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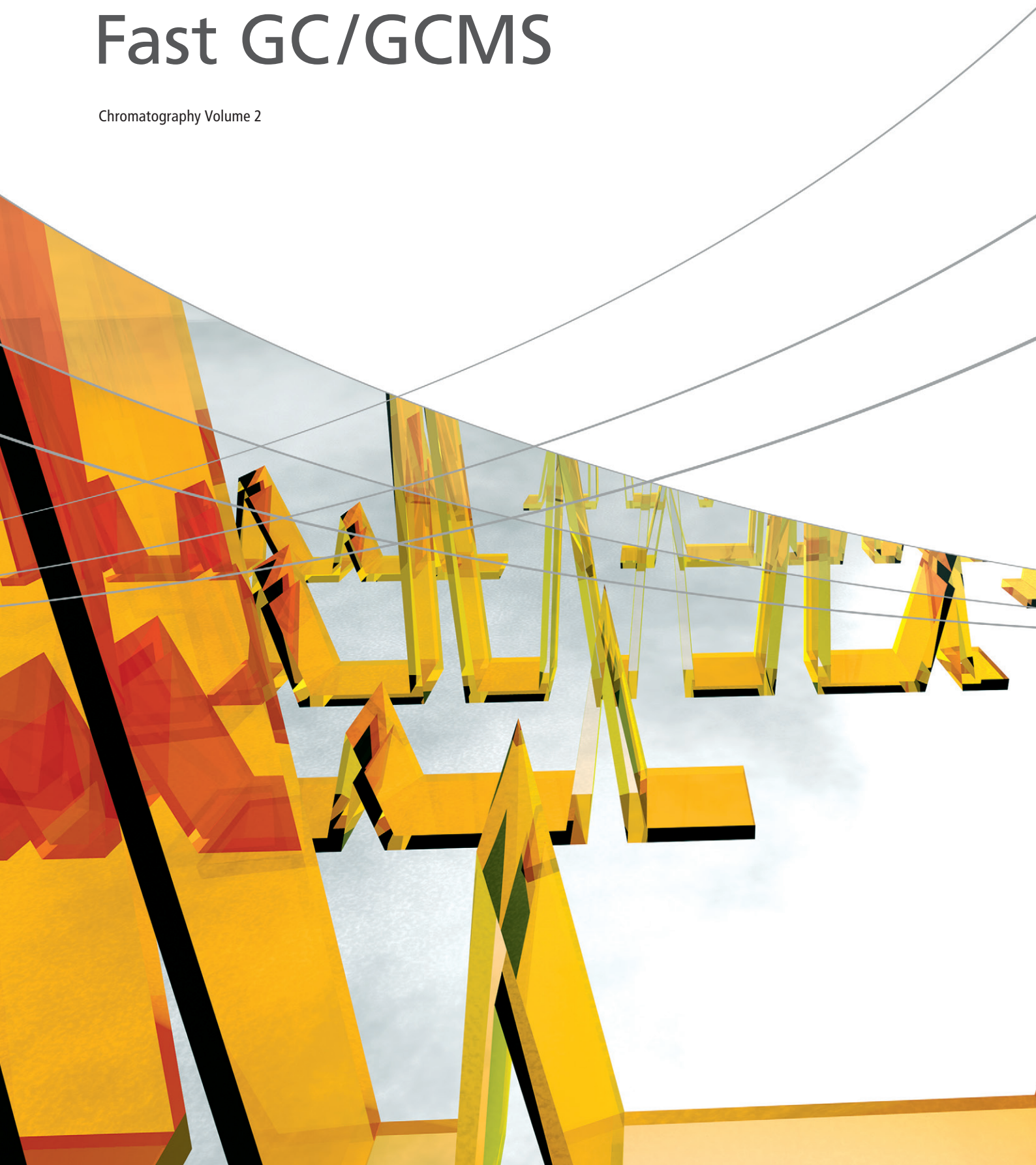
Application Handbook

Fast GC/GCMS

Chromatography Volume 2



Application Book

Fast GC/GCMS

Fast GC and GC/MS using narrow-bore columns:
Principles and Applications

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Content

I. Overview

Gas chromatography is a well-established technique, employed in many applicational fields such as environmental, food, petrochemical and pharmaceutical analysis [1].

The capillary columns used may have solid fillings (PLOT columns) or a liquid film as a stationary phase. The latter are employed in gas liquid chromatography (GLC), which is the subject of the present booklet. In GLC, analyte separation is achieved by means of a dynamic thermal equilibrium between the stationary phase (liquid) and mobile phase (gas). The dimensions of the columns employed, which vary depending on the application, generally range from inner diameters between 0.25 to 0.53 mm and lengths from 25 to 60 m. The film thickness selected, dependent on the boiling points of the analytes, usually ranges from 0.25 to 1 µm (in some cases up to 3 µm or even more).

Nowadays in daily routine work, apart from increased analytical sensitivity, demands are also made on the efficiency in terms of speed of the laboratory equipment. Regarding the rapidity of analysis, two aspects need to be considered:

1. **The costs in terms of time required, for example in quality control analysis**

2. **The efficiency of the analytical equipment employed**

It is well known that analytical time costs may be very high in standard GC applications. In the last few years, fast GC methods have been shown to be suitable for routine laboratory work. In this respect, the employment of narrow-bore columns is of particular interest [2-5].

These analytical tools enable a considerable reduction of analyses times while peak resolution is essentially maintained. Another approach worthy of mention is the use of multicapillary columns [6-8] with more than 900 capillary tubes with inner diameters of about 40 µm.

The present overview is focussed on the use of narrow-bore columns in fast gas chromatography. As mentioned, this type of approach enables substantial reductions in GC run-times without compromising the chromatographic resolution.

An example of the validity of this approach is illustrated in Figure I.1 (lower chromatogram) which reports a fast GC analysis (RTX-5 10 m, 0.1 mm ID, 0.4 µm film thickness) on a capillary column test mixture (Grob test mixture, Macherey und Nagel). The conditions were as follows: injection mode: split (200:1), average linear carrier gas velocity: 120 cm/s (502 kPa, H_2), temperature program: from 140 °C at 60 °C/min to 280 °C. A conventional application (DB 5 30 m, 0.25 mm ID, 0.25 µm film thickness) on the same matrix is also shown in the diagram (upper chromatogram). As apparent, the degree of separation is even better in the fast GC application while a speed gain of approximately 8 times is attained.

However, the GC hardware has to meet some requirements in order to enable the efficient use of narrow-bore columns. In the following chapters, general and fundamental issues relative to fast gas chromatography are discussed (injection systems, capillary columns, carrier gas and detector characteristics).

All the chromatograms shown were recorded with a Shimadzu GC-2010 or GCMS-QP2010 with an AOC-20i autoinjector and GCsolution or GCMSsolution software for data elaboration.

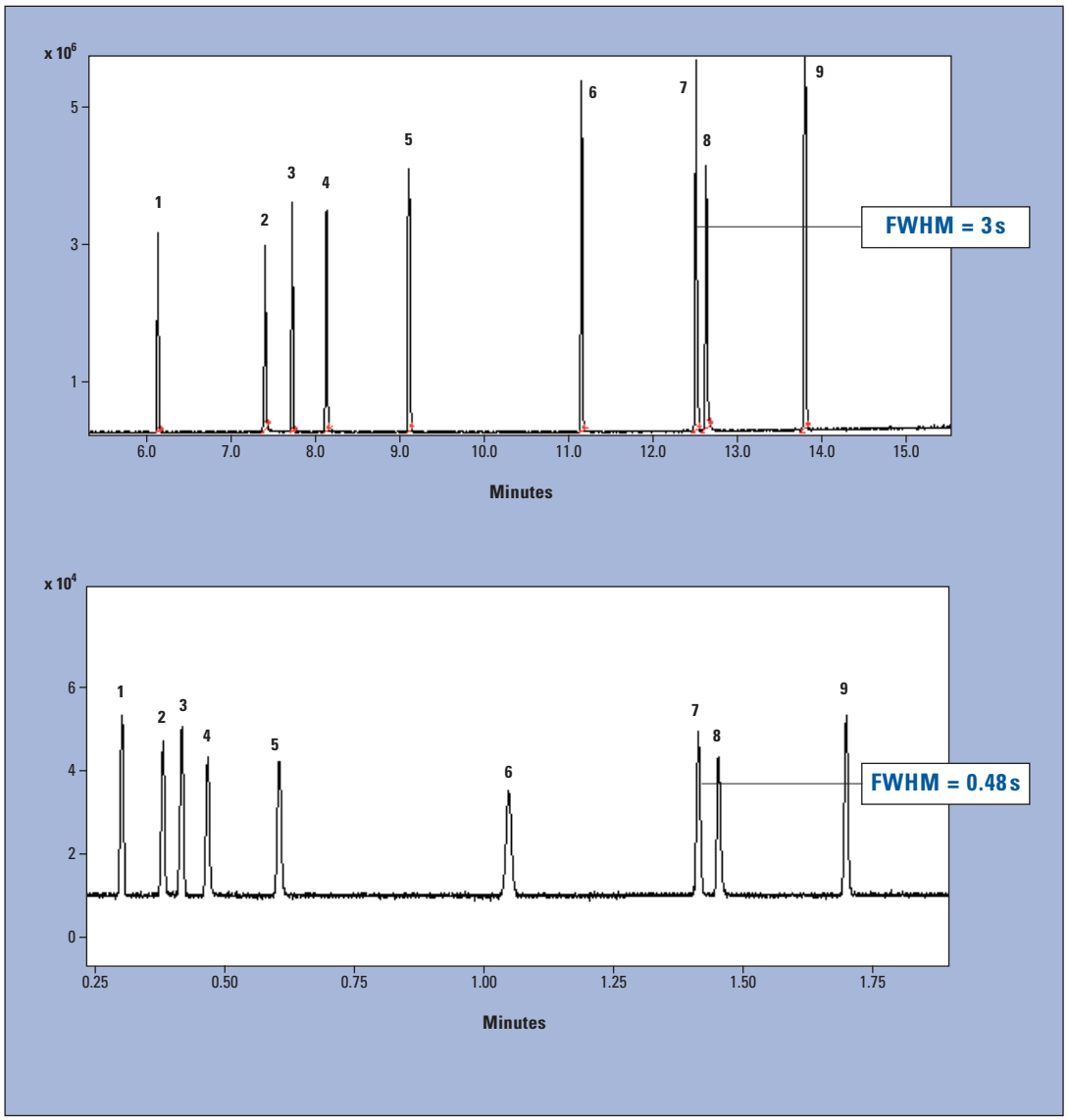


Figure I.1:

Top: Chromatogram recorded with a Grob test mixture using a DB5 30 m, 0.25 mm, 0.25 µm column.
Bottom: Chromatogram recorded with the Grob test mixture using a RTX-5 10 m, 0.1 mm, 0.4 µm column.

Peak identification:
1) n-Decane
2) n-Octanole
3) n-Undecane
4) 2.6-Dimethylphenole
5) 2.6-Dimethylaniline
6) Decane acid methyl ester
7) Undecane acid methyl ester
8) Dicyclohexylamine
9) Dodecane acid methyl ester

II. Basics of separation in fast GC

1. Column and stationary phase

Both the polarity and the boiling points of the sample analytes must be considered during the selection of a specific stationary phase material. Nowadays, several phase materials are available for typical fast GC applications.

An important issue in fast GC regards the narrow-bore column sample capacity, which is considerably lower than with conventional capillaries (this aspect will be discussed later).

Apart from the choice of the stationary phase, other important column parameters to be optimized are length, internal diameter and film thickness.

2. Length and peak resolution

The number of theoretical plates N of a column is a measure of its separation efficiency and is defined as [9]:

$$N = 16 \bullet \left[\frac{t_R}{w_b}\right]^2 \quad (1)$$

where w_b is the base peak width and t_R is the retention time. Peak resolution is of particular interest as the main aim is to reduce the analysis time while maintaining the column resolving power (Figure II.2). The resolution between two peaks is defined as:

$$R = \frac{\Delta t}{\frac{1}{2}[w_a + w_b]} \quad (2)$$

Resolution (R) on the other hand depends on the capacity factor k and the plate number N in the following equation [9]:

$$R = \frac{\sqrt{N}}{4} \frac{\alpha}{\alpha - 1} \frac{k'_2}{k'_2 + 1} \quad (3)$$

with k_2 = capacity factor of the more retained solute and
α = separation factor:

$$k' = \frac{t'_R}{t_M}, \quad \alpha = \frac{k'_2}{k'_1} = \frac{t'_{R2}}{t'_{R1}}$$

where t_M is the time required for an unretained analyte to pass through the column (generally referred to as dead time). The relationship between the length of the column, N and height of a theoretical plate (HETP) is as follows:

$$N = \frac{L}{HETP} \quad L = \text{column length} \quad (4)$$

thus the resolution is proportional to the square root of the column length:

$$R \propto \sqrt{L} \quad (5)$$

Consequently, doubling the column length achieves a gain of resolution of a factor of only 1.41. Therefore typical column lengths in fast GC are within the 10 - 15 m range.

- **Column length for fast GC: 10 - 15 m**

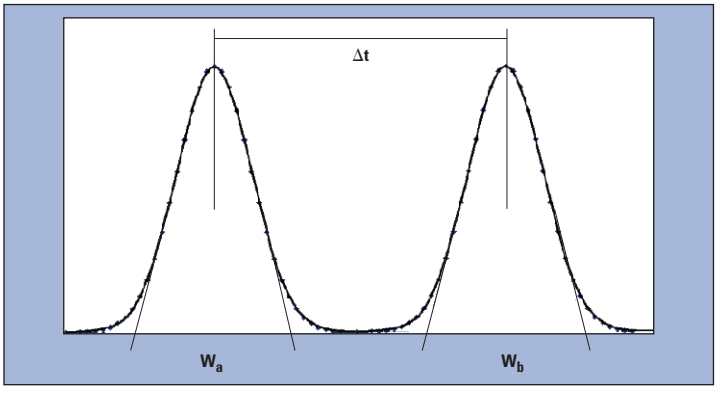


Figure II.1: Peak resolution parameters for two subsequent peaks in a chromatogram

3. Inner diameter and peak resolution

In general, the chromatographic peak width increases with the retention time due to resistance to mass transfer in the mobile and stationary phase contributions. The influence of the inner diameter with respect to the theoretical plate number is now considered. The basic equation for the retention of a substance is [9]:

$$K_D = k' \bullet \beta \qquad \beta \approx \frac{d_I}{4d_f} \quad (6)$$

where:
d_I, d_f = inner diameter/film thickness of the column
K_D = distribution constant
β = phase ratio

The distribution coefficient K_D is dependent on the temperature and the physical and chemical properties of the analytes and stationary phase. The retention time is therefore determined by the inner diameter, film thickness and length of the column for fixed material properties. For typical inner diameters and film thicknesses such as 0.25 mm and 0.25 µm, the phase ratio is equal to approximately 250. This is a typical phase ratio value for a medium boiling point analyte range. In general, this parameter is used by the analyst to make a first selection of the column dimension for a given distribution of analyte boiling points. Column manufacturers usually offer schematic tables in their catalogues giving an overview of typical β values for different applications. The value for β typically varies between 50 (columns with thick films for volatiles) and 530 (wide-bore columns, high boilers).

For further elucidation, the so called van Deemter curves [9] will be discussed in the following chapter where HETP values for different capillary columns are plotted versus the average linear carrier gas velocity [u].

