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Applications of Multi Column Switching Capillary GC-MS in Identification of Trace Impurities in Industrial Products

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Abstract

The separation and identification of trace components in industrial products is a well known analytical problem, particularly if they elute in low concentrations close to the major component. Current methods fail due to insufficient resolution and or the detection limits of existing systems.

In this paper the potential of a combination of programmed temperature sample introduction and dual oven multicolumn switching for the determination of trace impurities in industrial intermediates, is discussed and demonstrated on three examples.

It will be shown that a reliable identification of trace amounts of impurities in these industrial products is possible, with a fully optimized multi column switching system, without interference of the major components.

Introduction

The analysis of trace impurities in industrial products is a typical example of trace analysis, where both the selectivity and the sensitivity of the detection have to be fully optimized, in order allow a reliable MS identification.

Essentially these problems are related to the complexity of the samples, particularly if low concentrations of these impurities elute close together with the major component.Current methods, even those using high resolution capillary columns in single column GC-MS, appear deficient in many applications due to overloading of the major component.

In the present study the target impurities are selectively transferred to the mass spectrometer after elimination of the main part of the major component in a two oven, dual column GC-MS combination. The fraction of interest is accumulated and focused in a cryotrapped transfer line and then transferred to the second column by temperature programmed desorption.

This procedure not only allows an independent optimization of the separation in both columns, but also on-line refocusing of a fraction of interest which is required to match the detection limits of the mass spectrometer.

EXPERIMENTAL

Instrumentation. **Figure 1** represents a scheme of the various components used to configure the system employed for this work. The apparatus consists of a temperature programmable cold injection system (CIS-3, Gerstel GmbH, Mülheim an der Ruhr, Germany), two HP 5890 GC ovens (Hewlett-Packard, Avondale, USA), connected by a cryotrap interface (CTS-1, Gerstel GmbH, Mülheim an der Ruhr, Germany). The second oven is equipped with a mass selective detector (HP 5971 A, Hewlett-Packard, Avondale, USA).

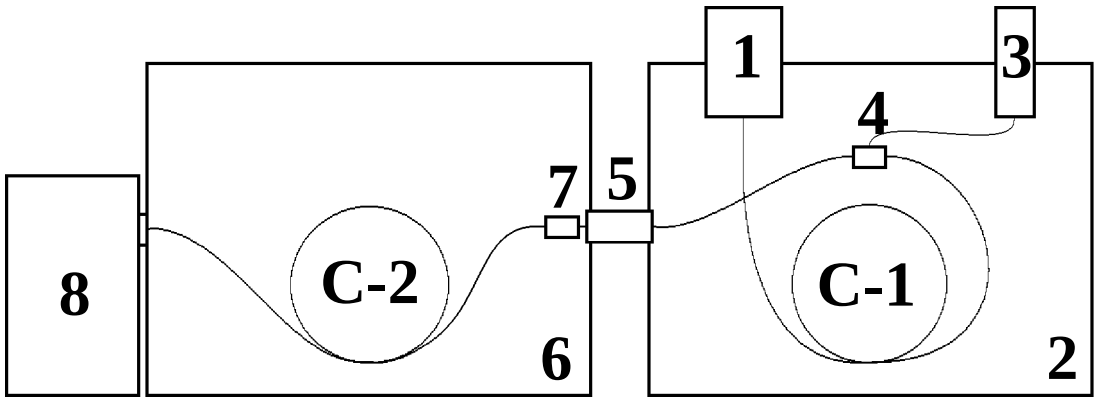


Figure 1. *Schematic diagram of the applied system which consists of a temperature programmable cold injection system with a septumless sampling head (1), a GC (2) configured with a monitor FID (3), column switching device (4) and pneumatics, connected via a heated transfer line incorporating a cryotrap (5) to a second GC (6) which has a second switching device (7) installed after the the transfer line with the main column to the msd (8).*

RESULTS

Identification of trace impurities in industrial products appear a rather difficult problem in capillary GC-MS, particularly for those components which elute closely before or after the major peak. Fundamentally sample size, detection limits and resolution are conflicting factors in the optimization of the identification. Transfer of too large amounts of the major component to the mass spectrometer will result in its overloading. In practice this means that the sample fraction to be transferred to the mass spectrometer can only be taken on the leading or tailing edge of the major peak in order to achieve a sufficiently pure mass spectrum.

