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COUPLING OF A HIGH-PRESSURE GAS CHROMATOGRAPH WITH A FOURIER TRANSFORM INFRARED SPECTROMETER

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SUMMARY

The coupled system has the advantage of providing a large dynamic range by combining the high loadability of the high-pressure gas chromatographic (HPGC) column and the possibility of optimizing the light-pipe to the optical system. A large dynamic range is essential in the investigation of the separation of complex mixtures in which minor components elute close to major components. In this instance the optimization of the optical system was realized by increasing the light-pipe diameter and adapting the HPGC column to the latter. The results are discussed in terms of loadability and dynamic range and HPGC columns are compared in these respects with capillary columns.

INTRODUCTION

The combination of gas chromatography with Fourier transform infrared spectrometry (GC–FT-IR)[1] has great potential for the analysis of complex mixtures[2–4]. In the elucidation of structures, especially when isomers are involved, this method can be a useful complement to gas chromatography–mass spectrometry (GC–MS)[5–7]. The detection limits of GC–FT-IR, also expressed as the minimum identifiable quantity (MIQ), can be as low as 10 ng under favourable conditions, but are generally of the order of 0.1–1 μg. As this is several orders of magnitude higher than that of GC–MS, this means that relatively large amounts of sample have to be injected, especially when minor components are of interest. However, the maximum injectable amount depends on the sample capacity of the GC column, which is limited to 0.1–10 μg when capillary columns are used. In this instance the small peak volumes also require the addition of a make-up gas flow in order to maintain the resolution of two succeeding peaks, which results in an increase in the detection limit. Nevertheless, the general conclusion is that because of the limited separation performance of packed columns, capillary columns are to be preferred[6–10].

However, high-pressure gas chromatography (HPGC)[11,12] using columns packed with small particles (<80 μm) provides relatively large plate numbers in combination with a high loadability and offers a good alternative for the analysis of complex mixtures. It is possible to adapt the geometry of the HPGC column (length,

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mean particle size, diameter) to the volume of the light-pipe of the FT-IR spectrometer. The latter can be optimized for the measurement process, without constraints with respect to the volume, which will always be larger in that event.

In this work the coupling of HPGC with FT-IR spectrometry has been tested. In a first set of experiments the existing light-pipe with a volume of about 200 μl and optimized for capillary GC was used, and the signal-to-noise ratio of this combination was determined. In a second set of experiments the diameter of the light-pipe was increased to improve the signal-to-noise ratio. With an HPGC column optimized for this light-pipe, which had a volume of 2 ml, the signal-to-noise ratio was again investigated. The dynamic range of a major and a minor component, which could be eluted without column overloading of the former and still with a library searchable spectrum of the latter, has been determined. The analysis of turpentine mixtures were carried out to confirm the applicability of this technique.

EXPERIMENTAL

Apparatus

The HPGC–FT-IR experiments were performed on a Nicolet 20SXB spectrometer, equipped with an air-cooled globar source, a KBr/Ge beam splitter and a medium-range wavelength liquid nitrogen-cooled MCT (mercury cadmium telluride) detector with a range of 4000–750 cm^{-1}. The detector and the light-pipes were built in a GC optical bench accessory. The IR spectra were recorded at a resolution of either 4 or 8 cm^{-1} with a mirror velocity of 40 cm/s and a data collection rate of 4 spectra/s, which were co-added before real-time Fourier transforms were computed. The computed data were stored as transmission spectra on a 35-Mbyte Winchester hard disk for later interpretation. The HPGC system consisted of a Packard Model 427 instrument (Packard Becker, Delft, The Netherlands) equipped with a dome-type pressure controller (IV Pressure, Middlesex, U.K.) to supply the high inlet pressures. The stainless-steel columns were 6 m × 1.2 mm I.D. and were slurry packed with 15% OV-101, cross-linked[13] on Spherosil XOB 005 with a mean particle size of 34 μm. The end of the column was connected to the light-pipe with a glass-lined capillary contained in a thermostated transfer pipe. This transfer pipe was constructed between the GC bench accessory and the adapted GC front entrance. The end of the light-pipe was connected to the GC flame ionization detector with a glass-lined capillary which was also contained in the transfer pipe. The dimensions of the two connecting capillaries were 500 mm × 0.5 mm I.D.

Chemicals

The carrier gas (helium) was purchased from Hoek-Loos (Amsterdam, The Netherlands). The standards and solvents were of GC grade from Fluka (Buchs, Switzerland) and Merck (Darmstadt, F.R.G.). The monoterpene mixtures (turpentines) were gifts from several sources.