With regard to the experimental curves, the HETP values are derived from the peak widths (eq. 1 and 4) and are plotted as a function of the average linear velocity of the carrier gas.
A typical curve is shown in Figure II.2 for 2 columns of differing inner diameter [10]. The plate height is characterized by a minimum value ($HETP_{min}$) at the optimum linear velocity [9].
Both columns have a β value of approximately 250. For columns with such a high phase ratio value, the resistance to mass transfer in the stationary phase can be neglected and $HETP_{min}$ can therefore be approximated to the column ID [10]:

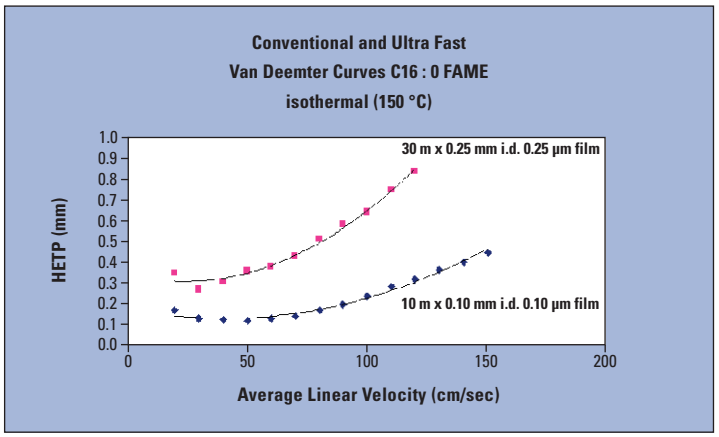


Figure II.2: Van Deemter curves [10] for 0.25 mm and 0.1 mm ID columns. The phase ratio is 250 in both cases.

$$HETP_{min} \; prop \; d_I \quad (7)$$

As seen from equation 7 and Figure II.2 the minimum theoretical plate height decreases linearly with the capillary column inner diameter. Furthermore, the ascending part of the curves rises more gradually, enabling the application of higher than optimum velocities with little loss in terms of resolving power. To conclude, the inner diameter of suitable columns for fast GC are:

- **Columns for fast GC: inner diameter ≤ 0.15 mm**

4. Film thickness and peak resolution

The linear relationship between peak resolution and stationary phase thickness requires the latter to be as thin as possible in fast GC.

On the other hand, it should also be suited to the boiling points of the analytes (see also β). Since the column sample capacity also decreases with the film thickness (less amount of stationary phase), the split ratio needs to be adjusted depending on the concentration of the sample. High split ratios ensure that the sample is transferred rapidly from the glass insert to the column (see III. Injection).

As a conclusion, a typical film thickness in fast GC of 0.1 µm (d_I = 0.1 mm, β = 250) is used. In specific cases of highly volatile compounds film thicknesses of up to 0.4 µm (β = 62.5 for 0.1 mm d_I) may be used.

- **Columns in fast GC: film thicknesses are typically 0.1 µm (≤ 0.4 mm)**

5. Type of carrier gas and average linear velocity

In fast GC applications, particular attention must be paid to the type of carrier gas used. The Van Deemter curves have different minima for different gas types [9]. This factor is shown in detail in Figure II.3.

As can be seen, the minimum HETP for the hydrogen curve is attained at a higher average linear velocity when compared to other carrier gas types. In addition, the ascending part of the curve rises more gradually for the hydrogen curve. The data illustrated in Figure II.3 were derived from a 0.25 mm ID column. In the case of smaller inner diameters, as already referred to, the ascending part rises even more gradually as mentioned in section 3.

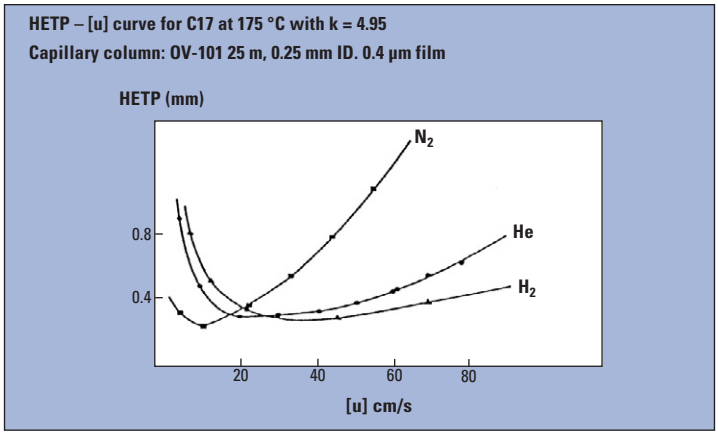


Figure II.3: Van Deemter curves measured using different carrier gases (Shimadzu Corporation, Kyoto, Japan)

In most applications, a linear temperature program is employed rather than isothermal analysis. Under isobaric conditions, average linear velocity decreases with increasing temperatures [9]. This is due to the fact that the gas viscosity increases linearly with temperature. Hence, the separation efficiency is reduced as the temperature increases (the optimum velocity is generally selected for the initial temperature) and the analysis time is also prolonged when compared to constant velocity conditions.

Consequently, the gas chromatograph should have an automatic pressure regulator in order to keep the average linear velocity constant over the entire temperature program. This issue leads directly to fast GC hardware requirements.

6. GC hardware requirements

The aforementioned issues have direct consequences on GC instrumentation requirements such as injection system, carrier gas pneumatics, column oven heating/cooling and detection. These aspects are summarized as follows:

GC instrument requirements

- fast injection → autoinjector, rapid injection, high split ratios (see chapter III.)
- reduced internal diameter → large head pressure, high maximum operational head pressure (up to 970 kPa)
- temperature program → average linear carrier gas velocity should be constant over the entire analysis (the constant linear velocity mode requires a pressure program)
- high separation efficiency → linear temperature ramps are higher compared to standard GC [70 °C/min linear and higher (ballistic)]
- high final temperature → fast cooling of the GC oven (2 min from 280 °C to 100 °C)
- high concentration range → high split ratios should be available (total flow of up to 1200 mL/min)
- sharp peaks in fast GC → high sampling rates and low filter time constants (250 Hz, 4 ms-conventional detectors)

The data in brackets refer to specifications of the GC-2010.

In the example illustrated in Figure I.1 (see page 9), a 120 cm/s average linear velocity was applied. In order to obtain this velocity an initial pressure of 502 kPa was required at the initial temperature of 140 °C. The gas chromatograph maintains the average linear velocity constant over the temperature program (60 °C/min up to 280 °C).

This is achieved by the application of a pressure program automatically calculated by the GC software, and leads to a final pressure of 660 kPa at 280 °C. The cooling time for this analysis is below 2 minutes and the cycle time is under 4 minutes.

III. Injection requirements in fast GC

Injection requirements in fast GC

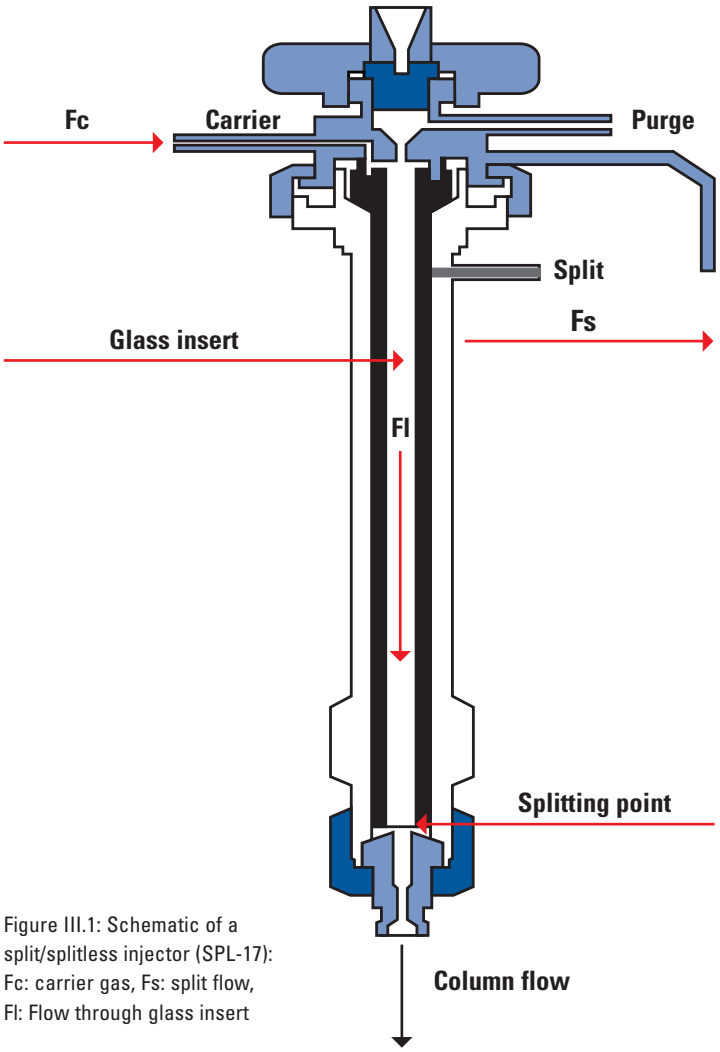


Figure III.1: Schematic of a split/splitless injector (SPL-17): Fc: carrier gas, Fs: split flow, Fl: Flow through glass insert

As can be observed in Figure I.1 (see page 9), the peak widths at half height (FWHM) are below 0.5 s, much less if compared to conventional GC (about 3 s). The peak width is affected by the time needed to transfer the sample, vaporized in the glass insert, onto the column. The sample transfer must be fast enough (movement of syringe plunger, purge speed of the glass insert).

In the case of a relatively slow sample transfer rate (such as in splitless injection, see Figure III.1), this results in an initial sample band broadening on the first part of the column [11], which has a considerable effect on the whole separation efficiency. The well-known solvent effect indicated by Grob [11] is not applicable as the column initial temperature has to be set below the solvent boiling point, making the analysis time longer, and in addition the film thickness is very small. This requires that the glass insert is not overloaded with vapor after liquid injection [11].

The sharpness of the peaks is also affected. For example, a 1 µL n-hexane injection into a split/splitless injector results in a vapor volume of about 175 µL at 280 °C and a head pressure of 100 kPa. In the case of acetone as solvent the vapor volume under the same conditions is about 310 µL. Typical glass insert volumes on the other hand are within 1-2 mL.

Whenever splitless injection is applied in fast GC, a reduced volume glass insert and high pressure injection are required. In general, sample transfer has a profound influence on peak shape and needs to be optimized:

Samples with a high concentration: high split ratio

At low concentration ranges (low split ratio or splitless injection):

1. Use of glass insert with small inner diameter to enhance purging with carrier gas.
2. In the case of splitless injection: high pressure injection.

1. Glass insert

Figure III.2 shows the effect of glass insert dimensions on peak width. Here the Grob test mix was analyzed with a stan-

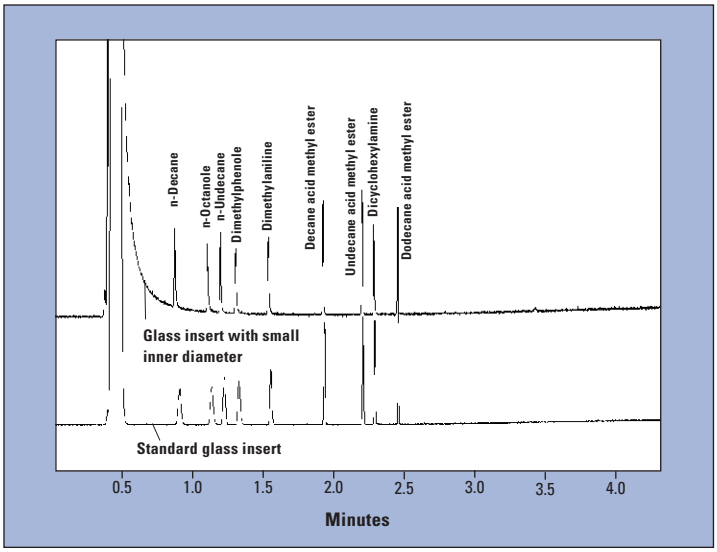


Figure III.2: Chromatograms relative to a Grob test mixture.
Top: reduced ID (inner diameter) glass insert = 1 mm.
Bottom: standard glass insert, 4 mm ID.

dard glass insert (4 mm inner diameter – bottom) and a glass insert with a 1 mm ID (top). All other parameters remained unchanged. In particular, the peak widths of the less retained volatile components were narrower when the glass insert dimension was reduced. The effect of purging, which was more effective for the reduced ID glass insert, is clearly demonstrated. The split ratio was 40:1 in both cases. For increased split ratios the peak widths were also narrower when using the standard glass insert.

In the chromatogram illustrated in Figure I.1 (see page 9), a 200:1 split ratio was selected. For peak no 1, the peak width measured with the standard glass insert was FWHM = 0.42 s (split ratio 200:1) in contrast to 1.56 s in Figure III.2 – bottom (split ratio 40:1).

2. High pressure injection

As discussed in chapter II (section 5), the carrier gas average linear velocity has a great influence on the column separation efficiency. The applied head pressure is therefore of great importance after sample transfer to the column. In this respect, it is possible to apply an increased pressure just for sample transfer (typically for 30 s to 1 min). After this period the pressure is dropped automatically to the analytical pressure to ensure peak resolution. This operation mode is defined as high pressure injection. Obviously, the purging of the glass insert is increased when compared to standard conditions. In chapter V (section 1), where analysis of organophosphorous pesticides is discussed, high pressure injection (600 kPa) was applied in combination with a splitless injection technique in order to optimize peak shapes.

3. Sample capacity of capillary columns

The maximum amount of sample which may be introduced onto a capillary column without overloading is lower for narrow-bore columns. When excessive sample amounts are injected onto a capillary, peak fronting effects are observed [9]. The generation of asymmetric peaks may obviously lead to a substantial loss in resolution. Consequently, the injected sample amount must be below a threshold value, as may be observed in Figure III.3 [10]. Here the plate number (calculated from the peak width according to eq. 1) and hence separation efficiency is plotted as a function of sample amount for two columns of different internal diameter. It can be seen that for standard columns (0.25 mm ID) up to 50 ng solute quantities may be injected with little or no loss of separation efficiency. For a narrow-bore column with a 0.1 mm ID, analyte amounts of up to 1 ng may be injected without losing separation efficiency.