This is illustrated in the first example aiming at the determination of impurities in an intermediate. In single column GC-MS it appears impossible to achieve a reliable identification, due to overloading or malfunctioning of the mass spectrometer. Multi column switching is therefore the most attractive approach to solve these problems. A nonselective long thick film capillary column (50m x 0.32mm x 1.05µm) was selected as pre-column while the separation efficiency of wide bore columns appeared not sufficient.

Both the fractions, at the leading as well as at the tailing edge, were transferred to the second (analytical) column with an intermediate cryo focussing and temperature programmed desorption step. The thermal desorption, the temperature program of the second oven and the MS-run are started simultaneously. In this way the separation efficiency can be optimized for both columns.

The pitfalls and possibilities of this approach are illustrated in **Figure 2**. The TIC chromatogram of 1 µl of the intermediate sample is given in **Figure 2a**. Obviously identification of the peaks # 2 and #3 is questionable due to coelution of a relatively large part of the major peak and the respective impurities.

In **Figure 2b** a splitless introduction of 1 µl of the sample on the pre-column shows similar problems for the corresponding peaks. For peak #1 excessive peak broadening due to a reversed "solvent-effect" does not allow a reliable identification.
A representative chromatogram of the overall separation of a 1 µl sample, is presented in **Figure 2c**. The major peak is nearly completely vented after the pre-column (**Figure 2b**). In this way a reliable identification is achieved, while the main component does not influence the mass spectra of the impurities 1-3 even in the ppm-range.

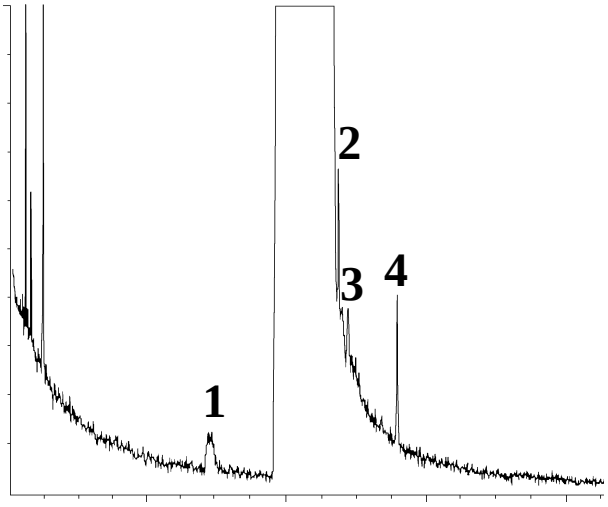


Figure 2a. *Single column chromatogram of an intermediate (TIC), 25 m HP-1, split ratio 1:100.*

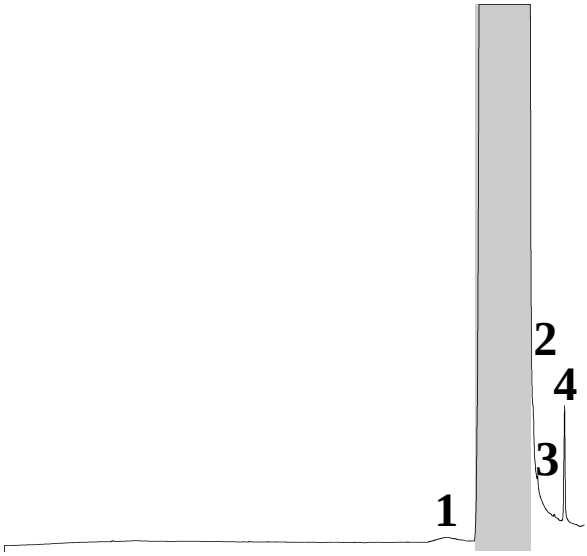


Figure 2b. *Multi column analysis of an intermediate, precolumn chromatogram (FID), marked part of the main compound vented.*

Analysis conditions.

