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Applications of Mass Flow Controlled Multi Column Switching in On-Line Capillary GC/MS

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KEYWORDS

PTV-injection, multi column switching, cryotrapping, capillary GC-MS, industrial applications

Abstract

The separation and analysis of low concentrations of organic compounds in complex sample matrices, such as petroleum products, waste and drinking water, food, beverages and pharmaceutical products is a rather complex analytical problem. Current methods are hampered by insufficient resolution obtained by single capillary columns even if they have rather high plate numbers.

In this paper the potential of a combination of programmed temperature sample introduction and mass flow controlled multi column dual oven capillary gas chromatography and on-line mass spectrometry will be discussed and illustrated.

The effect of cold trapping in between the columns for components with a moderate volatility will be demonstrated for different applications dealing with the determination of trace impurities in various main products such as gasoline, aromatics, steroids and aniline.

Introduction

Due to ever increasing demands for resolution, sample volume and detection limits in capillary GC nowadays, multi column switching is becoming increasingly important. Essentially these problems are related to the complexity of the samples and the required compatibility of sample size, input band width, column properties, detector specifications and the actual concentrations of the components of interest in the sample.

To realize adequate analysis a number of clean-up and/or enrichment steps, or solvent elimination for diluted samples prior to separation, are needed in order to achieve the required separation efficiency and detection limits. The identification by an on-line coupled MS-system is another breakpoint in the analysis of such complex mixtures, particularly if they elute in low concentrations close together with a major component. Multi column switching is, therefore, an attractive approach to solve these problems, particularly if high and low concentrations have to be determined simultaneously.

The aim of this paper is to demonstrate the possibilities of a combination of temperature programmed sample introduction, multi column dual oven capillary GC, coupled on-line with mass spectrometry in order to enhance identification. The effect of cryotrapping at the inlet of the second column will be emphasized.

EXPERIMENTAL

Instrumentation. The system consists of a combination of a manual or automatic injection (HP 7673, Hewlett-Packard, Avondale, USA), a temperature programmable cold injection system (CIS-3, Gerstel GmbH, Mülheim an der Ruhr, Germany), a multi column switching system (MCS A or MCS P, Gerstel GmbH, Mülheim an der Ruhr, Germany),2 Ovens (HP 5890 series II, Hewlett-Packard, Avondale, USA) with a cryotrapsystem (CTS-1, Gerstel GmbH, Mülheim an der Ruhr, Germany) in between and a mass selective detector (HP 5971, Hewlett-Packard, Avondale, USA) as illustrated in **Figure 1**.

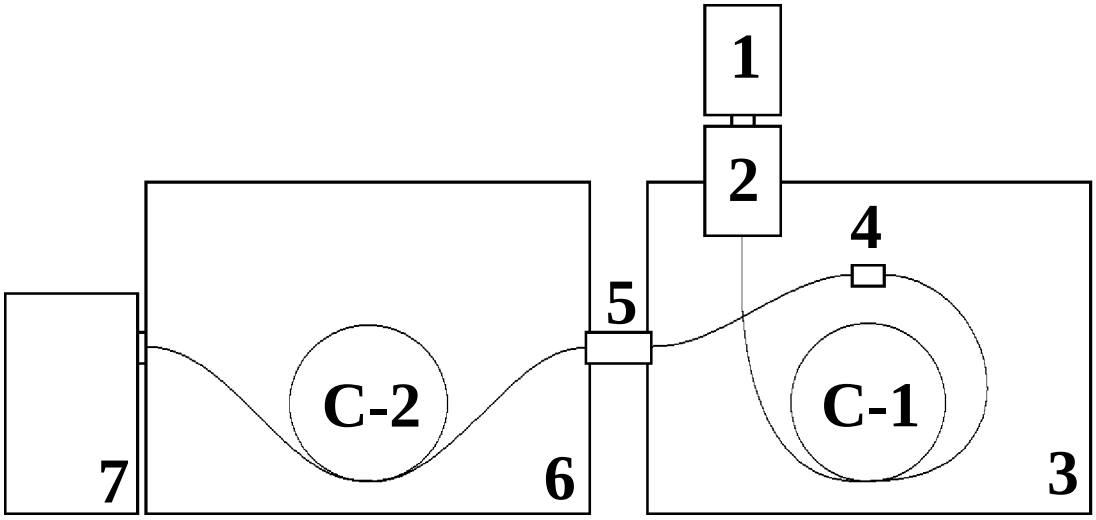

Figure 1. *Schematic diagram of the applied system consisting of a manual or automated injector, a temperature programmable cold injection system with septumless sampling head (2), a GC (3) configured with monitor-FID, column switching device (4) and MCS A or MCS P-pneumatic, connected via a heated transferline with included cryotrap (5) to a second GC (6) with a mass selective detector (7).*

