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Review

Direct coupling of reversed-phase liquid chromatography to gas chromatography

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Abstract

Direct approaches for coupling reversed-phase liquid chromatography to gas chromatography are reviewed. The following four main solutions have been devised to overcome the problems of direct injection of large volumes of water to the GC: retention gap techniques using retention gaps with special deactivation, loop-type interface, programmed temperature vaporizer interface and vaporizer interface. Advantages and disadvantages of the different solutions are discussed. The paper has been written from the viewpoint of practical use.

Keywords: Reviews; Liquid chromatography–gas chromatography; Interfaces, LC–GC

Contents

1. Introduction

The aim of coupling of liquid chromatography (LC) to gas chromatography (GC) is to minimize manual sample pretreatment, which is usually required before chromatographic analysis. The LC–GC coupling allows the high sample capacity and wide flexibility of LC to be coupled with the high

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separation efficiency and many selective detection methods available in GC. The sample preparation, that is, the clean-up and preconcentration, can be done selectively by LC, and the final separation by the more efficient GC.

A large number of the samples has an aqueous sample matrix, including most biological samples and many environmental samples. Coupling of reversed-phase (RP) LC to GC is more complicated than coupling of normal-phase (NP) LC but for taking advantage of the whole range of analytical possibilities, RPLC–GC coupling is required. The problems in coupling arise from the aqueous eluents used in RPLC. Water is not a suitable solvent for GC as it hydrolyses the siloxane bonds in GC columns causing re-activation of silylated surfaces and deterioration of the stationary phase. Furthermore, the properties of water are not good for retention gap techniques: water has a poor ability to wet the surface of the retention gap and does not swell any of the commonly used stationary phases. Added to this, water forms a very large volume of vapour per volume of liquid more than seven-times as much as hexane, for example. One further disadvantage of direct injection of aqueous eluents is that salts and non-volatile matrix constituents will be introduced into the GC system, where they will interfere with the performance of the system.

The problems of RPLC–GC coupling have been tackled in two ways. Direct solutions to the problem of aqueous eluents rely on special techniques [1–18], whereas indirect solutions avoid them by phase switching, i.e., replacing the water with suitable organic solvent before the GC analysis [19–26]. For routine applications, a direct approach seems to be more tempting, as it is simpler and less complicated than indirect solutions. Four main solutions have been devised to overcome the problems of direct injection of large volumes of water to the GC, namely retention gap techniques using special retention gaps [1–4], loop-type interface [5–7], programmed temperature vaporizer (PTV) interface [8–11] and vaporizer interface [12–14]. In this review, different solutions of direct large volume RPLC– GC coupling are described excluded micro-RPLC–GC coupling. The emphasis is on the RPLC–GC technique with vaporizer/pre-column solvent split/gas discharge interface.

2. Direct coupling of RPLC to GC

2.1. On column interface: retention gap techniques using retention gaps with special deactivation

In the on-column interface the sample fraction is pushed by the LC pump in the flow of the carrier gas through the on-column injector to the retention gap. The sample is usually injected below the pressure-corrected boiling point of the solvent and the solvent is evaporated in the retention gap. The length of the retention gap can be shortened or the fraction volume increased by using partially concurrent solvent evaporation (PCSE) technique, in which most of the solvent is evaporated concurrently during the injection [27].

The drawback of the transfer techniques is that three interdependent parameters have to be optimized: length of the flooded zone determining the length of the retention gap, the transfer rate and the rate of evaporation of the solvent. If a solvent vapour exit is used, the closure of the exit is critical. Dirty samples containing non-volatile impurities may also be problematic since the impurities tend to remain on the wall of the retention gap, changing the retaining power of the pre-column.

Retention gap techniques rely on the wettability of the retention gap with the solvent. If the wettability is not sufficient, the film is not uniform, the flooded zone increases in length and becomes unstable, and it is then impossible to estimate reliably the required length of the retention gap. The length of the flooded zone is dependent not only on the sample volume but also on temperature, pressure, viscosity and surface tension of the liquid; inner diameter of the pre-column; and the injection rate. Water is a tricky solvent for retention gap techniques; because of its high surface tension, it does not wet properly any of the commonly used deactivated retention gaps.

Retention gap techniques with the on-column interface can be used for coupling LC to GC. In fact, for NPLC–GC, this approach is often preferred, as it allows analysis of both volatile and non-volatile solutes. Deactivation of the retention gap for polar compounds and different solvents is necessary to obtain good wettability and create good peak shapes. Furthermore, the deactivation should be both thermostable and chemically stable.

As mentioned earlier, water does not wet the surfaces of commonly used retention gaps, and in addition, the large vapour volume of water makes the evaporation process very time-consuming. The most serious problem with water, however, is that water hydrolyses the deactivation layer thus producing active sites inside the retention gap. A few special applications have been reported in which retention gaps have been coated with Carbowax-type phases [1–4].