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		25 m Ultra-2 (Hewlett-Packard)	
		d_i = 0,2 mm	d_f = 0,33 µm
Pneumatics:			
Carriergas	He	p_i = 170 kPa	split x:30
Control flow		p_c = 45 kPa	10 ml/min
		p_{c1} = 41 kPa	
FID	H_2, 30 ml/min	Air, 300 ml/min	N_2, 30 ml/min
Temperatures:			
CIS	60°C;	↗ 280°C;	12°C/s
Oven 1	60°C;	↗ 280°C;	10°C/min
Oven 2	60°C;	↗ 280°C;	10°C/min
CTS	280°C;	↘ -150°C;	12°C/s
		↗ 280°C;	12°C/s
FID	300°C		
MSD	280°C		
Detectors:			
Monitor detector in GC 1	FID		
Main detector in GC 2	MSD	Scan 30-350 amu	

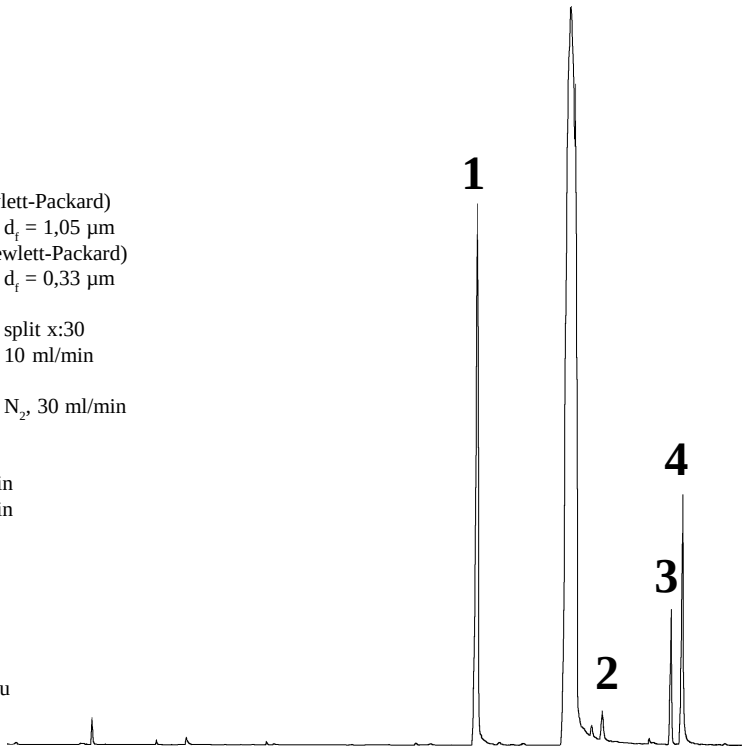


Figure 2c. *Multi column analysis of an intermediate, main column chromatogram (TIC).*

In the second example (**Figure 3**) the identification of the impurities which elute close to either the monomer or the dimer of acrylic acid is discussed. The chromatogram in **Figure 3a** shows a TIC-chromatogram which will be obtained under normally used operating conditions. Comparison of precolumns with different lenghts, diameters and film thicknesses have learned us, that a long column with thick film is required to achieve optimum results. Therefore also in this case the same precolumn (50m x 0.32mm x 1.05µm) is used.

Comparing the TIC chromatogram , given in **Figure 3a**, to the FID chromatogram of the precolumn, the overloading of the mass spectrometer is obvious.