The pneumatics of the multi column switching systems used in this study are presented in **Figure 2a** and **b**.

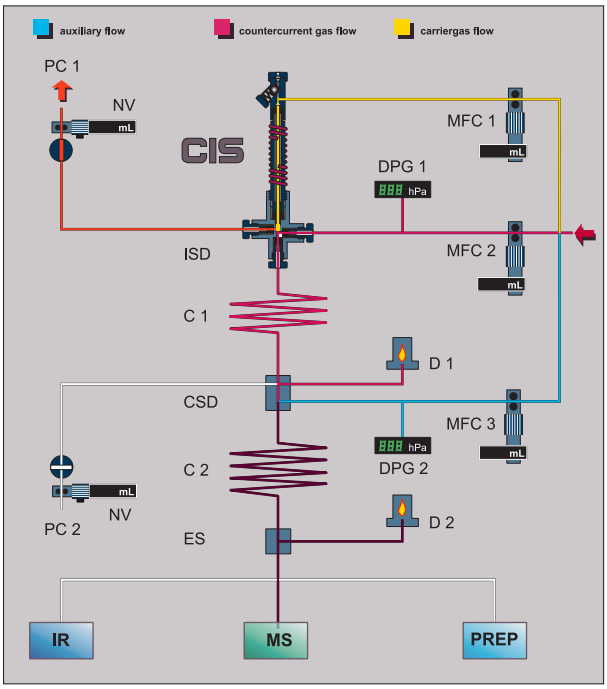

Figure 2a. *Schematic design of a dual column MCS P system. Solvent flush prior to the first column NV1 and MFC2, both open.*

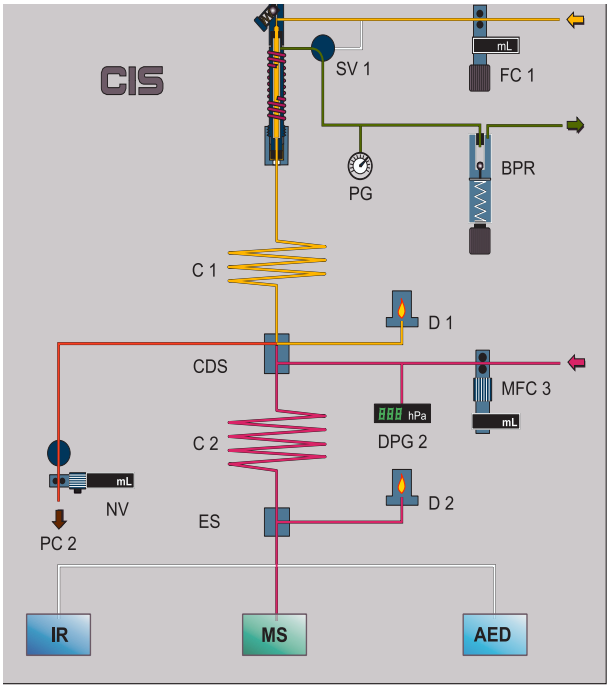

Figure 2b. *Schematic design of the multi column MCS A system. Solvent flush via splitline, MFC3 open.*

The switching pneumatics of both systems are mass flow controlled. The carrier gas flow of the MCS P system is mass flow controlled, the carrier gas flow of the MCS A system is pressure controlled.

Results

Multi column switching is the most powerful approach for analytical and preparative separation of components which can hardly or not at all be separated in single column systems. This is illustrated below for 5 different applications all dealing with the analysis of trace components, which elute very close to or together with a major component or the determination of trace impurities in highly pure products.

Example 1. Multi column determination of benzene and 1-me-cyclopentene in gasoline.