One approach to improve the wettability is to add an organic solvent to the water [5]. The organic solvent must have a higher boiling point than water, or it will evaporate first, leaving water droplets on the wall of the capillary which, in the flow of carrier gas, could accumulate and flush the whole column. Azeotropic mixtures are useful, because their boiling point is virtually independent on pressure changes.

Retention gap techniques are not yet of practical use for direct coupling of RPLC and GC because of the lack of water-resistant deactivation of the retention gaps. Although some successful applications of RPLC–GC methods with retention gap techniques have been reported [1–4], also failures of these retention gaps to withstand water in the long run have been reported [28–30].

2.2. Loop-type interface with concurrent eluent evaporation

The loop-type interface has been specially designed for LC–GC coupling [31]. The interface is usually used with fully concurrent eluent evaporation (FCSE) techniques, where the solvent is concurrently evaporated during the injection. The oven temperature is kept above the boiling point of the solvent at the applied inlet pressure. The vapour pressure of the evaporating solvent quickly exceeds the inlet pressure and stops the plug of liquid from entering further into the retention gap. The vapours leave the column by expansion (vapour overflow technique) and the carrier gas flow starts only after the evaporation is completed. Concurrent eluent evaporation volatilizes all of the solvent during the transfer and virtually no liquid floods to the GC column. Since there is no solvent trapping, volatile components are either lost by co-evaporation with the solvent if a solvent vapour exit (SVE) is used or else they give rise to broadened peaks.

With this technique, no wettability is required and aqueous eluents can be transferred directly to GC. The deteriorating effect of water is far less pronounced when the water is in vapour form. The limitation of the system is that, in the absence of solvent and phase soaking effects, it is practically impossible to analyse volatile analytes. With concurrent eluent evaporation of aqueous eluents, the first perfect peaks elute some 100–150°C above the transfer temperature. Therefore, only solutes with elution temperatures above 230–260°C can be analysed [32]. With co-solvent trapping the volatility range can be widened to solutes eluting above 110–140°C as has been described using butoxyethanol as co-solvent [5,6].

2.3. Programmed temperature vaporizer

Direct transfer of aqueous effluents can also be accomplished with the PTV interface although it has not yet widely been applied in RPLC–GC coupling [8–11].

In transfer of large sample volumes in a PTV injector, the split valve is open during the transfer of sample fraction. The solvent is selectively eliminated via the split valve, while less volatile analytes are retained on the packing material. An additional purge time is used to remove remaining solvent from the liner, after which the analytes are thermally desorped from the liner and transferred into the GC column. The important parameters to be taken into account are the design of the liner, the initial liner temperature, the inlet pressure, the purge flow-rate, the transfer flow-rate, the additional purge time, the sample volume and solvent properties [33,34].

With water, it is neither possible to use sub-zero initial conditions, nor create a solvent film in the porous glass bed inside the liner, which are the typical ways to reduce the losses of volatiles in PTV techniques. Therefore, liners packed with adsorptive materials, such as Tenax, have to be used, which in turn restricts the analysis of high-boiling compounds. In principle, there are two ways to separate water from the analytes in the liner of the PTV, either by evaporation or non-evaporative mode. The liner is

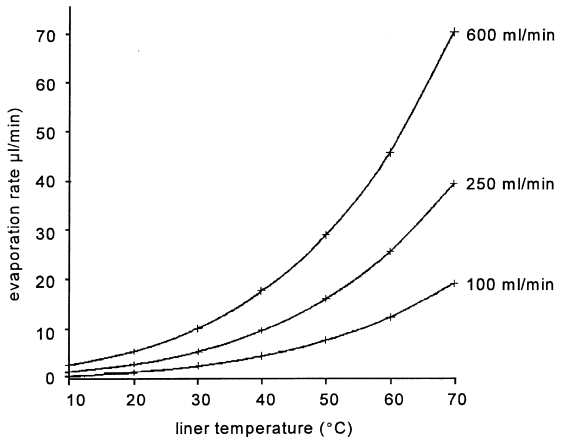

Fig. 1. Evaporation rate of water as a function of linear temperature and purge flow-rate (from Ref. [9]).

packed with suitable material, and it acts as a GC pre-column or as solid-phase cartridge, respectively.

The PTV interface with evaporative mode is limited to relatively small fraction volumes because of the slow evaporation of water at temperatures below the boiling point. The solvent evaporation rate is dependent on the saturated vapour volume under given conditions, i.e., at given inlet pressure and temperature. At 20°C, for example, the saturated vapour volume for 1 μl of solvent is 0.4 ml for pentane, 1.2 ml for *n*-hexane, 4.8 ml for methanol, 7.1 ml for 1,4- dioxane and 59.6 ml for water [33]. This means that elimination of water will require more than eight-times as much time as 1,4-dioxane, even though it has a similar boiling point with water (b.p. 101°C). It is possible to increase the evaporation rate by increasing the purge flow, however, the rate of evaporation is still slow (Fig. 1). In practice, the evaporation rates are even lower than shown in Fig. 1 due to cooling of the liner by the evaporation process. Furthermore, for GC systems it has been shown that the breakthrough volumes for packed PTV liners with water as solvent can be very small [35].

