

The sample liquid was introduced at controlled flow-rate, as with an HPLC pump or an autosampler with adjustable injection rate. It entered the vaporising chamber through a narrow bore capillary to minimise evaporation inside the transfer line. The capillary ended on top of the packing to ensure continuous evaporation (and prevent droplets from falling onto the hot packing). The packing was positioned near the upper end of the heated zone to keep the heated section of the transfer line short. It must be of low resistance against the gas flow and must chemically resist water.

2.4. Pneumatics of the vaporiser (PTV1)

When water or water–methanol is injected at a rate, e.g. of 100 μl min^{-1}, vapours are produced at almost 100 ml min^{-1}. The flow-rate must be high enough to discharge this vapour safely and possibly

dilute it with carrier gas to reduce the dew point. As evaporation is not always smooth or constant, the system must cope with temporarily higher rates of vapour formation. Finally, vapours of water and methanol are more viscous than hydrogen (the carrier gas used). For these reasons, the gas flow-rate was adjusted to at least twice the rate of vapour formation (around 200 ml min^{-1}).

The gas supply was designed to produce an approximately constant flow-rate. This allowed conditions to be adjusted, rendered the flow-rate independent of the evaporation rate, and eliminated the danger of high vapour pressure stopping or even reversing it. An inlet pressure far above that for chromatography was applied onto a flow restriction.

During desorption and gas chromatographic separation, the vaporising chamber was purged inwards to the column. This was preferred to a purge outwards through the top of the vaporiser because it ensured that high boiling solute material deposited in the T-piece protruding from the heated injector reached the separation process. The restriction in the carrier gas supply line was exchanged for a far stronger one (switching a rotating valve), feeding carrier gas at a low flow-rate. A minor proportion of it purged the sample supply line outwards, while the rest went into the separation column.

Backflush of the sample line passed through a small vial that collects the liquid: since water-containing solvent mixtures are extremely viscous, they easily plug the narrow bore capillary that serves as a restriction.

2.5. Pneumatics of the trap (PTV2)

The gas supply to the trap (PTV2) was pressure-regulated, but with a restriction to limit the flow-rate. During injection, with the vapour exit open, the flow-rate was restricted to 25 ml min^{-1}. This purged the exit and prevented vapours from entering the supply line. During chromatography, this restriction had no effect since the flow-rate was low.

The trap (PTV2) contained a wide (2 mm I.D.) liner with short plugs of packing to keep the resistance against the gas and vapour flow to a minimum. This minimises pressure at the T-piece below PTV1 and keeps the flow-rate in the separation column low. With a column flow-rate of about 0.5 ml min^{-1} and discharge of the vapours at 200 ml min^{-1}, the split ratio in the T-piece was about 400:1, i.e. 0.25% of the sample entered the separation column during sample introduction.

3. Experimental

3.1. Reagents and standards

The system was tested with a mixture containing methyl esters of the fatty acids C_6 to C_{28} (E6 to E28, Fluka, Buchs, Switzerland). Stock solutions of 100 mg l^{-1} were prepared in hexane, 1-propanol and methanol. Working solutions were prepared daily by diluting the stock solutions with hexane, 1-propanol or methanol–water (1:1). Solutions in methanol–water showed rapidly decreasing peak areas for E24 to E28 because of low solubility.

3.2. Instrumentation

The system was constructed on a Carlo Erba (Milan, Italy) 5300 gas chromatograph equipped with two on-column injectors and PTV injectors mounted to the bottom of the on-column injectors (i.e. inside the oven), and a flame ionisation detection (FID) system. Data were recorded on a D-2500 integrator (Merck, Darmstadt, Germany).