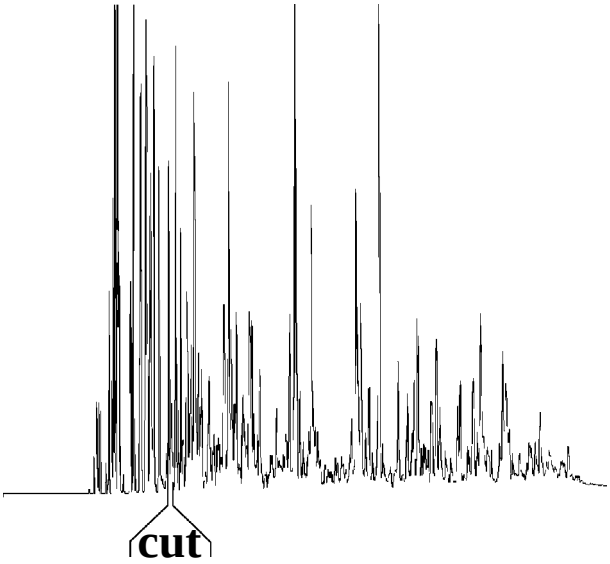

Figure 3a. *Precolumn chromatogram, 1 µl, splitless, marked components transferred to the main column.*

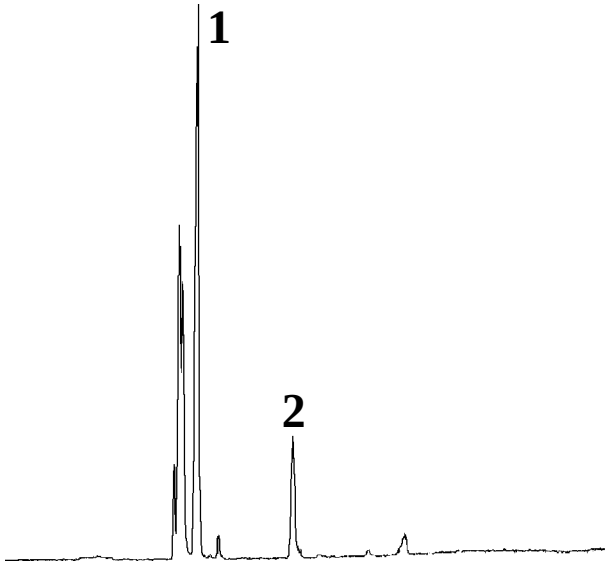

Figure 3b. *Main column chromatogram (TIC).*

Analysis conditions.

System:

MCS A, 2 columns, 2 ovens, CTS, MSD

Columns:

Pre-column in GC 1	50 m HP-1 (Hewlett-Packard)	
	d_i = 0.32 mm	d_f = 1.05 µm.
Main column in GC 2	50 m Wg-11 (WGA)	
	d_i = 0.25 mm	d_f = 0.2 µm.

Pneumatics:

Carriergas	He	p_i = 100 kPa	split x:50
Control flow		p_c = 30 kPa	10 ml/min
FID	H_2, 30 ml/min	Air, 300 ml/min	
	N_2, 30 ml/min		

Temperatures:

CIS	40°C;	↗ 320°C;	12°C/s.
Oven 1	50°C;	↗ 280°C;	5°C/min.
Oven 2	50°C;	↗ 120°C;	5°C/min.
CTS	220°C;	↘ -150°C;	12°C/s;
		↗ 220°C;	12°C/s.

Detectors:

Monitor detector	FID	
Main detector	MSD	Scan 10-350 amu

Compounds:

1. 1-Me-Cyclopentene
2. Benzene

Example 2. Multi column analysis of m-,p-xylene in ethylbenzene.