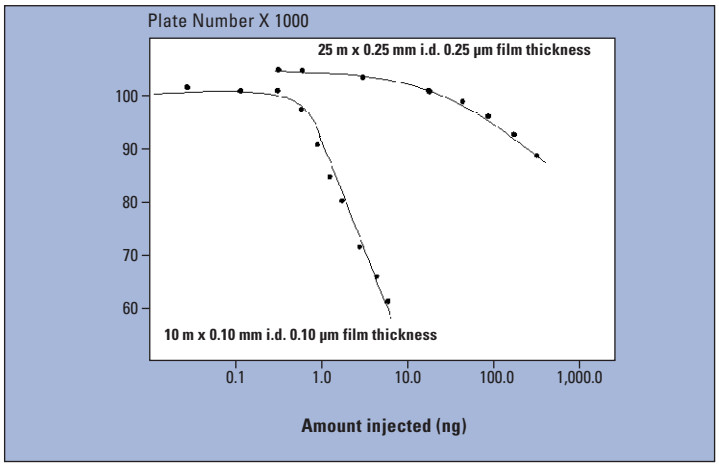


Figure III.3: Number of theoretical plates as a function of sample amount for two different columns

IV. Detector requirements in fast GC

Filter time constant and sampling frequency

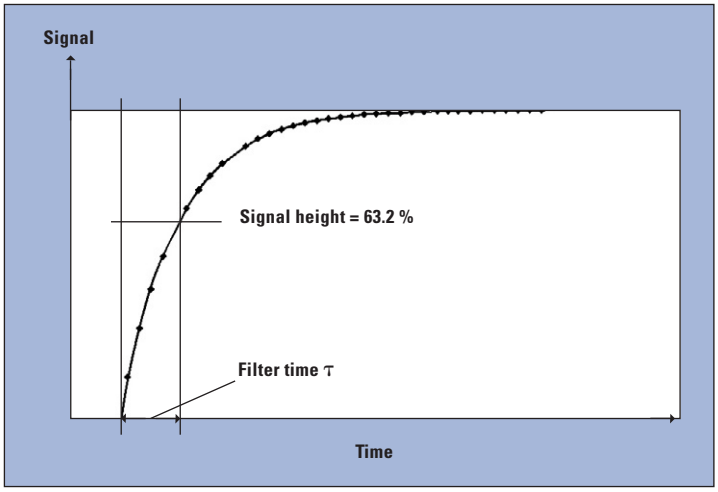


Figure IV.1: Definition of filter time constant τ

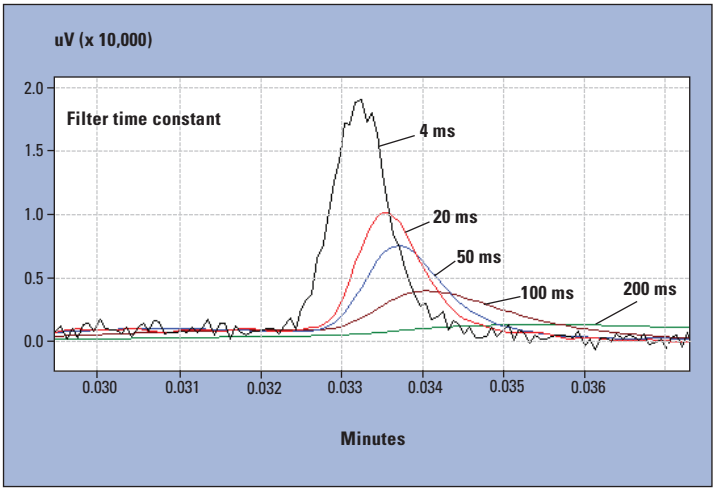


Figure IV.2: FID signal of chlorodecane. The filter time constant τ was changed from 4 to 200 ms. The sampling frequency was 250 Hz in all cases.

1. Conventional detectors

In this section, conventional detectors such as the flame ionization detector (FID), electron capture detector (ECD), flame photometric detector (FPD) and flame thermionic detector (FTD or NPD) are discussed.

Mass spectrometric detection is described in the next section. As mentioned, typical fast GC peak widths are 0.5 s or less. The detection system must meet a series of requirements in order to maintain the peak width at column outlet. In this section the requirements for FID are discussed, but the principles are valid for all of the conventional GC detectors. In general, detector peak broadening may be caused by two factors. Firstly, the possible presence of dead volumes in the sample path. Modern GC detectors are generally characterized by low dead volumes. Furthermore, make-up gas is employed to optimize peak shapes through an additional flow (typically 30 mL/min). For mass flow dependent detectors (FID, FPD, FTD) this feature enhances sensitivity [9].

In modern GC, the detector signal is digitalized in the detector electronics and the A/D converter passes digital data to the PC. Due to the presence of RC chain-containing circuits, any signal amplifier has a certain response time with the presence of some smoothing effect. This should not influence the peak width which is determined by the chromatographic process prior to the detector (injection system, column). The parameter of detector electronics regarding the response time is usually referred to as filter time constant (FTC) [12]. The electronic detector signal amplifier cannot follow a signal in an infinitely fast way. It needs a certain time to follow rapid signal changes. In Figure IV.1 this parameter is visualized graphically [12]. A theoretical step increase of signal is shown here and the response of detector amplifiers indicates that it follows the signal with some time delay ($1-1/e^t$). The time interval which the detector electronics needs to reach the (1-1/e) fraction of such a step signal is defined as filter time constant.

This parameter should be selectable [12] together with the number of data points recorded across a peak. In an experiment, the influence of this parameter on real peak shapes was measured. The effects of the injection system and column on band broadening were reduced as follows:

1. **A 0.1 mm ID glass insert and a 0.2 µL injection volume of just one compound (chlorodecane) with a high split ratio (600:1).**
2. **Use of a 1 m column with a 0.1 mm ID and 0.1 µm film thickness; isothermal analysis at 200 °C.**
3. **Detector make-up gas flow of 60 mL/min.**

Chlorodecane was diluted in methanol. Figure IV.2 shows the chlorodecane peak which elutes at 0.0332 min under isothermal conditions. The filter time constant τ was varied from 4 ms to 200 ms. It can be clearly obser-

ved that increases in the filter time constant affects both the peak retention time and shape as predicted from theory [12]. The full width at half maximum for a τ value of 200 ms (a standard parameter in many GC systems) is about 3 s, whereas for a τ value of 4 ms the FWHM value is about 40 ms. The effect of the filter time constant on peak shape obviously has a drastic effect on resolution as shown in Figure IV.3. The figure illustrates two kerosene very fast GC chromatograms with applied filter time constants of 100 and 10 ms respectively. The improvement in terms of peak resolution is evident in the 10 ms FTC analysis. This experiment shows the importance of detector parameter optimization in terms of peak resolution. In addition, the FTC has a considerable influence on the signal-to-noise ratio (S/N). Figure IV.4 shows the normalized signal-to-noise ratio as a function of the filter time constant. These curves are plotted for different peak widths. For a peak width of 0.1 s the optimum filter time constant is 20 ms with regard to the S/N ratio. The optimum FTC value under such conditions is also dependent on the sample concentration and ranges between 4 and 20 ms.

A further electronic parameter of importance is the sampling rate or, in other words, the number of data points acquired per second which are transferred from the A/D converter to the PC. The number of points must be sufficient for the proper reconstruction of a Gaussian peak (minimum 10 to 15 data points). If the number of data points is too low, data reproducibility is reduced. The filter time constant and the sampling frequency parameters necessary for the range of peak widths observed in gas chromatography were summarized by J.V. Hinshaw [12]. The latter reported that for peak widths between 0.1 and 0.5 s the filter time constant and sampling rate should be about 10 ms and 20 to 100 Hz respectively.

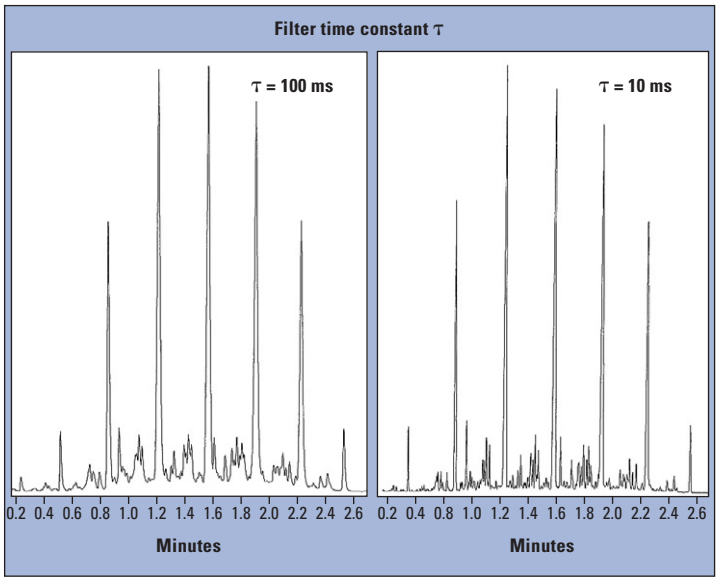


Figure IV.3: Chromatograms relative to a kerosene sample recorded at a filter time constant τ of 100 ms and 10 ms respectively

2. Mass spectrometric detector (quadrupole MS)

The most common mass spectrometric detector used in gas chromatography is the quadrupole MS. With regard to fast GC/MS analysis, the MS detector obviously needs to be fast enough for the rapid eluting analyte bands. For identification purposes, GC/MS applications are carried out in the full scan mode in order to perform a MS library search. In this operation mode, every data point corresponds to a complete mass spectrum over the mass range selected (scan).

After peak assignment, the SIM mode (selected ion monitoring) may be used in order to increase the analytical sensitivity.

In order to attain this data, two parameters of the GC/MS hardware must be considered: firstly, the mass range selected by the analyst must cover all the analyte ion fragments in order to ⏵

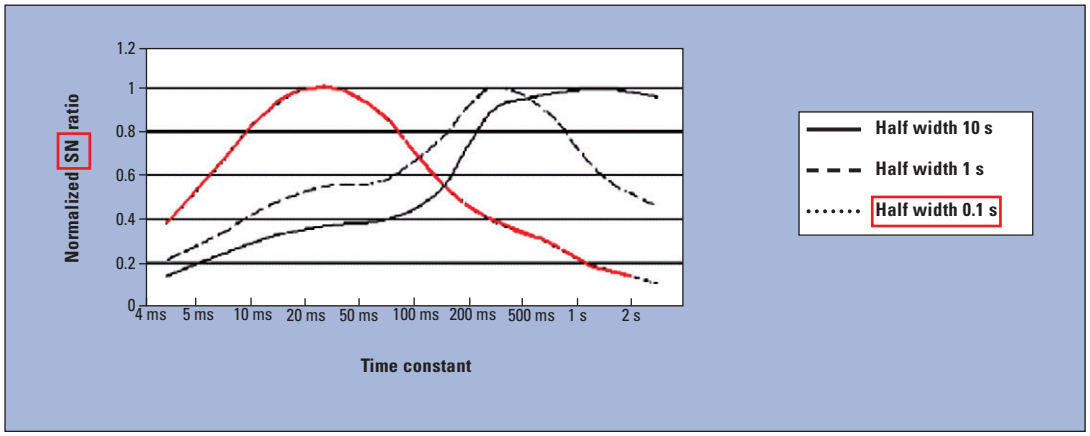


Figure IV.4: Signal-to-noise ratio as a function of the filter time constant and for different peak widths (source: GC-2010 operation manual)

perform a library search for component identification (scan). In this case, the scan speed should be high enough so that the relative intensities of the fragments do not change significantly from point to point across a narrow peak. In this respect, a low scan speed would result in low quality library matches. Secondly, the sampling frequency, which corresponds to the number of scans (or the number of SIM data points) per second, is, as aforementioned, a fundamental parameter. Fast GC/MS applications require a high quadrupole scan rate (up to 10,000 amu/s) and, in addition, a low inter-scan dead time (reset time of the electronics) so that the sampling rate may be sufficiently high (up to 50 Hz/100Hz in scan/SIM modes for the GCMS-QP2010). This situation is shown in Figure IV.5.

The true scanning speed of the quadrupole is calculated by the scan range divided by the interval time minus the RF setup time which ranges from 5 to 10 ms for the GCMS-QP2010. In Figure IV.6 this is demonstrated by experimental data. A linalool peak was scanned with a 20 Hz scanning frequency and a selected mass range of 30 to 350 amu. The analysis was carried out with a SPB5 10 m, 0.1 mm, 0.1 µm column. The peak width at half height is about 0.6 s and about 1.2 s at the base resulting in 24 data points across the peak. As can be seen, the quality of the spectra in three points across the chromatographic peak is good (a Wiley library search was performed). The spectra similarities, 94, 96, 94, indicate that there is no skewing.

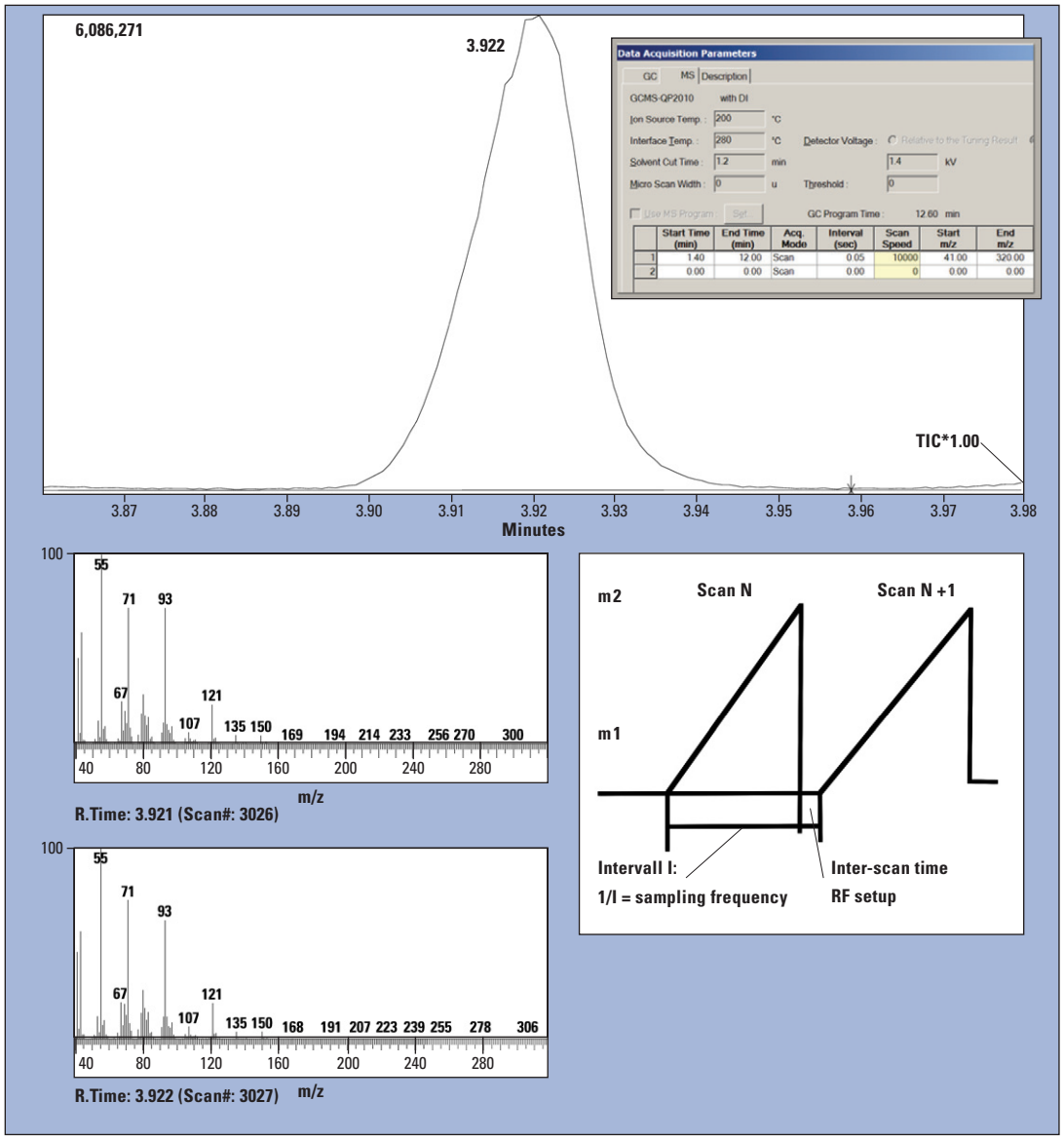


Figure IV.5: Definition of scan speed, inter-scan delay and sampling frequency for a quadrupole MS

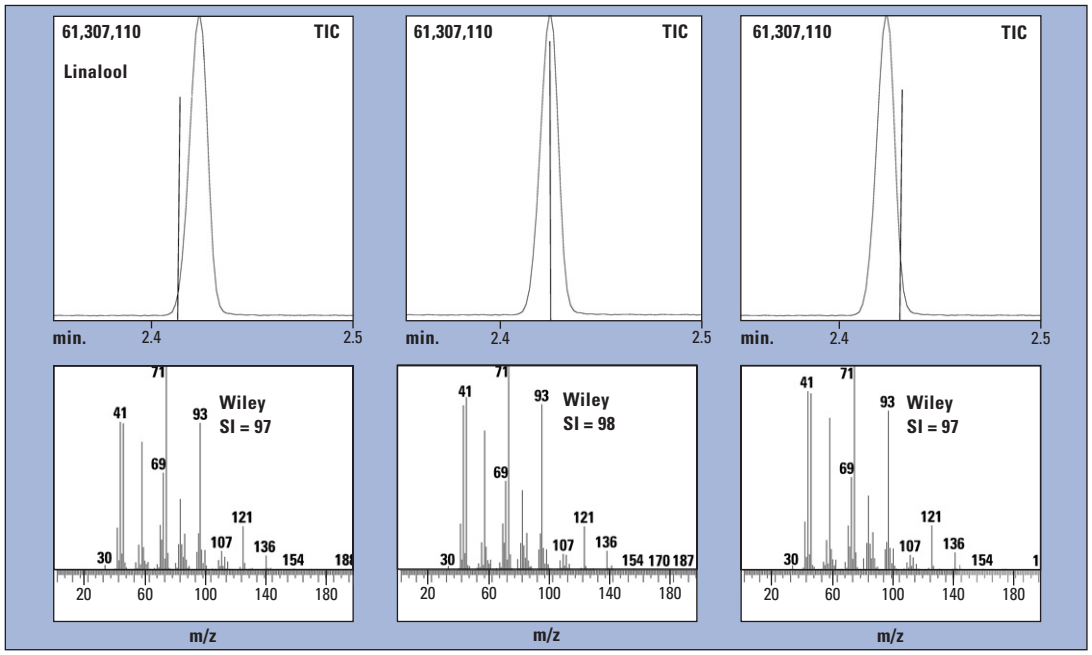


Figure IV.6: Linalool peak generated by a narrow-bore column (FWHM 0.6 s) and the spectra recorded at the beginning, apex and end of the peak after background subtraction. Spectra similarities are 94, 96, 94 using the Wiley MS library.