2.4. The vaporizer/pre-column solvent split/gas discharge interface

The vaporizer/pre-column solvent split/gas discharge interface for RPLC–GC coupling is schematically shown in Fig. 2. The vaporizer system is constructed of a vaporizing chamber connected to a pre-column [12,13,36]. The chamber is partially filled with Carbofrit, and internally coated with thin layer of polyimide. The polyimide layer protects the glass surface from water, and also glues the packing material into the inner wall of the chamber. The pre-column is connected to a SVE and to the analytical column. More details can be found in Refs. [12,13,36].

The chamber is kept clearly above the boiling point of the solvent. This is necessary because evaporating water strongly cools the chamber. The carrier gas flow-rate has to be relatively high to remove the water vapors through the pre-column and SVE. The minimum gas flow-rate is dependent on the amount of water in the eluent, and on the transfer flow-rate. For a transfer flow-rate of 0.1 ml/min aqueous eluents, the gas flow-rate should exceed 120 ml/min.

Vapours are discharged through the pre-column and the SVE located between the pre-column and the analytical column by the carrier gas. The solvent–solute separation takes place in the pre-column instead of the vaporizing chamber. In gas discharge systems, vaporization occurs in a stream of carrier gas and therefore, solvent evaporation is possible below the standard boiling point of the solvent, owing to the dilution of vapours with the carrier gas. For the same reason, the inlet of the column may also be below the normal boiling point of the solvent.

The most obvious drawback of the vaporizer/pre-column solvent split/gas discharge interface is that the method is limited to relatively non-volatile analytes [12,13]. The most volatile analytes are lost together with the solvent vapours. To maximise solvent–solute separation, and thus, to minimize the losses of volatile analytes, the oven temperature should be as low as possible. As the recondensation of aqueous eluents into GC columns is not acceptable, the oven temperature during transfer must be above the dew point (d.p.), i.e., the point at which the solvent starts to recondense. The dew point of the eluent is therefore, the lower temperature limit for the transfer. The transfer temperature is the key point of this technique, and therefore, it has to be taken