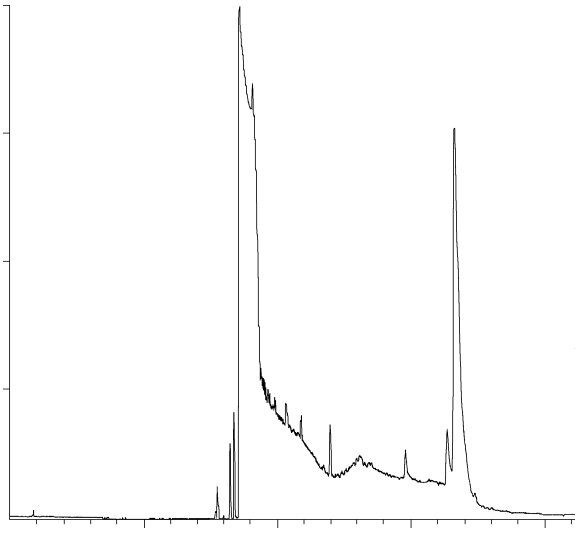


Figure 3a. *Single column chromatogram of acrylic acid (TIC).*

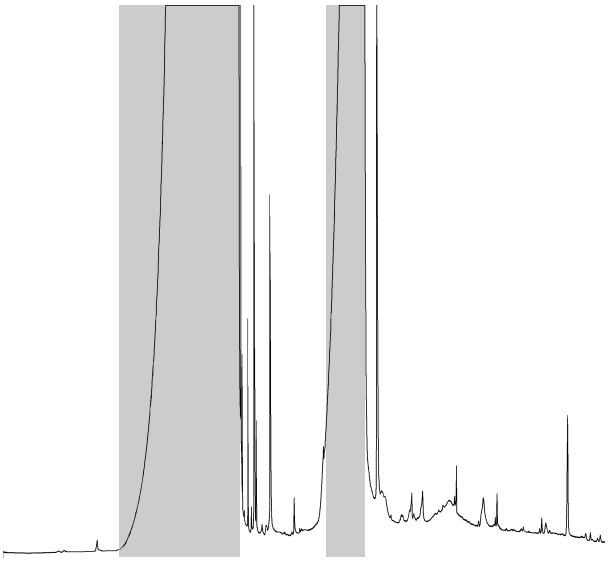


Figure 3b. *Multi column chromatogram of acrylic acid, precolumn chromatogram (FID), marked parts of the main compounds vented.*

Analysis conditions.

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	(polar)	60 m Stabilwax-DA (Restek)	
		d_i = 0,25 mm	d_f = 0,5 µm
or	(apolar)	60 m SB-1 (IAS)	
		d_i = 0,25 mm	d_f = 0,2 µm

Pneumatics:

Carriergas	He	p_i = 150 kPa	split x:20
Control flow		p_c = 45 kPa	10 ml/min
		p_{c1} = 40 kPa	
FID	H_2, 30 ml/min	Air, 300 ml/min	N_2, 30 ml/min

Temperatures:

CIS	60°C;	↗ 280°C;	12°C/s	
Oven 1	50°C;	↗ 130°C;	5°C/min	
		↗ 280°C;	10°C/min	
Oven 2 (polar C.)	50°C;↗	180°C;	10°C/min	
		↗ 220°C;	5°C/min	
or (apolar C.)	50°C;	↗ 150°C;	5°C/min	
		↗ 280°C;	10°C/min	
CTS	280°C;	↘ -150°C;	12°C/s	
		↗ 280°C;	12°C/s	
FID	300°C			
MSD	280°C			

Detectors:

Monitor detector in GC 1	FID	
Main detector in GC 2	MSD	Scan 30-350 amu

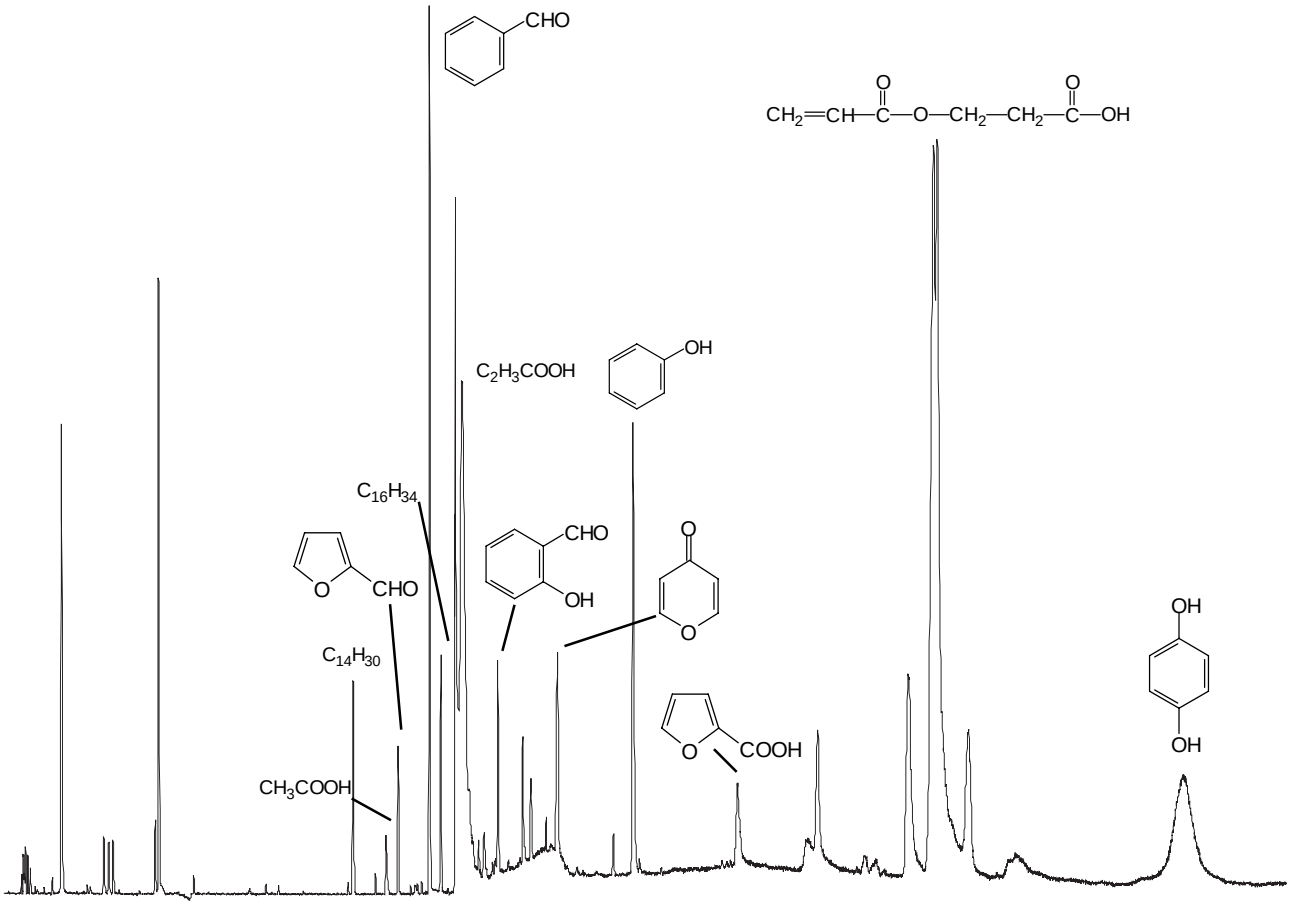


Figure 3c. *Multi column analysis of acrylic acid, main column chromatogram (TIC, polar column).*

