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COUPLING OF A HIGH-PERFORMANCE LIQUID CHROMATOGRAPH WITH A FOURIER TRANSFORM INFRARED DETECTOR

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SUMMARY

The characteristics of a liquid chromatograph-interfaced Fourier transform infrared spectrometer are plotting of five simultaneous chromatograms in five operator-selected infrared bands and storage of interferograms during elution, which permits the infrared spectra of the solutes to be obtained.

The main parameters of the system (width of the detection spectral region, nature and thickness of the flow cell, linearity range) have been determined and compared with those of classical detection systems. The usual eluents in reversed-phase chromatography (alcohols, water, acetonitrile) are hardly compatible with IR detection but the method was found to be suitable for adsorption chromatography, especially with chlorinated eluents (limit of detection about 1 μg injected). The system is a powerful means of identifying solutes in adsorption chromatography, and incompletely resolved chromatographic peaks can be further resolved by the spectral substraction technique. The method has been applied to the separation and identification of additives in mineral oils.

INTRODUCTION

Various detection methods are used in high-performance liquid chromatography (HPLC). Some of them, such as ultraviolet absorptiometry, fluorimetry and thin-layer electrochemistry, are very sensitive but not universal, whilst differential refractometry, which is a general method, is not sensitive enough. Mass spectrometry is a very powerful technique but is difficult to use with HPLC. Therefore, the number and capabilities of detection methods in liquid chromatography should be extended,

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especially in the field of petroleum for the detection of saturated hydrocarbons, and in the field of fatty compounds for the detection of esters.

Infrared (IR) spectroscopy, commonly used in organic analysis, would be expected to be useful with liquid chromatography for the identification and the quantitative analysis of solutes in the effluent. However, it is difficult to apply this method because most of the common solvents used in liquid chromatography are opaque in large spectral regions. Common IR solvents ($CHBr_3$, CHI_3, $CHCl_3$, CCl_4, CS_2) are rarely used in liquid chromatography.

Some work has been carried on classical IR coupling[1–4] and Fourier transform infrared (FTIR) coupling[5–10] in some particular instances. This paper describes a systematic investigation of the capabilities and characteristics of FTIR detection in HPLC.

With FTIR techniques the quality of spectra is greatly improved, and intricate data manipulations can be achieved[11,12]. The liquid chromatograph-interfaced FTIR spectrometer is now used to solve complex analyses requiring simultaneous chromatographic and spectrometric discrimination.

The advantages of FTIR over the classical IR technique are discussed. We have determined the characteristics of the method and made a full study of the influence of the nature of the mobile phase, which makes it possible to define the chromatographic fields in which this detection method can be used. We have studied the capabilities of FTIR for identification even with incompletely resolved chromatographic peaks. Finally, the application of the method to the separation and the identification of mineral oil additives is described.

EXPERIMENTAL

Apparatus

Experiments were performed with a liquid chromatograph assembled from commercially available modules consisting of an Altex 380 pump (Altex, Berkeley, CA, U.S.A.), a Rheodyne six-port sampling valve with a 20-μl loop, a Rheodyne six-port backflush valve to elute strongly retained solutes and a Nicolet 7199 FTIR spectrometer (Nicolet Instrument Corp., Madison, WI, U.S.A.).

The nature of the cell materials will be discussed later, but we used four commercial flow cells from Nicolet: two 0.2 and 1 mm KBr and two 0.2 and 1 mm ZnSe flow cells.

For comparisons with classical detection systems, a Waters R-401 refractometer (Waters Assoc., Milford, MA, U.S.A.), a Spectromonitor III spectrophotometer (Laboratory Data Control, Riviera Beach, FL, U.S.A.) and a Varian A 25 plotter (Varian, Palo Alto, CA, U.S.A.) were used.

Stationary phases

The stationary phases were commercially available LiChrosorb Si 60, LiChrosorb Alox T, LiChrosorb RP-18 (Merck, Darmstadt, G.F.R.) and Woelm N alumina (Prolabo, Paris, France).

Column packing techniques

The columns were prepared by using the high-pressure slurry packing tech-

nique, with ethanol as filling liquid. The slurry liquid for silica and bonded silica was carbon tetrachloride. For alumina we preferred the mixture 1,1,2,2-tetrabromoethane–dioxan (80:20).