V. Applications in food analysis

1. Organophosphorous pesticides in food matrices

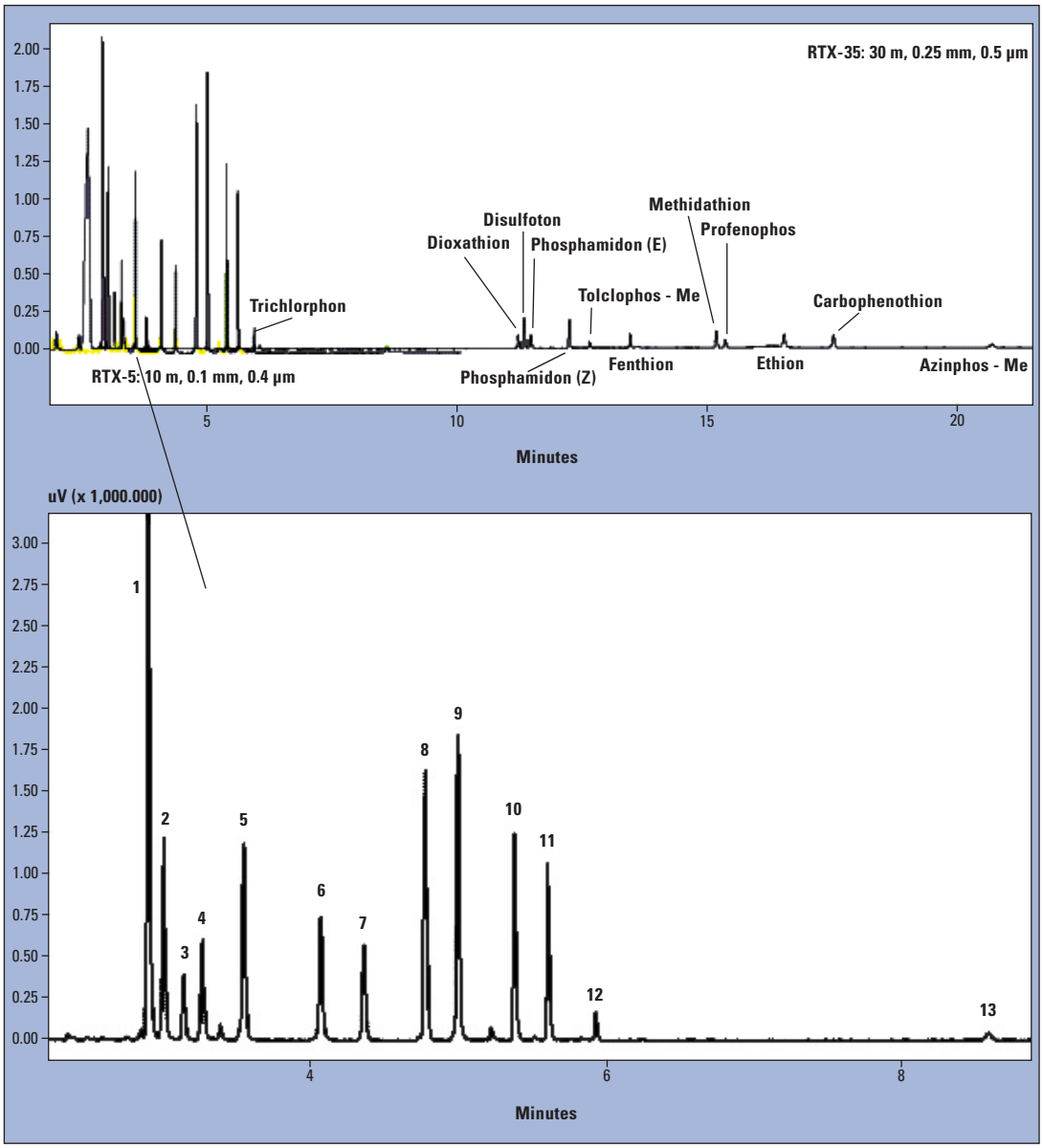


Figure V.1: **Top:** conventional GC chromatogram of organophosphorous pesticide standards in a tomato extract. Concentrations vary beween 125 and 1,000 pg. **Bottom:** fast GC organophosphorous pesticide analysis carried out with a RTX-5 : 10 m, 0.1 mm, 0.4 µm column.

Peak identification: 1. Dichlorphos, 2. Trichlorphon, 3. Dioxathion, 4. Phosphamidon (E), 5. Disulfoton, 6. Phosphamidon (Z), 7. Tolclophos methyl, 8. Fenthion, 9. Methidathion, 10. Profenophos, 11. Ethion, 12. Carbophenothion, 13. Azinophos methyl

Organophosphorous pesticides (OPPs) are widely used in agriculture in order to protect a broad range of products. Unfortunately, the presence of these toxic compounds is often detected in foods.

The maximum allowable concentrations of OPPs in foods is, however, strictly controlled [13]. In Germany, the well-known DFG S19 (Deutsche Forschungsgemeinschaft) is employed for the determination of traces of these substances in foods. This Standard is also present in European regulations as DIN EN 1528-3, DIN EN 12393-2. In addition, these methods define the procedure for the determination of organochlorine, nitrogen-containing and other types of pesticides. The procedure steps are mainly: 1. extraction and partition, 2. gel permeation chromatography, 3. mini silicagel chromatography and 4. analysis with GC-FTD, GC-FPD or GC/MS.

A chromatogram relative to an OPP-spiked (amount range between 125 and 1,000 pg) tomato matrix is shown in Figure V.1. The column used was a RTX-35 30 m, 0.25 mm, 0.5 µm. The figure also shows the result obtained with a RTX-5 (5 % phenyl), 10 m, 0.1 mm, 0.4 µm column under fast GC conditions [14] (temperature program from 100 °C (1 min) at 80 °C/min to 220 °C at 10 °C/min to 240 °C at 50 °C/min to 320 °C; carrier gas: H_2 (120 cm/s). The injection volume was 2 µL in the splitless mode. In order to increase the sample transfer speed (see above) a 600 kPa high pressure injection was applied for 1 minute. The peak widths (FWHM) are approximately 3 s in the standard analysis and, below, 0.5 s in the chromatogram obtained with the narrow-bore column. As the area in general is determined by the sample amount which was not changed (both runs were carried out in the splitless mode) the signal-to-noise ratio was higher in the fast GC experiment. The retention time of azinophos methyl was 22 minutes in the standard analysis and 9 minutes in the fast result.

A chromatogram derived from a black tea analysis is shown in Figure V.2. The analytical result indicated a contamination of dioxathion (225.2 pg), phosphamidon (67.1 pg), disulfoton (217 pg), dichlorphos (243 pg), ethion (145.1 pg) and azinophos methyl (244.8 pg).

The limit of detection in a fast GC application may be derived, for example, from the results

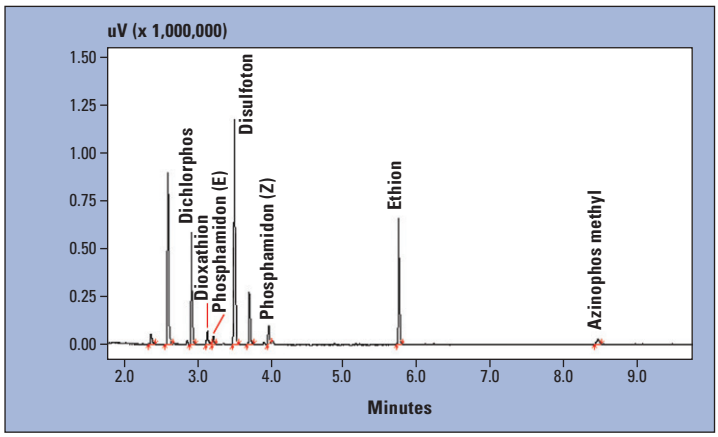


Figure V.2: Fast GC chromatogram of a black tea sample. For concentrations see text.

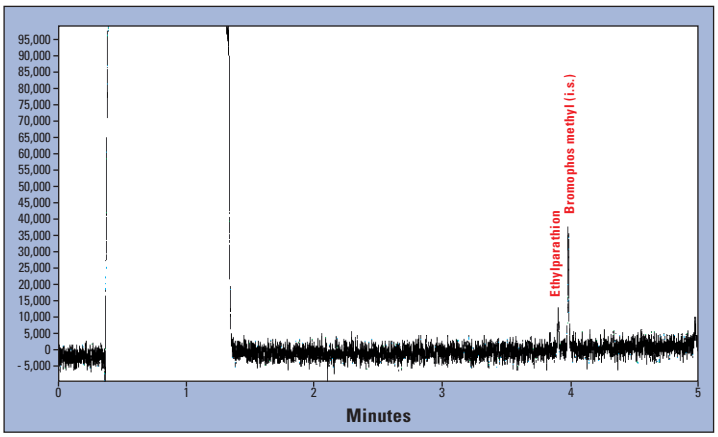


Figure V.3: Fast GC chromatogram of an olive oil sample. For the quantitative determination of ethylparathion, bromophos methyl was added as internal standard; concentration ethylparathion: 3 ppb.

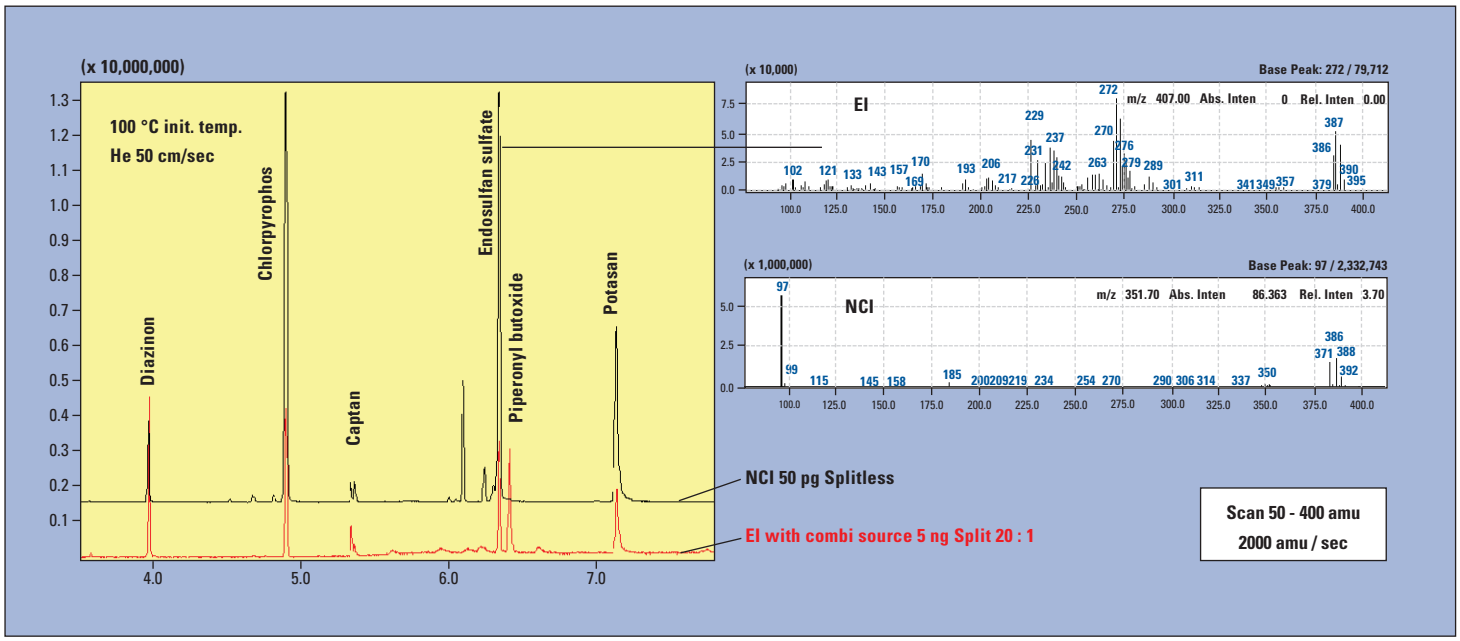


Figure V.4: Total ion chromatograms (TIC) of an OPP standard mixture analysis carried in the EI and NCI modes

shown in Figure V.3 [15]. The data shown were obtained from an olive oil sample. A 3 ppb contamination of ethylparathion was determined by using internal standard (bromophos methyl) calibration. During sample preparation, 2 g of olive oil were added to 2 mL of hexane. The internal standard (0.01 ppm bromophos) was then added. A liquid extraction with acetonitrile was then carried out and, following this, 7.5 mL was taken from the acetonitrile phase and dried. Finally, 2 mL of hexane was added before GC injection.