Procedures

Recording the chromatogram. At the moment of the injection of the sample, the recording of the IR spectra was started. The FT-IR spectrometer computes five "chemigrams", which represent the average absorbances over a pre-specified wave-

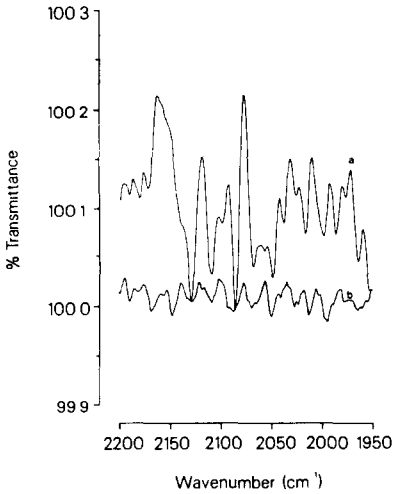


Fig. 1. Scale-expanded region 100% line at room temperature used to calculate the RMS value. The measurement is the ratio of a 32-scan co-added spectrum in the background to a co-added 32-scan spectrum. (a) LP1; (b) LP2.

number interval (window) plotted as a function of time. The chemigram windows were chosen in accordance with the nature of the solutes under analysis. The chromatogram is simultaneously monitored by flame ionization detection (FID). After the analysis a Gram–Schmidt orthogonalization can be performed in order to compute a reconstructed chromatogram.

Reference spectra. Infrared spectra of Δ^3-carene and α-terpineol were obtained by injecting 2 μl of a 3% solution in hexane at an oven temperature of 210°C. The spectra of the eluted peaks were recorded at a resolution of 4 cm^{-1} and stored in the vapour-phase library of the Environmental Pollution Agency (EPA) to be utilized in a computer search algorithm to facilitate and verify identification of the minimum identifiable quantity.

Minimum identifiable quantity (MIQ). We injected a series of solutions with decreasing concentrations of different compounds. All spectra files underlying the chromatographic peak of the compound were combined with the help of a weighting function using the system routines of the spectrometer. Then the computer search routine was carried out to identify the eluted peak with a EPA library and the Aldrich vapour-phase library. The smallest quantity which is correctly identified in this way is considered to be the MIQ.

Maximum loadable quantity (MLQ). A series of solutions with increasing concentration of *n*-decane and 2-heptanone were injected. The amount of solute which caused a peak distortion of 30% due to mass overloading of the column was chosen as the maximum loadable quantity. The peak distortion is defined as the percentage increase in peak width at half-height in comparison with that obtained on injecting small amounts.

Root mean square of the noise. The 100% line noise level was recorded at a wavenumer interval of 2200–1950 cm^{-1} for both light-pipes at room temperature (see Fig. 1). The record was obtained by a co-added 32-scan spectrum to a second co-

TABLE I

DIMENSIONS OF THE LIGHT-PIPES AND THE ROOT MEAN SQUARE OF THE NOISE LEVEL OF THE 100% LINE AT 20°C

Light-pipe	*Volume (μl)*	*I.D. (mm)*	*Type*	*RMS (% transmission)*
LP1	180	1.2	Suitable for CGC	0.047
LP2	1880	4.2	Custom made	0.009

added 32-scan spectrum. The root mean square (RMS) of this signal was determined (Table I). The first spectrum represents the baseline spectrum, which is generally used as a reference.

Major–minor analysis. Real samples were used to test the prediction with respect to the dynamic range. Major–minor ratios were determined by measuring the peak heights of the FID signal.

Construction of the larger light-pipe. A precision-bore borosilicate tube (150 mm × 4.2 mm I.D.) was plated with a gold-foil cylinder of thickness 0.10 mm. The gold foil was cut to the required size with a tolerance of about 0.1 mm, rolled up and inserted in the glass tube. Next the still overlapping edges of the foil were forced into adjacent positions, by pulling a plastic cone (slightly oversized) throught the tube by means of a steel wire.

THEORY

In order to separate a complex mixture in which minor-components elute close to major components, the separation method first requires a given number of theoretical plates, N_{req}. Second, it must be possible to acquire detailed spectral information on the minor component under conditions where the major components do not overload the separation system. The ability to deal with this situation is indicated by the dynamic range, which in the present context can be defined as the ratio of the MLQ of a major compound that can be handled by the separation system to the MIQ of a minor compound that gives a correctly identified spectrum.

The optimal speed of separation and resolution for packed columns are obtained when the particle size is such that at the available pressure the column operates at the minimum of the theoretical plate height *vs.* flow velocity curve. According to Knox and Saleem[14], this is valid when the inlet pressure is limited and the minimum value of the reduced plate height is the same for all particle sizes. When in addition to N_{req} the inlet pressure is chosen, then the particle size, the length of the column and the separation time are determined. However, the diameter of the column, d_c, can be freely chosen without a decrease in separation performance.

This brings us to the second criterion, the dynamic range. If we assume the MLQ to be proportional to the volume of stationary phase per theoretical plate[15], then this will be proportional to the cross-section, A, of the column and so to the square of the column diameter:

$$\text{MLQ} \approx d_c^2 \tag{1}$$

The MIQ, however, can be expressed as the minimum concentration of a component in the light-pipe, $c_{i,\min}$. Assuming the peaks to have a Gaussian shape, this can be written as

$$\text{MIQ} = c_{i,\ \min} \cdot \sigma_{v,\text{tot}} \cdot \sqrt{2\pi} \tag{2}$$

