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Programmed Cold Sample Introduction and Multidimensional Preparative Capillary Gas Chromatography

Part I: Introduction, Design and Operation of a New Mass Flow Controlled Multidimensional GC System

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1 Introduction

Capillary gas chromatography is a widely used separation technique for the analysis of complex samples with sufficient volatility. Maximum resolution and efficiency, large sample volumes, and highly sensitive detectors are frequently required for many applications.

Despite the availability of a great variety of sample introduction systems, highly efficient columns, sensitive detectors, and sophisticated instrumentation, many samples cannot be analyzed with sufficient qualitative and quantitative reliability. Essentially, these problems are related to the complexity of the sample and the compatibility of sample size, the input band width, and column properties such as phase ratio, film thickness, diameter, etc. Interfacing of the column with the injection and detection system, as well as detector specifications (e.g. volume, time constants) and the actual operating conditions are also important limiting factors. For more and more applications a detailed multicomponent analysis of mixtures with a wide range of volatilities, polarities, and concentrations is required. Matrix isolation and off- or on-line enrichment techniques are particularly attractive to achieve the requested detection limits for the lower concentrations in those samples.

Unfortunately the demands for the detectability of low concentrations are conflicting in many situations with the required resolution and the sample capacity of the columns and/or the existing

Key Words:

Preparative capillary GC
Large sample volumes
Cold injection system
Temperature programmed vaporization
Multicolumn switching

Summary

A new design of a mass-flow controlled multidimensional switching system for capillary gas chromatography is introduced and discussed. Large sample amounts can be introduced with a required input band width onto the first column. A combination of cold sample introduction and successive high speed programmed heating of the injector liner is used for this purpose. The potential of such an approach for selective and fast high resolution separations with series coupled wide bore, thick film columns is emphasized, and illustrated for various concentrations.

sample introduction systems. For instance, narrow bore columns offer high plate numbers per unit length ($n \sim 1/d_c$) and short analysis times ($t_r \sim d_c - d_c^2$), dependent on the pressure drop across the column [1]. Unfortunately these columns have a low sample capacity ($\sim d_c^3$) and a relatively small working range (W_o), being the ratio of the column sample capacity (Q_s) and the minimum detectable amount (Q_o) [2, 3]. Wide bore columns, which have a rather high sample capacity, show a low separation efficiency and are relatively slow.

Considering the effect that the required plate number is decreasing considerably with increasing selectivity of the stationary phase, the combination of a sample introduction system that can accept relatively large sample volumes (5–100 μ l) and a multidimensional switching system with selective wide bore thick film columns, is highly attractive.

In this paper a new, mass flow controlled multidimensional switching system is introduced in combination with a temperature programmed cold injection system. The system permits cold sample introduction and successive high speed temperature programmed desorption of the sample, which has been deposited in the cold liner of the injection system with a low heat capacity. The aim of this paper is to introduce, discuss, and illustrate the possibilities of an optimal combination of the introduction and selective multidimensional separation of large complex samples.

2 Experimental

2.1 Columns

Column 1: $L = 25$ m; i.d. = 0.53 mm; $d_f = 5$ μ m; stationary phase = OV-1 (Hewlett Packard, Avondale, PA, USA); Column 2: $L = 3$ m; i.d. = 0.53 mm; $d_f = 3$ μ m; stationary phase = OV-1 (Hewlett Packard, Avondale, PA, USA); Column 3: $L = 5$ m; i.d. = 0.53 mm; $d_f = 5$ μ m; stationary phase = OV-1 (home made); Column 4: $L = 25$ m; i.d. = 0.53 mm; $d_f = 5$ μ m; stationary phase = OV-17 (home made).

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Figure 1

Schematic design of a single column system. a: split (MFC1 = open, MFC2 = closed, NV = open) or first stage of solvent elimination (MFC1 = open, MFC2 = open, NV = open). b: splitless or second stage of solvent elimination (MFC1 = open, MFC2 = closed, NV = closed). AT = adsorption trap; C = column; CIS = programmed cold injection system; D = detector; DPG = digital pressure gauge; ES = effluent splitter; IS = inlet switching device; MFC = mass flow controller; NV = needle valve.

