

On-line combination of liquid chromatography and capillary gas chromatography : preconcentration and analysis of organic compounds in aqueous samples

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On-Line Combination of Liquid Chromatography and Capillary Gas Chromatography. Preconcentration and Analysis of Organic Compounds in Aqueous Samples

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Capillary GC
Coupled LC-GC
Large injection volumes
Trace analysis
Aqueous samples

Summary

This paper describes the design of a new, versatile, and low-cost on-line LC-GC interface that allows the fast and reliable introduction of large sample volumes onto a capillary GC column. The sample introduction procedure consists successively of: evaporation of the entire sample (LC fraction), selective removal of the solvent and simultaneously cold-trapping of the solutes, splitless transfer of the solutes to the GC column, on-column focusing, GC separation and detection. Quantitative and qualitative aspects of various experimental parameters are evaluated and optimum conditions are reported. The applicability of the method is demonstrated on a synthetic aqueous sample of chlorinated pesticides.

1 Introduction

In chromatography there is an increasing interest in the analysis of very low concentrations of organic compounds in complex samples. As these concentrations are often too low to be determined directly, sample preconcentration techniques have to be applied. Among them the combination of liquid chromatography and capillary gas chromatography is very promising.

As a pre-separation technique, liquid chromatography adds selectivity to the high efficiency of capillary gas chromatography, thus improving the overall separation potential. Moreover, when LC is employed for sample preconcentration, the LC-GC combination provides a very sensitive analytical technique.

GC analyses of off-line LC pre-separated fractions is a universally adopted analytical procedure [1-3]. Generally only a small part of the total volume of the LC fraction is used for GC analysis. Direct introduction of the entire LC fraction, however, drastically improves the detectability of trace

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compounds, while contamination, losses, and the overall analysis time are considerably reduced. In addition, it is easily automated.

For the on-line LC-GC combination two possible approaches occur: the adjustment of LC to GC requirements, resulting in a micro-LC version [4,6], or the adaption of the GC instrument to the introduction of very large volumes of liquid sample, typically 20-1000 μl . Injection techniques appropriate for the introduction of such large sample volumes include PTV injections [7,9], injections on a packed pre-column [10,11], a specially designed injection device incorporating a 500 μl reservoir [12], and several on-column injection techniques using very long retention gaps [13] or applying concurrent solvent evaporation [14,17]. The latter has been used successfully in the on-line combination of LC and GC [14-17]. The on-column injections, however, require long sampling times and the applications are limited to non-polar solvents.

The design, the optimization and the evaluation of a new LC-GC interface, that allows the fast introduction of large sample volumes onto a capillary GC-column, are presented in this paper.

2 Experimental

2.1 System Design

A schematic design of the LC-GC interface is given in Figure 1.

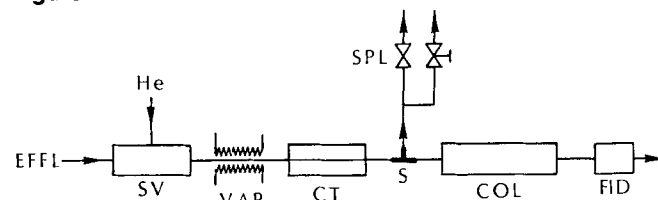


Figure 1

Schematic design of the LC-GC interface design. EFFL = LC effluent, SV = sampling valve, VAP = vaporizer, S = all-glass low dead volume T-splitting device, CT = cold-trap, COL = GC-column, SPL = splitter valves, FID = Flame ionization detector.

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The system consists of a sampling valve connecting the LC and GC instruments, a vaporizer, a short fused silica capillary cold-trap and a specially designed low dead volume t-splitting device.

Two different sampling valves were used during this study. They are given in detail in **Figure 2**.

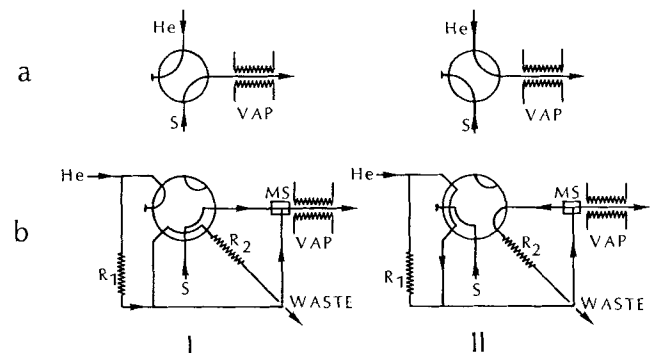


Figure 2

Sampling valves. a. 4-port switching valve b. 6-port switching valve. I. Sample introduction. II. GC-analysis and back flush. S = sample; R₁, R₂ = restrictions; MS = mixing + splitting device; VAP = vaporizer.