Where $\sigma^2_{v,\text{tot}}$ is the total peak variance in volume units. If we consider the increase in σ^2_v due to mixing in the light-pipe to be negligible, then $\sigma^2_{v,\text{tot}}$ is equal to the peak variance due to peak broadening effects in the column, $\sigma^2_{v,\text{col}}$. According to the equations of Knox and Saleem[14], it can be derived[16] that the standard deviation of a peak eluting from the column is

$$\sigma_{v,\text{col}} = CA \cdot \frac{N_{\text{req}}}{P_1} \tag{3}$$

Where C can be considered contstant and P_1 is the outlet pressure. If we substitute eqn. 3 in eqn. 2 with the assumption made above, we obtain

$$\text{MIQ} = C \cdot \frac{c_{i,\min} \cdot A N_{\text{req}} \cdot \sqrt{2\pi}}{P_1} \tag{4}$$

The conclusion is that

$$\text{MIQ} \approx d_c^2 \tag{5}$$

Increasing the diameter of the column does increase the MLQ, but also leads to an increase in MIQ, which would be of the same proportion when $c_{i,\min}$ is constant. It is obvious that, under such conditions, the use of larger d_c values will not increase the dynamic range of the system.

However, the MIQ can be decreased by modifying the light-pipe dimensions. The large peak volumes eluting from a packed column with large d_c values allow the dimensions of the light-pipe to be adapted to the optical requirements and to obtain the optimal signal-to-noise ratio at a given c_i. This is equivalent to obtaining lower $c_{i,\min}$ values. Thus, contrary to what Eqn. 5 would suggest, the MIO increases less than in proportion to the square of d_c.

The increase in $c_{i,\min}$ obtained on modifying the light-pipe dimensions depends partly on the instrumental limitations. According to the Lambert–Beer law, the light absorption of the solute is proportional to its concentration, its absorptivity and the length of the light-pipe. An increase in signal-to-noise ratio can also be obtained via the light throughput, by increasing the light-pipe diameter. Owing to the limitations of the GC optical bench accessory we could not increase the length. Therefore, a better optical performance could be pursued only by increasing the diameter, which is only effective as long as the beam size is limited by the light-pipe. Although a light-pipe diameter of 2 mm would be sufficient for this purpose (the beam diameter being 2 mm in the present system), we decided to construct a light-pipe of 4.2 mm I.D., in order to show clearly the capability of HPGC to deal with large light-pipe

volumes. Under other instrumental conditions this volume could be exploited in a much more effective way also by increasing the light-pipe length.

RESULTS AND DISCUSSION

The coupling of the HPGC and FT-IR instruments give rise to two practical problems. The maximum scan speed of the spectrometer is approximately 5 s^{-1}. The standard deviation of the peaks in units of time (σ_t) has to be long enough in relation to the scan time. From Table II it can be concluded that the σ_t for the unretarded component and hence for the retarded components is sufficient.

The second matter of concern is the pressure in the light-pipe. This pressure is caused by the relatively high flow-rate and the restriction in the capillary connection between the light-pipe and the FID. The KBr windows, which are pressed on the light-pipe with small springs, could be pushed away, causing leakage. The pressure calculated using the Hagen–Poiseuille equation in a form that accounts for the high pressure ratios, as given, *e.g.*, by Guiochon[17], caused no problem during analysis and was 0.04 MPa.

Signal-to-noise ratio

According to Griffiths[1] and Giss and Wilkins[18], miniaturization of the light-pipe in order to increase the concentration and to adapt the light-pipe to capillary GC, for instance, has its drawbacks. The loss of light energy can be important, especially when the inner diameter of the light-pipe is much smaller than the diameter of the light beam. We increased the light-pipe diameter from 1.2 to about 4.2 mm; its volume than became about 2 ml and the column dimensions were chosen such that the peak volumes were more than 1 ml. In this way the chromatographic resolution could be maintained. The column parameters are given in Table II.

In order to compare the RMS of the noise levels of both light-pipes, we recorded the noise of a 100% line (Fig. 1) as described under *Procedures*. The noise level of the light-pipe of I.D. 1.2 mm and suitable for capillary GC, LP1, appeared to be five times greater (see Table I) than that of the light-pipe with the larger di-

TABLE II

PARAMETERS OF THE INSTALLED COLUMN

Parameter	*Value*
Column length (m)	6
Inner diameter (mm)	1.2
Inlet pressure (MPa)	5.3
Particle size (μm)	34
Number of theoretical plates	50 000
Retention time of unretarded component (s)	180
σ_{t_0} (s)	0.75
σ_{v_0} (μl)	800
Carrier gas	Helium
Pressure in the light-pipe (MPa)	0.04

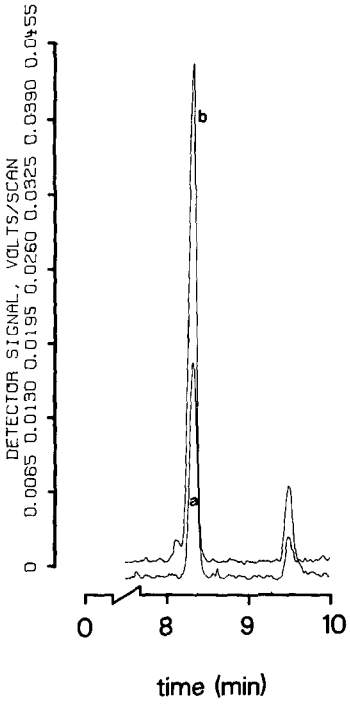


Fig. 2. Gram–Schmidt reconstructed chromatograms of 2 μl of 1% (v/v) solution of Portuguese turpentine in hexane. Chromatographic conditions: oven temperature, 180°C; light-pipe temperature, 250°C; carrier gas, helium; inlet pressure, 5.0 MPa; spectral resolution, 4 cm^{-1}. (a) LP1; (b) LP2.