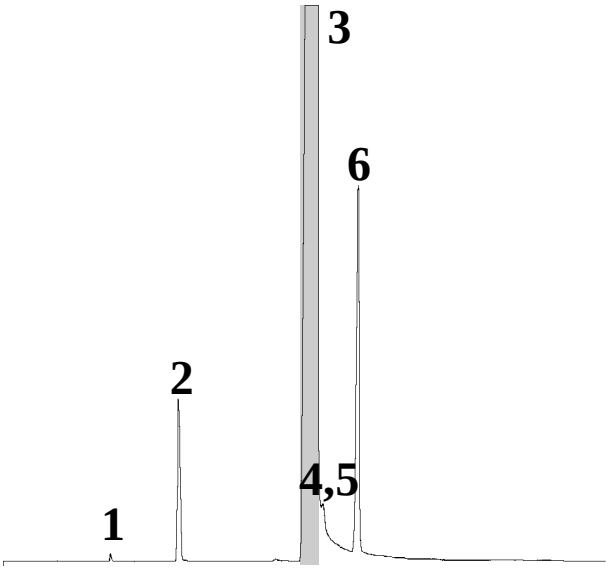

Figure 4a. *Precolumn chromatogram, 1 µl, split ratio x:30, marked compound flushed.*

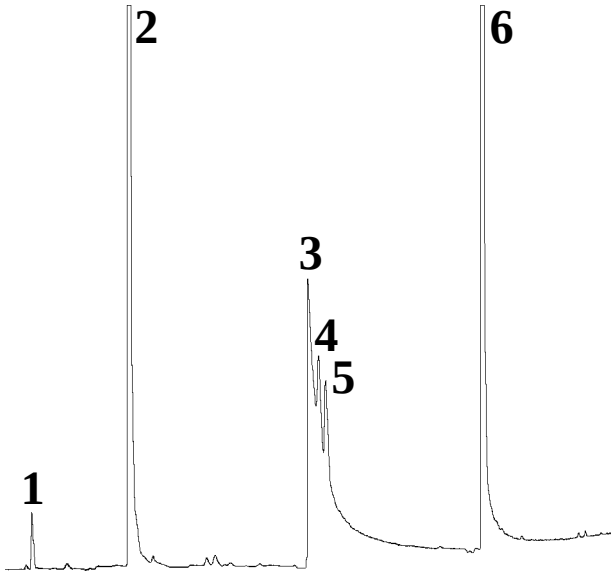

Figure 4b. *Main column chromatogram, without CTS.*

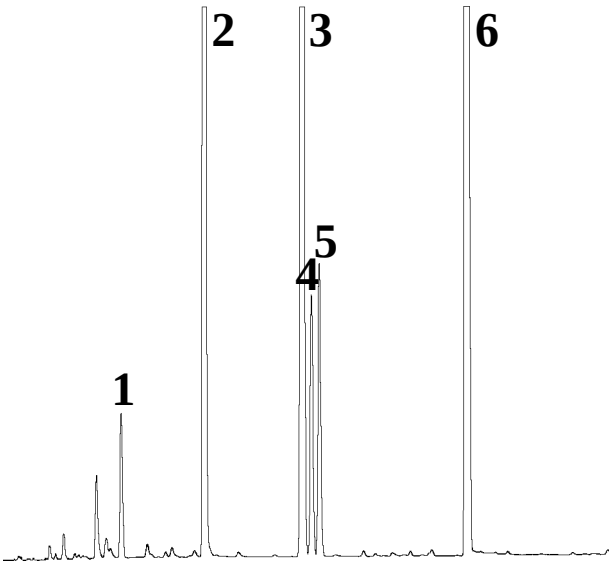

Figure 4c. *Main column chromatogram, with CTS.*

Analytical conditions.

System:

MCS A, 2 columns, 2 ovens, with and without CTS

Columns:

Pre-column in GC-1	25 m Ultra-1 (Hewlett-Packard)	
	d_i = 0.32 mm	d_f = 1.02 µm.
Main column in GC 2	30 m CP-Wax (Chrompack)	
	d_i = 0.32 mm	d_f = 1.2 µm.

Pneumatics:

Carriergas	He	p_i = 130 kPa	split x:40
Control flow		p_c = 50 kPa	10 ml/min
FID	H_2, 30 ml/min	Air, 300 ml/min	
	N_2, 30 ml/min		

Temperatures:

CIS	60°C;	↗260°C;	12°C/s.
Oven 1	70°C.		
Oven 2	50°C;	↗180°C;	3°C/min.
CTS	200°C;	↘-150°C;	12°C/s;
		↗200°C;	12°C/s.