The 4-port switching valve was used in most of the experiments. The cold-trap capillary is passed through the vaporizer and connected directly to the 4-port valve. The 6-port valve system was designed to enable back flushing of the switching valve in order to avoid memory effects. A memory- and dead volume free mixing and splitting device was constructed by sliding a 50 μm i.d. capillary into a 320 μm i.d. column, as shown schematically in **Figure 3**.

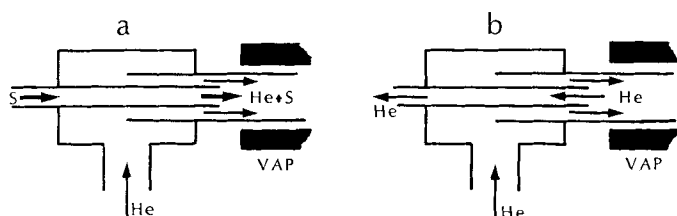


Figure 3

Mixing and splitting device of the 6-port valve system (Swagelok^R 1/16" union-T). a. Sample introduction. b. GC analysis and back flush. S = sample; VAP = vaporizer.

In addition, the mixing of the sample with helium provides a more gentle evaporation. During sampling, the carrier gas flow through the cold-trap is limited by a restriction (R₁ in Fig. 2b). In this way an early breakthrough of volatile compounds can be avoided.

The vaporizer and the low dead volume T-splitting device are schematically presented in **Figure 4**.

In the vaporizer the cold-trap capillary is passed through a closely fitting brass insert, placed in the heated GC-injection port. The column connections to the T-splitter can be made either by Swagelok^R reducing unions (1/8" \times 1/16") or by polyimide glue.

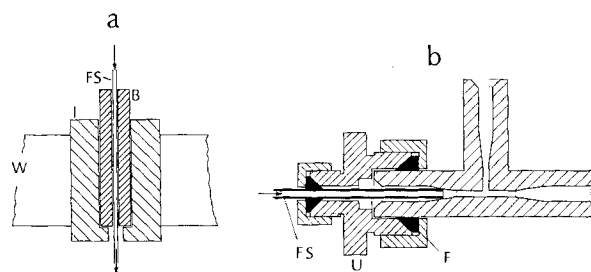


Figure 4

Schematics of the vaporizer (a) and the all-glass low dead volume T-splitter (b). FS = fused silica capillary; I = GC injection port; W = GC oven wall; B = Brass insert, L = 100 mm, o.d. = 6 mm; U = reducing union (1/8" \times 1/16"); F = Vespel ferrule.

2.2 Sample Transfer

Because of the need of an easy exchange of stock solutions in studying the introduction of large sample volumes, the samples were delivered by a pressurized glass container instead of using an LC pump. The sample container was connected to either one of the switching valves by means of a flexible fused silica capillary (0.6 m \times 50 μm i. d.). The amount of liquid introduced in this way was determined gravimetrically.

After evaporation of the entire sample in the vaporizer, the solutes are retained in the cold-trap while the solvent vapor is passed and largely removed via the split vent. The cold-trap is a short fused silica capillary column installed in the GC oven compartment, connecting the valve system to the splitting device. In order to avoid recondensation of the solvent, the trap temperature (*i. e.*, the initial oven temperature) is maintained slightly above the solvent boiling point.

After introduction of the desired sample volume, the valve is switched. Simultaneously the splitter valve is closed and the GC oven temperature program is started. On increasing the oven temperature the trapped solutes are transferred to the GC column via the T-splitting device. Back diffusion of solvent vapor to the column is prevented by a parallel split line incorporating a needle valve, thus establishing a small constant gas flow.

Unless stated otherwise, the analyses were performed according to the standard experimental conditions of **Table 1**.

Table 1

Standard experimental conditions.

