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New Developments in Multi-Dimensional Capillary Gas Chromatography

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Multi-Dimensional, Multi-Column Switching, Backflush, Early Vapor Exit, Venting, Large Volume Injection.

Abstract
Multi-dimensional capillary gas chromatography has been used for many years to aid in the determination of trace impurities in relatively pure products, to isolate analytes from complex matrices, and to improve chromatographic resolution.

Major drawbacks to these systems have been the complexity of the hardware, difficulty of use, and system instability. A new line of multi-dimensional systems will be presented that overcome these drawbacks by using septumless sample introduction, microprocessor controlled proportional valves and electronic mass flow controllers, valveless switching, integrated analyte cold trapping, and complete Windows™ based software control. The line consists of three systems that are designed to cover all multi-dimensional applications.

Examples of these systems' use will be presented covering food and flavors, industrial chemicals, environmental analysis, and large volume injection.

Single Column Switching System SCS

The SCS is a simple switching system for solving a wide range of problems. The system allows switching or venting between the inlet and the analytical column. This feature is especially valuable when doing large volume injection in combination with a PTV type inlet, because it prevents solvent vapor from entering the column.

The systems' performance can be enhanced by adding a retention-gap or short pre-column. This permits the use of the early vapor exit technique for large volume injection, and also provides protection for the column and detector by venting high boiling compounds or unwanted interferences. By adding EPC pneumatics to the inlet, GC runtime can be further reduced by backflushing unwanted compounds.

Another configuration places the switching device between the analytical column and detector. Here the decision to vent whole fractions or even single compounds can be made after full chromatographic separation. The SCS can easily be installed in either new or existing GCs and can also be upgraded to the DCS or MCS systems.

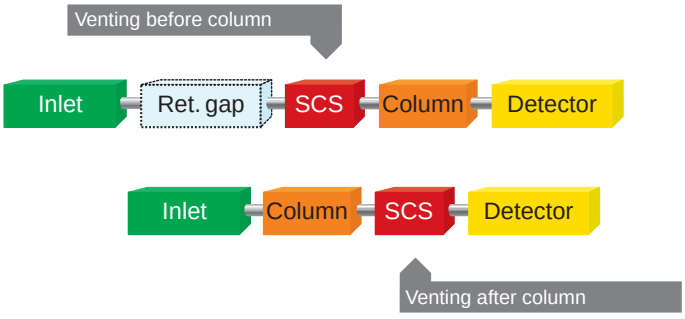


Figure 1. Single column switching system SCS.

The example of diesel fuel demonstrates the after-column venting technique. 1 µl of diesel fuel (1:100 in hexane) is injected onto the analytical column. Figure 2 shows the chromatogram without venting. Figure 3 shows the same sample, but this time the solvent is vented and the high boiling components are backflushed.

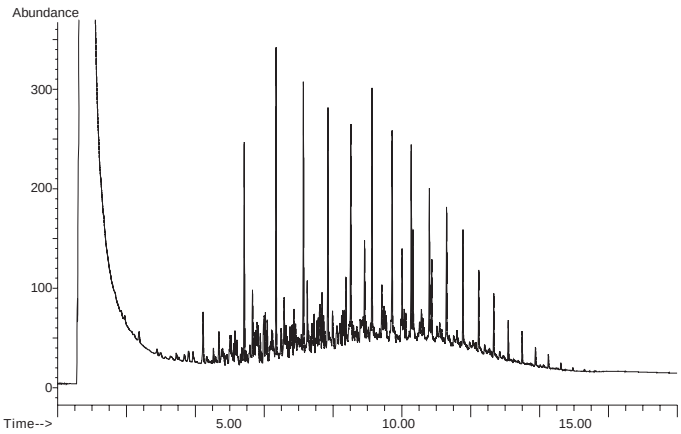


Figure 2. Diesel, 1:100 in hexane, without venting.

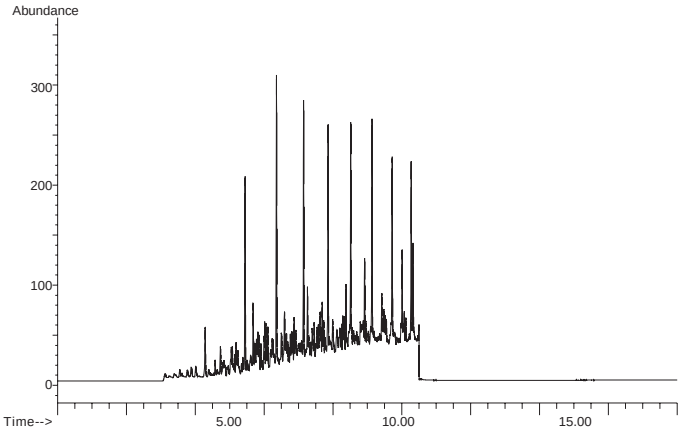


Figure 3. Diesel, 1:100 in hexane, venting and backflush.