GC/MS data:

In GC/MS, the electron impact (EI) mode for analyte ionization is most widely employed. However, in recent years the chemical ionization mode has become more popular. Sensitivity may be considerably enhanced for electrophilic molecules by negative chemical ionization (NCI) ➧

Substance	EI Peaks (Da)	NCI dominant Peaks (Da)
Methamidophos	94, 141, 126, 111, 110, 128	-
Methomyl	58, 105, 88, 73, 115, 162	-
Diazinon	304, 179, 137, 152, 276, 199	169
Chlorpyriphos-OEt	314, 187, 258, 244, 97, 125, 351	313, 315, 212, 214
Captan	79, 117, 149, 264, 301, 182, 236	150, 149
Endosulfan sulfate	229, 272, 239, 207, 170, 387	97, 386
Piperonyl butoxide	176, 177, 149, 178	-
Potasan	192, 328, 176, 300, 272, 148	328, 192

Table V.1: EI and NCI dominant peaks observed with the organophosphorous pesticides

Comparison of the sensitivities in EI and NCI

Higher sensitivity in NCI mode ← → **Higher sensitivity in EI mode**

> 10 times	2 - 10 times		Equality		2 - 10 times	> 10 times	
Bifenox	Dichlofluanid	Dicofol Bunkaibutu	p,p'-DDT	Aldin	Fosthiazate	Chlorfentezinedeg	Mepronil
Fenvalerate	Fenalimol	Malathion	Dimethoate	Thiobencarb	Acephate	Metamidophos	Propiconazol
Chlorfenapyr	Pendimethalin	Parathion	δ-Lindane	Permethrin	Terbacil	EPTC	Lenacil
Cyfluthrin	Dieldrin	Dimethylvinphos	Cafenstrole	Pyributicarb	Pyraclofos	Propamocarb	Tebucanzole
Pyrethrin-2	Edifenphos	Pyrifenox-Z	Fluvalinate-1	p,p'-DDD	Penconazol	Chlorpropham	Etoxazole
MEP	Tefluthrin	Parathion methyl	Pyrifenox-E	Chlorpyrofos	Uniconazolep	Terbufos	Tebufenpyrad
EPN	Cypermethrin	Kresoxim methyl	Diflufenican	Bitertanol	Fensulfothion	Benfuresate	Pyriproxyfen
Fenpropathrin	Thifluzamide	Folpet	Hexaconazole	Isofenphos	Cyhalofop buthyl	Dimethenamid	Pyrimidifen
Acrinthrin	Acetamiprid	Cyanazine	Thiometon	Quinalphos	Butachlor	Alachlor	Mefenacet
Trifluralin	PAP, Phenthoate	Cadusafos	Diazinon	p,p'-DDE		Metolachlor	Triadimenol
Phosalone	Pyrethrin-1	Tolclofos methyl	Prothiofos	Pirimiphos methyl		Diethofencarb	Etrimfos
Cyhalothrin	Endrin	Pretilachlor	Difenoconazole	p,p'-DDT		Fenthion	Chlorobenzilate
β-CVP	Deltamethrin	Malathion	Pyridaben	Halfenprox		Fludioxonil	Esprocarb
Flucythrinate	β-BHC	Captafol	Teraconazole	Ethoprophos		Methoprene	Thenylchlor
Butamifos	α-BHC	Flutolanil	Chinomethionate	Dichloros		Paclobutrazol	Tricyclazole
γ-BHC			Bifenthrin			Flusilazole	Isoprocarb
Captan			Inabenfide			Cyproconazole	
Imibenconazole			Myclobutanil				

Table V.2: Classification of sensitivities with EI and NCI modes for pesticides

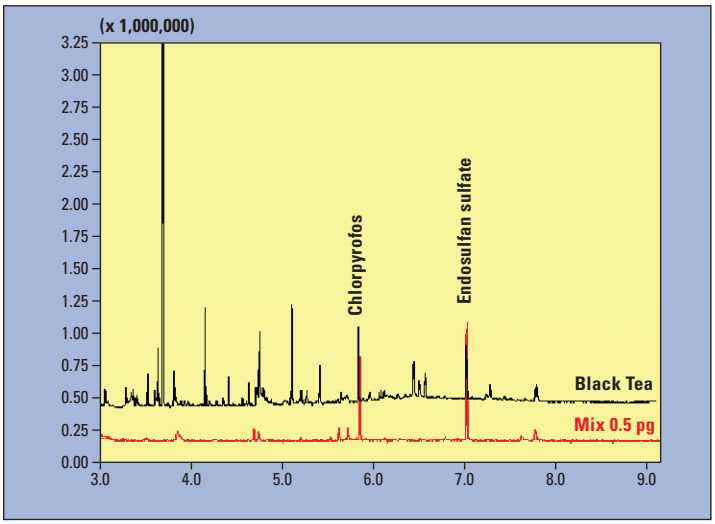


Figure V.5: Black tea and standard compound mixture (0.5 ppb of each compound) TIC chromatograms (NCI mode)

using iso-butane, methane or ammonia as reagent gas. The selectivity is also helpful when peak coelutions are observed with other matrix components [16]. In order to identify pesticides the EI mode of the NCI/PCI/EI combi source was used in these experiments. The NCI masses of the compounds were then determined by comparison of the EI and NCI scan data. In Figure V.4, the GC/MS results attained for a standard using a RTX-5 10 m, 0.1 mm, 0.1 µm column and using both modes are shown. The resulting spectra similarity is comparable with the result obtained using the standard method. In this experiment, the scan range was 50 to 400 amu with a scan frequency of 20 Hz. The amounts of the two standards were 5 ng (EI) and 50 pg (NCI). While the MS response is enhanced drastically for diazinon, chlorpyrofos, endosulfan sulfate and potasan, the signal increase is less for captan, while for piperonyl butoxide there is almost no signal at all. To illustrate the different spectra generated by the two modes, the corresponding spectra of endosulfan sulfate are also shown.

With regard to EI, a typical fragmentation is observed; in the case of NCI only the masses 384, 386, 388 together with a dominant 97 fragment are present. Table V.1 reports data concerning different dominant fragments observed in EI compared with NCI for the compounds measured here. Figure V.5 shows a TIC chromatogram of a real sample (black tea) indicating a contamination of chlorpyrofos and endosulfan sulfate. Also shown is a chromatogram relative to a standard mixture containing 0.5 pg of each component.

Table V.2 shows a list of pesticides and a classification in terms of sensitivity in each mode [16]. As NCI is characterized by a very high selectivity, it can also prove useful when matrix components interfere with the peaks of interest. For a more complete overview of pesticides screened with a combination of EI and NCI, please consult reference [16].

In conclusion, a combination of EI and NCI as well as mass spectra library search for both modes is a powerful tool for pesticide analysis.

2. The analysis of organochlorine pesticides in food matrices using GC-ECD and NCI GC/MS

Organochlorine (OCP) pesticides are commonly measured using ECD or MS (NCI mode) detectors.

In conventional GC analysis using standard columns of about 30 m length with a 0.25 mm inner diameter and 0.25 µm film, the typical run time for an OCP standard solution containing 23 compounds is about 30 minutes (Figure V.6; for quantitative results refer to Table V.3). The retention time of p,p'-DDD is about 21.5 minutes. The column used in this application was a 5 % phenyl; the temperature program was as follows: from 100 °C (1 min) to 170 °C, at 50 °C/min (1 min), then to 220 °C at 5 °C/min, then to 260 °C at 10 °C/min, then to 280 °C (10 min) at 20 °C/min using N_2 as carrier gas with an initial pressure of 77 kPa corresponding to an average linear velocity of 23 cm/s. The injection was carried out in the splitless mode (1 µL).

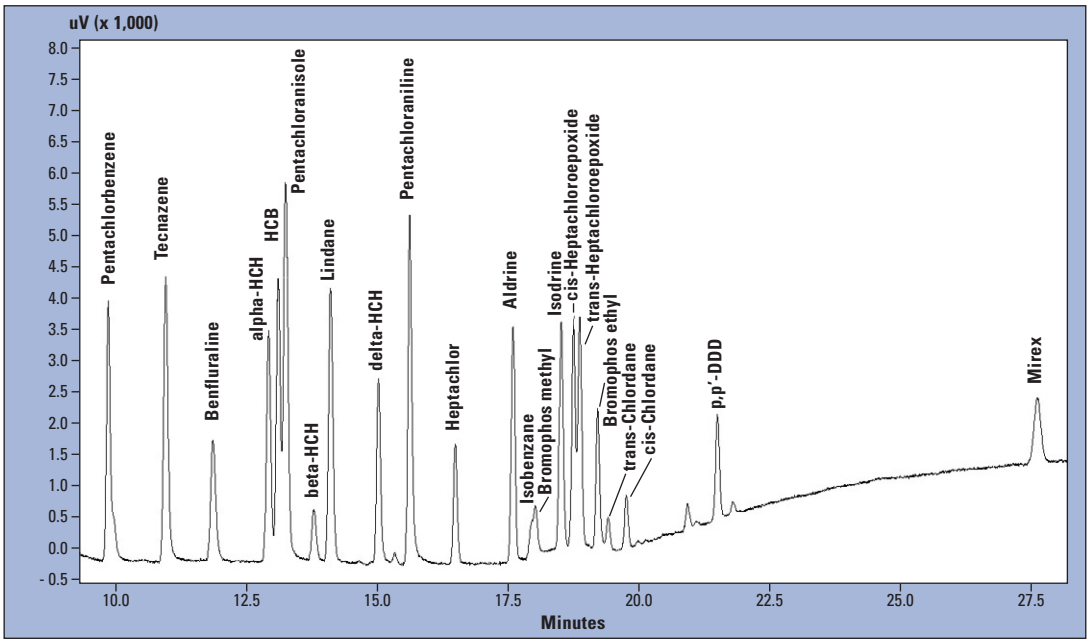


Figure V.6: Conventional GC analysis of an OCP standard mixture (23 compounds) using a RTX-5 30 m, 0.25 mm ID, 0.25 µm column. For operational conditions refer to text.

The application was then carried out using a fast GC method with a CPsil 8 9 m, 0.1 mm, 0.1 µm column and H_2 as carrier gas. The result is shown in Figure V.7. As can be seen, all 23 compounds are better separated and the retention time of p,p'-DDD was less than 3.6 minutes. The temperature program applied was as follows: from 80 °C (1 min) to 280 °C (3 min) at 60 °C/min with an initial head pressure of 324 kPa and an average linear velocity of 100 cm/s (H_2) which was constant during the entire analysis. The selected filter time constant and sampling frequency were 20 ms and 63 Hz respectively. The injection volume was 1 µL with a split ratio of 40:1. The ECD make-up gas flow was 80 mL/min. The signal-to-noise ratio of α-HCH in the rapid application is about 440:1 (split) while the same measured 220:1 in the splitless conventional application, indicating an increased sensitivity.

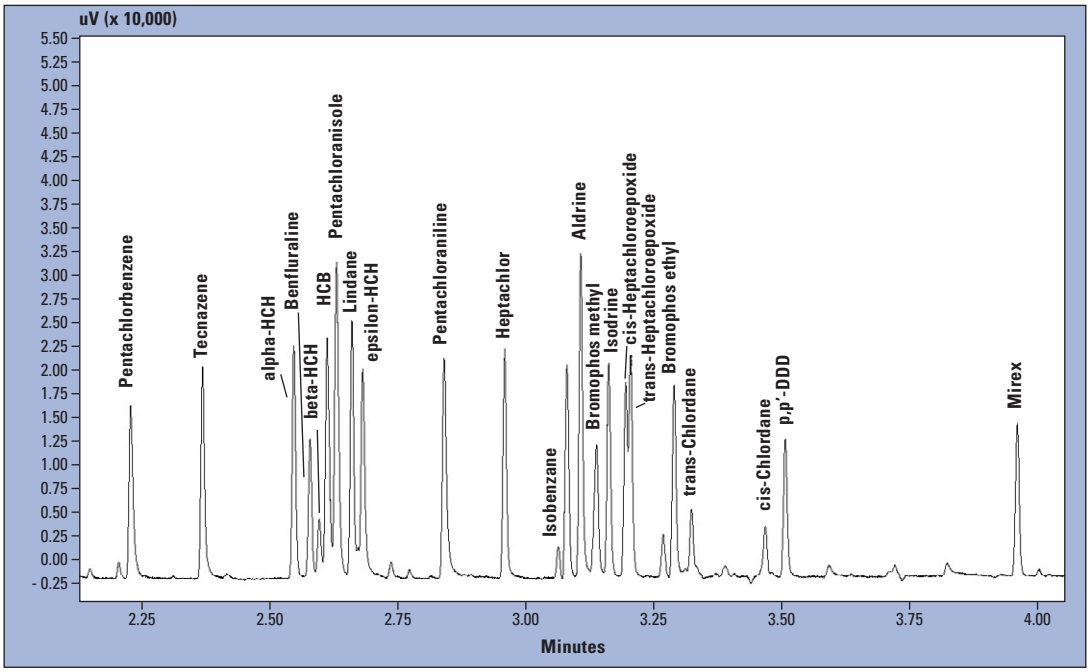


Figure V.7: Fast analysis of the OCP standard mixture containing 23 compounds with a CP SIL 8 9 m, 0.1 mm, 0.1 µm column. For retention times and concentrations see Table V.3.

The full width at half maximum of α-HCH, for example, is about 0.5 s which is a typical value for these types of columns, demonstrating the suitability of the ECD-2010 for fast analysis in the field of organochlorine pesticides. The limit of detection for α-HCH (considering a signal-to-noise ratio of at least 3) was about 0.1 ppb. The method was then applied to a grape sample. The resulting chromatogram is shown in Figure V.8. Contaminations of chlorpyrofos at a concentration of 0.53 ng/mL (corresponding to 0.48 ng/kg grapes) and ⏵

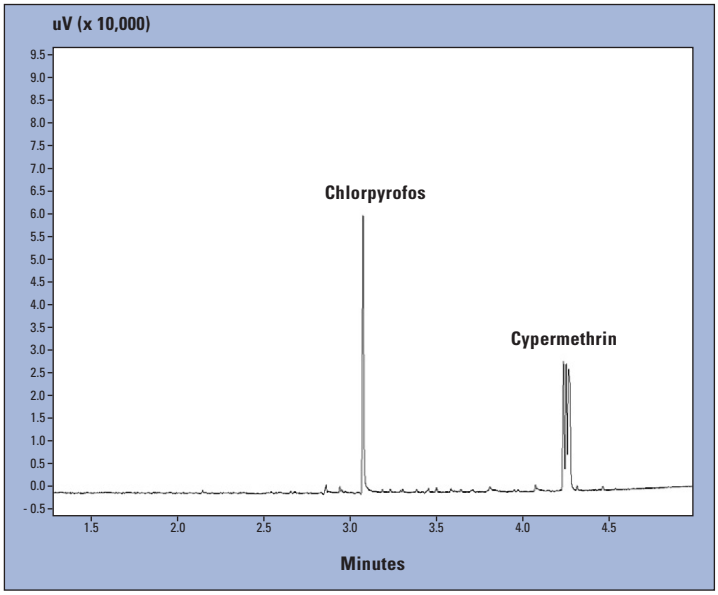


Figure V.8: Fast GC-ECD result for a grape sample: chlorpyrofos 0.53 ng/mL (corresponds to 0.48 mg/kg grapes) and cypermethrin 0.55 ng/mL (corresponds to 0.5 mg/kg)

		RT	Conc (ppb)
01 Pentachlorobenzene	Target	2.23	21.3
02 Tecnazene	Target	2.37	22.5
03 Benfluraline	Target	2.58	52.8
04 α-HCH	Target	2.548	22.1
05 HCB	Target	2.613	24.1
06 Pentachloroanisole	Target	2.631	20.6
07 β-HCH	Target	2.598	20.4
08 Lindane	Target	2.662	28.8
09 Δ-HCH	Target	2.818	23.2
10 ϵ-HCH	Target	2.683	1
11 Pentachloroaniline	Target	2.842	26
12 Heptachlor	Target	2.96	30.4
13 Aldrine	Target	3.109	21.7
14 Isobenzane	Target	3.065	5
15 Bromophosmethyl	Target	3.139	22.6
16 Isodrine	Target	3.163	22.04
17 cis-Heptachloroepoxide	Target	3.196	25
18 trans-Heptachloroepoxide	Target	3.206	25
19 Bromophosethyl	Target	3.291	50.36
20 trans-Chlordane	Target	3.325	5
21 cis-Chlordane	Target	3.469	5
22 p,p'-DDD	Target	3.508	22.4
23 Mirex	Target	3.961	21.84

Table V.3: Concentration of the OCP standard. Chromatogram shown in Figure V.6.

cypermethrin at a concentration of 0.55 ng/mL (corresponding to 0.5 ng/kg) were found.