Sample	volume	40–100 μl
	flow rate	40 $\mu\text{l}/\text{min}$
Cold-trap	type	uncoated fused silica
	dimensions	2 m \times 0.25 mm i.d.
	temperature	70 $^{\circ}\text{C}$
Vaporizer	temperature	250 $^{\circ}\text{C}$

2.3 Gas Chromatography

The equipment was built on top of a HP 5880 gas chromatograph (Hewlett Packard, Avondale, PA, USA) provided with a FID and an ECD detector. Throughout this study two different separation columns were used: a. a home-made fused silica SE-54 column ($L = 15$ m, i. d. = 0.31 mm, $d_f =$ approximately 0.3 μ m), temperature program: 70 $^{\circ}$ C up to 280 $^{\circ}$ C at 8 $^{\circ}$ /min, and b. a 11.5 m \times 0.2 mm i. d. crosslinked OV-1 fused silica column ($d_f = 0.11$ μ m) (Hewlett Packard, Avondale, PA, USA), programmed from 70 $^{\circ}$ C up to 280 $^{\circ}$ C at 20 $^{\circ}$ /min.

Synthetic stock solutions containing *n*-hydrocarbons in redistilled *n*-hexane were prepared in concentrations of 100 ng/ml (100 ppb m/v).

3 Results and Discussion

3.1 Accuracy and Reproducibility

In order to examine the extent to which quantitative sample transfer ("recovery") could be achieved, the LC-GC sample introduction was compared to on-column injectors of 1 μ l of a more concentrated stock solution. The cold-trap capillary was connected to a HP on-column injector for this purpose. During on-column sampling the splitter valve was closed.

The recoveries as well as the relative standard deviation (RSD) of reproduced sample introduction are given in Table 2.

Table 2

Recovery and reproducibility ($n = 5$) of sample transfer by the LC-GC interface for the 4-port (a) as well as the 6-port valve system (b).

Hydrocarbon	Recovery (%)	RSD (%)	
		(a)	(b)
<i>n</i> -C15	14	5.6	—
<i>n</i> -C16	22	8.6	—
<i>n</i> -C20	102	1.7	2.7
<i>n</i> -C22	99	2.0	2.8
<i>n</i> -C24	99	1.1	5.2
<i>n</i> -C26	98	0.6	3.4

Solutes with a volatility less than *n*-C20 are retained quantitatively by the uncoated cold-trap, whereas more volatile compounds are partly vented via the splitter. The reproducibility is excellent for non-volatiles and still surprisingly good for the incompletely recovered solutes. In agreement with this, the detector response for non-volatile compounds correlates very well with the sample volume introduced by the 4-port valve (cf. Figure 5). The corresponding correlation coefficients are 0.999 for *n*-C20 and only 0.96 for *n*-C16.

Similar results were obtained for the 6-port valve system: for hydrocarbons with 20 up to 30 carbon atoms, the correlation coefficients exceeded the value of 0.998 .

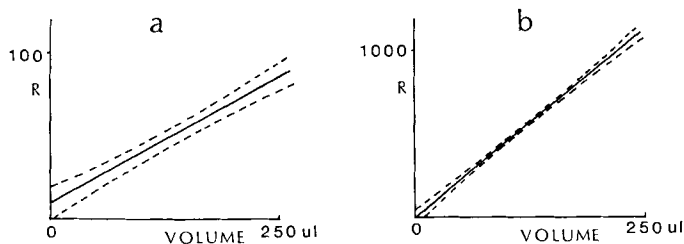


Figure 5

Correlation between sample volume and detector response (R) for *n*-C16 (a) and *n*-C20 (b), including the 95% reliability intervals.

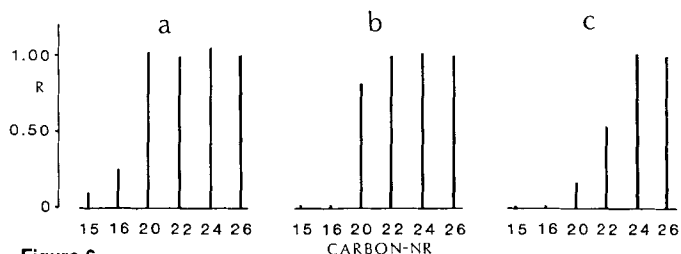


Figure 6

Recoveries (R) of several *n*-hydrocarbons at different cold-trap temperatures. a = 70 $^{\circ}$ C; b = 80 $^{\circ}$ C; c = 100 $^{\circ}$ C.