Analysis Conditions Figures 2-3.

PTV:	split 1:10 30°C, 12°C/s, 350°C (5 min)
Column:	12 m HP-1 (Hewlett-Packard), d_i= 0.20 mm, d_f= 0.33 µm
Pneumatics:	He, P_i= 93 kPa cut 1 = venting 0-3 min cut 2 = backflush at 10.4 min
Oven:	40°C (3 min), 20°C/min, 300°C (1 min)

The other example shows chromatograms from an environmental standard of 175 compounds at a concentration of 20 ppm each in dichloromethane. First, 1 µl of the undiluted standard is injected in splitless mode, then 100 µl of a 1:100 dilution of the standard in dichloromethane is injected.

This time a megabore pre-column is installed as a retention gap, and a cryotrap is used to cryofocus the analytes at the beginning of the analytical column. 100 µl are injected on-column into the megabore capillary, the solvent is separated from the analytes and vented.

The compounds of interest are cryofocussed and then transferred to the analytical column.

With this technique it is possible to achieve 100% recovery of compounds with boiling points starting at that of benzene.

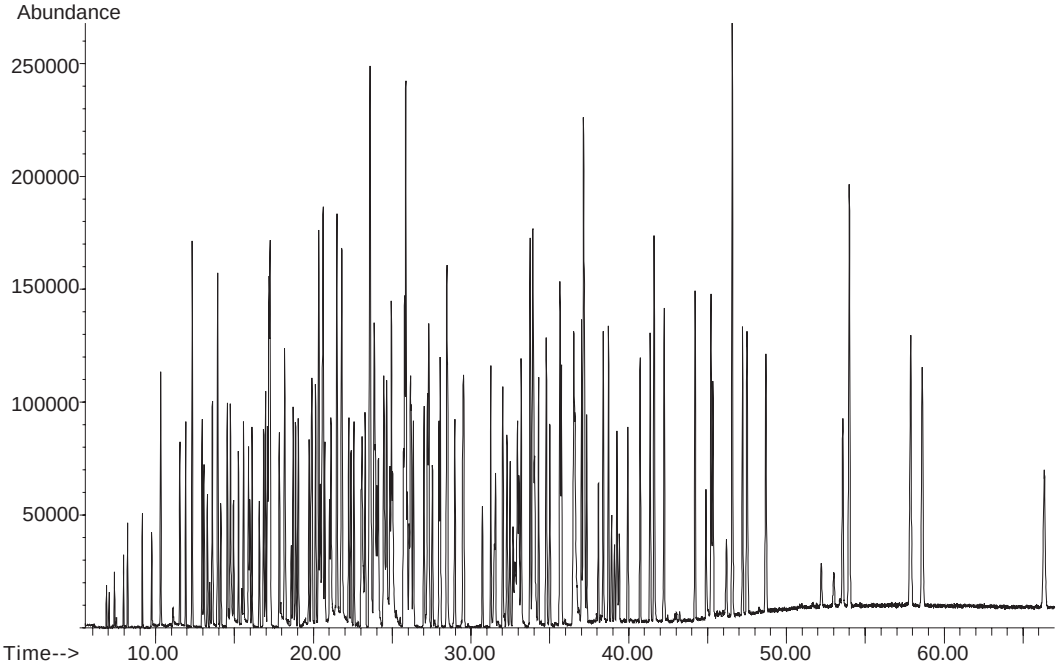


Figure 4. 1 µl of a 175-compound standard, undiluted.