In order to apply a splitless injection technique, high pressure injection in combination with a slightly thicker film needs to be used (Figure V.9). For this application, a 10 m, 0.18 mm, 0.4 µm (5 % phenyl) column was used with a 100 °C initial temperature for 1 min then at 60 °C/min up to 280 °C (3 min). The carrier gas was H_2 and the linear velocity was 120 cm/s over the entire run. All other parameters were unchanged. Again considering α-HCH, the calculated detection limit is about 0.01 ppb in this case.

The determination of organochlorinated pesticides in food matrices can be performed very well using fast GC-ECD with the ECD-2010. The measured detection limits were below 0.1 ppb for several compounds using a split of 40:1 and about 0.01 ppb using the splitless technique.

In the case of GC/MS, negative chemical ionization may be considered as ideal in order to promote a thermal electron capture process inside the ion source using a reagent gas (methane). Low energy secondary electrons originate from the impact of the electrons emitted from the MS filament onto the reagent gas molecules. The ions produced then pass through the mass filter just as in EI. Only the polarities of the instrument are reversed. It is very interesting to compare the results obtained by employing NCI GC/MS with those obtained with the ECD. Figure V.10 illustrates data relative to six organochlorine compounds recorded in the SIM mode. The concentrations employed were between 0.4 and 0.6 ppb. The signal-to-noise ratios observed for t-heptachloroepoxide and p,p'-DDE are 28:1 (mass 71) and 210:1 (mass 70) respectively. If a minimum signal-to-noise ratio of 3:1 is considered, the limits of detection are similar to the ECD results. The calibration curve for t-heptachloroepoxide is also illustrated, showing a good correlation.

In conclusion, EI and NCI in combination is a very powerful tool for screening of organophosphorous or organochlorine pesticides.

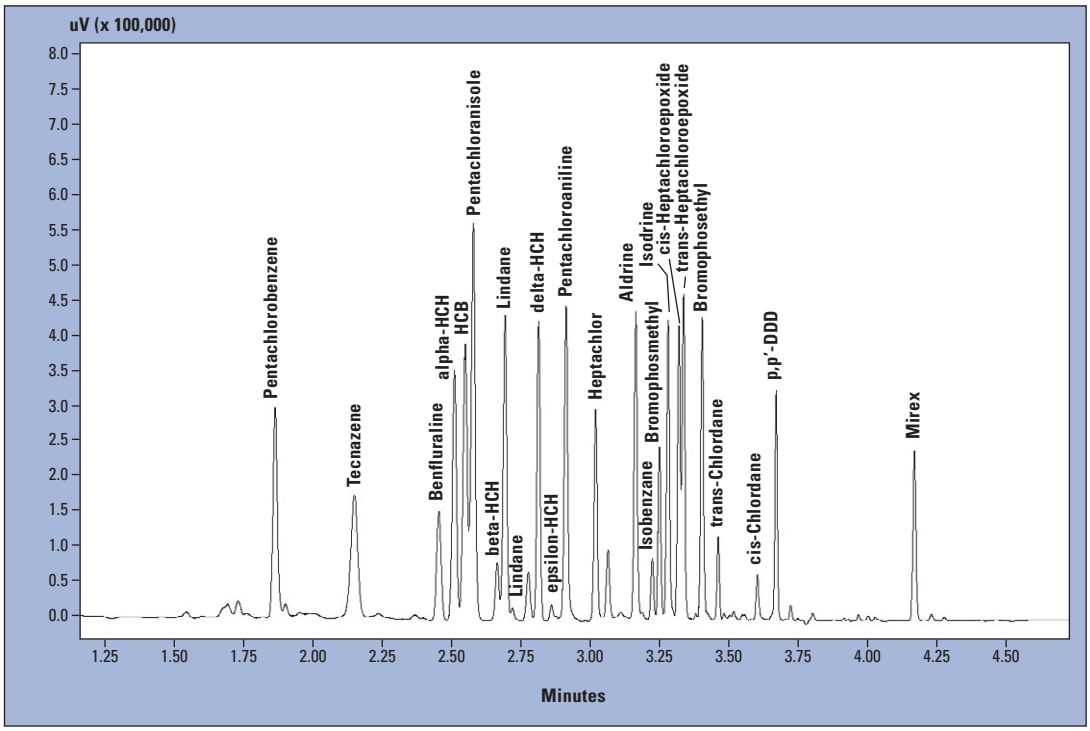


Figure V.9: Fast GC chromatogram relative to an OCP standard mixture. Injection volume: 1 µL, in the splitless mode, high pressure pulse 400 kPa. Column: RTX-5 10 m, 0.18 mm, 0.4 µm.

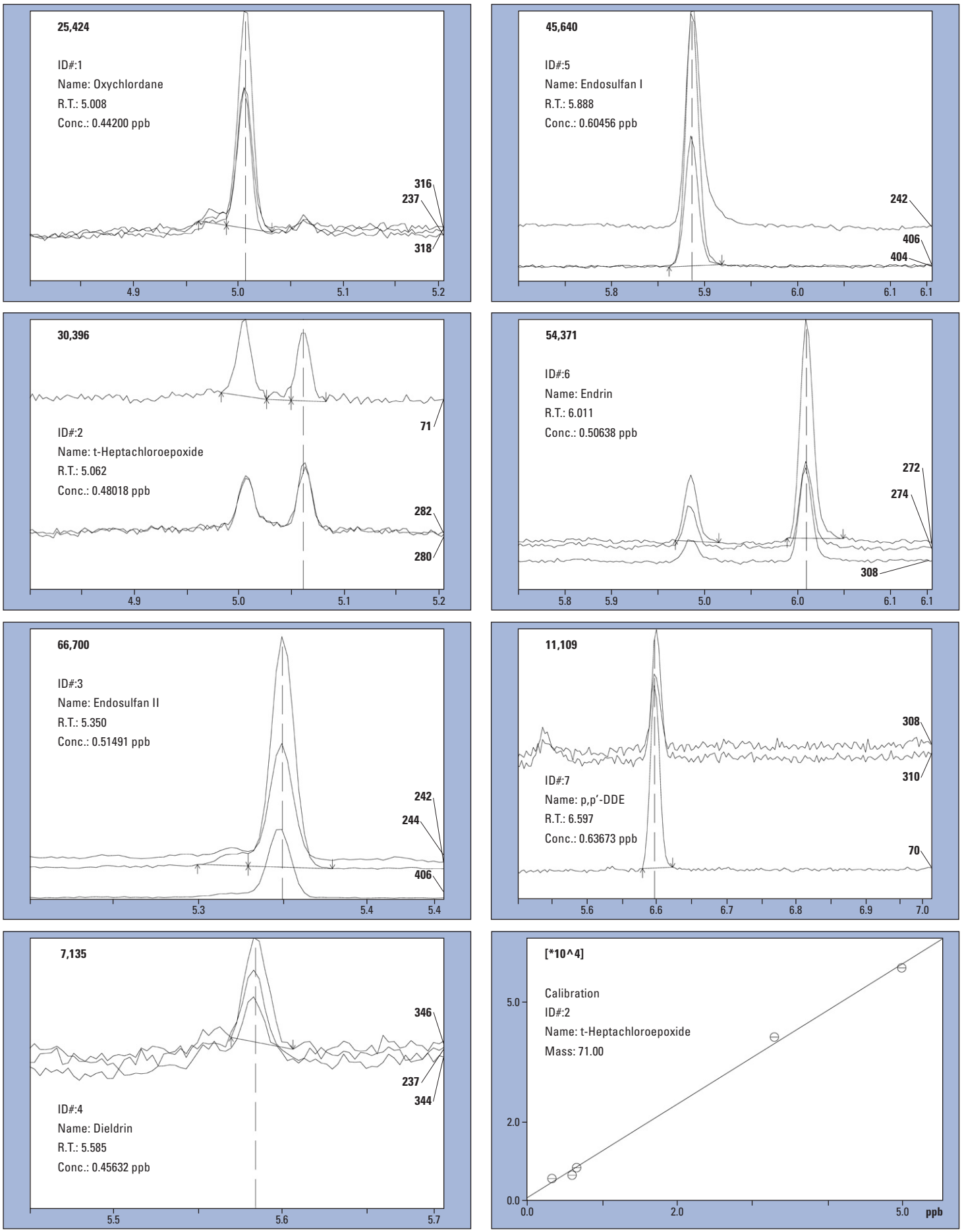


Figure V.10: NCI (methane) GCMS data recorded in SIM mode (figures on the graphs refer to the selected mass traces) with an organochlorine standard containing oxychlordane, t-heptachloroepoxide, endosulfan I, dieldrin, endosulfan II, endrin and p,p'-DDE. Concentration of each compound is 0.4 to 0.6 ppb.

3. Analysis of butter fatty acid methyl esters (GC-FID)

Fatty acids (FAs) have essential physiological functions in the human body and therefore have an important influence on human health.

In particular, ω3 unsaturated fatty acids are of great importance as they can not be produced by the human metabolism. FAs such as eicosanic acid (EPA) and docosahexanioc acid (DHA) have a beneficial influence on immunological, heart and allergic diseases, diabetes and cancer [17]. As a consequence, the determination of lipidic profiles in foods is very important. The composition of fats and oils in natural matrices may be very complex and conventional GC separations can therefore be time-consuming. It must be added that prior to GC injection, the FAs must be converted into their respective methyl esters in order to increase volatility and decrease polarity.

A conventional GC application carried out with butter FAMEs is illustrated in Figure V.11 [18]. The separation may be considered to be quite complex and with the column type used (Carbowax 30 m, 0.25 mm ID, 0.25 µm film), the total analysis time exceeds 30 minutes.

In contrast, the result obtained with a fast GC method is shown in Figure V.12 (Supelcowax 10 m, 0.1 mm ID, 0.1 µm film) [18]. The resolution may be considered to be approximately the same but the total analysis time is reduced by a factor of 17. The parameters applied in the conventional analysis were as follows: injection volume: 1 µL (1:10 in hexane); split ratio: 1:50 (250 °C); temperature program: 50 °C to 250 °C at 3.0 °C/min; head pressure: 53 kPa at constant average linear velocity; carrier gas: H_2; [u]: 36.2 cm/s; detector: FID (250 °C), H_2: 50 mL/min, air: 400 mL/min, make-up: 50 mL/ min kPa (N_2); sampling rate: 40 ms; filter time constant: 200 ms.

The parameters applied in the fast analysis were as follows: injection volume: 0.2 µL (1:20 in hexane); split ratio: 1:200 (250 °C); temperature program: 50 °C to 250 °C at 90.0 °C/min; head pressure: 400 kPa at constant average linear velocity; carrier gas: H_2; [u]: 116.0 cm/s; detector: FID (250 °C) H_2: 50 mL/min, air: 400 mL/min, make-up: 50 mL/min kPa (N_2); sampling rate: 4 ms (250 Hz); filter time constant: 20 ms.

The correlation between fast and conventional GC data is very good, as can be derived from Table V.4, which reports relative peak area percentages for both applications. For more details see reference [18].

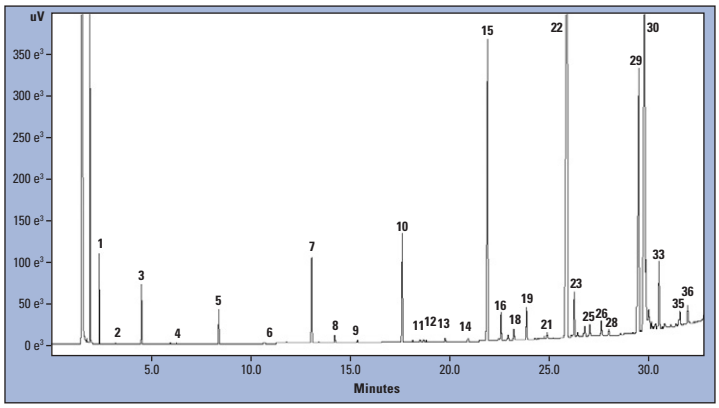


Figure V.11: Conventional GC chromatogram of butter FAMEs using a wax column: 30 m, 0.25 mm, 0.25 µm. For experimental conditions refer to text.

Table V.4: Comparison of relative peak areas for conventional and fast GC. Area reproducibility over 5 successive runs was below 1 % RSD.

	Conventional (run time: 33.0 minutes)	Ultra-fast (run time: 2.0 minutes)
C4 : 0	1.4	1.6
C6 : 0	1.4	1.3
C8 : 0	1.1	1.1
C10 : 0	2.7	2.8
C10 : 1	0.2	0.2
C12 : 0	3.5	3.5
C14 : 0	11.6	11.8
C14 : 1	1.0	0.9
C15 : 0	1.3	1.1
C16 : 0	32.0	32.0
C16 : 1	1.8	1.8
C17 : 0	0.7	0.6
C17 : 1	0.3	0.3
C18 : 0	10.7	10.1
C18 : 1	24.2	24.2
C18 : 2	3.0	2.7
C18 : 3	0.5	0.6

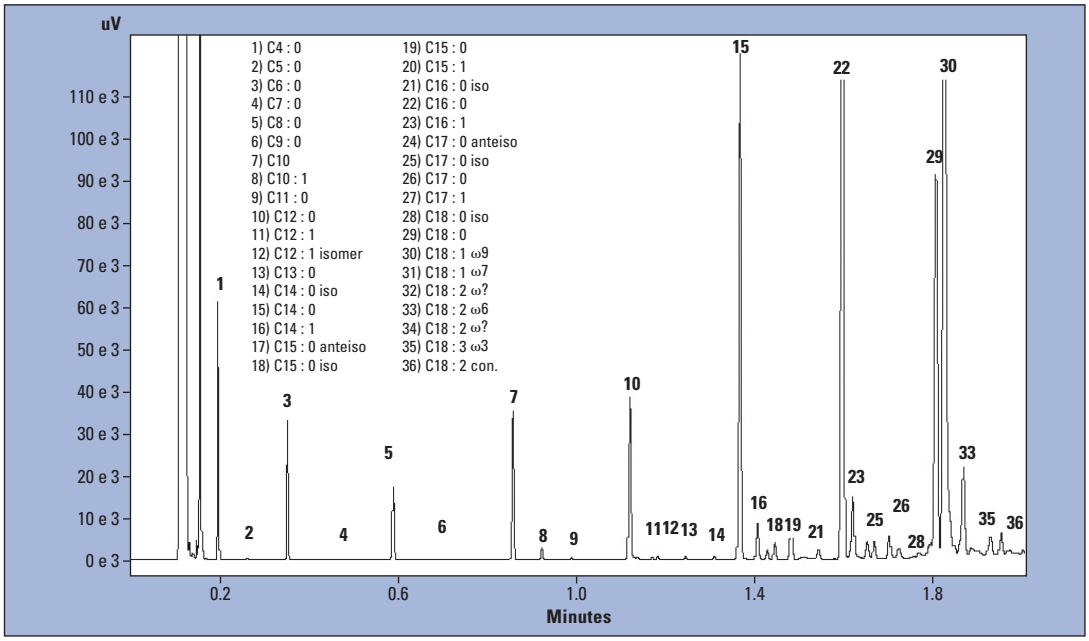


Figure V.12: Fast GC chromatogram of butter FAMEs using a wax column: 10 m, 0.1 mm, 0.1 µm. For experimental conditions refer to text.