Figure 2

Schematic design of a dual column system. a: Series coupled columns. (MFC1 = open, MFC2 and 3 = closed, both needle valves (NV1 and 2) = closed). b: Series coupled columns, solvent elimination mode. (MFC1 = open, MFC2 = open, MFC3 = closed, NV1 = open, NV2 = closed). Abbreviations: see Fig. 1; CS = column switching device.

2.2 Instrumentation

A HP 5880 gas chromatograph provided with a double level 4 GC-terminal and equipped with a HP 7671A auto sampler (Hewlett Packard, Avondale, PA, USA) was modified for this study. A programmed Cold Injection System – CIS – (Gerstel GmbH, Mülheim a/d Ruhr, FRG) that allows high speed thermodesorption and transfer of interesting fractions of the sample, which has been deposited temporarily in the injector, onto the column, was made compatible with the GC instrument and the autosampler. A newly designed prototype of a mass flow controlled switching device system was installed in the GC oven. A preliminary series of experiments were performed with a single 25 m wide bore (0.5 mm i.d.) thick film (5 μ m) OV-1 column (Hewlett Packard, Avondale, PA, USA). The column inlet was connected to an inlet switching device and an effluent splitter as shown in **Figure 1**.

In principle, the system can be used for both hot and cold split as well as hot and cold splitless sample introduction. It allows solvent elimination in the cold splitless mode, which is particularly interesting for on-line enrichment of diluted samples. A schematic design of these operation modes is given in Figures 1a and 1b.

For the second series of measurements a dual column system is used, as shown schematically in **Figure 2**. The system consists of an inlet switching device (IS) between the CIS and the first column, a 3 m wide bore (0.5 mm i.d.) thick film (3 μ m) OV-1 column switching device (CS), two FID detectors (D_1 , D_2), an effluent splitter and two adsorption traps. The first trap is placed in the injector vent line (AT1) and the second one between the first and the second column (AT2). Compared to the set-up given in Figure 1 for a single column system, an additional flow controller is required in order to block the entry of the eluent of the first column has to be avoided. In that case a small flow in the connecting lines between the outlet and the inlet of the column switching device (CS) is required (counterflow).

Obviously, a third separation dimension is optional, by using a liner packed with a selective column packing material.

As shown in **Figure 3a** the solvent can also be partly or totally flushed after the first column. The first of these options can be applied in order to complete the solvent flush of the inlet splitter. Dependent on whether MFC3 is open or closed the column effluent of the first column can be

either vented via AT2 or transferred to the second column. Parallel chromatograms can be registered by both detection systems. In case of total solvent flush after the first column, the inlet splitter is not functional and can be omitted (cf. Figure 3b).

3 Results and Discussion

The importance of selectivity is clearly demonstrated by the following expression:

$$n_{\text{req}} = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{1 + k}{k} \right)^2$$

Where

n_{req} = required plate number

R = resolution

α = selectivity factor or relative retention time

k = capacity factor

Increasing of the selectivity factor (α) from 1.01 to 1.5 results in a thousand-fold decrease of the required plate number. For columns with a reasonable pressure drop, using H_2 carrier gas and a column diameter 0.25 mm, for a component with a capacity ratio $k = 5$, a baseline separation of two adjacent peaks ($R = 1$) requires a column length of about 25 m and 2 cm for α values of 1.01 and 1.5, respectively. Although

Figure 3

Schematic design of a dual column system with and without inlet splitter. a: Series coupled columns: – First column only or solvent elimination after the first column (MFC1 = open, MFC2 = closed, MFC3 = open, NV1 = closed, NV2 = open). – First and second column simultaneously in parallel (MFC1 = open, MFC2 = closed, MFC3 = open, NV1 = closed, NV2 = open). b: Series coupled columns without inlet splitter. For comments see Fig. 3A. Abbreviations see Fig. 2.