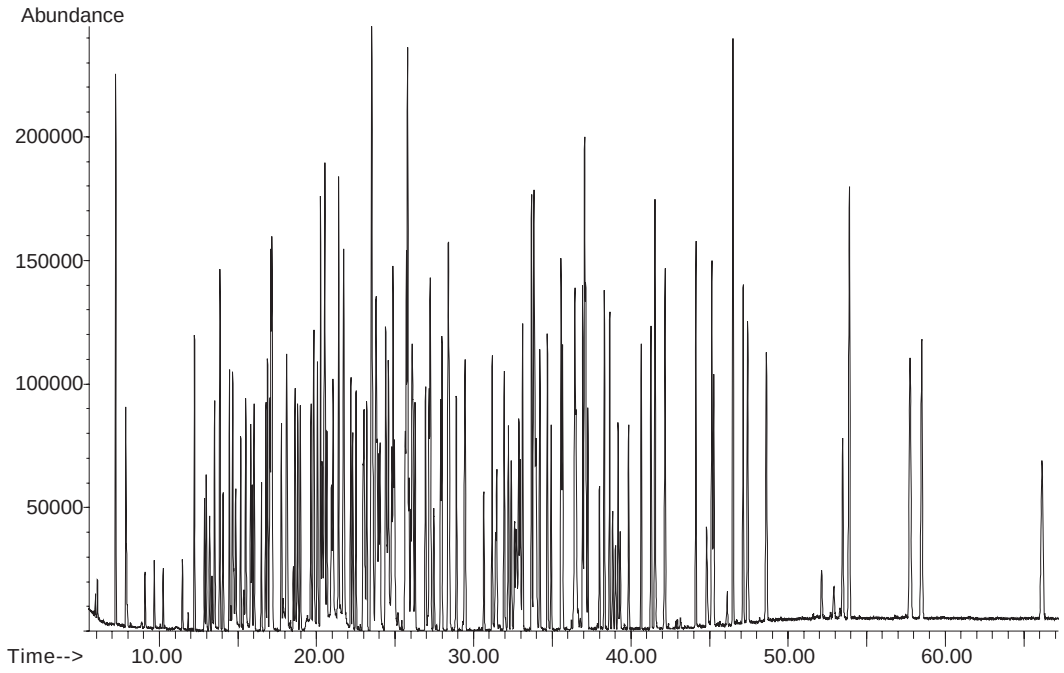


Figure 5. 100 µl of a 175-compound standard, diluted 1:100.

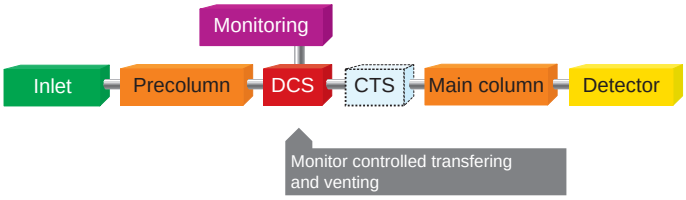
Analysis Conditions Figures 4-5.

PTV:	60°C, 12°C/s, 280°C (3 min)	Oven 1:	40°C (1 min), 10°C/min, 250°C (60 min)
Column 1:	25 m SB 1 (IAS), d_i= 0.53 mm, d_f= 1.0 µm	Oven 2:	50°C (1 min), 5°C/min, 280°C (3 min)
Column 2:	50 m HP-1 (Hewlett-Packard), d_i= 0.32 mm, d_f= 1.05 µm	CTS:	-150°C (25 min), 20°C/s, 280°C (5 min)
Pneumatics:	He, P_i= 120 kPa cut = venting 0-1 min		

Dual Column Switching System

DCS

The DCS is a versatile switching system for solving complex problems. It incorporates all SCS capabilities, but greatly increases its applicability by adding electronic mass flow controlled switching and a valveless, low dead volume crosspiece that also provides „real-time“ monitoring of the sample analysis. The system can be installed as a single or dual oven system, with or without cryofocussing options, and therefore, allows classical multi-dimensional separations to be performed as well as on-line analyte enrichment or sample clean-up.



It can be used for a wide range of applications such as:

1) Optimizing separations through column phase selection between pre-column and analytical column.
2) Elimination of sample matrices, and isolation of compounds of interest in complex mixtures.
3) On-line analyte enrichment by combining a high sample capacity pre-column with a high resolution analytical column.

The chromatograms show the analysis of a „medicinal“ off-odor in a shampoo. Due to the complexity of the sample, standard analysis methods failed, and only a multidimensional approach could solve the problem. The off-odor was identified as the flame retardant 2,6-dibromophenol. The shampoo was contaminated because it was made in the same reactor as the phenol, but the reactor was not cleaned sufficiently.

Figure 6. Dual column switching system DCS.