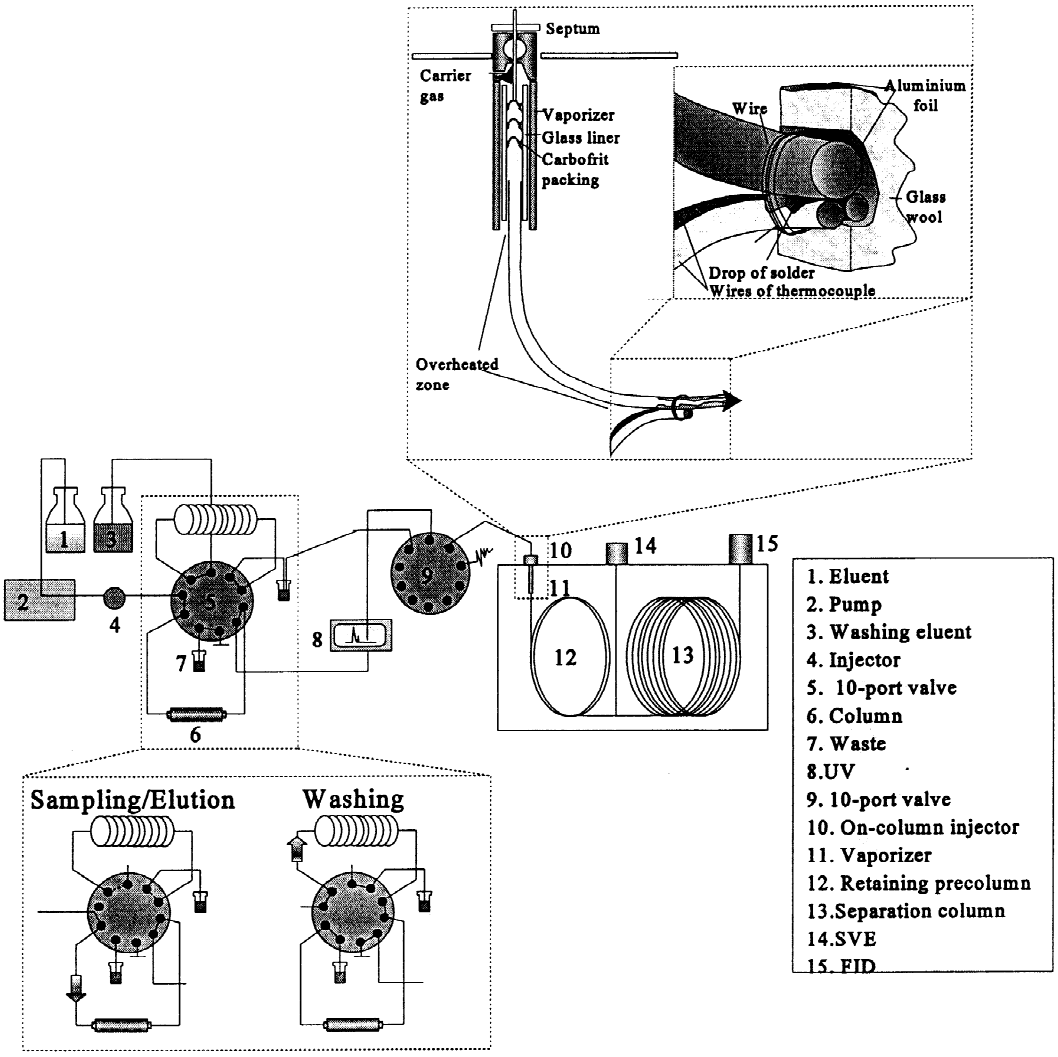

Fig. 2. Schematic figure of RPLC–GC system with the vaporizer/pre-column solvent split/gas discharge interface, and the measurement of the dew point. FID=Flame ionization detector.

into account in optimization of LC separation, limiting the choices in LC eluent composition and LC flow-rate in some respects.

Stability of the vaporizing chamber is critical. The polyimide layer, that deactivates the glass surface, has to be uniform and the packing material must be well immobilized. If the polyimide layer is too thin or it is not uniform there will be adsorption of the analytes onto the inner wall of the vaporizing chamber, indicated by reduced peak areas. Loose particles of the packing material, on the other hand, tend to accumulate to the press-fit T-piece, and can partially block it. This will result in reduced gas flow-rates, and thus, the optimized transfer conditions are no longer valid [13].

The transfer line from the transfer valve (see Fig. 2), must be carefully placed. It should be in touch with the packing material to obtain smooth evaporation. The evaporation takes place mainly in the first centimetre of the packing material [37]. This is

noticed by introducing tap water, containing some inorganic salts to the chamber. The salts are precipitated in the first section of the packing material, indicating where the evaporation process takes place.

It is important to minimize the resistance of the column system to obtain high carrier gas flow-rate through the pre-column with relatively low inlet pressures. Therefore, a short and wide-bore pre-column is the best choice for the system. There is no substantial improvement in using longer retaining pre-columns because, owing to the increased resistance, higher inlet pressures have to be used to get the required gas flow-rate [12,13]. The dew point is then increased, and the higher oven temperature during transfer cancels out the increased retention power of the longer column.

Although the retention power of the retaining pre-column can be enhanced by increasing the film thickness of the column or by using more strongly retaining phases, this does not necessarily lead to better results. This is due to the high carrier gas flow-rates (>400 ml/min) during transfer, which result in relatively broad initial bands of the solutes, which need to be refocused. When the retaining pre-column and separation columns have the same phase ratios and there is no refocusing effect, the peaks for the analytes are broadened, relative to the situation where the retaining pre-column has higher phase ratio than the separation column. A weak retention gap effect is needed for refocusing and, therefore, a retaining pre-column with thinner film is better, even though the retention of the volatiles has to be compromised.

The stability of the GC column system is good when the oven temperature is kept above the dew point of the eluent, and there is no recondensation of aqueous eluent. Slight recondensation at low temperatures does not affect the performance of the column system, but large amounts of flooding water will cause deterioration of the stationary phase of the pre-column [13].

To meet the requirements of optimal transfer conditions and GC analysis, several compromises have to be made in LC separation. As the LC eluent is directly transferred to the vaporizing system, it is not possible to use non-volatile additives in the LC eluent. The LC mobile phase has to be chosen to give sufficient separation of matrix compounds from the analytes of interest, while minimizing the separation between the analytes in order to decrease the fraction volume. The volume of the analyte fraction should be small, because large volume of mobile phase, i.e., carrier gas and solvent vapors, pushes the analytes further into the pre-column, and thus elongates the initial bands.

The proportion of water has a strong influence on the dew point of the eluent mixture, and therefore on the transfer temperature. For example, the decrease in water content from 50 to 15% decreased the dew point of the eluent by 22°C, which increases the retention power of the retaining pre-column substantially [12]. In choosing the LC flow-rate, there are two restricting factors. First, due to strong cooling of the vaporizing chamber by evaporating water, the transfer flow-rate should not exceed some 150–200 μl/min. Second, as high degree of dilution of the eluent vapours is required to obtain a low dew point, low LC flow-rates are favoured. Therefore, a compromise between fast analysis and optimal transfer conditions has to be made.

Since the dew point is affected by the degree of dilution of solvent vapours with the carrier gas, a decrease in transfer flow-rate allows lowering of the oven temperature during the transfer. It has been shown, that a reduction of the transfer flow-rate by a factor of two, i.e., from 100 to 50 μl/min lowered the dew point by some 20°C [12]. However, this also increased the LC analysis and transfer time. To shorten the analysis time, higher flow-rates can be used during sampling and flushing than during the transfer.