3.2.1. PTV injectors

The vaporiser consisted of a permanently heated PTV injector (PTV1). This contained a 7.50 cm×1 mm I.D.×1.5 mm O.D. glass liner packed with 2 cm of Carbofrit (Restek, Bellefonte, PA, USA) positioned 2 cm below its upper end. At the lower end, the packing material was kept in place by a piece of glass-fibre filter of about 1 mm thick (from a cigarette smoking machine). At the upper end, a 4 mm piece of a 0.5 mm I.D.×0.9 mm O.D. glass capillary was fused into the liner. To the bottom end of the glass liner, a press-fit T-piece was fused with a 2 cm piece of 0.53 mm I.D. fused-silica capillary from which the polyimide had been removed. The length of the liner plus the upper leg of the press-fit T-piece corresponded to the length of the PTV body (10 cm), avoiding cold zones.

A 100 mm×2 mm I.D.×2.8 mm O.D. glass liner

was installed in PTV2. About 2 cm above its bottom, this liner was packed with 1 cm of Tenax TA, 1 cm of Tenax GR and 0.5 cm of Carbotrap, which was kept in place with plugs of glass-wool.

The retaining precolumn between PTV1 and PTV2 consisted of a 50 cm×0.53 mm I.D. capillary coated with a 0.5-μm film of PS-255 (a methylpolysiloxane, Fluka) or a 25-cm section of the same capillary elongated by a 25 cm×0.53 mm I.D. deactivated uncoated fused-silica capillary. The 20 m×0.25 mm I.D. separation column was coated with an 0.6-μm film of PS-255.

3.2.2. Pneumatics

The carrier gas (hydrogen) was supplied to the vaporising chamber, PTV1 in Fig. 2, at 250 kPa. Between the manometer and the on-column injector, a rotating switching valve (V1) was installed. During injection, the gas passed through a 280 cm×0.25 mm I.D. fused-silica tube (restriction R1) at about 240 ml min^{-1}. For desorption and separation, the valve was switched to a 15 cm×50 μm I.D. fused-silica tube (restriction R2). The gas was supplied to the trap (PTV2), at 50 kPa through a 1.5 m×0.25 mm I.D. steel capillary tube (restriction R3).

3.2.3. Supply of the sample

The test samples were introduced through the switching valve (V2) with a 100-μl sample loop (0.53 mm I.D. fused-silica tube). The loop content was driven through a 25 cm×0.1 mm I.D.×0.17 mm O.D. fused-silica capillary and the on-column injector into the vaporiser (PTV1) by a syringe pump (Phoenix 20, Carlo Erba) that fed methanol–water (1:1). The injector was closed with a cap designed for the LC–GC on-column interface of the Dualchrom 3000 (Carlo Erba).

The transfer line was backflushed through an 0.8-ml autosampler vial, connected to V2 by a short 0.32 mm I.D. fused-silica capillary inserted through the septum. A 1 m×50 μm I.D. fused-silica capillary was the restriction at the outlet; it allowed around 0.05 ml min^{-1} to pass. Some two-thirds of the autosampler vial were filled with methanol to keep the gas phase saturated with vapour.

For injections of hexane, the autosampler vial was removed, because hexane did not plug the restriction

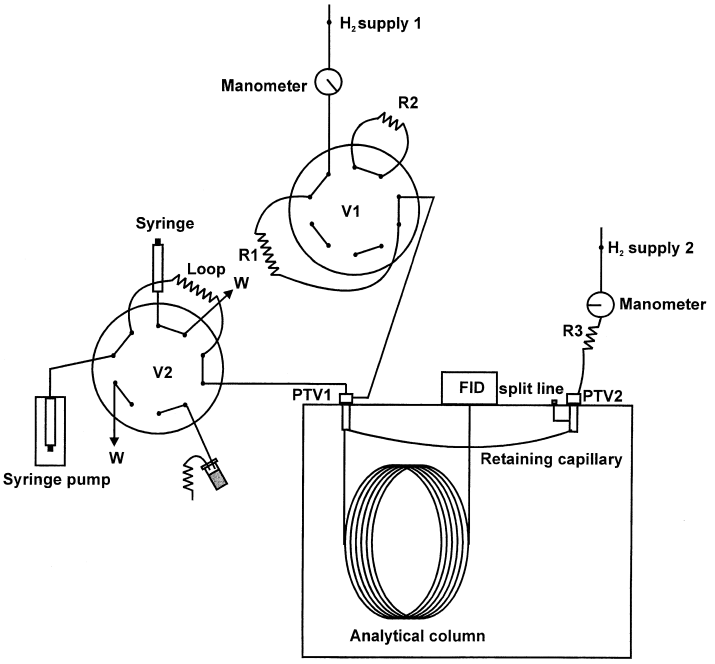

Fig. 2. Experimental set-up. R1, R2, R3: restrictions; W: waste; V1, V2: valves.

and because the higher vapour pressure meant that an increase in temperature was needed to push hexane vapours backwards into PTV1.