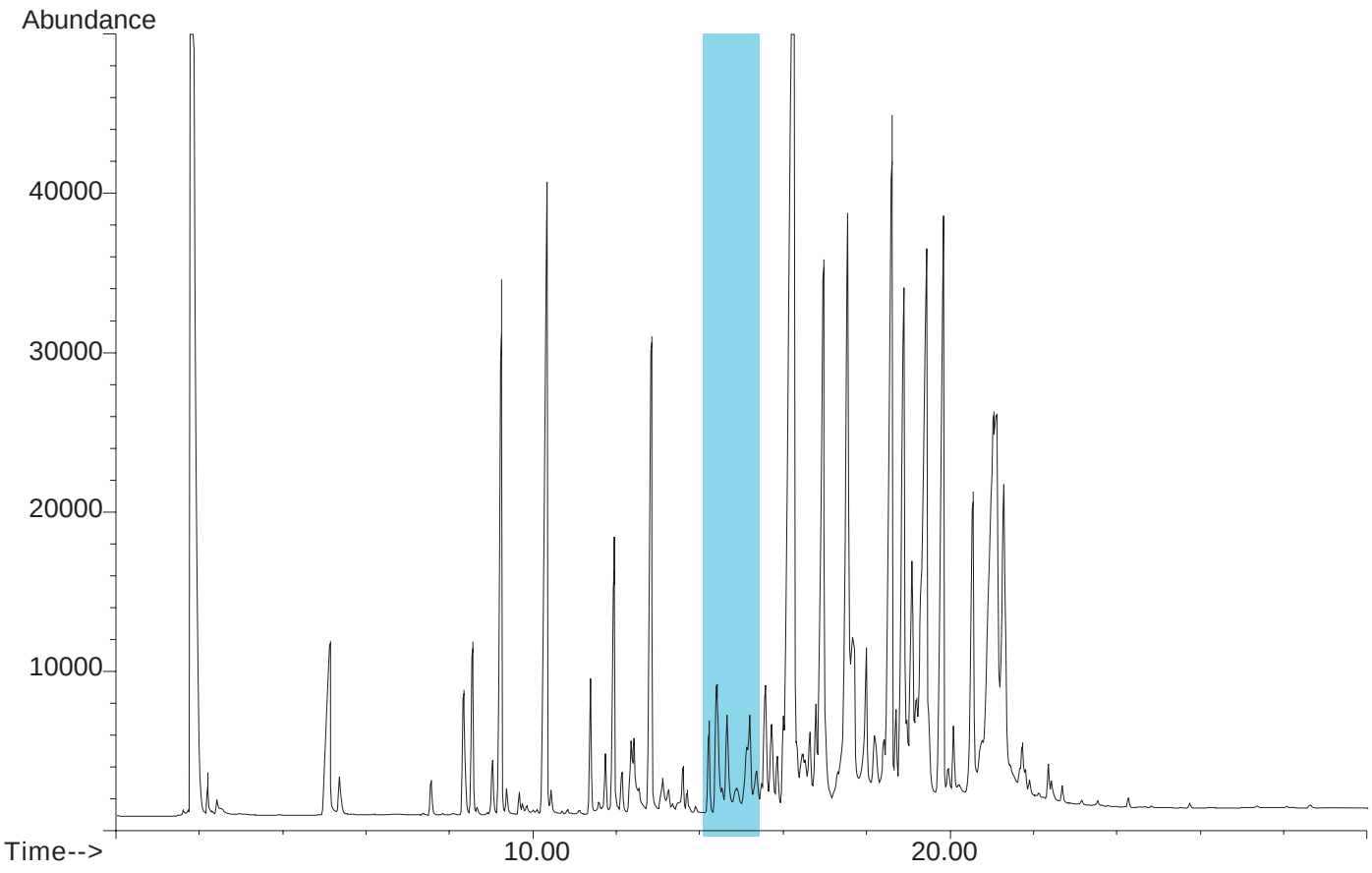


Figure 7. Shampoo-Extract, pre-column chromatogram (FID), marked compounds transferred.