3.2 Influence of the Cold-Trap Temperature

As shown already by Table 2, a quantitative sample transfer is obtained for compounds which are less volatile than *n*-C20 at a cold-trap temperature of 70 $^{\circ}$ C. Increasing this temperature results in a faster solute transport along the cold-trap capillary and consequently more of it is lost. The effect of the cold-trap temperature on the recovery of some hydrocarbons is shown in Figure 6. Even a small temperature elevation results in a considerable increase of the losses for the more volatile compounds.

As demonstrated by the example of Figure 7, a decrease of the cold-trap temperature below the boiling point of the solvent gives rise to serious losses and/or bad peak shapes. This is due to recondensation of the solvent, which results in passage of the solutes through the cold-trap capillary.

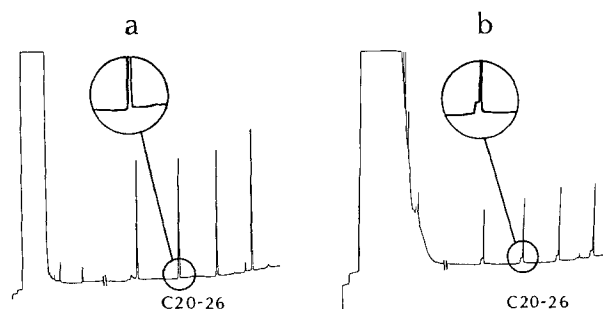


Figure 7

The effect of recondensation of the solvent. a: cold-trap at 70 $^{\circ}$ C; b: cold-trap at 65 $^{\circ}$ C; even numbered hydrocarbons *n*-C20-*n*-C26.

3.3 Influence of the Cold-Trap Stationary Phase Film Thickness

On increasing the stationary phase film thickness, the retention time of the solutes in the cold-trap is increased as well. **Figure 8** shows considerable improvements in the recoveries of volatile solutes when the uncoated cold-trap is replaced by a cold-trap with a stationary phase coating ($2\text{ m} \times 0.25\text{ mm}$ i. d., $d_f = 0.14\text{ }\mu\text{m}$, immobilized OV-1, homemade).

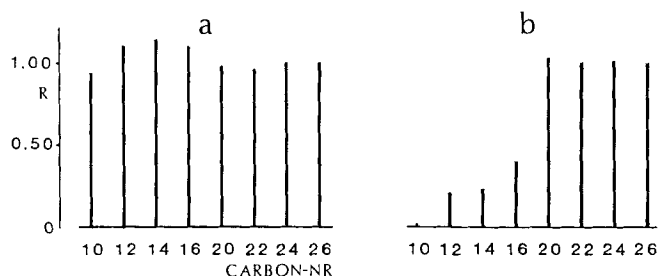


Figure 8

Comparison of the recoveries (R) on a coated and an uncoated capillary cold-trap for $n\text{-C}10\text{-}n\text{-C}26$ (4-port valve system). a: $2\text{ m} \times 0.25\text{ mm}$ i. d., immobilized OV-1, $d_f = 0.14\text{ }\mu\text{m}$, b: $2\text{ m} \times 0.25\text{ mm}$ i. d., uncoated and non-deactivated.

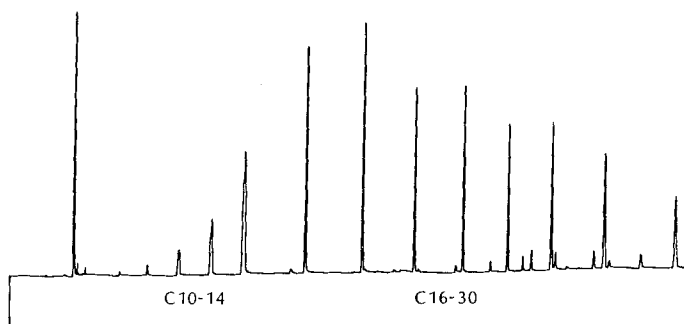


Figure 9

Chromatogram of $100\text{ }\mu\text{l}$ of a hydrocarbon solution ($n\text{-C}10\text{-}n\text{-C}14$, even numbered $n\text{-C}16\text{-}n\text{-C}30$, 100 ppb in $n\text{-hexane}$) using a coated cold-trap ($5\text{ m} \times 0.31\text{ mm}$ i. d., CP SIL 5 CB, $d_f = 0.11\text{ }\mu\text{m}$) in combination with the 6-port valve system.