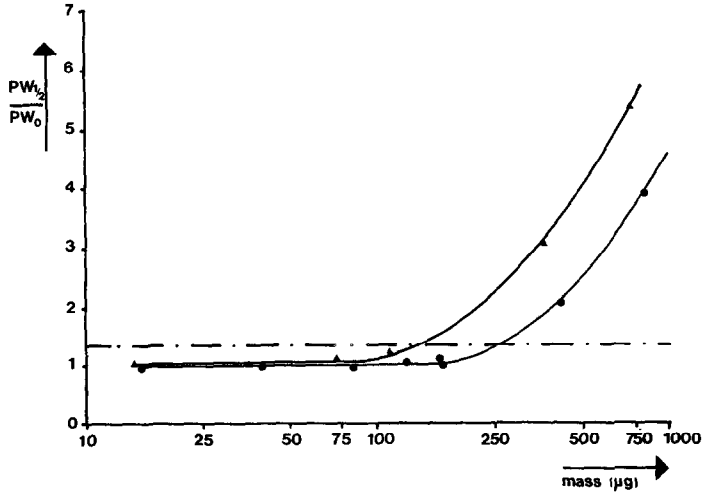
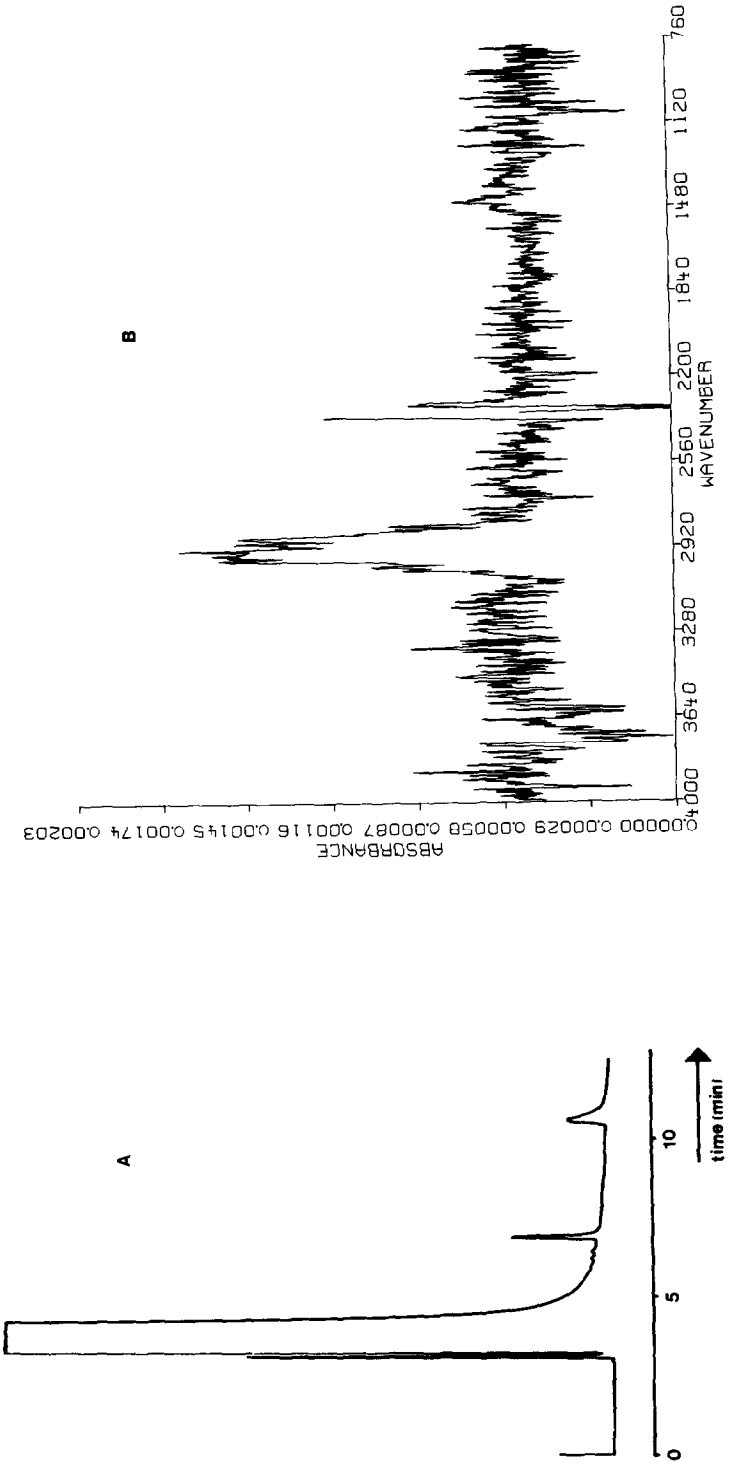


Fig. 3. Ratio of the peak width at half-height ($PW_{1/2}$) of a solute to the peak width at half-height of the same solute when small amounts are injected (PW_0) as a function of the injected mass. ▲, *n*-Decane; ●, 2-heptanone.