3.3. Procedure

3.3.1. Introduction of the sample

The sample loop was filled manually with the text mixture. The loop content was transferred to the GC by pumping methanol–water (1:1). Restriction 1 (R1) in V1 directed the carrier gas from PTV1 to PTV2 and through the opened valve of the on-column injector. PTV1 was at 300°C. PTV2 was at the oven temperature (80°C for samples in hexane and 100°C for those in methanol–water). An FID system estimated the time needed to eliminate most of the solvent vapour.

3.3.2. Desorption

After the solvent vapours were discharged, the carrier gas flow was reversed and the analytes swept into the analytical column. The outlet of the on-column injector was closed and V1 switched to R2, thus purging PTV1. PTV2 was then heated to 300°C and the GC program started. After 3 min, the oven temperature increased to 300°C at 10°C min^{-1}; 30 s after PTV2 had reached 300°C (the FID signal came back to the initial value), the split line was opened (6 ml min^{-1}).

4. Results and discussion

4.1. Displacement of the packing in PTV1

After the first large volume injections of the methanol–water solution, a decrease in peak areas, mainly of the medium and later eluted compounds, was observed. The upper end of the packing in PTV1 was not secured and most of the Carbofrit displaced upwards, leaving an almost empty liner. This was probably due to the violent evaporation in the hot chamber.

Glass wool or a piece of glass-fibre filter did not withstand the displacement of the packing material. The problem was solved by fusing a piece of glass capillary into the liner above the Carbofrit. The transfer line passed through it and ended on top of the packing.

4.2. Retention of analytes

Fig. 3 shows in which part of the vapour outlet the solutes were retained. A 50-μl volume of a solution in methanol–water (1:1) was injected at 50 μl min^{-1}. During sample introduction, the oven was at 120°C. The 50 cm×0.53 mm I.D. retaining pre-column was used. E10 to E20 formed sharp peaks. They were retained in the packing material of PTV2. This was confirmed by their absence when the packing material of PTV2 was removed. E22 formed a broadened peak, while those of the later eluted components became sharper again. These compounds were trapped in the retaining precolumn. E22 was spread over the whole length, and hence formed an initial band 50 cm long. The higher esters were retained in a shorter section of the precolumn.

Peak broadening of components trapped in the precolumn can be avoided by shortening the retaining precolumn (since E22 passes into PTV2) or by

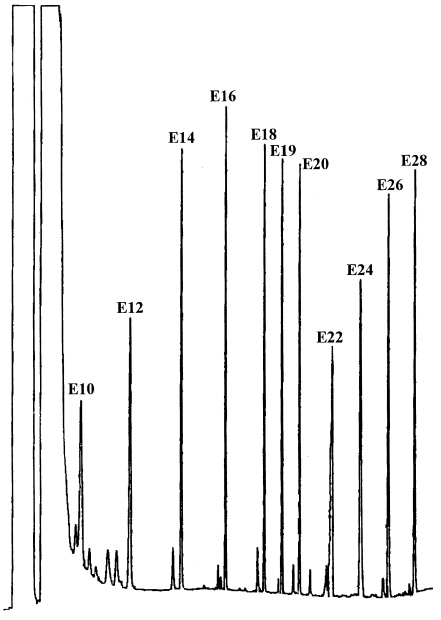

Fig. 3. Chromatogram from 50 μl of a solution of 1 mg l^{-1} in methanol–water (1:1) at 50 μl min^{-1}. For other conditions see text. Most minor peaks in Figs. 3–7 are sample impurities.

reducing film thickness in order to obtain a reconcentration in the inlet of the separation column by the retention gap effect.