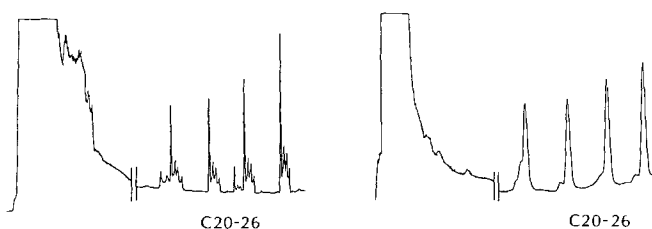


Figure 10

Chromatograms after damaging of the cold-trap stationary phase film.

The applicability of coated cold-traps is determined by the stability of the immobilized stationary phase, the resistance of the stationary phase coating to solvent damage, as well as by the refocusing capacity of the GC column. This phase gradient refocusing, *i. e.*, the reduction of the band width of

the deposited solutes in the cold-trap by the stationary phase film inside the GC column, is directly proportional to the retention ratio and thus the ratio of the film thicknesses of the separation column and the cold-trap capillary.

As shown by **Figure 9**, using a coated cold-trap, compounds more volatile than $n\text{-C}20$ are also quantitatively trapped ($n\text{-C}14\text{-}n\text{-C}18$). Components with a volatility higher than $n\text{-C}14$ are partly lost during trapping. Because in this experiment the film thickness of the cold-trap and the GC column are of the same order, no phase gradient refocusing can be expected. Obviously $n\text{-C}14$ is deposited along a considerable length of the cold-trap capillary, whereas the less volatile hydrocarbons are deposited as reasonably narrow bands in the cold-trap.

The application of coated cold-traps requires a very careful selection of the immobilized stationary phase. In contact with the liquid solvent the stationary phase swells and becomes very vulnerable. We assume that in the environment of boiling solvent sheets of the stationary phase film are torn off the inner column wall and are deposited further downstream in the cold-trap capillary, in the T-splitter, or even in the GC-column. Apart from the reduced trapping capacity, this irregular stationary phase distribution causes peak splitting or extreme peak broadening (**Figure 10**). Using a coated cold-trap like the one of Fig. 7a ($2\text{ m} \times 0.25\text{ mm}$ i. d., immobilized OV-1, $d_f = 0.14\text{ }\mu\text{m}$), connected to the 4-port valve system, clogging of the GC column was observed. With the combination of the 6-port valve system and the cold-trap, presented in Figure 8, none of these problems have occurred during a period of about four months.

3.4 Influence of the Vaporizer Temperature

The LC-GC interface performance is hardly affected by the vaporizer temperature. Only when the vaporizer temperature is far below the solute elution temperature, compounds may remain trapped in the vaporizer as they are not submitted to the GC oven temperature program (*e. g.* at a vaporizer temperature of $150\text{ }^\circ\text{C}$ less than 25% of $n\text{-C}30$ hydrocarbon, eluting at $280\text{ }^\circ\text{C}$, was recovered).

3.5 Influence of Sample Flow Rate

When the sample flow rate is too high, incomplete evaporation occurs and the solutes are transported with the liquid solvent along the cold-trap. Similar to the observations on recondensation at too low cold-trap temperatures, bad peak shapes result (**Figure 11**).

For the quoted experimental conditions a sample flow rate of $150\text{ }\mu\text{l}/\text{min}$ is the upper limit.