A
0
5
10
time (min)
B
ABSORBANCE
0.000000 0.000029 0.000058 0.000087 0.000116 0.001145 0.001174 0.002203
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760
WAVENUMBER

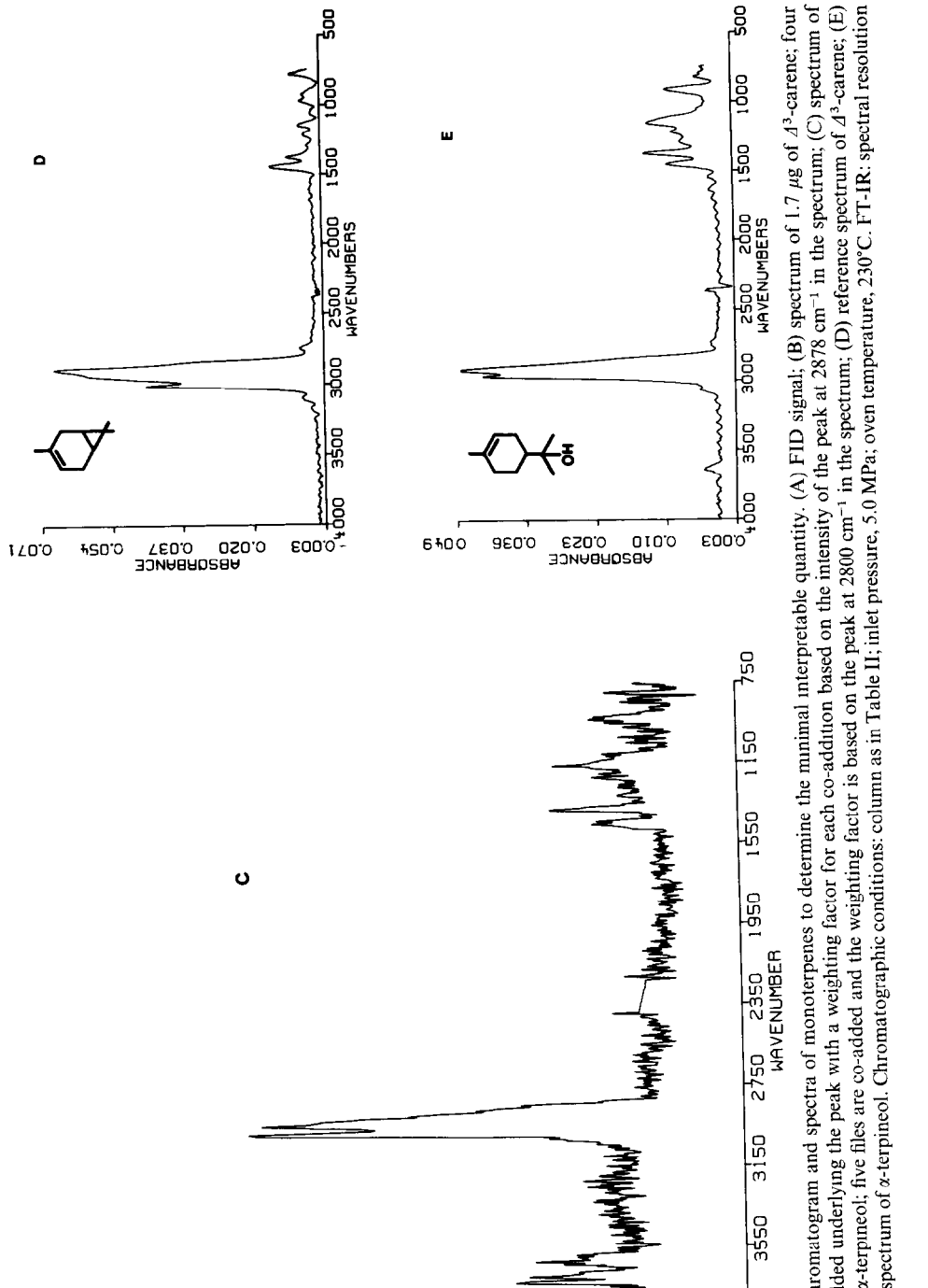


Fig. 4. Chromatogram and spectra of monoterpenes to determine the minimal interpretable quantity. (A) FID signal; (B) spectrum of 1.7 μg of Δ^3-carene; four files co-added underlying the peak with a weighting factor for each co-addition based on the intensity of the peak at 2878 cm^{-1} in the spectrum; (C) spectrum of 2.3 μg of α-terpineol; five files are co-added and the weighting factor is based on the peak at 2800 cm^{-1} in the spectrum; (D) reference spectrum of Δ^3-carene; (E) reference spectrum of α-terpineol. Chromatographic conditions: column as in Table II; inlet pressure, 5.0 MPa; oven temperature, 230°C. FT-IR: spectral resolution 4 cm^{-1}

ameter, LP2. Fig. 2 illustrates the difference in noise level between the two light-pipes. In both combinations a 1% (v/v) solution in hexane of Portuguese turpentine was injected. Fig. 2 shows that the noise level is much lower with LP2. Because this aspect does extend the dynamic range we decided to continue the experiments with LP2.