VI. Application in the petrochemical field

Kerosene analysis (GC-FID)

GC analysis of kerosene may be considered to be a very common quality control procedure in the petrochemical field.

An increase in sample throughput is of the highest interest in this industrial sector. In Figure VI.1, the chromatogram recorded with a conventional 30 m column is shown (temperature program: 40 °C (2 min) at 2 °C/ min to 220 °C (3 min); carrier gas H_2, linear velocity: 59 cm/s). The total analysis time is about 72 min. The predominant peaks, in an equally spaced order, are kerosene paraffines. The transition to a fast method was achieved using a RTX-1 MS, 10 m length, 0.1 mm ID, 0.1 µm stationary phase thickness column. The result of the fast GC analysis is shown in Figure VI.2.

In this case the analysis time is about 2.3 min with a 31.3 fold speed gain. The applied average linear velocity was 85.3 cm/s (H_2 as carrier gas) with a greatly accelerated temperature program. The split ratio was set at 800:1 with the gas saver function activated (10:1 after 1 min).

The temperature program was set from 40 °C up to 150 °C at 80 °C/ min, and up to 250 °C at 70 °C/ min and finally up to 350 °C at 50 °C/min; the FID filter time constant and sampling frequency were set to 10 ms and 125 Hz respectively.

The chromatographic resolution is very comparable with that of the conventional analysis. The peak widths of the narrowest peaks are less than 0.5 s (FWHM).

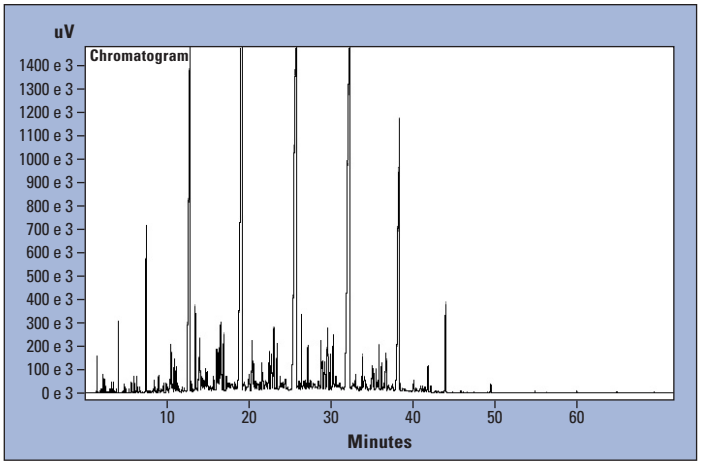


Figure VI.1: Conventional GC chromatogram recorded with a kerosene sample: RTX-1MS, 30 m, 0.25 mm ID, 0.25 µm

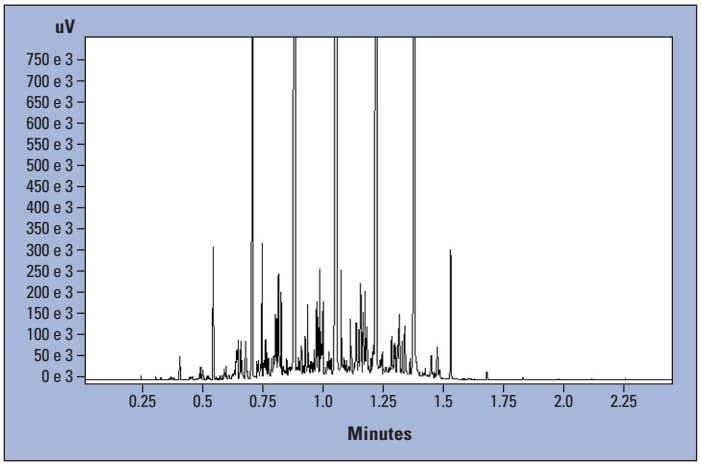


Figure VI.2: Fast GC chromatogram relative to a kerosene sample: RTX-1MS, 10 m, 0.1 mm ID, 0.1 µm

VII. Applications in the fields of flavors and fragrances

1. Potential allergens in perfumes

In the 7th Amendment to the European Cosmetics Directive, as published in the Official Journal N° L 66 of the European Union on March 11, 2003, 26 compounds are defined as potential allergens. This regulation requires that the presence of these 26 fragrance ingredients must be indicated on the label of finished cosmetic products if their concentrations exceed a threshold of 0.01 % for rinse-off and 0.001 % for leave-on products. These compounds are referred to as potential allergens, as they may or may not induce an allergic reaction. Among the 26 materials indicated, two are natural extracts (oak moss and tree moss) so the method as specified below is restricted to the determination of 24 volatile chemicals [19]. These compounds are listed in Table VII.1.

It must be emphasized that the determination of these components, which is usually carried out using quadrupole GC/MS equipment, is very complex and time-consuming. An example of such an application carried out with pure standard compounds is illustrated in Figure VII.1. The concentration of each compound was about 400 ppm, with a total of 26 peaks (including isomers) separated on a CP SIL 5 50 m column with 0.25 mm ID and 0.25 µm film thickness [temperature program: 50 °C (1 min) to 210 °C at 2 °C/min, to 280 °C at 10 °C/min (10 min). Carrier gas: He; average linear velocity 34.4 cm/s; split ratio 300:1]. As the analysis time is more than 75 minutes, the aim is to decrease this extensive GC run time in order to increase the sample throughput.

Figure VII.2 shows a fast GC/MS application carried out on a mixture of standard allergens with a RTX-5 10 m, 0.1 mm ID, 0.1 µm column [temperature program: 70 °C (1 min) to 180 °C at 25 °C/min to 280 °C (1 min) at 80 °C/min. Carrier gas: He; constant linear velocity: 40 cm/s; split 300:1]. In order to evaluate the resolution attained in both applications, two chromatographic expansions are compared in Figure VII.3. As can be seen, the degree of peak separation is better in the fast application (citral and anisyl alcohol are resolved) while a speed gain of a factor of about 11 is observed. Peak FWHM values were on average approx. 0.5 s; a mass range of 30 to 350 amu and a 20 Hz acquisition rate were applied. The quality of the resulting spectra, provided by the GCMS-QP2010, was very high with similarities ranging between 94 and 98 (Wiley library). Linearity was measured between 4 and 400 ppm and a regression coefficient of 0.9995 was attained which indicates excellent analytical

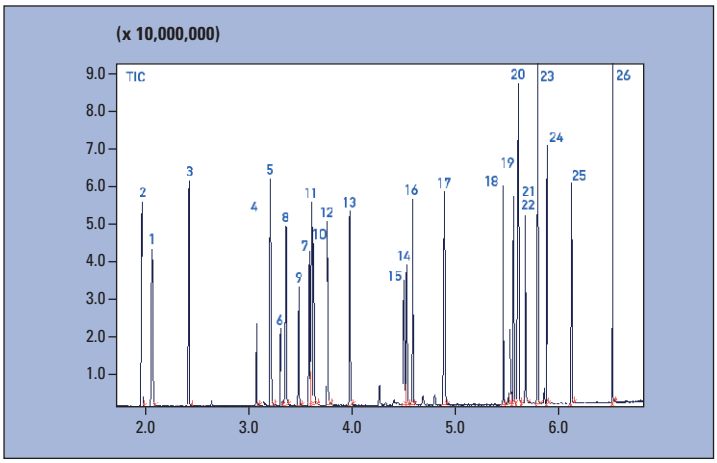


Figure VII.2: Fast GC/MS chromatogram relative to an allergen standard mixture carried out with a RTX-5 10 m, 0.1 mm, 0.1 µm column

01 Benzyl alcohol	14 Coumarin
02 Limonene	15 Iso-eugenol
03 Linalool	16 Methyl gamma ionone
04 Methyl heptin carbonate	17 Lilial
05 Citronellol	18 Amyl cinnamic aldehyde
06 Citral (Neral)	19 Lyral
07 Cinnamic aldehyde	20 Amyl cinnamic alcohol
08 Geraniol	21 Farnesol 1
09 Citral (Geranial)	22 Farnesol 2
10 Anisyl alcohol	23 Hexyl cinnamic aldehyde
11 Hydroxy citronellal	24 Benzyl benzoate
12 Cinnamyl alcohol	25 Benzyl salycilate
13 Eugenol	26 Benzyl cinnamate

Table VII.1: Compounds defined by the IFRA as potential allergens

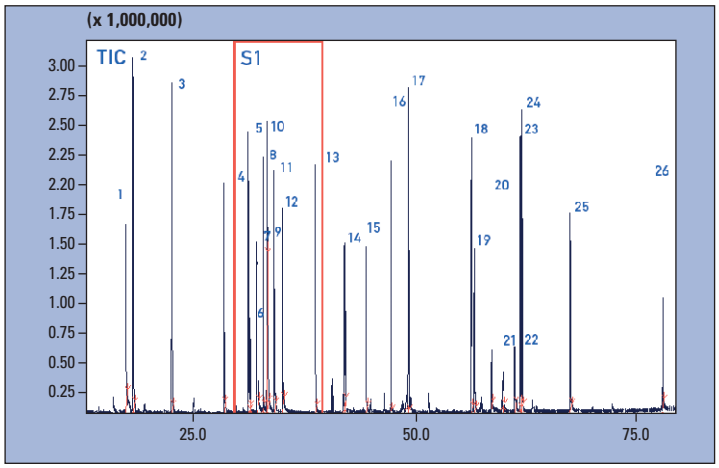


Figure VII.1: Conventional GC/MS chromatogram relative to an allergen standard mixture carried out with a CP SIL-5 50 m, 0.25 mm, 0.25 µm column

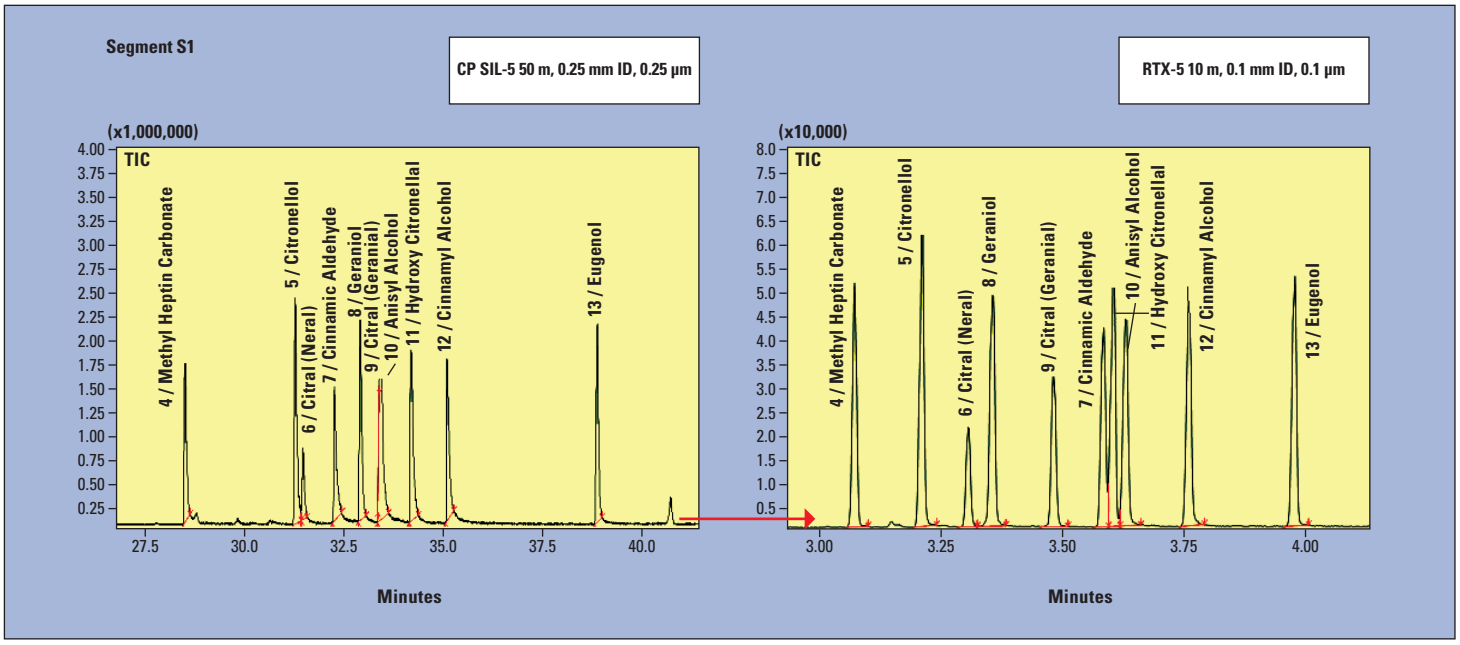


Figure VII.3: Chromatographic expansions relative to Figure VII.1 and Figure VII.2

precision. To illustrate, calibration curves for limonene and lyral are shown (Figure VII.4).

The method was then applied to real-world samples. The TIC result of an Eau de Toilette sample, diluted in acetone (1:100), is shown in Figure VII.5. The allergens found (concentrations refer to the dilution) are methyl gamma ionone (74.5 ppm), lilial (129.7 ppm), lyral (99.4 ppm) and benzyl salicylate (96.6 ppm). The spectral similarities were between 93 and 98 using a commercial MS library (Wiley).