Chemicals

Carbon tetrachloride, diisopropyl ether, acetonitrile and dioxan were of Chromasol grade and were purchased from SDS (Valdonne, France). Chloroform and heptane were of LiChrosolv grade and were obtained from Merck. Methanol and ethanol were of analytical-reagent grade from Prolabo. Fluorinert was purchased from 3M (Saint-Paul, MI, U.S.A.). 1,1,2,2-Tetrabromoethane and all solutes were Merck reagents. The water used was doubly distilled.

PRINCIPLE OF FOURIER TRANSFORM INFRARED SPECTROSCOPY

Disadvantages of classical systems

With a classical IR spectrophotometer, the spectral resolution increases with decreasing slit width, while the transmitted energy decreases. To obtain a sufficient resolution, the slit width must be as small as possible. Then, the measurement time in every spectral region must be increased in order to obtain a large enough signal. As a consequence, too small an amount of energy falls on the detector per unit time. An improvement can be achieved by collecting simultaneously all the spectral element energies, which is realized with FTIR.

Principle

A Michelson interferometer (Fig. 1) consists of two mirrors (one stationary and one movable at a constant speed) at right-angles to each other, and a beam splitter bisecting the angle between the two mirrors. The two beams resulting from the splitting interfere and the interference pattern depends on the light path difference

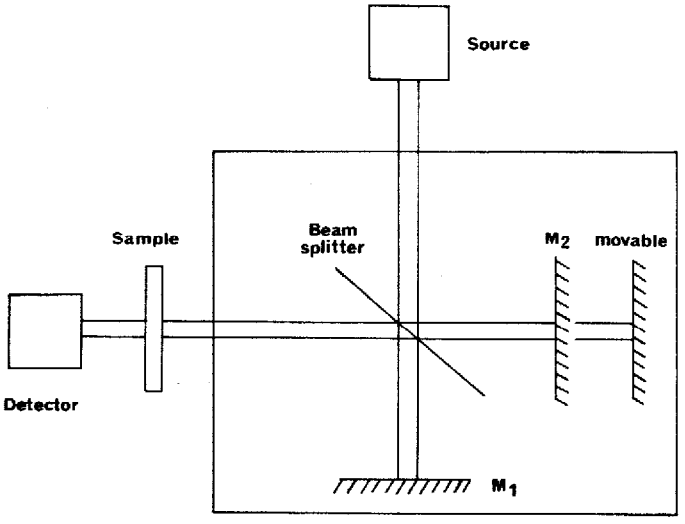

Fig. 1. Michelson interferometer.

between the beams. This difference can be changed by driving the movable mirror M_2.

If the incoming light is a strictly monochromatic radiation (wavenumber $\bar{\nu}_0$, luminance G_0), the interference pattern is given by

$$I(x) = G_0 \cos^2 \bar{\nu}_0 x = \tfrac{1}{2} G_0 (1 + \cos 2\pi \bar{\nu}_0 x)$$

where $I(x)$ is the output intensity as a function of the path difference x(cm), $\bar{\nu}$ the wavenumber (cm^{-1}) and $G(\bar{\nu})$ the spectral intensity distribution function (or the spectrum of the source).

The intensity $I(x)$ consists of two parts, one constant and one variable. The variable part is

$$I'(x) = \tfrac{1}{2} G_0 \cos 2\pi \bar{\nu}_0 x$$

The resultant intensity for incoming light composed of several monochromatic radiations is the sum of the intensities of each radiation. For a continuous spectrum spreading from $\bar{\nu}_1$ to $\bar{\nu}_2$, the interferogram is given by

$$I''(x) = \int_{\bar{\nu}_1}^{\bar{\nu}_2} G(\bar{\nu}) \cos 2\pi \bar{\nu} x \, d\bar{\nu}$$

which is the Fourier transform of the spectrum of the source $G(\bar{\nu})$.