3. Optimization of transfer conditions

Finding optimal conditions for large volume injection or on-line transfer of LC fractions to GC is not straightforward: several, often interdependent parameters have to be taken into consideration. Furthermore, the optimization usually has to be made by trial and error. The oven temperature during injection or transfer is perhaps the most critical parameter. A difference of a few degrees may well determine the success of the analysis. Since most large volume transfer techniques include a solvent

vapour exit for solvent venting, an additional parameter needs to be adjusted.

Depending on the technique, the oven temperature during injection or transfer should be such that either no solvent recondenses in the column inlet or that recondensation is restricted to an amount limited by the capacity of the uncoated pre-column to retain liquid (Table 1).

In retention gap techniques, the oven temperature should be below the dew point to obtain flooding of the eluent and in loop-type interface with concurrent eluent evaporation above the boiling point of the solvent at the applied inlet pressure. In PTV and vaporizer techniques, the oven temperature should be above the dew point of the eluent to prevent water from recondensing into the GC pre-column. The dew point of given solvent is dependent on the carrier gas flow-rate, inlet pressure and the transfer flow-rate.

In overflow techniques, it is relatively easy to determine the optimal oven temperature during transfer, since the boiling point of the solvent is directly dependent on the inlet pressure, and the boiling point can be calculated. In gas discharge systems the situation is more complicated, because the carrier gas flow dilutes the eluent vapours, leading to a lower boiling point. In gas discharge methods, therefore, it is better to refer to the dew point of the solvent, below which the solvent vapours starts to condense or above which there is no flooding liquid. With high carrier gas flow-rates, the dilution is stronger and the dew point is lowered. However, the increase in gas flow-rate also requires an increase in the inlet pressure, which partially eliminates this benefit.

The carrier gas flow-rate plays an important role in retention gap techniques, and in PTV and vaporizer interfaces. High carrier gas flow-rates are favoured with the vaporizer interface for aqueous eluents since the higher the gas flow-rate the higher the degree of dilution of the eluent vapours and thus, the lower the dew point. On the other hand, increased gas flow-rates require increased inlet pressures, which has an increasing effect on the minimum transfer temperature. However, to a certain point, the increasing carrier gas flow-rate has a dominating effect on the dew point as can be seen in Fig. 3 for a water–methanol mixture [12]. By increasing the gas flow-rate from 100 to 500 ml/min, the dew point is decreased by 20 degrees. Also for retention gap techniques, a high gas flow-rate is attractive, as it accelerates the rate of evaporation.

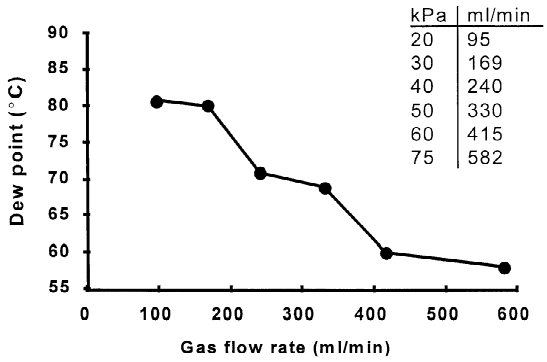

Fig. 3. The effect of gas flow-rate on the dew point of water–methanol mixture (85:15, v/v) (from Ref. [12]).

There are different ways to determine the dew point of the solvent during the transfer. For techniques, where recondensation must be avoided, one way is to add water-soluble compounds into the sample [12,13]. These compounds will spread within

Table 1
Approaches for large volume injections or transfers in the GC system; vapour discharge process, optimal oven temperature during injection or transfer and suitability of recondensation

Method	Discharge by	Oven temperature	Recondensation
Loop-type interface: FCSE	Overflow	Far above b.p.	No
On-column interface: retention gap techniques	Gas discharge	Far below d.p.	Yes
On-column interface: PCSE	Gas discharge	Below d.p.	Yes
PTV solvent split	Gas discharge	At or above d.p.	No
PTV splitless	Gas discharge	Below/above b.p.	Yes/no
PTV splitless	Overflow	Above b.p.	No
Vaporizer/pre-column solvent split	Gas discharge	Below/at or above d.p.	Yes/no
Vaporizer/pre-column solvent split	Overflow	Above b.p.	No

Table 2
The techniques, for which direct measurements of solvent evaporation or recondensation from the outer column wall can be utilized

Large volume technique	Optimized condition
Vaporizer/pre-column solvent split/gas discharge interface	Oven temperature during the transfer
On-column injection/transfer: Retention gap technique	(1) Length of flooded zone (2) Closure of solvent vapour exit
Loop-type interface: fully concurrent solvent evaporation	Length of evaporation zone

the column by recondensed water which will result in broadened peaks. The broadening can be used as indicator of recondensation. Carbowax compounds, which have relatively high solubility in water serve well as indicator compounds as they form clearly broadened peaks with recondensation [7].