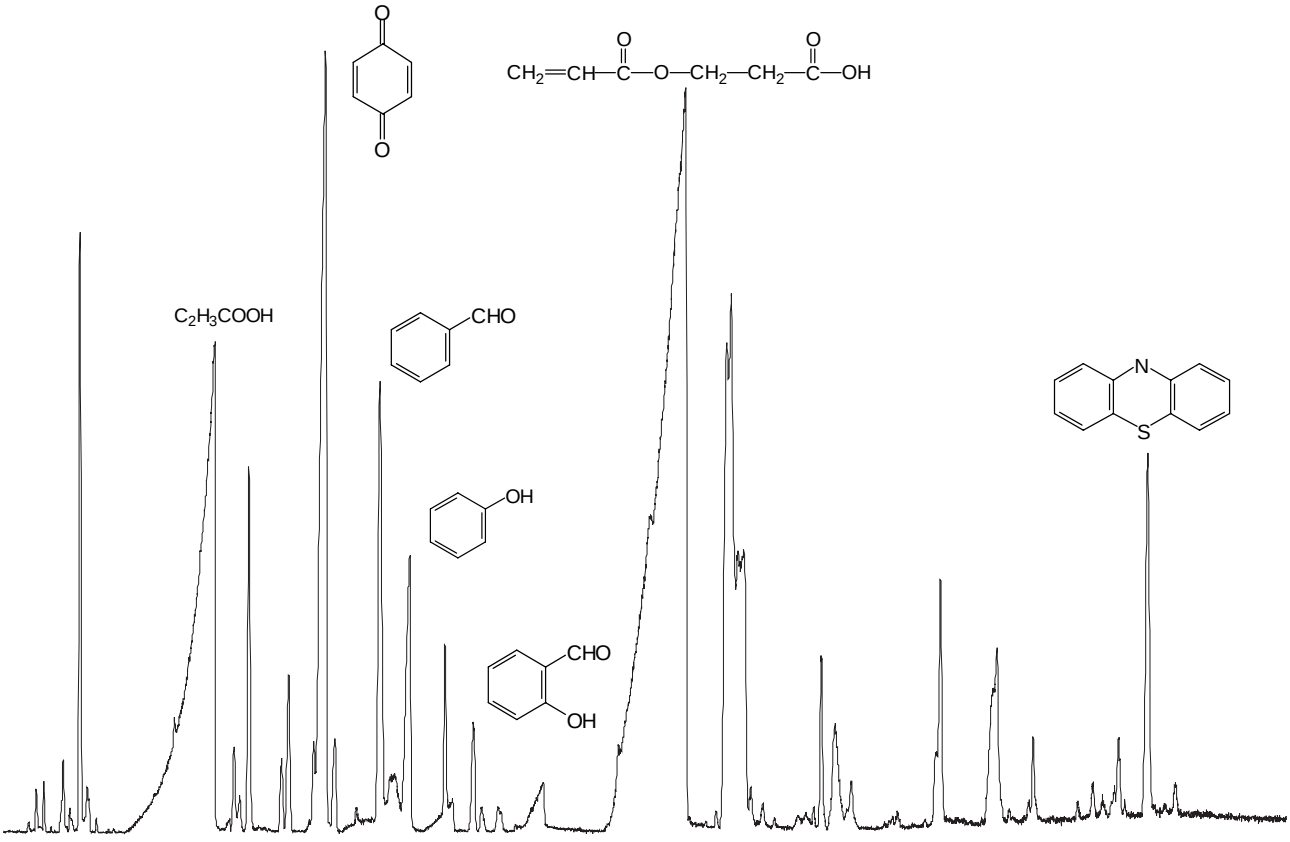
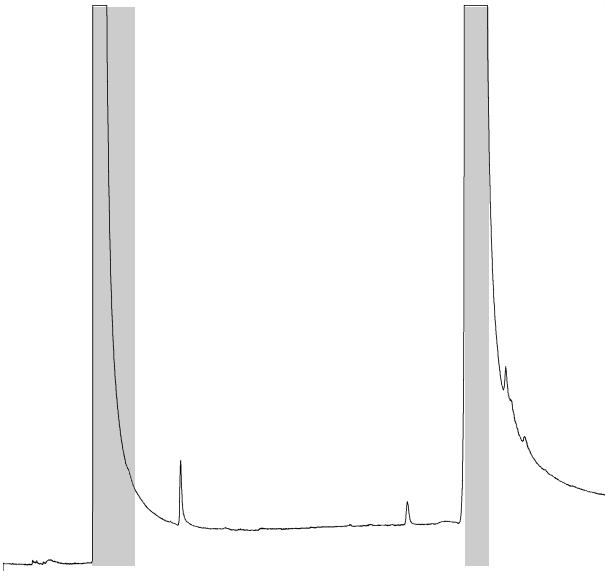


Figure 3d. *Multi column analysis of acrylic acid, main column chromatogram (TIC, apolar column).*

The identification of trace impurities in a phenyl-substituted heterocyclic compound of high purity, slightly diluted in DMF, is illustrated in **Figure 4**. A 1µl (splitless) TIC chromatogram of the sample is presented in **Figure 4a**. The final result, which is demonstrated in **Figure 4b** is a convincing example for the succesful approach presented in this paper without any further explanation.



Analysis conditions.

Columns:

Pre-column in GC 1		50 m CP-Sil 19 (Chrompack)
		d_i = 0,53 mm d_f = 2,0 µm
Main column in GC 2		25 m Ultra-2 (Hewlett-Packard)
		d_i = 0,2 mm d_f = 0,33 µm

Pneumatics:

Carriergas	He	p_i = 150 kPa	split x:30
Control flow		p_c = 45 kPa	10 ml/min
		p_{c1} = 40 kPa	
FID	H_2, 30 ml/min	Air, 300 ml/min	N_2, 30 ml/min

Temperatures:

CIS	60°C;	↗ 280°C; 12°C/s
Oven 1	80°C;	↗ 220°C; 5°C/min
Oven 2	50°C;	↗ 120°C; 5°C/min
		↗ 280°C; 10°C/min
CTS	280°C;	↘ -150°C; 12°C/s
		↗ 280°C; 12°C/s
FID	300°C	
MSD	280°C	

Detectors:

Monitor detector in GC 1	FID	
Main detector in GC 2	MSD	Scan 30-350 amu

Figure 4a. *Multi column analysis of a phenyl-substituted heterocyclic compound, precolumn chromatogram (FID), marked part of the components vented.*