The interesting variable is the spectrum of the source $G(\bar{\nu})$, because it determines the absorption of the sample, *i.e.*, the absorbance as a function of the wavenumber. It is given by the Fourier transform of the interferogram:

$$G(\bar{\nu}) = \int_{-\infty}^{+\infty} I''(x) \cos 2\pi \bar{\nu} x \, dx$$

The main disadvantage of interferometry is that little information is available from it without further processing. It is necessary to convert the interferogram into a spectrum by calculating its Fourier transform with a fast computer. Before the publication of the Cooley–Tukey algorithm in 1965[14] it often took several days of computer time to process the data, but the algorithm reduced the computation time by several orders of magnitude. Later, minicomputers were developed and their coupling with a Michelson interferometer resulted in the capability for on-line short-time Fourier transformations. With this final advantage, FTIR spectroscopy moved into the analytical laboratory to stay.

The process of obtaining the spectrum of the source from the interferogram offers several advantages over direct recording of the same spectrum by classical IR spectroscopy.

Signal-to-noise ratio

Felgett[15,16] demonstrated that the signal-to-noise ratio greatly increases with

this interferometric method, because the detector views all the wavenumbers all the time during the mirror displacement, giving rise to what is termed the multiplex advantage[17].

With a classical spectrophotometer, if M spectral elements are to be measured during time T, each spectral element is measured during T/M; the multiplex advantage makes possible the measurement of each spectral element during T[18]. If the fluctuations are not correlated and the background noise does not increase with the simultaneous incoming of all the spectral elements, the signal-to-noise ratio increases with respect to the square root of the exploration time. The signal-to-noise ratio increases with respect to $\sqrt{M}$ (generally about 150-fold). The method is then all the more interesting as the studied spectrum contains more spectral elements.

Available energy

Jacquinot[19] showed that the available energy is more important with an interferometer than with a classical spectrophotometer. The interferometric system does not require slits or dispersive or filtering systems, which are the limiting elements of energy throughput. Therefore, the available amount of energy is 100–200 times greater than with a classical instrument.

Multiscanning capability

With the two preceding advantages, the time for driving the mirror can be short and the interferogram can be recorded in a few seconds. This makes possible the co-addition of successive interferograms[20]. As the signal increases with respect to the number of scans and noise with respect to the square root of the number of scans, the signal-to-noise ratio increases with respect to the square root of the number of scans, the computational time remaining unchanged.

PRINCIPLE OF HPLC–FTIR COUPLING

Detection of liquid chromatographic eluates using FTIR was achieved in two ways. The first, developed by Griffiths and co-workers[21–23], consists in detecting the solutes after removal of the solvent using a carousel with 32 positions of deposition of the solutes. The effluent from the HPLC column passes on to powdered potassium chloride, then the solvent is completely evaporated. The solute deposited on the surface of the potassium chloride powder is subsequently analysed by diffused reflectance FTIR spectroscopy. The best advantage of this off-line technique is the possibility of analysing collected samples by any method (other than IR especially), but it needs a second detector to detect chromatographic peaks and start the solvent removal system. Moreover, the complex mechanical concept of the carousel makes it difficult to achieve.

The second technique, developed by Vidrine and co-workers[7–10] using a Nicolet 7199 FTIR spectrometer, realizes on-line detection via a flow cell. Its main advantages are the following: real-time plotting of the integrated adsorbance in each of up to five operator-selected IR bands against time, so as to produce five simultaneous specific chromatograms; disk storage of effluent interferograms, which after Fourier transform provide the spectra; (the spectra of the solutes are obtained after division

of the effluent spectra by the eluent spectrum); and possible intricate data manipulations with the computer system.

CHARACTERISTICS OF THE COUPLING

Width of the detection spectral region

During elution, chromatograms are plotted in real time in five different spectral regions. The influence of the spectral region width on peak height was examined.

A narrow spectral region is interesting for detecting a solute with a previously known IR absorption maximum. The spectral region must then be centred on that maximum. The narrower the spectral region, the higher is the chromatographic peak (nevertheless, under 6 cm^{-1}, the peak height cannot be increased because the background noise becomes too great).

A wide spectral region makes possible the detection of many solutes with the same organic function. The peaks are generally smaller but random noise decreases because of its averaging on all the wavenumbers of the spectral region. The detection of carbonyl derivatives with chloroform as the eluent illustrates these results (Fig. 2). In the 1685–1678 cm^{-1} window, only acetophenone can be detected properly. In the 1725–1675 cm^{-1} window, the six derivatives are detected, but the acetophenone peak height is smaller.