3.6 Influence of Solvent Type

Injection techniques employing the solvent effect for solute focusing [13-17] are limited to non-polar solvents due to wettability problems of the coated column inner wall by polar solvents. Consequently, LC-GC interfaces based on

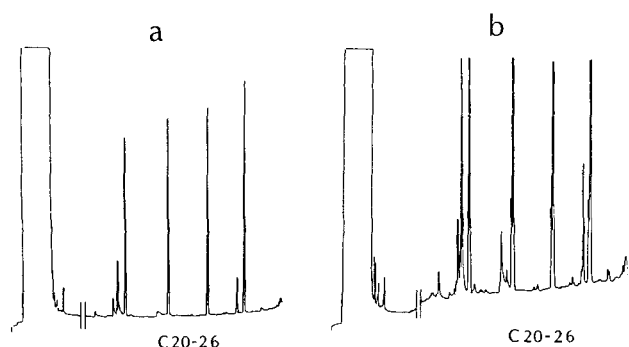


Figure 11

Effect of the sample flow rate on the peak shape in combination with the 4-port valve system. a: 100 µl/min. b: 300 µl/min; hydrocarbons even-numbered nC20–nC26.

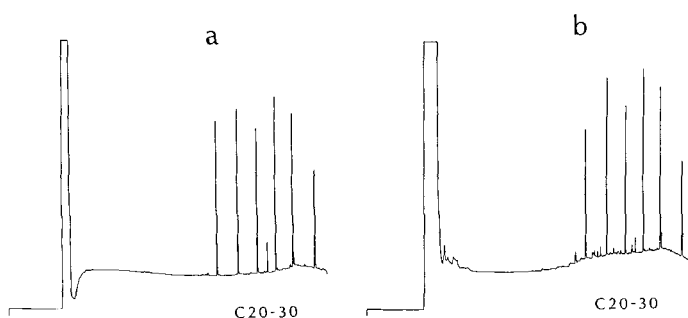


Figure 12

Chromatograms of 100 ppb solutions of hydrocarbons (even numbered n-C20–n-C30) in n-hexane (a) and methanol respectively (b); sample volume = 100 µl, sample flow rate = 100 µl/min in combination with the 6-port valve system.

on-column sampling can only be applied for straight phase LC effluents. Nowadays, however, reversed phase HPLC has become the predominant LC technique.

In our equipment the entire sample with a volume from 20 up to 1000 µl is evaporated, followed by cold-trapping and on-column phase gradient refocusing. This process is not influenced by the solvent polarity, as shown in **Figure 12**, where comparative chromatograms of hydrocarbon solutions in methanol respectively and n-hexane are given, which are introduced under equal conditions. Neither the peak areas nor the peak shapes are affected by the solvent type.

3.7 Introduction of Extremely Large Sample Volumes

Figure 13 shows a chromatogram of 1000 µl of a n-hexane solution containing 10 ppb of even-numbered n-hydrocarbons (C20–C30). On introduction at a flow rate of approx. 100 µl/min, a large solvent peak appears.

After adjustment of the zero signal and attenuation, contaminant peaks appear as well. They correspond to concentrations of 1–50 ppb w/v. Obviously the purity of the redistilled hexane was not sufficient. This example illustrates

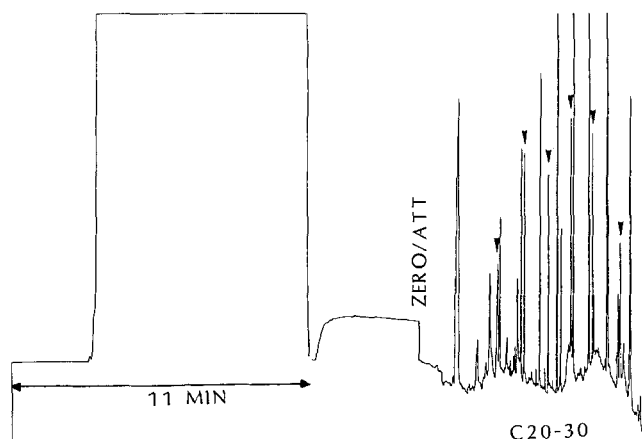


Figure 13

Chromatogram of 1000 µl of a diluted n-hydrocarbon sample n-C20–C30, 10 ppb w/v/compound, the hydrocarbons are indicated by arrows.