A more direct way to determine the dew point is to measure temperature changes on the outer column wall [14] (Fig. 2). Recondensation of solvent releases heat, and evaporation consumes it. This phenomenon can be utilized for finding the optimal oven temperature during transfer. Direct measurement of temperature changes on the outer wall of the capillary offers a useful way of detecting both evaporation and recondensation. This phenomenon can be exploited also for other techniques (Table 2), for example for the optimization of the length of flooded zone in retention gap techniques, and as signal for optimal closure of solvent vapour exit [14].

For vaporizer interface, the optimal point for measurement of temperature changes is dependent on the carrier gas flow-rate [14]. The hot gas–solvent vapour mixture leaving from the vaporizing chamber heats the first few centimetres of the column inlet considerably above the oven temperature. As the transfer begins, the temperature is increased even though there is no recondensation because the eluent vapours can transfer more heat than the carrier gas alone. Clearly, measurements in this section of the column will not give reliable information about recondensation. Conversely, measurements should not be made too far from the entrance where there is no more recondensation: there the column is still flooded, but the solvent is driven to this section from the recondensation zone by the carrier gas. The recondensation zone will be relatively broad, because recondensation is an oscillating process: the recondensing solvent heats the capillary at the first site where the temperature is above the dew point and recondensation thus starts just a little bit further along the pre-column. The process is then repeated, as this site will also cool. Moreover, the recondensation is more vigorous and occurs earlier when the oven temperature is substantially lower than when it is near to the dew point. The optimal point for measurement is some 6–10 cm from the column attachment to the vaporizer, depending on gas flow-rate [14].

For aqueous eluents, the recondensing process is not as smooth as for organic solvents and the direct measurement of aqueous mixtures is made especially with high carrier gas flow-rates. Therefore, the addition of water soluble compounds offers a good alternative way to detect or ensure the dew point.

4. Applications

4.1. On-column interface with retention gap techniques

Direct transfer of water containing eluents to GC has been applied in RPLC–GC analysis only to test sample mixtures [1–4] as will be briefly discussed below.

An on-column interface with Carbowax-coated retention gap has been used for the RPLC–GC analysis of naphthalene and biphenyl as test compounds [1]. The eluent was a mixture of acetonitrile–water (75:25, v/v). Another application of Carbowax-coated retention gaps has been reported, using phenanthrene as test mixture [3,4]. The eluent was an azeotropic mixture of acetonitrile–water

(84:16, v/v) with a flow-rate of 175 μl/min during the transfer of 200 μl fraction. The results showed, that if more than ca. 1 μl of water is left in the retention gap after the azeotropic solvent mixture has evaporated, the peaks start to distort or areas to collapse [4].

4.2. Loop-type interface with concurrent solvent evaporation

Only one application has been reported using loop-type interface for direct transfer of RPLC eluents into GC for the analysis of atrazine in water [5]. Ten ml of water was injected into an ODS column with water–methanol–1-propanol (57:38:5, v/v/v) as eluent. The flow-rate was 400 μl/min and the volume of the fraction transferred into the GC system 150 μl. The analytical column, which had the same stationary phase as the retaining pre-column, was coated with Carbowax 20M, which had a high retention power for the atrazine. This was necessary to obtain high elution temperature for the analyte of interest (here 250°C), which is necessary for the loop-type interface with aqueous solvents. The critical parameters of the technique were the oven temperature during the transfer and the volume of the transferred fraction. Over the optimum transfer temperature (112°C with a fraction of 150 μl) peak broadening became evident. Also, with a LC fraction of 250 μl, the peak broadening was evident also with the transfer temperature of 112°C. The method was highly specific for atrazine, the limit of detection being better than 15 ppt.

Concurrent eluent evaporation with co-solvent trapping increases the volatility range of the technique. Butoxyethanol has been shown to be suitable as co-solvent for aqueous mixtures [6,7]. It boils at 171°C and forms an azeotropic mixture with water. Principles of the technique have been reported, but it has not been applied to real samples. The use of co-solvent made it possible to analyse compounds eluting only a few degrees higher than the transfer temperature.

4.3. Programmed temperature vaporizer interface: analysis of cholesterol and stigmasterol

The RPLC–GC method with PTV as the interface, has been applied to analysis of cholesterol, stigmasterol, *b*-sitosterol and campesterol in olive oil [10,11]. The LC preseparation was carried out in a silica-column, with a water–methanol gradient. The fraction from LC was transferred to a PTV, which was kept at 30°C. The glass liner was packed with Tenax. During transfer, the inlet of the pre-column was not connected to the PTV. After transfer, the GC pre-column was reinstalled to the PTV, the analytes were desorbed from the liner and the analysis was started. Limits of detection were 110–302 ng/ml for the analytes.

With the low transfer temperature (30°C) and the high transfer flow-rate (some 1500 μl/min), the method resembles the non-evaporative mode.

4.4. Vaporizer/pre-column solvent split/gas discharge interface: analysis of phthalates in water samples and pesticides in red wines

RPLC–GC with the vaporizer/pre-column solvent split/gas discharge interface has been applied to the analysis of phthalates in surface and drinking waters [12] and to the analysis of pesticides in red wines [13].