Maximum loadable quantity

The MLQ was determined as described under *Procedures*. As an acceptable peak distortion caused by mass overloading we chose 30%. The experimental results are shown in Fig. 3, where the ratio of the peak width a half-height and that of a peak obtained when small amounts were injected is plotted against mass of solute. It can be seen in Fig. 3 that the observed MLQ for *n*-decane is 130 μg and the MLQ for 2-hexanone is 250 μg on this column. The column used was loaded with 15% stationary phase (OV-101) and was designed to have 50 000 theoretical plates (see Table II).

Minimum identifiable quantity

Series of mixtures contianing Δ^3-carene and α-terpineol were eluted with the use of LP2 under the conditions shown in Fig. 4. The MIQ for Δ^3-carene was 1.7 μg and for α-terpinol 2.3 μg. Fig. 4b and c are the IR spectra of these MIQs. Fig. 4d and e represent the library spectra of these compounds.

Two interesting observations can be made here. The first concerns the position of the compound in the chromatogram. It is obvious that especially in isothermal GC, owing to the higher concentration in the mobile phase, the earlier the solute is eluted the lower will be the MIQ limits. The second observation concerns the library search. If the compounds has a unique spectrum in the reference library used, then the interference with other spectra is low and the recognizability for the library search routine wil be good. This explains the difference between the MIQs of Δ^3-carene and α-terpineol. These results are satisfactory if we compare them with those of Kalasinsky and McDonald[19], who also found detection limits of a few micrograms. However, in the latter instance a three times longer light-pipe was used.

Dynamic range: MLQ/MIQ

The above discussions of MLQ and MIQ give an insight into the magnitude of the dynamic range of a coupled HPGC–FT-IR system. The dynamic range expressed as the mass ratio MLQ/MIQ is about 100 when LP2 is used.

Comparison with standard and thick-film capillary columns

The comparison can be carried out by considering some basic relationships. The MLQ and MIQ values, necessary in such a comparison, applicable to the same type of compound, phase system, etc., can be related in this way to those observed here. We first deal with the standard capillary, for which we take dimensions of 25 m × 0.25 mm I.D. and a maximum film thickness of 0.4 μm. Such a column has an amount of stationary phase of 0.35 μg per theoretical plate, where one plate in the HPGC column contains 7 μg of stationary phase. The MLQ value for the HPGC column is 20 times larger.

The MIQ value for the capillary is different from that observed here, because

of three effects: (i) the optical signal-to-noise ratio at a given solute concentration in the light-pipe, (ii) the smaller peak volume (less dilution) delivered by the capillary and (iii) the effect of dilution by the make-up gas.

The optical signal-to-noise ratio is expected theoretically to be three times (the ratio of the effective areas) better with the larger cell. In fact, we observed (see Table I) an improvement of a factor five.

The effects (ii) and (iii) mentioned above can be summarized by considering the σ_v value of a peak after the addition of the make-up gas. This value has to be adjusted by means of the make-up gas flow-rate to a value (in comparison with the light-pipe volume) such that no unacceptable decrease in resolution occurs (law of additivity of chromatographic variances). All properly designed configurations will have comparable compromises in this respect: the ratio of σ_v to light-pipe volume will be the same for all types of columns. The conclusion is that the dilution effect is proportional to the light-pipe volume: in the present context this means that the capillary has an advantage of a factor of 10 (the ratio of the two light-pipe volumes).

Summarizing these effects, we obtain an improvement in dynamic range of a factor of at least 6 for an HPGC column in the present equipment because there is a 20-fold larger MLQ, a 3–5-fold improvement in instrumental signal-to-noise ratio and a 10-fold loss because of extra dilution.

The comparison with thick film capillaries, which are of increasing popularity in this field, is complicated because there is a combination of decreasing chromatographic performance with better dynamic range properties. This will be the subject of a subsequent paper, and for the present discussion the following remarks may suffice. Using a film thickness of 1 μm (2.5 times that of the example quoted above) precludes the generation of a high chromatographic resolving power in a reasonable time. This follows directly from the Golay equation in combination with a diffusion coefficient of 10^{-11} m^2 s^{-1} in the film. For instance, 50 000-plate columns would require elution times of at least three times the 200 s observed for the HPGC column. A similar calculation shows that the generation of 50 000 plates with a retention time for the unretarded component of 200 s dictates a film thickness of less than 0.5 μm ($k' = 3$, $D_l = 10^{-11}$ m^2 s^{-1}; D_l is the diffusion coefficient in the film), which represents a column that is hardly different from that in the preceding section.