Detectors:

Monitor detector	FID
Main detector	FID

Compounds:

1. Benzene
2. Toluene
3. Ethylbenzene
4. m-Xylene
5. p-Xylene
6. Styrene

Example 3. Multi column analysis of by-products in steroids.

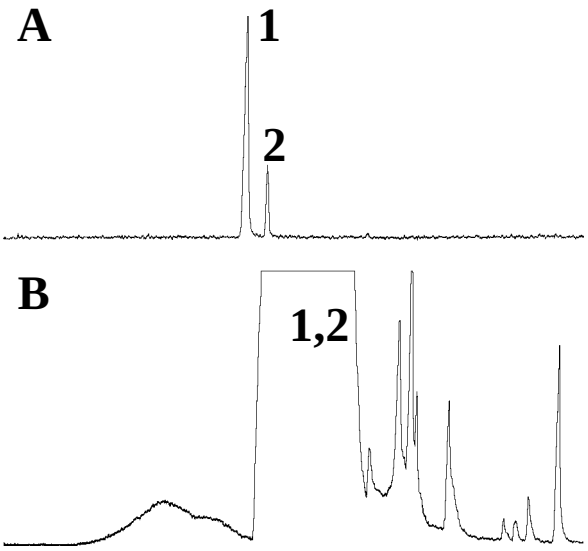

Figure 5a. *Single column analysis in split (A) and on-column (B) mode.*

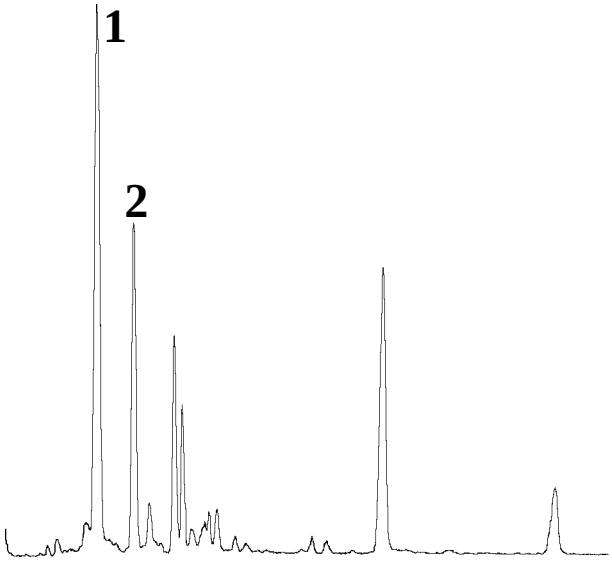

Figure 5b. *Multi column analysis (TIC), main compounds flushed.*

Analysis conditions.

System:

MCS P, 2 columns, 2 ovens, MSD

Columns:

Pre-column in GC 1	10 m SB-1 (IAS)	
	d_i = 0.32 mm	d_f = 0.1 µm.
Main column in GC 2	50 m SB-1 (IAS)	
	d_i = 0.32 mm	d_f = 0.1 µm.

Pneumatics:

Carriergas	He	1.0 ml/min	10ml/min
Control flow	PC 1	0 ml/min	20 ml/min
	PC 2	0 ml/min	8 ml/min
FID	H_2, 30 ml/min	Air, 300 ml/min	
	N_2, 30 ml/min		

Temperatures:

CIS	60°C;	↗ 320°C;	12°C/s.
Oven 1	50°C;	↗ 280°C;	15°C/min.
Oven 2	50°C;	↗ 280°C;	10°C/min.
Transferline	280°C.		

Detectors:

Monitor detector	FID	
Main detector	MSD	Scan 30-450 amu

Compounds:

1. Steroid X
2. Steroid Y

Example 4. Multi column analysis of impurities in aniline.