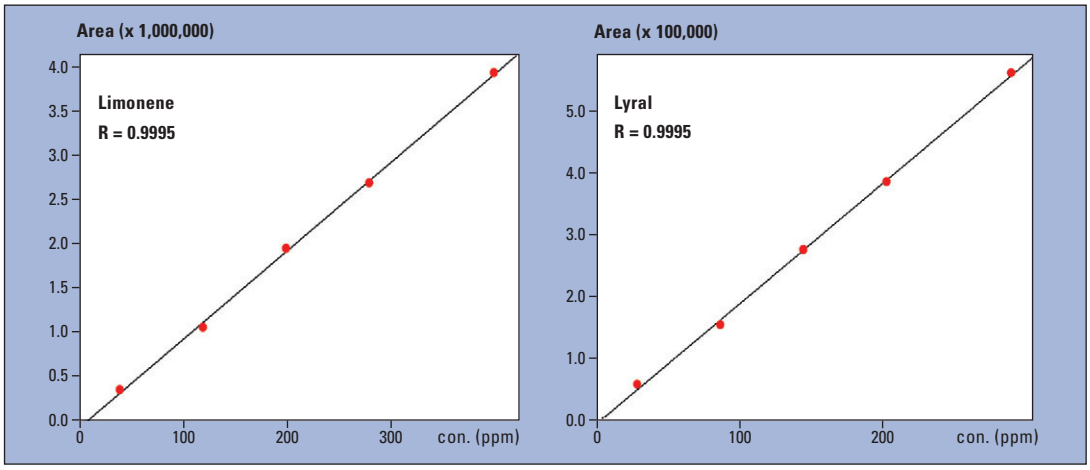


Figure VII.4: Calibration curves determined with fast GC/MS for limonene and lyral

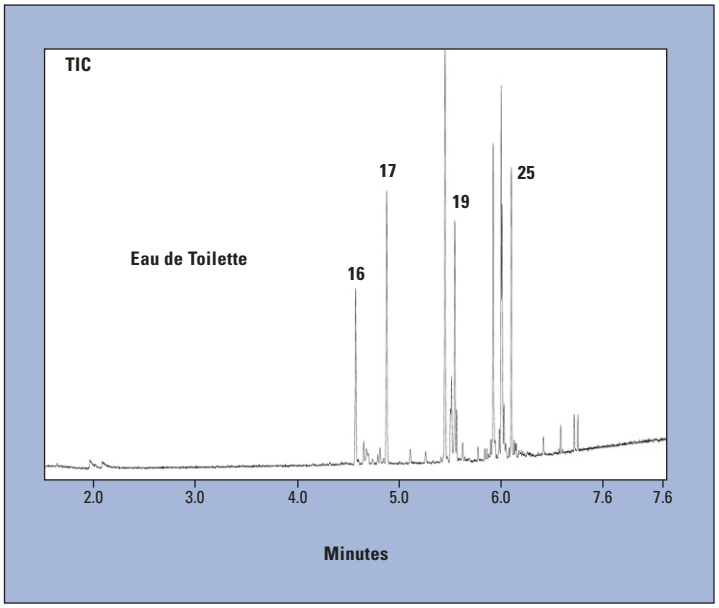
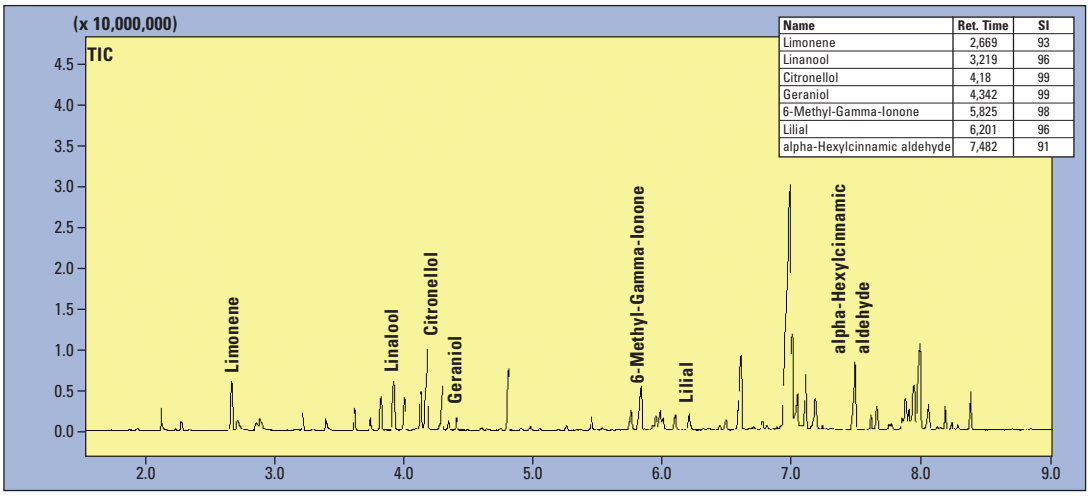


Figure VII.5: Fast GC/MS analysis of allergens in a sample of Eau de Toilette. The peak numbers refer to Table VII.1.

The method was also applied to a higher concentrated perfume. Figure VII.6 shows the chromatographic result obtained with a 10 % solution (acetone) of a perfume using a SPB 5 10 m, 0.1 mm, 0.1 µm column (injection volume: 1 µL; split ratio: 500:1; average linear velocity: 50 cm/s; temperature program: 50 °C (0.5 min) to 200 °C at 20 °C/min, to 280 °C at 50 °C/min; MS: scan range 41 to 320 amu, 20 scans/s at 10,000 amu/s scan rate). The identification of the potential allergen compounds was carried out by the finder function of the GCMSsolution software. In this case the whole TIC is searched for a library match with the compounds of interest. This is also shown in the same figure. Seven allergens were identified with a high similarity using the aforementioned commercial library.



Name	Ret. Time	SI
Limonene	2,669	93
Linanool	3,219	96
Citronellol	4,18	99
Geraniol	4,342	99
6-Methyl-Gamma-Ionone	5,825	98
Lilial	6,201	96
alpha-Hexylcinnamic aldehyde	7,482	91

Figure VII.6: Fast GC/MS TIC data relative to a perfume and obtained with a SPB-5 10 m, 0.1 mm, 0.1 µm column

2. Quality control of flavors

In the flavor industry, routine quality control analyses are applied to a high number of samples. In this field, the analysis of essential oils is widespread and may be considered as a complex task. Chromatograms relative to geranium and limette essential oil analysis carried out on a DB WAX 10 m, 0.1 mm, 0.2 µm column are reported in Figure VII.7 and Figure VII.8.

The essential oils were diluted in ethanol at a concentration of 5 %. The GC program was set from 40 °C (0.5 min) to 230 °C (at 50 °C/min) with a 60 cm/s constant average linear velocity (hydrogen). The injection volume was 1 µL with a split ratio of 400:1. About 30 important flavor components were separated and identified in less than 5 minutes.

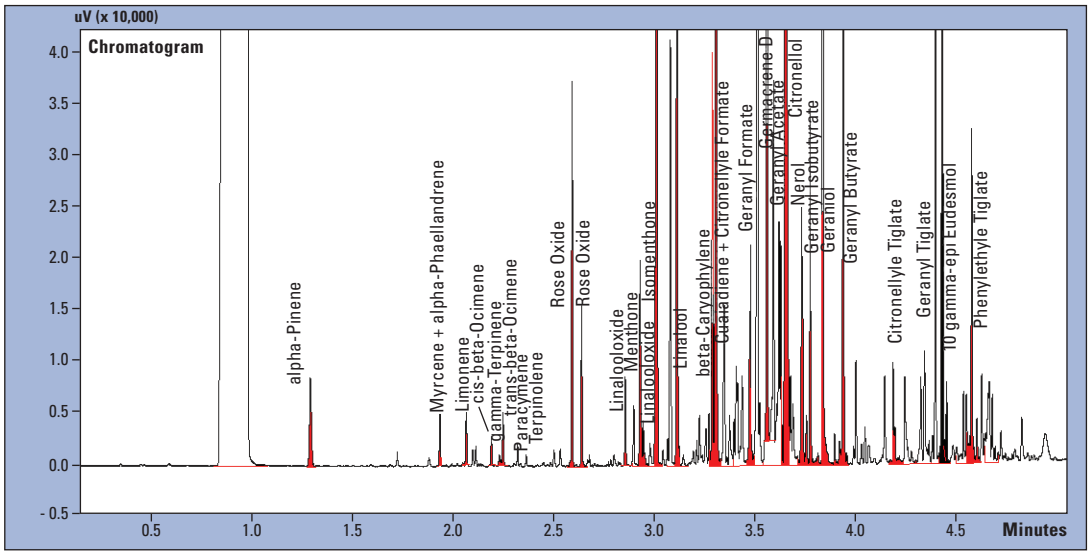


Figure VII.7: Fast GC/MS chromatogram (DB wax 10 m, 0.1 mm, 0.2 µm) of a geranium essential oil (5 % in ethanol)

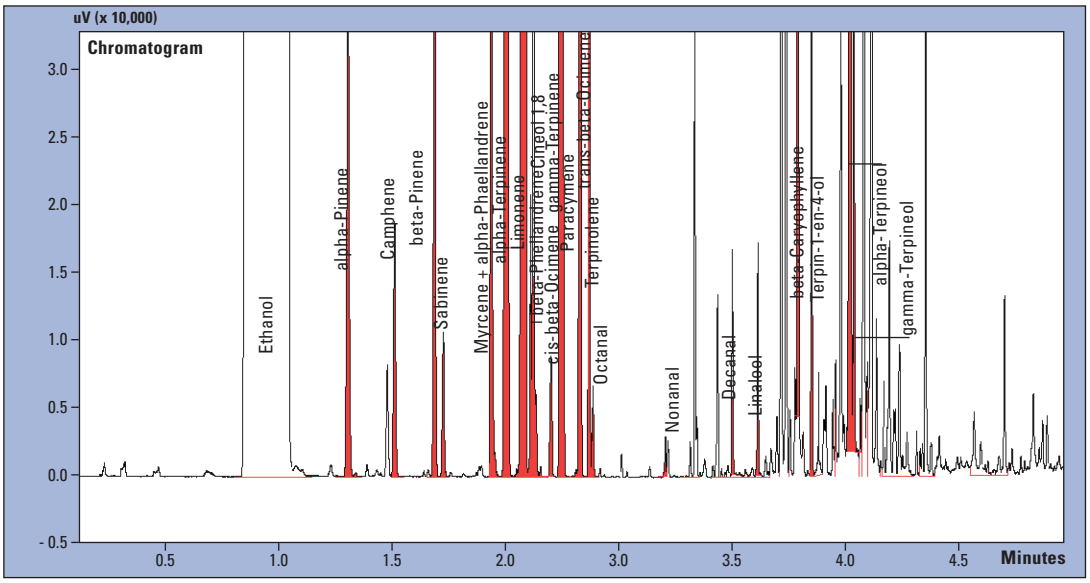


Figure VII.8: Fast GC/MS chromatogram (DB wax 10 m, 0.1 mm, 0.2 µm) of a limette essential oil (5 % in ethanol)

VIII. Application in the environmental field

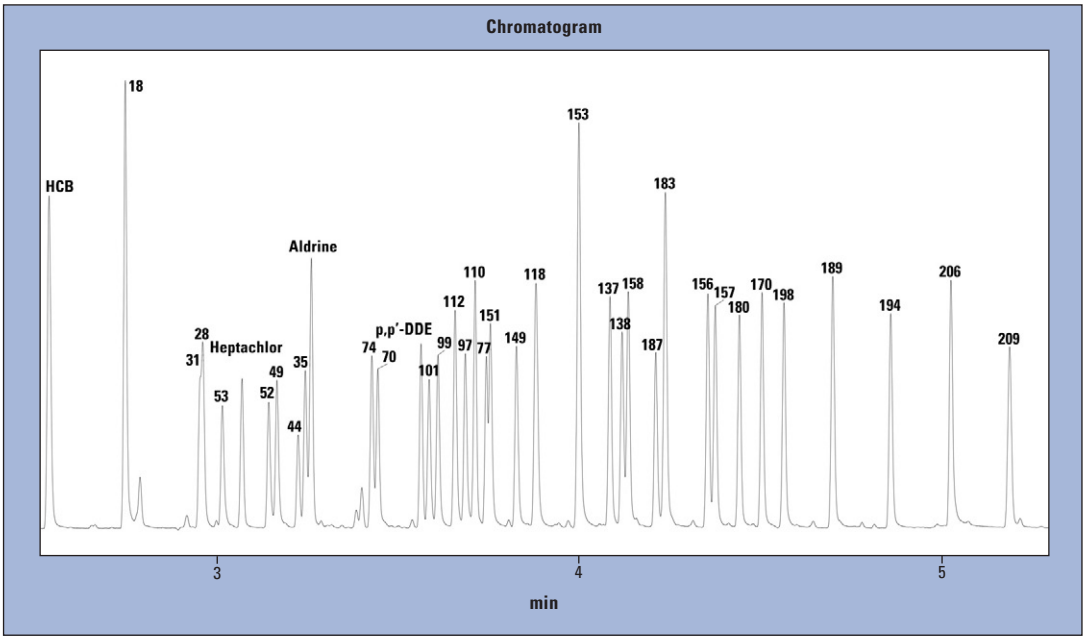


Figure VIII.1: GC-ECD chromatogram of 38 PCBs using a SPB5 10 m, 0.1 mm, 0.1 µm column. Concentrations are about 0.1 ppb.

PCB analysis with GC-ECD detection

The analysis of PCBs in different matrices such as water or sludge is still an important issue in the environmental field. These applications are achieved by using either GC-ECD or NCI GC/MS. The results obtained by using GC-ECD are shown in Figure VIII.1.

The chromatogram was attained by injecting a mixture of 38 standard PCBs (Table VIII.1). The column used was a SPB1, 10 m, 0.1 mm, 0.1 µm, with an oven program of 90 °C (2 min) at 40 °C/min to 290 °C and a constant average linear velocity of 50 cm/s (He). The injection volume was 1 µL with a split ratio of 10:1 (0.1 ppb for each compound). The ECD current was set to 1 nA. The filter time constant and sampling frequency were 20 ms and 100 Hz respectively. In order to avoid detector band broadening, a make-up gas flow of 100 mL/min was applied.

Table VIII.1: List of PCBs contained in the standard

Compound		RT
HCB	Target	4,537
18	Target	4,746
31	Target	4,953
28	Target	4,957
53	Target	5,011
Heptachlor	Target	5,065
52	Target	5,138
49	Target	5,161
44	Target	5,219
35	Target	5,238
Aldrine	Target	5,255
74	Target	5,42
70	Target	5,437
p,p'-DDE	Target	5,555
101	Target	5,577
99	Target	5,601
112	Target	5,648
97	Target	5,676
110	Target	5,703
77	Target	5,734
151	Target	5,745
149	Target	5,816
118	Target	5,869
153	Target	5,987
137	Target	6,072
138	Target	6,105
158	Target	6,122
187	Target	6,197
183	Target	6,223
156	Target	6,339
157	Target	6,36
180	Target	6,426
170	Target	6,488
198	Target	6,548
189	Target	6,681
194	Target	6,839
206	Target	7,004
209	Target	7,165

IX. Summary

The reduction of analytical cycle times in routine applications has become increasingly important in order to increase productivity or to acquire quick and correct results in quality control processes.

The narrow-bore column approach is a very effective way of decreasing GC run times while maintaining a high degree of peak resolution. The application of these methods is increasing in routine laboratory work, also due to improved column and GC instrumental technology. In fact, modern-day GC systems fulfill the analytical requirements of narrow-bore capillaries.

Literature

[1] Matter, L. (Ed.), Food and Environmental Analysis by Capillary Gas Chromatography, Hüthig, 1997

[2] van Es, A., High Speed Narrow-Bore Capillary Gas Chromatography, Hüthig, Heidelberg, 1992

[3] van Ysacker, P. G.; Janssen, H.-G. Snijders, H. M. J.; Cramers C. A.; J. High Resol. Chromatogr. 18 (1995) 397

[4] Broske, A. D. et al, Abstract A05 and A21, 20th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 26-29, 1998

[5] David, F. et al., Abstract P53, 20th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 26-29, 1998

[6] Cook, W. S., Today's Chemist at Work 1 (1996) 16

[7] Sandra, P. et al., Experiments with fast Multicapillary GC, presented at the 18th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 20-24, 1996

[8] van Lieshout, M. et al., J. Micro. Sep. 11 (2) (1999) 155

[9] Schomburg, G., Gaschromatographie, Grundlagen, Praxis, Kapillartechnik, VCH

[10] Mondello, L. et al., J. Chrom. A, 1035 (2004) 237

[11] Grob, K., Classical Split/Splitless Injection, Hüthig

[12] Hinshaw, J. V., LCGC (2002) vol 15, p. 152

[13] Leoni, V. and D'Alessandro De Luca, E., Essenz. Deriv. Agrum., 1978, 48, 39-50.

[14] Kempe, G. and Baier, H.-U., Organophosphorous pesticides determined in natural matrices with GC-FPD, GC-FTD and GCMS: medium and narrow-bore columns, presented at 25th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 14-17, 2002.

[15] Mondello, L., 22th International Symposium on Capillary Chromatography, Riva del Garda, Italy May 2002

[16] Kondo, S. et al., Euroanalysis conference, 2004

[17] Han, J. J. and Yamane, T., Lipids, 1999, 34, 989-995

[18] Mondello, L., J. Microc. Sep. 12 (1) 41-47, 2000

[19] www.ifraorg.org

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