Practical examples

To test the validity of the thus determined dynamic range, some practical samples were analysed. The example of a minor compound eluting close to a major component in a complex mixture is shown in Fig. 5. A 1-μl volume of a 25% (v/v) turpentine solution in hexane was eluted and shows major and minor peaks in mass ratios up to 50. Fig. 5a is the FID signal and Fig. 5b the Gram–Schmidt reconstructed chromatogram. The chromatogram shows an example of a minor component (peak 2), which elutes close to a major component (peak 1). For these two compounds the mass ratio is about 50. Fig. 5c shows that the library search results in a fairly good match and the MIQ of this component represents a few micrograms. When we injected more than 3 μl, peak 1 overloaded the column and disturbed the elution of the minor peak. We conclude that the dynamic range of the system is well over 100 and is in good agreement with what we predicted in the above discussion.

Another example is given in Fig. 6 and shows the analysis of a 3-μl pine oil

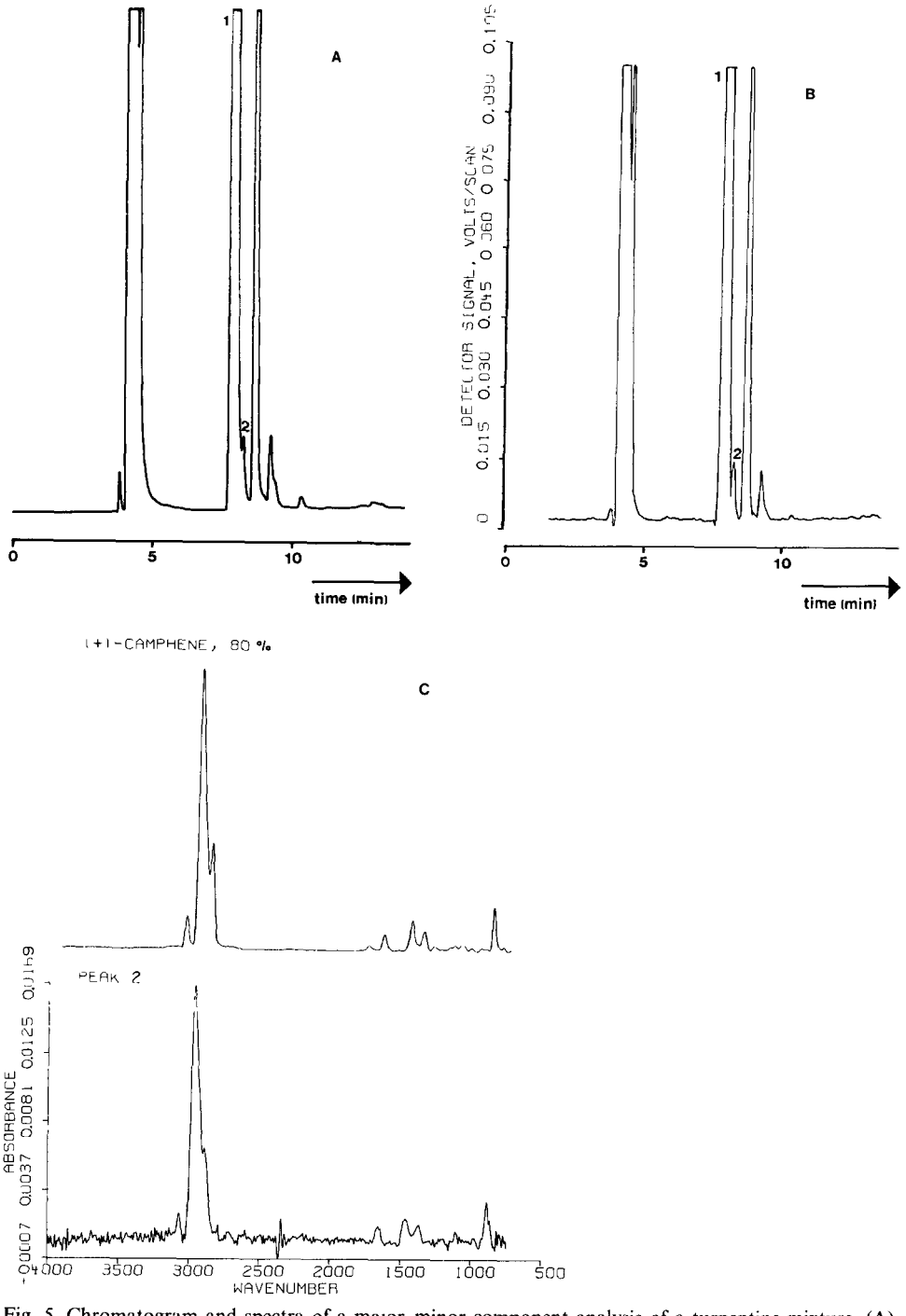
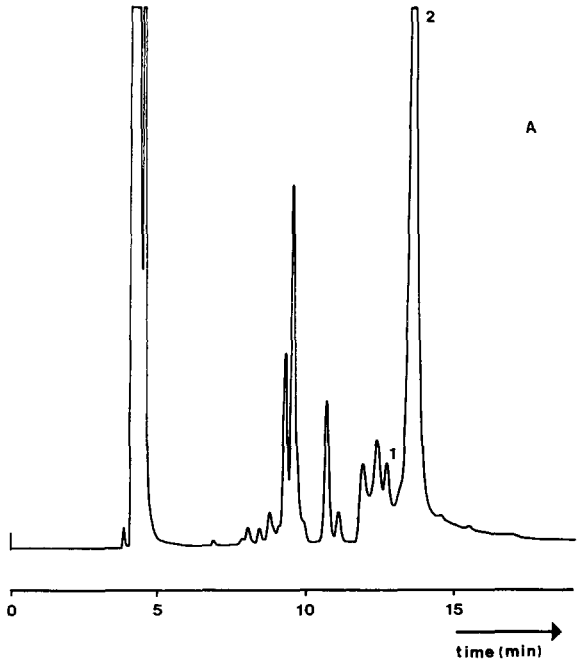