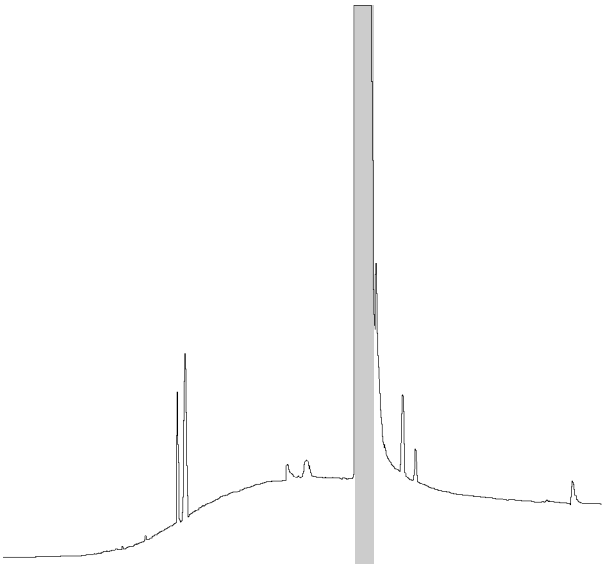

Figure 6a. *Precolumn chromatogram, 1 µl, split ratio x:10, marked compound flushed.*

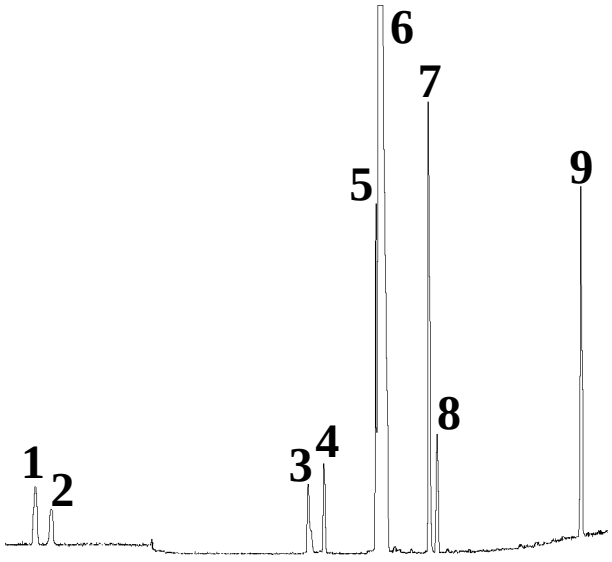

Figure 6b. *Main column chromatogram (TIC), without CTS.*

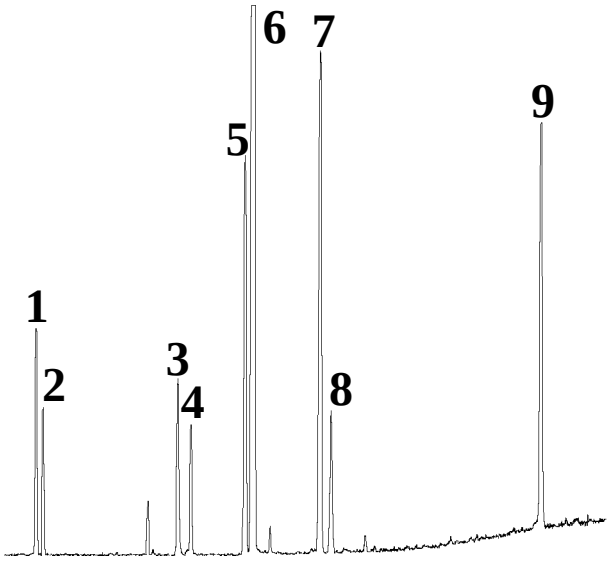

Figure 6c. *Main column chromatogram (TIC), with CTS.*

Analytical conditions.

System:

MCS A, 2 columns, 2 ovens, with and without CTS

Columns:

Pre-column in GC-1	25 m OV-17 (home made)	
	d_i = 0.32 mm	d_f = 1.0 µm.
Main column in GC 2	50 m HP-1(Hewlett-Packard)	
	d_i = 0.32 mm	d_f = 1.05 µm.

Pneumatics:

Carriergas	He	p_i = 60 kPa	split x:15
Control flow		p_c = 45 kPa	10 ml/min
FID	H_2, 30 ml/min	Air, 300 ml/min	
	N_2, 30 ml/min		

Temperatures:

CIS	60°C;	↗260°C;	12°C/s.
Oven 1	50°C;	↗200°C;	10°C/min.
Oven 2	40°C;	↗260°C;	10°C/min.
CTS	220°C;	↘-150°C;	12°C/s;
		↗220°C;	12°C/s.