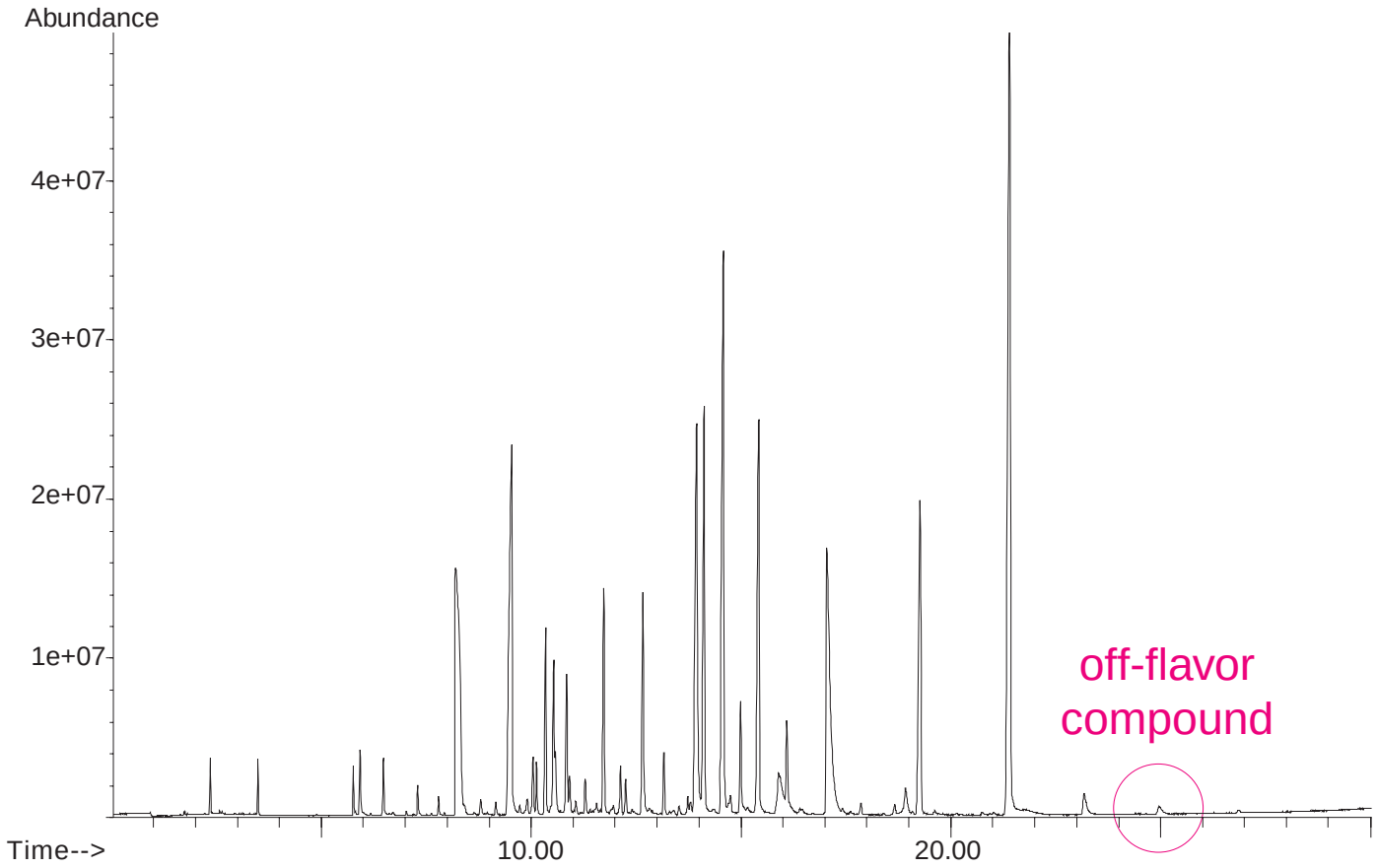


Figure 8. Shampoo-extract, main column chromatogram (MSD), separation of transferred fraction.

Analysis Conditions Figures 7-8.

PTV:	60°C, 12°C/s, 280°C (3 min)
Column 1:	25 m SB 1 (IAS), d_i= 0.53 mm, d_f= 1.0 µm
Column 2:	50 m HP-1 (Hewlett-Packard), d_i= 0.32 mm, d_f= 1.05 µm
Pneumatics:	He, P_i= 120 kPa cut = venting 0-1 min
Oven 1:	40°C (1 min), 10°C/min, 250°C (60 min)
Oven 2:	50°C (1 min), 5°C/min, 280°C (3 min)
CTS:	-150°C (25 min), 20°C/s, 280°C (5 min)

Multi Column Switching System MCS

The MCS is the most advanced column switching system available, providing unsurpassed flexibility for gas chromatographic analysis. It incorporates all the features of the SCS and DCS, and adds independent flow control of both the pre-column and analytical column. Since the flow control of the second column is achieved by controlling pressure at the crosspiece, the system is compatable with EPC pneumatic systems. This capability allows the MCS to optimize separations or perform on-line clean-up using a combination of capillary columns with different diameters, lengths, and flows.

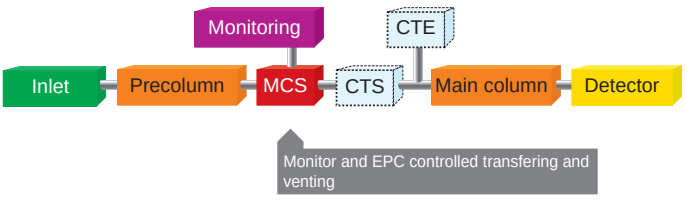


Figure 9. Multi column switching system MCS.

Figures 10 and 11 show the multi-dimensional analysis of oxygenates in a decene cut. Peak shapes of compounds eluting close to the main component are usually distorted and can‘t be analysed. Transfer of only the desired fraction of compounds onto a different polarity column eliminates this effect and easily allows the identification of the oxygenates.