Fig. 4 shows chromatograms obtained when there is no packing in PTV2. In Fig. 4a, the retaining precolumn was the same as in Fig. 3: 50 cm×0.53 mm I.D. In Fig. 4b, it was shortened to 25 cm, with a 25 cm×0.53 mm I.D. deactivated uncoated fused-silica capillary added to reach PTV2. During the injection, the oven was at 100°C; 100 μl of methanol–water solution was injected at 100 μl min^{-1}. E6 to E16 were lost. The lower oven temperature than in Fig. 3 increased the retention power of the retaining precolumn so that it trapped more than half of the E20. The peak was again broad owing to spreading throughout the precolumn. When the coated section of the precolumn was reduced to half (Fig. 4b), E20 became sharper, but its area decreased. Later eluted peaks were also sharp in Fig. 4a because these

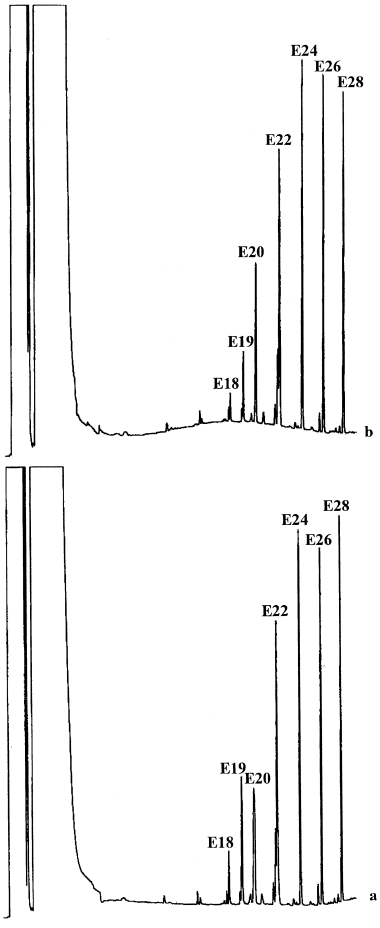

Fig. 4. Chromatograms from 100 μl of a solution of 0.5 mg l^{-1} in methanol–water (1:1) at 100 μl min^{-1} with a retaining capillary of: (a) 50 cm×0.53 mm I.D. coated with a 0.5-μm film of PS-255; (b) 25 cm×0.53 mm I.D. coated with a 0.5 μm film of PS-255 plus 25 cm×0.53 mm I.D. deactivated uncoated fused-silica capillary. For other conditions see text.