wide bore columns have a relatively low efficiency, they can be used for separation and analysis of complex mixtures in multidimensional systems with an optimized selectivity. The power of multidimensional capillary GC has been studied and advocated by many chromatographers [4–15]. Considering the potential of this multidimensional approach, however, its application is amazingly limited, although sophisticated instrumentation of high quality is available. Most probably, the existing systems are considered rather complicated and sometimes difficult to optimize. They are used so far mainly for analytical applications and sample amounts of 1–50 ng per component. This is most probably due to the limited sample capacity of the available columns. Application of wide bore thick film columns, which have a rather large sample capacity, is therefore a highly interesting area for analytical as well as preparative multidimensional capillary GC. It allows on-line and off-line combination with MS (also for lower concentrations), FTIR, NMR, and other less sensitive hyphenated detectors, for identification purposes. In this paper we briefly introduce an extremely promising combination of a temperature programmed cold injection system and a new design of a multidimensional switching system in combination with wide bore thick film columns.

The gas flows are mass flow controlled, so that the optimization of the system, which is operated either manually or automatically, is fairly easy and reproducible.

Sample sizes up to 100 μl can be handled in the so-called "solvent flush" mode for diluted samples. The interesting part of the sample, with a volatility sufficiently different from the solvent, is deposited in the cold liner of the injector. Large sample quantities ($>10 \mu\text{l}$) are introduced so far by repeated injections. The deposited sample fraction is successively completely transferred to the column by high speed temperature programmed heating of the liner (12°C/s). After thick film or if necessary cold trap refocusing of the components, they are separated in the respective column switching systems. The sample inlet band is refocused prior to the start of the separation by a careful adjustment of the desorption time and column operating conditions such as initial temperature and initial hold time, etc. Various operational modes have been described in the experimental part at this stage. The potential of the system for multidimensional preparative separations is emphasized and illustrated using wide bore thick film non-polar

Figure 4

Series coupled columns (cf. Fig. 2 a). Column temperature = 80°C ; column 1 = OV-1, $L = 3 \text{ m}$, $d_i = 3 \mu\text{m}$, i.d. = 0.5 mm ; column 2 = OV-1, $L = 25 \text{ m}$, $d_i = 5 \mu\text{m}$, i.d. = 0.5 mm . Carrier gas = helium; $p_i = 0.3 \text{ bar}$. Injection system = CIS, Injection temp. = $100^\circ\text{C} \rightarrow 12^\circ\text{s} \rightarrow 300^\circ\text{C}$. $v_i = 0.1 \mu\text{l}$. Components: 1 = ethylbenzene (19 %); 2 = m/p-xylene (58 %); 3 = o-xylene (4 %).

Figure 5

Operating conditions, see Fig. 4. The arrow indicated parts in the chromatograms a_1 , a_2 and a_3 are transferred to column 2 (chromatograms b_1 , b_2 and b_3).

columns, in this study. Aspects like purity of the isolated peaks in relation with recovery and losses due to intended or accidental inaccurate peak cutting are demonstrated by a series of chromatograms of a non diluted industrial solvent sample. The examples focus on the effects of preseparation, timing of the switching, sample quantity on purity and recovery for components of various concentrations of components which are hardly or not at all separated on the first column. The experiments are performed with a dual column system in the splitless mode (cf. Figures 2 b and 3 a).

The separation of the sample on the first (a) and the second (b) column is illustrated in Figure 4. The peaks 1–3 which are co-eluting at the end of the first column, are separated after the second column in the series coupled operation mode. In the following we will concentrate on the separation of this group of alkylaromatics.