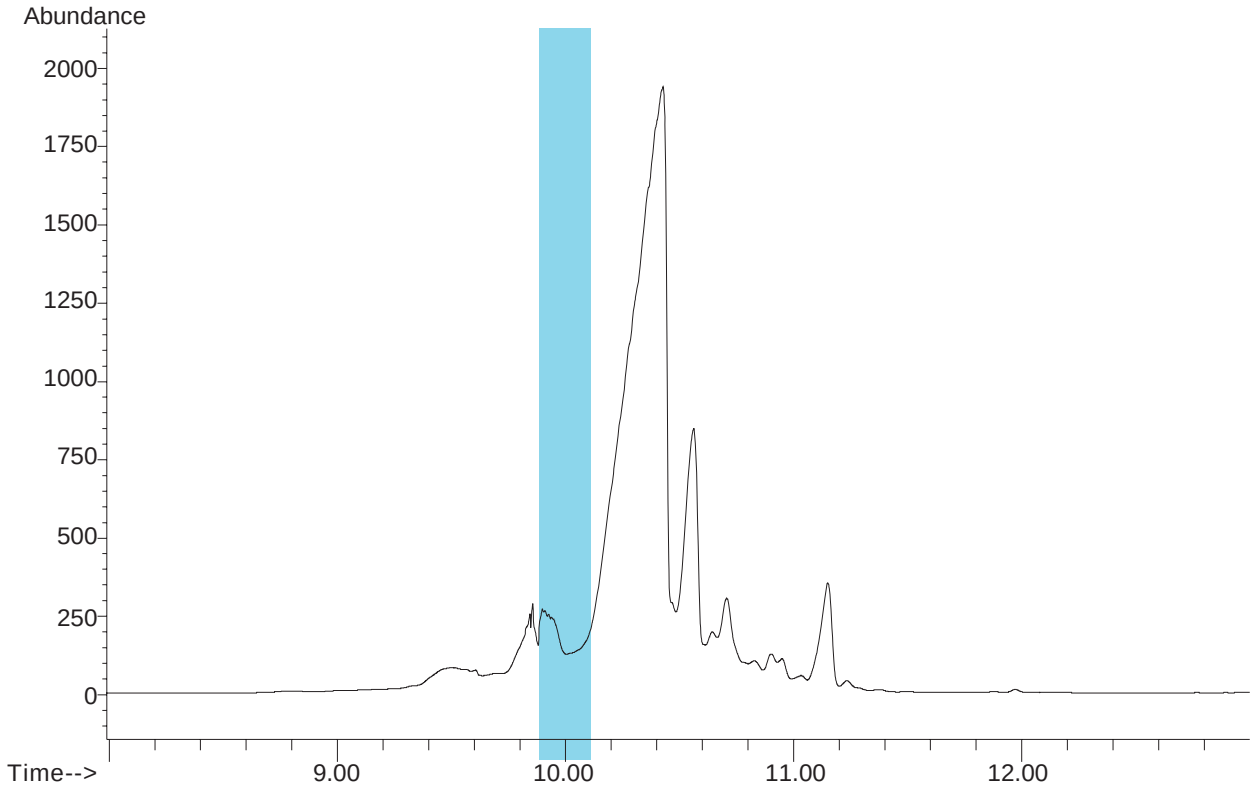


Figure 10. Pre-column chromatogram of a decene-cut (FID), marked compounds transferred.