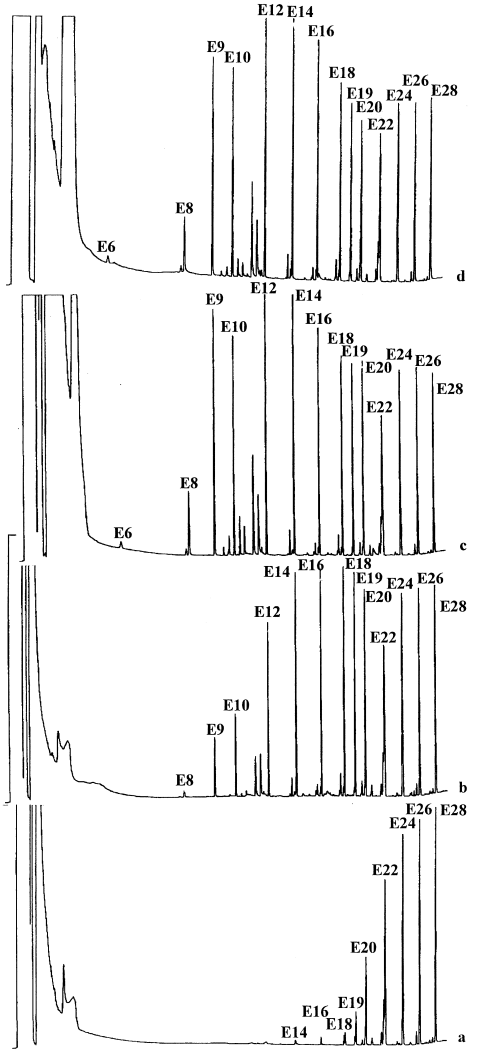

Fig. 5. Chromatograms from 100 μl of a solution of 0.5 mg l^{-1} in methanol–water (1:1) at 100 μl min^{-1} using a liner in PTV2 packed with: (a) empty liner; (b) 1 cm of Tenax TA; (c) 1 cm of Tenax TA plus 1 cm of Tenax GR; (d) 1 cm of Tenax TA, 1 cm of Tenax GR and 0.5 cm of carbon. For other conditions see text.

components were retained in the inlet of the precolumn. The results shown below were obtained with the 25 cm retaining precolumn.

Fig. 5 shows how the packing of PTV2 affect the retention of volatile solutes. 100 μl of a solution in methanol–water (1:1) was injected at 100 μl min^{-1}, with the oven at 100°C. Before reversing the gas flow, the oven cooled to 40°C to separate the volatile components from the solvent better. Fig. 5a was from an empty liner. E14 to E20 were increasingly retained by the retaining capillary. Fig. 5b, with 1 cm of Tenax TA in the liner, shows strong improvement. For Fig. 5c, 1 cm of Tenax GR was added. Here E6 is visible and quantitative peak areas were obtained starting from E9. Adding Carbotrap (Fig. 5d) did not noticeably improve retention. This was not because of excessive adsorption to the Carbotrap, as shown by the fact that desorption at 350°C for 2 min did not improve the result.

4.3. Oven temperature

The lower the temperature of the retaining precolumn and PTV2, the stronger the retention of the volatiles. However, oven temperature must exceed the dew point of the solvent (methanol–water, 1:1) to avoid recondensation. Fig. 6 shows the chromatogram obtained by injecting 100 μl of the methanol–water (1:1) solution at 50 μl min^{-1}, and keeping the oven at 80°C. This temperature was decreased to 40°C before the flow was reversed. The peak areas of E8 and E9 increased by 16 and 30% more than with injection at 100°C, respectively.

The minimum oven temperature, i.e. the dew point of the solvent vapours, is determined by the injection rate: a higher rate reduces dilution of the vapours. In fact, injection at 100 μl min^{-1} required the oven to be at 100°C.

4.4. Sample volume

To check whether the system works for large sample volumes, 500 μl were injected (Fig. 7). The sample in methanol–water (1:1) (0.1 mg l^{-1}) was injected at 100 μl min^{-1} and an oven temperature of 100°C. The oven was cooled to 40°C before the flow was reversed. More volatiles were lost because of the

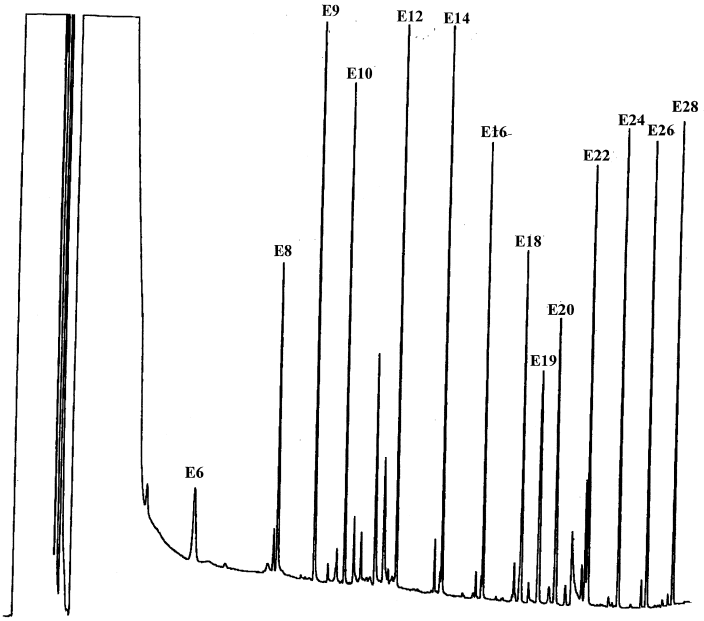

Fig. 6. Chromatogram from 100 μl of a 0.5 mg l^{-1} sample in methanol–water (1:1) at 50 μl min^{-1} with an oven temperature of 80°C. For other conditions see text.