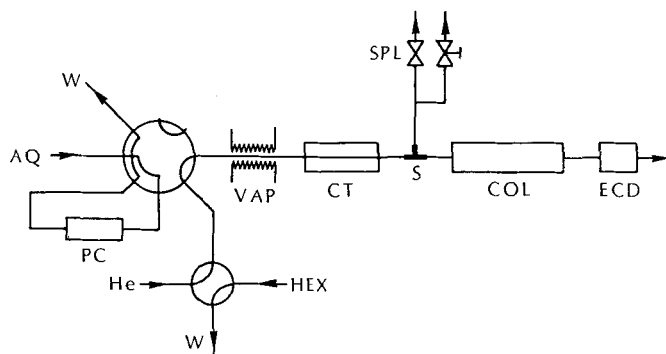


Figure 14

Equipment for the on-line combination of LC-preconcentration and HRGC separation. AQ = aqueous sample, PC = pre-column, W = waste, HEX = n-hexane, CT = cold-trap, VAP = vaporizer, S = T-splitting device, SPL = splitter valves, COL = GC column, ECD = electron capture detector.

the limitations of all kinds of applications of ultra-trace analysis: the availability of highly pure solvents and gases and extremely clean glassware, tubing, syringes, etc.

3.8 The On-Line Combination of LC and GC

The purpose of this work was the accomplishment of the on-line combination of LC-preseparation or LC-preconcentration and capillary GC separation. Although additional research is required for further improvement of this system, a preliminary example of the analysis of a diluted aqueous sample of chlorinated pesticides is presented. The equipment for pre-concentration, extraction, and sample transfer is shown in **Figure 14**.

A six-port valve incorporating a C-18 modified silica pre-column (10 mm × 2 mm i. d., $d_p = 20\mu\text{m}$) is supplementary to the evaluated equipment. A 12 ml sample volume of the aqueous solution containing approx. 100 ppt/compound was passed over the pre-column. After drying of the pre-

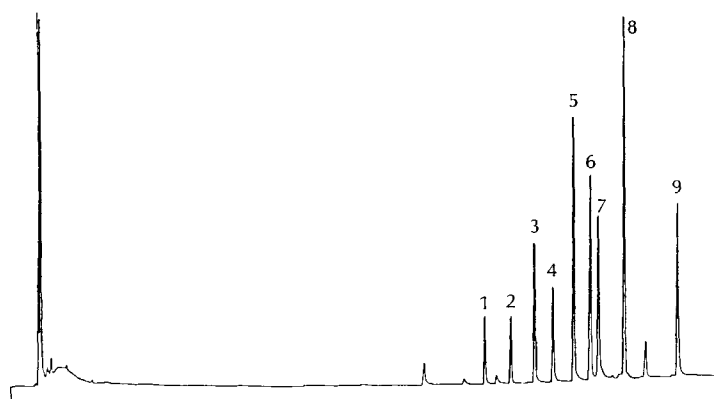


Figure 15

Chromatogram of chlorinated pesticides concentrated from 12 ml aqueous sample containing 100 ppt/compound, and extracted with 70 μ l *n*-hexane. Cold-trap: L = 2 m, i. d. = 0.25 mm, uncoated. 1 = γ -HCH; 2 = heptachlor; 3 = aldrin; 4 = heptachlorepoide; 5 = *o,p*-DDE; 6 = *p,p*-DDE; 7 = endrin; 8 = *p,p*-DDD; 9 = *p,p*-DDT.

column by the combination of He-flushing and applying vacuum, the pre-column was extracted by a small amount of *n*-hexane (ca. 70 μ l). The resulting chromatogram is shown in Figure 15.

4 Conclusions

The presented on-line LC-GC interface enables the reliable introduction of large liquid sample volumes (20–1000 μ l) onto a capillary column in a relatively short time. The 6-port valve system appears an attractive device for sample transfer, allowing back flushing in order to avoid memory effects and gentle evaporation of the solvent.

The performance of the LC-GC interface is mainly determined by the efficiency of the capillary cold-trap. Because the trapping temperature should be as low as possible, but always above the boiling point of the solvent, low boiling solvents are most advantageous. The presence of a stationary phase film inside the cold-trap benefits the recovery of more volatile components, but reduces the effect of phase gradient refocusing by the GC column. Compounds less volatile than *n*-C14 can be trapped quantitatively on a short thin film capillary cold-trap.

The performance of the LC-GC interface is hardly affected by the vaporizer temperature nor by the sample flow rate unless it is too high in relation to the vaporizer temperature and length.

Polar and non-polar solvents, as well as extremely large sample volumes can be introduced so that the system can be applied for ultra trace analysis of organic compounds in a wide variety of samples.

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