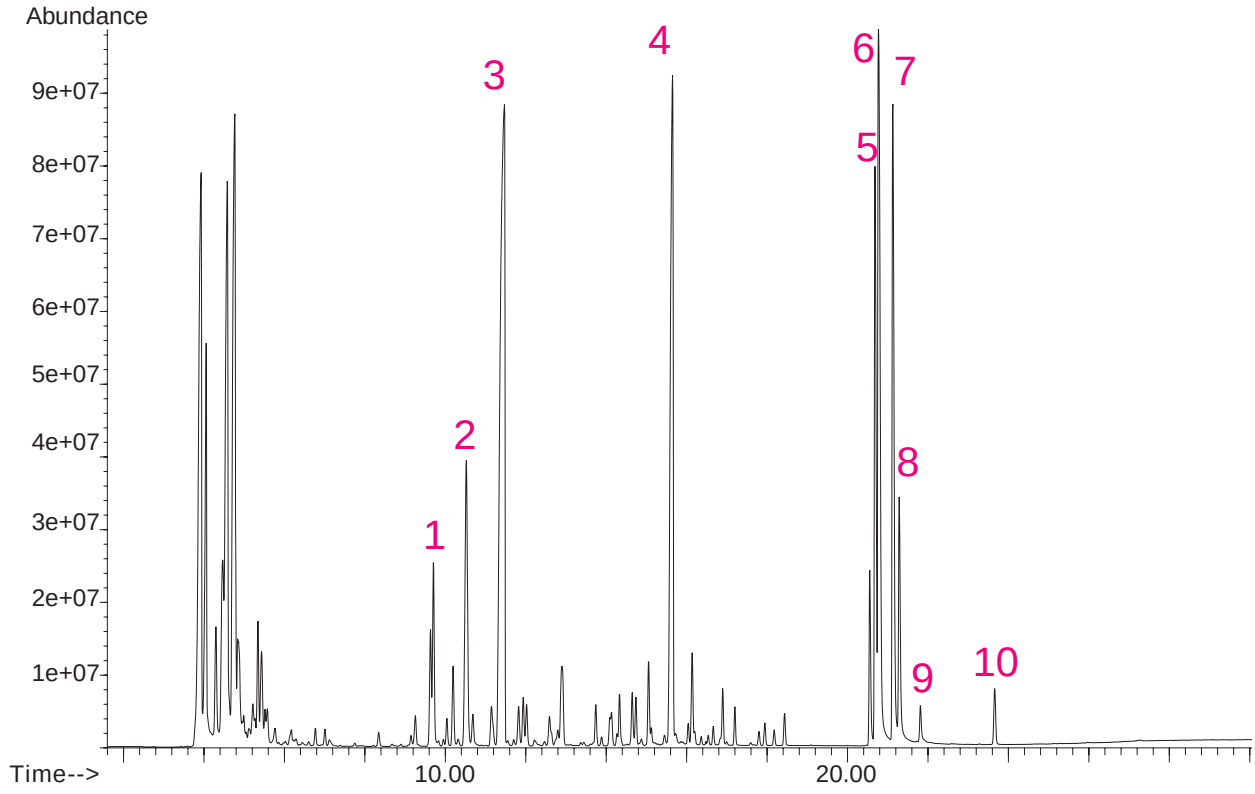


Figure 11. Main column chromatogram of the transferred fraction (MSD).

Figure 12 and 13 show the analysis of a naphtha sample. Here the complexity of the naphtha is the problem, no capillary column is able to separate all compounds sufficiently. The transfer of only a fraction, e.g. between two straight hydrocarbons, makes it possible to achieve the resolution necessary to identify even trace compounds.

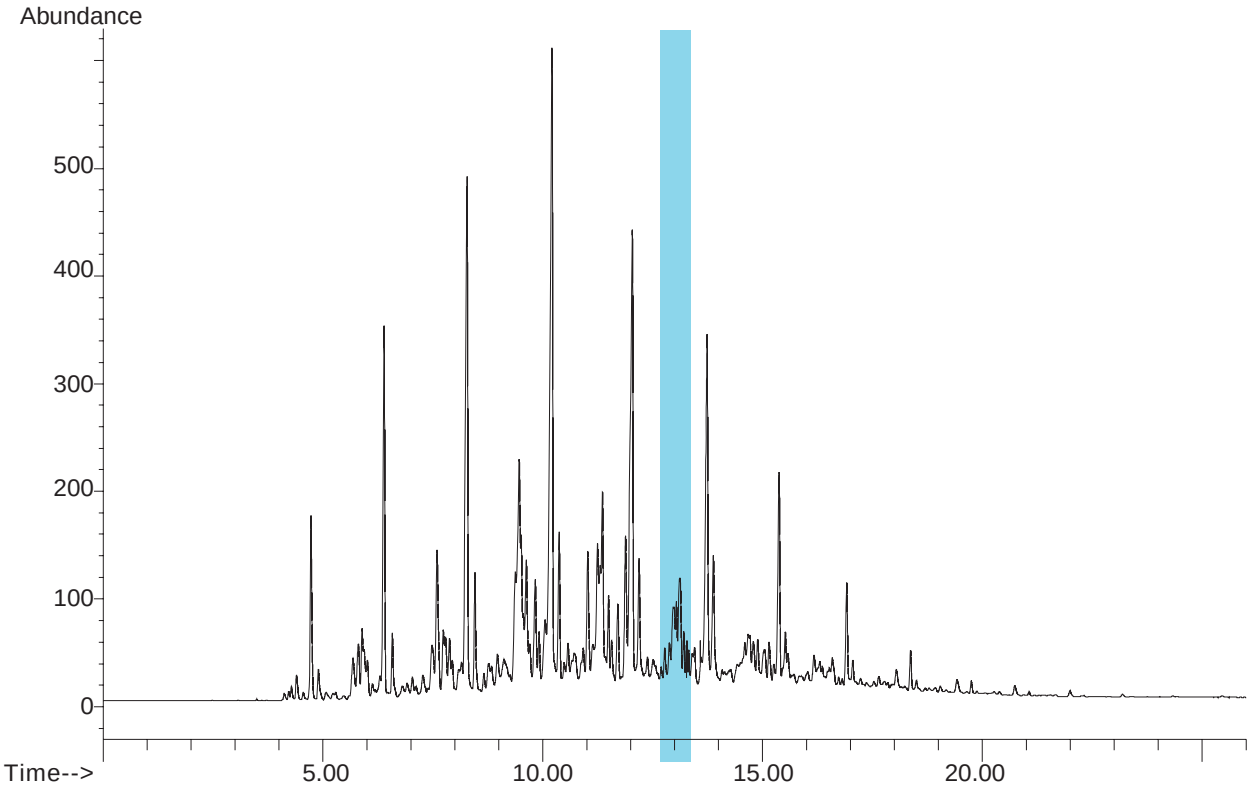


Figure 12. Pre-column chromatogram of naphtha, marked compounds transferred.