3.1 Effect of Switching and Preseparation on Recovery and Purity

In Figure 5 the parts indicated by arrows in the first chromatograms (a_1 – a_3) are

Figure 6

Operating conditions for chromatograms a_1 and b_1 , see Fig. 4. Operating conditions for chromatograms a_2 and b_2 , see Fig. 4, except column temperature: 40 °C (4 min) $\rightarrow$ 5°/min $\rightarrow$ 150 °C.

transferred to the second column in order to demonstrate a selective recovery of *m* + *p*-xylene (peak 2 in Figure 4b). The ethylbenzene peak (#1) that is present in the first part of the mixed (major) peak at the end of the first column is still present after the second column if a high recovery is intended as shown in Figures 5 a_1 –5 b_1 and 5 a_2 –5 b_2 . The *o*-xylene (peak #3) content, however, is reduced to a negligible level. Obviously, the purity of the main peak (#2) can be improved at the cost of recovery. In Figure 5 b_3 also the ethylbenzene peak is completely removed. Although the recovery has dropped considerably, a quantity of approximately 20 μ g has been left in this latter case.

Simultaneous isolation of two or more peaks is also possible. This is demonstrated in Figures 6 b_1 and b_2 . Sample transfer of the arrowed parts of the unresolved peaks in the first column results in an extremely pure *o*-xylene peak (#3 in Figure 4), while the ethylbenzene peak (#1 in Figure 4) is also already fairly pure. The concentration of *m/p*-xylene has decreased from 58 % v/v in the original sample to about 1 % v/v. This result can easily be improved by optimization of the separation in the first column, e.g. by changing the operating conditions or using a selective precolumn. Obviously, a slight improvement of the separation in the first column results simultaneously in a higher purity and an increased recovery ($\approx$ 15 μ g) of the ethylbenzene peak at the end of the second column.

3.2 Effect of Sample Quantity on Recovery and Purity

Although a tenfold increase in injection volume results in a more serious peak overlap in the first column, it can be seen in Figure 7 that optimization of either purity or recovery can easily be obtained by trial

Figure 7

Operating conditions, see Fig. 4, except sample volume: 1 μ l.

and error. Considering the *o*-xylene peak (4 % v/v in the original sample) as a reference peak and comparing the recoveries of ethylbenzene (19 % v/v in the original sample) in Figures 7 b_1 and 7 b_2 , expectedly a smaller fraction of the *m/p*-xylene was transferred to the second column in the latter case. Although this recovery amounts to about 25 % of the quantity originally present in the sample, the absolute amount appears to be about 40 μ g with a high degree of purity. The *m/p*-xylene peak is reduced to less than 1 % of its original value.

Finally, although this is not the ultimate limit of sample load, one of the major compounds of a non-diluted 10 μ l bergamot oil sample, linalyl acetate, is isolated in a temperature programmed run as

shown in Figure 8. A combination of a 5 m thick film OV-1 and 25 m thick film OV-17 column was used for this purpose. The isolated quantity is estimated about 250 μ g.

4 Conclusions

Multicolumn separations with wide bore thick film capillary columns in combination with a new design of a mass flow controlled universal switching device and a temperature programmed cold injection system are highly attractive for preparative capillary gas chromatography of complex samples, particularly for low concentrations. The system is applicable for on- and off-line identification by means of GC/MS (also for low concentrations) and FTIR, NMR and

Figure 8

Column 1: $L = 5$ m, i.d. 0.53 mm, $d_f = 5$ μ m, OV-1. Column 2: $L = 25$ m, i.d. 0.53 mm, $d_f = 5$ μ m OV-17 (home made). Carrier gas = nitrogen, injection volume = 10 μ l, injection system: C.I.S.; 50 °C (0) $\rightarrow$ 12 °/s $\rightarrow$ 300 °C. Column: 90 °C (1) $\rightarrow$ 10 °/min $\rightarrow$ 230 °C. The arrow indicated part in Fig. 8a is transferred to the second column (8b).

other hyphenated detectors that require minimum sample amounts above 10 μ g, per component. The combination can also be applied for high resolution GC analysis of diluted samples and with normal bore columns by selective solvent flush prior to separation. Sample introduction by means of available automatic samplers appears no problem.

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