LC was used for clean-up and preconcentration of the analytes. As much as 10 ml of water could be injected opposite to only 1 ml of wine. With larger samples of wine, matrix compounds disturbed the performance of the LC column.

The LC mobile phase was chosen to give sufficient separation of matrix compounds from the analytes of interest, while keeping the fraction volume minimal. In optimization, compromise was made between the efficient removal of the matrix components and the low fraction volume. It was possible in both applications to remove all the matrix compounds, but the fraction volumes then increased substantially (>900 μl).

The LC flow-rate during transfer to the GC must not exceed some 150 μl/min because of the cooling effect of the evaporating water and because the dew point of the solvent is dependent on the transfer rate, with low rates favoured. To shorten the analysis time, higher flow-rates were used during sampling and flushing: 1000 μl/min for water samples and 700 μl/min for wine samples. For pesticide analysis an additional washing step was required to remove

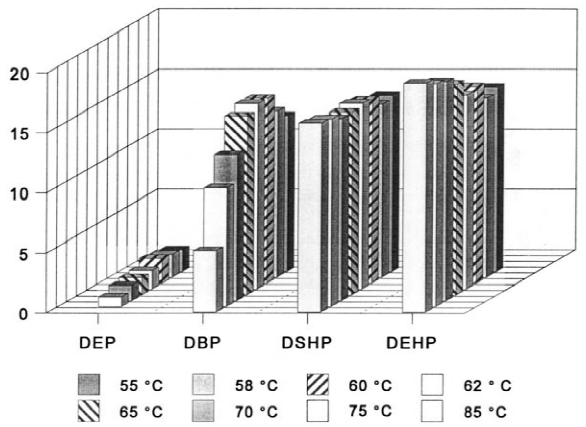

Fig. 4. Effect of transfer temperature on the retention of phthalates.

the disturbing matrix compounds: the column was washed with 10% ethanol in water for 1 min in backflush mode. During transfer a flow-rate of 100 μl/min was used for phthalates and 50 μl/min for pesticides. For phthalates, the lower transfer flow-rate did not significantly increase the retention of relatively volatile phthalate, DBP, and the method did not allow quantitative analysis of the most volatile phthalate, DEP, even with low LC flow-rates. For pesticides, the decrease of flow-rate from 100 to 50 μl/min made it possible to lower the oven temperature during transfer to such an extent that analysis of vinclosolin, the most volatile of the pesticides studied, was possible. With higher transfer flow-rates this did not succeed.

The importance of low oven temperature during the transfer on the retention of volatile analytes is shown in Figs. 4 and 5. The most volatile compound, diethyl phthalate, did not retain quantitatively on the pre-column at the transfer temperatures required for aqueous eluents. The retention of dibutyl phthalate, however, could be markedly increased by lowering the transfer temperature to the dew point (60°C). At the two lowest temperatures (55 and 58°C), there was eluent recondensation in the pre-column, but this did not result in losses of the analytes. By lowering the transfer flow-rate to 50 μl/min, the dew point was lowered, but not enough to enable the analysis of diethyl phthalate. As can be seen from chromatogram in Fig. 5, lindane and dimethoate, which eluted before vinclosolin, could not be quantitatively analysed. However, the analysis of more volatile pesticides would most probably be possible with some modifications to the vaporizing system.

No losses of phthalates occurred during the sampling step, as shown by a comparison of spiked samples analysed by LC–GC–MS with the same amount of standards directly injected to the GC–MS through the loop in the transfer valve. Recoveries in

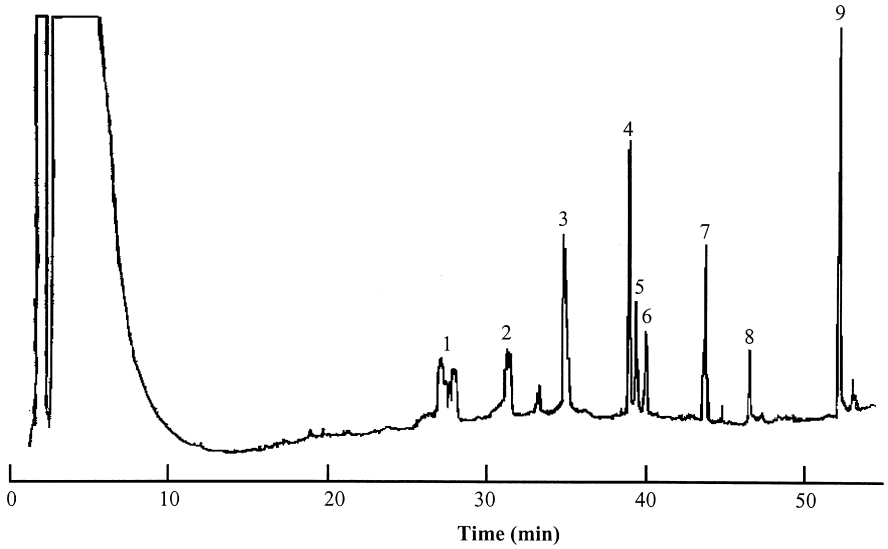

Fig. 5. RPLC–GC chromatogram of spiked red wine sample demonstrating the analytical range. Peaks: 1=Dimethoate, 2=lindane, 3=vinclosolin, 4=quinalphos, 5=procymidone, 6=endosulfan α, 7=endosulfan β, 8=carbophenthion and 9=tetradifon.