Fig. 5. Chromatogram and spectra of a major–minor component analysis of a turpentine mixture. (A) FID signal; (B) Gram–Schmidt reconstructed chromatogram; (C) spectrum of peak 2 with its vapour-phase library spectrum. Chromatographic conditions as in Fig. 4. FT-IR· spectral resolution 4 cm^{-1}.



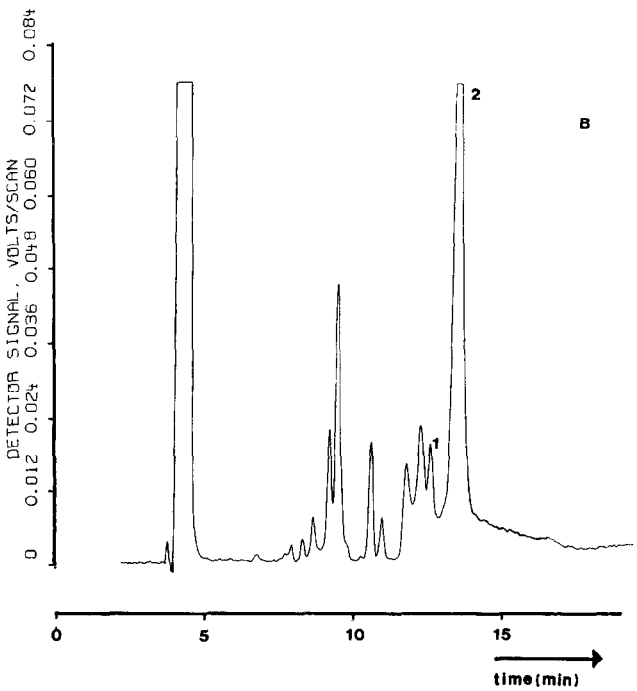


Fig. 6.

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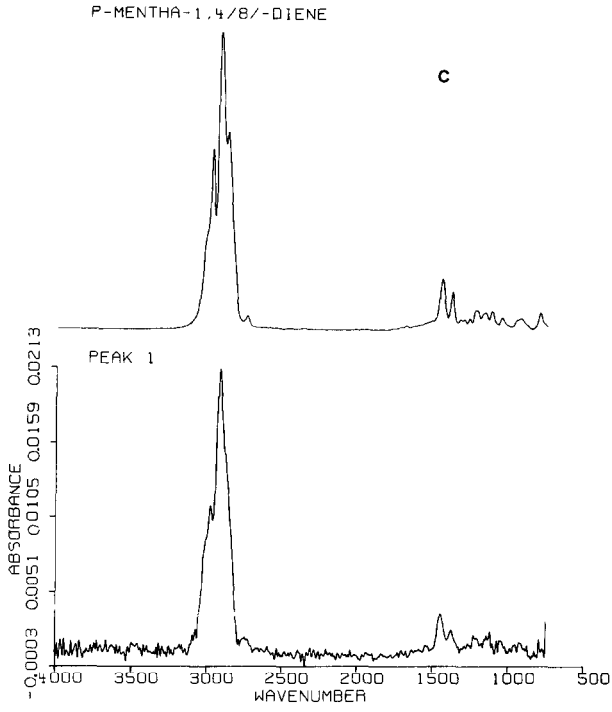

Fig. 6. Injection of 3 μl of pine oil. (A) FID signal; (B) Gram–Schmidt reconstructed chromatogram; (C) spectrum of peak 1 with its library spectrum. Chromatographic conditions as in Fig. 4 but with a temperature programme from 190–250°C at 10°C/min. FT-IR: spectral resolution 4 cm^{-1}.

sample. In this instance the minor component (peak 1) elutes in front of the major component (peak 2). The mass ratio is about 20 in this instance. Peak 1 is identified as *p*-mentha-1,4(8)-diene (Fig. 6c) and its MIQ is 5 μg. Overloading effects disturbed the chromatographic resolution of the two peaks when we injected more than 10 μl. From these data, the dynamic range of the system is 70, which is lower than predicted but still reasonable.

CONCLUSIONS

The study of major–minor component problems preferably requires the use of a separation system with a large dynamic range. For this purpose we used packed HPGC columns, which offer the advantage of a higher loadability and large elution volumes. Compared with capillary columns, the scale of the separation system is considerably larger. The latter aspect has the advantage that the diameter of the light-pipe could be increased without a decrease in resolution. A greater light-pipe diameter resulted in a decrease in the RMS noise level, which in turn resulted in a larger dynamic range. An even larger gain in this respect is to be expected with the use of longer, rather than thicker, light-pipes. However, with the present system this possibility could not be explored.

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