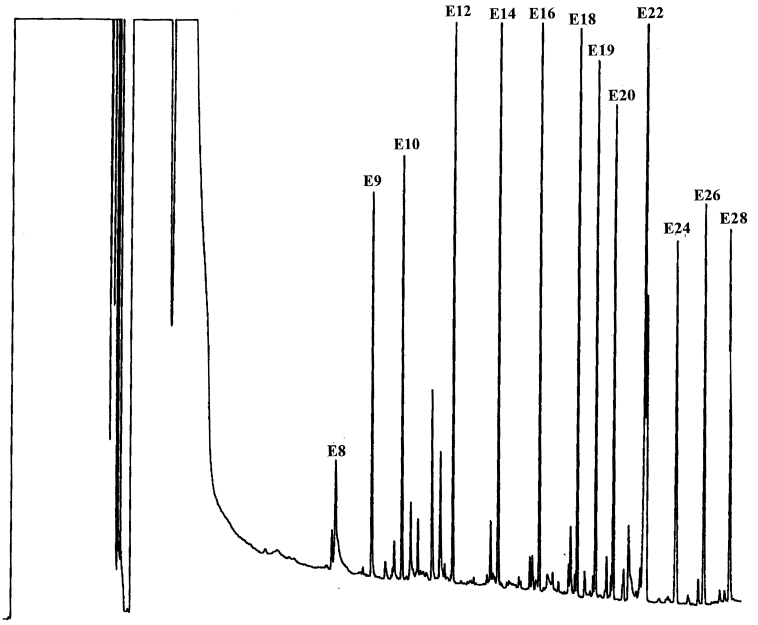

Fig. 7. Chromatogram from 500 μl of a solution of 0.1 mg l^{-1} in methanol–water (1:1) at 100 μl min^{-1}. For more conditions see text.

larger volume of vapour driving them through the traps. E8 to E28 were determined.

4.5. Recoveries

Peak areas obtained by 100 μl injections (0.5 mg l^{-1} in methanol–water) at 100 μl min^{-1} were compared with those obtained by a manual 2 μl injection of a more concentrated solution in 1-propanol (25 mg l^{-1}). The oven, PTV1 and PTV2 were kept at 80°C. PTV1 was then heated to 300°C and, after elution of the solvent (observed by the FID), analysis was started as usual. Quantitative recoveries were obtained for analytes beyond E9 (Table 1). Relative standard deviations for the well-retained components were between 2 and 3% (n=6).

Table 1
Recoveries of 100 μl injections at 100 μl min^{-1} and reproducibility of the system

Compound	Recovery (%)	RSD (%)
E6	5	8
E8	39	8
E9	89	6
E10	94	3
E12	96	2
E14	94	3
E16	90	2
E18	93	3
E19	92	3
E20	92	2
E22	94	2
E24	93	2
E26	91	4
E28	91	5

5. Conclusions

The swing system was conceived for the large volume injection of water-containing samples or on-line transfer from RPLC. It adds a packed column to the vapour outlet of the vaporiser/precolumn solvent split system and greatly improves performance for the more volatile components: while methyl stearate was the first component which could be quantitated, it is now methyl nonanoate.

The swing system competes with alternative techniques, such as on-line extraction with an organic solvent or phase switching through a packed bed (solid-phase extraction–GC) [20]. The advantage of

phase switching is that nonvolatile materials, such as salts and humic acids in natural waters, can be eliminated. The swing system is expected to be highly competitive in on-line RPLC–GC, where extraction is more difficult. Solvent evaporation is not a partitioning process and leaves all the solute material in the GC system, provided that the boiling point is sufficiently high. It is therefore a suitable process for GC.

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