Detectors:

Monitor detector	FID	
Main detector	MSD	Scan 10-300 amu

Compounds:

1. Benzene
2. Cyclohexane
3. Cyclohexylamine
4. Cyclohexanol
5. Phenol
6. Aniline
7. Toluidine
8. Nitrobenzene
9. Dicyclohexylamine

Example 5. Multi column analysis of impurities in styrene.

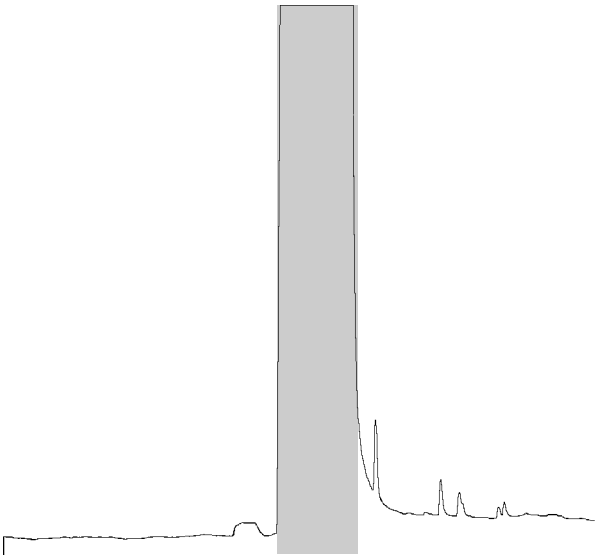

Figure 7a. *Precolumn chromatogram, 0.5 µl, split ratio x:30, marked compound flushed.*

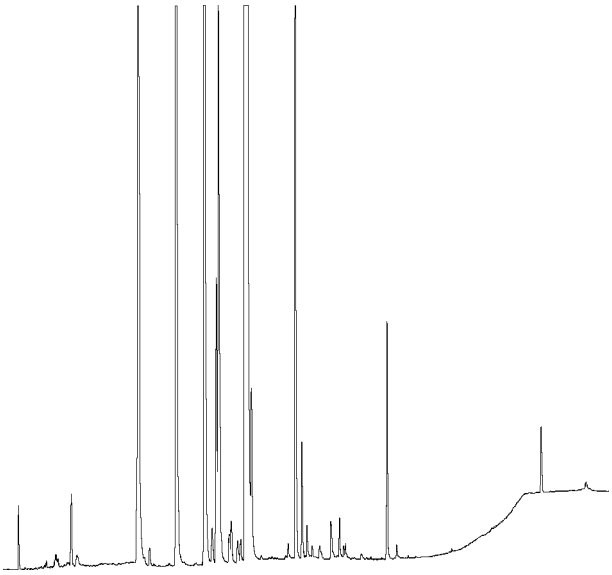

Figure 7b. *Main column chromatogram, with CTS.*

Analytical conditions.

System:

MCS A, 2 columns, 2 ovens, CTS

Columns:

Pre-column in GC-1	25 m Ultra-2 (Hewlett-Packard)	
	d_i = 0.32 mm	d_f = 0.52 µm.
Main column in GC 2	30 m DB-Wax (Restec)	
	d_i = 0.32 mm	d_f = 0.25 µm.

Pneumatics:

Carriergas	He	p_i = 120 kPa	split x:30
Control flow		p_c = 65 kPa	10 ml/min
FID	H_2, 30 ml/min	Air, 300 ml/min	
	N_2, 30 ml/min		

Temperatures:

CIS	60°C;	↗ 260°C;	12°C/s.
Oven 1	60°C;	↗ 150°C;	5°C/min.
Oven 2	40°C;	↗ 70°C;	5°C/min;
		↗ 180°C;	10°C/min.
CTS	150°C;	↘ -150°C;	12°C/s;
		↗ 150°C;	12°C/s.

Detectors:

Monitor detector	FID
Main detector	FID

CONCLUSIONS

Mass flow controlled dual oven multi column switching in combination with on-line coupled MS is a user friendly, very powerful tool for the analysis of complex samples with a wide range of volatilities, polarities and concentrations. High quality mass spectra are obtained after enrichment of volatile trace components.

Cryotrapping at the inlet of the analytical column results in a significant improvement of the separation of critical peak pairs and the reproducibility of the analysis.

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