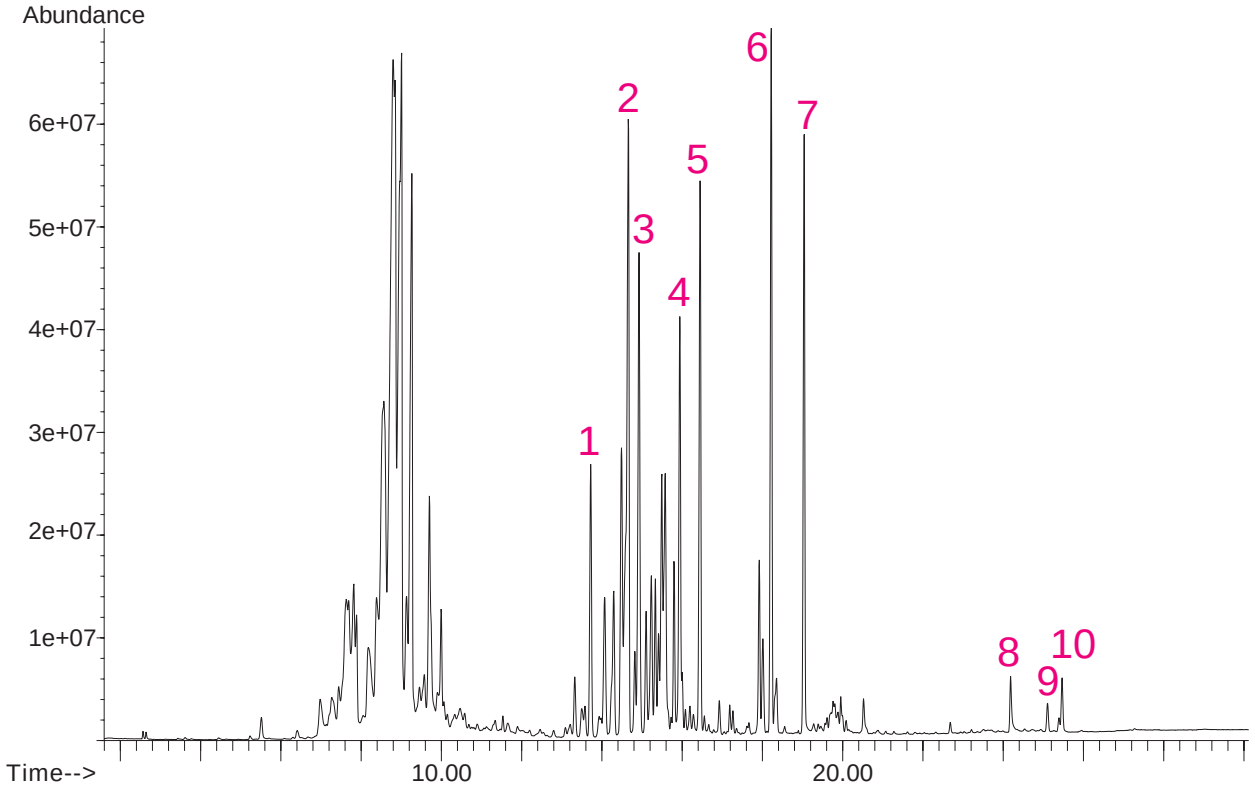


Figure 13. Main column chromatogram of the transferred fraction (MSD).

Table I. List of compounds figure 11.

No.	Compound	No.	Compound
1	C_3-Benzenes	6	2-Methyl Pentanoic Acid
2	3-Octanone	7	3-Methyl Pentanoic Acid
3	2-Octanone	8	4-Methyl Pentanoic Acid
4	1-Heptanol	9	Hexanoic Acid
5	2-Ethyl Butanoic Acid	10	Phenol

Table II. List of compounds figure 13.

No.	Compound	No.	Compound
1	tert-Pentylbenzene	6	Methylindene
2	Pentylbenzene	7	Nonanol
3	1,6-Dimethylindane	8	Caprylic Acid
4,5	Dihydromethyl indene	9,10	C_2-Phenol

Analysis Conditions Figures 10-13.

PTV: 60°C, 12°C/s,
300°C (5 min)

Column 1: 30 m HP-1 (Hewlett-Packard),
d_i= 0.32 mm, d_f= 1.05 µm

Column 2: 50 m HP-InnoWax (Hewlett-Packard),
d_i= 0.25 mm, d_f= 0.25 µm

Pneumatics: He, P_i= 80 kPa
cut = transfer 12.7 - 13.25 min

Oven 1: 50°C, 10°C/min,
300°C (10 min)

Oven 2: 40°C (1 min), 5°C/min,
100°C, 10°C/min
240°C (30 min)

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