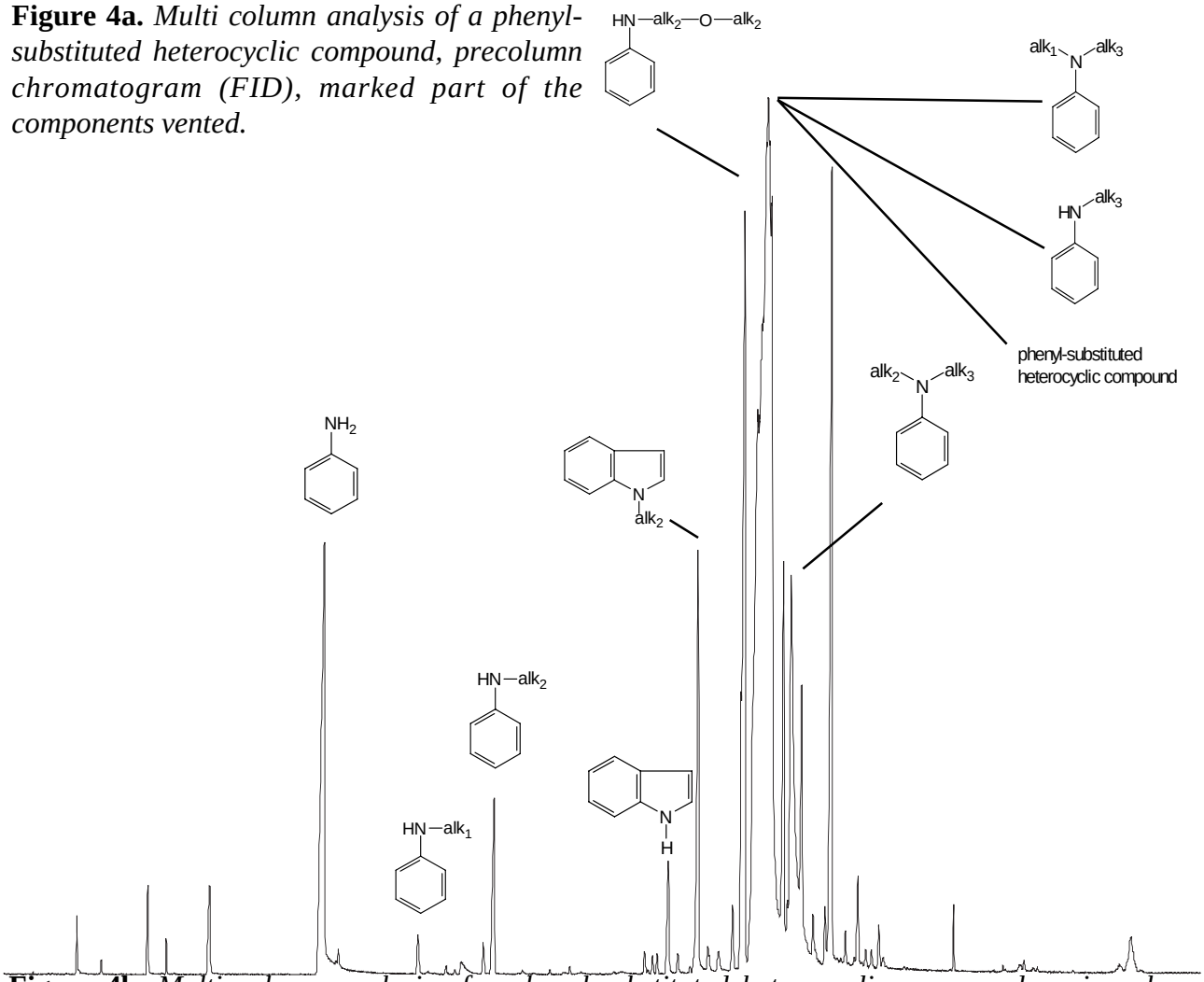


Figure 4b. *Multi column analysis of a phenyl-substituted heterocyclic compound, main column chromatogram (TIC).*

Conclusion

The application of user friendly two oven dual column switching GC-MS systems is a highly recommandable approach for the identification of trace impurities in industrial products.

Cryotrapping and successive thermodesorption of the selected fraction , in between the columns, allows an optimal separation efficiency for both columns.

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