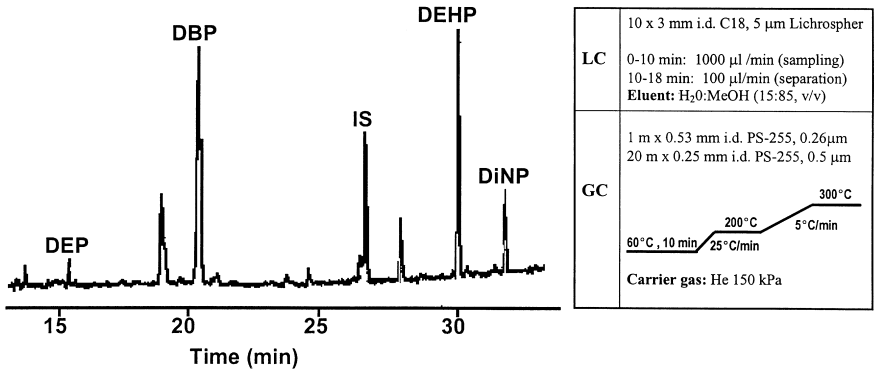

Fig. 6. RPLC–GC–MS chromatogram of water sample containing phthalates. Peaks: DEP=diethyl phthalate, DBP=dibutyl phthalate, I.S.=benzyl butyl phthalate, DEHP=diethylhexyl phthalate and DiNP diisononyl phthalate (from Ref. [7]).

the LC clean-up of wine samples were excellent except for procymidone. The limits of quantification for phthalates were 5–10 ng/l for the RPLC–GC–MS procedure. For pesticides, the limits were higher (8–10 μg/l) due to the less sensitive flame ionization detection (FID).

Some river and drinking water samples from the Zurich area were analysed for phthalates, and some authentic red wines from different areas for pesticide residues. Measurable amounts of phthalates were found in most of the water samples, with concentrations in the range 5–500 ng/l (Fig. 6). Traces of pesticides were detected in the red wines in the range 8–36 μg/l.

5. Conclusions

Relatively few applications of direct RPLC–GC methods have been reported. The properties of water makes the direct transfer relatively difficult. Compared to indirect solutions for RPLC–GC coupling, the primary advantage of direct solutions is the simplicity. No phase-switching is needed, which simplifies the methods and facilitates automation, and makes them attractive for routine analysis. The advantages and disadvantages of the different direct RPLC–GC solutions are listed in Table 3.

The on-column interface with special retention gaps and stationary phases are not yet of practical

Table 3
Comparison of direct solutions for RPLC–GC coupling

	On-column	Loop-type	PTV	Vaporizer
Suitability for aqueous samples	Poor	Good	Relatively good	Good
Temperature range (°C)	>90–110	>240 (>120[a])	>130–150	>170
Ruggedness	Poor	Good	Relatively poor	Good
Transfer conditions	Complicated to adjust	Easy to adjust	Complicated to adjust	Fairly complicated to adjust
Transferred volume	Up to 50–200 μl	Up to 100–200 μl	Up to millilitre	Up to millilitre
Disadvantages	difficulties with stability of retention gaps; many parameters to be optimised	Suitable only for high-boiling analytes	Many parameters to optimise; time-consuming transfer; limited applicability to high-boiling analytes	Not suitable for volatiles
Advantages	Suitable also for relatively volatile analytes	Easy to adjust easy to adjust	Suitable also for relatively volatile analytes	Simple; easily automated

[a] With co-solvent.

use for direct coupling of RPLC and GC. More development is needed in the field of deactivation methods and stationary phases to obtain columns, that are applicable to routine analysis.

The main limitation of loop-type interface with concurrent eluent evaporation is that it is restricted to high-boiling analytes. Even though the use of co-solvent allows the analysis of relatively volatile analytes, with the co-solvent, the optimization is more difficult both in LC and GC.

The use of a PTV as an interface between RPLC–GC allows the analysis of relatively volatile analytes but the analysis of high-boiling compounds is restricted. Special attention has to be paid to the optimization of different parameters, including packing material, transfer and gas flow-rates, transfer temperature and purge time. The transfer time is typically long, due to evaporation characteristics of water.

The vaporizer/pre-column solvent split/gas discharge interface provides a simple interface for RPLC–GC coupling which is suitable also for routine applications. The technique is, however, limited only to relatively non-volatile analytes. To minimize the losses, the transfer conditions have to be carefully optimised. Two parallel methods for the optimization have been reported, which make the optimization less time consuming and more reliable.

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