Flow cell

The nature of the flow cell is a specific characteristic of on-line detection. During elution the flow cell is located in the IR beam, in the dried air sample compartment. A compound for an IR cell is characterized by its compatibility with all solvents and especially its insolubility in water, its transmission ability, *i.e.*, its refractive index, and its cut-off wavenumber. The properties of some common compounds are given in Table I.

The most useful compound have low water solubility, refractive index and cut-off wavenumber. However, as shown in Table I, there is no ideal compound and the choice of the material depends on the experimental conditions.

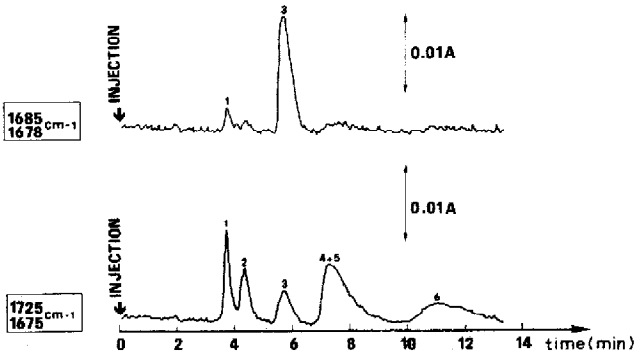

Fig. 2. Influence of the position of the spectral region on the detection of solutes. Column: 5 cm × 4.8 mm (¾ in.) I.D. Stationary phase: Woelm N alumina, d_p 3–6 μm. Mobile phase: chloroform with 100 ppm of water; flow-rate, 1 ml min^{-1}. FTIR detection (0.2 mm KBr flow cell). Solutes: 1 = ethyl benzoate; 2 = ethyl formate; 3 = acetophenone; 4 = acetone; 5 = cyclohexanone; 6 = dibutyl phthalate.

TABLE I

PROPERTIES OF COMPOUNDS USED IN IR CELLS

Compound	*Solubility in water*	*Refractive index (at 2000 cm^{-1})*	*Cut-off wavenumber (cm^{-1})*
NaCl	Soluble	1.52	650
KBr		1.53	400
CsBr		1.67	250
CsI		1.74	200
ZnSe	Insoluble	2.5	500
AgCl		2.0	450
BaF_2	Barely soluble	1.45	850

Four commercial flow cells were studied: two 0.2 and 1 mm ZnSe flow cells and two 0.2 and 1 mm KBr flow cells. The corresponding volumes are 3 and 12 μl for 0.2 and 1 mm thicknesses, respectively.

The nature of the solvent prescribes the choice of the compound. KBr, which is water soluble, cannot be used with aqueous–organic mixtures, nor with pure alcohols because slight absorbance of the cell could occur. ZnSe is then to be preferred, even if such a material gives, under the same experimental conditions, a four times smaller signal than KBr. With other eluents, KBr is to be preferred because of its better transparency.

The choice of the cell thickness depends on the type of the detection spectral regions. With a perfectly transparent solvent in the chosen spectral region, a 1 mm flow cell must be preferred because the instrumental noise is constant whatever the flow cell is, while the amount of solute present in cell is five times greater with a 1 mm than with a 0.2 mm cell. In contrast, when significant regions of solvent opacity exist [lower than 2 absorbance units (A.U.), however], an increasing cell thickness makes the intensities of these bands greater. The energy falling on the detector is smaller, so the signal-to-noise ratio decreases and detection of the solutes becomes more difficult. A 0.2 mm flow cell must then be preferred. Regions with solvent absorbances greater than 2 A.U. are useless and masked by the background noise.

Linearity range

Two methods can be used to study the detector linearity. The first consists in determining the chromatographic peak area for different concentrations of the solute (classical method in chromatography). The second consists in measuring on an IR spectrum obtained during elution the variations of the height of a characteristic IR band with different concentrations. The same conclusions can be drawn with these two methods; the second is illustrated in this paper.

Two cases have been investigated: acetophenone in chloroform ($k' = 0.1$) and *o*-methylanisole in carbon tetrachloride ($k' = 3$) (Fig. 3). The linearity of the IR band height with the amount injected is well established. In the studied concentration range (10–600 μg) the Beer–Lambert law still holds.

Limits of detection

Two methods similar to those considered for the study of the detector linearity

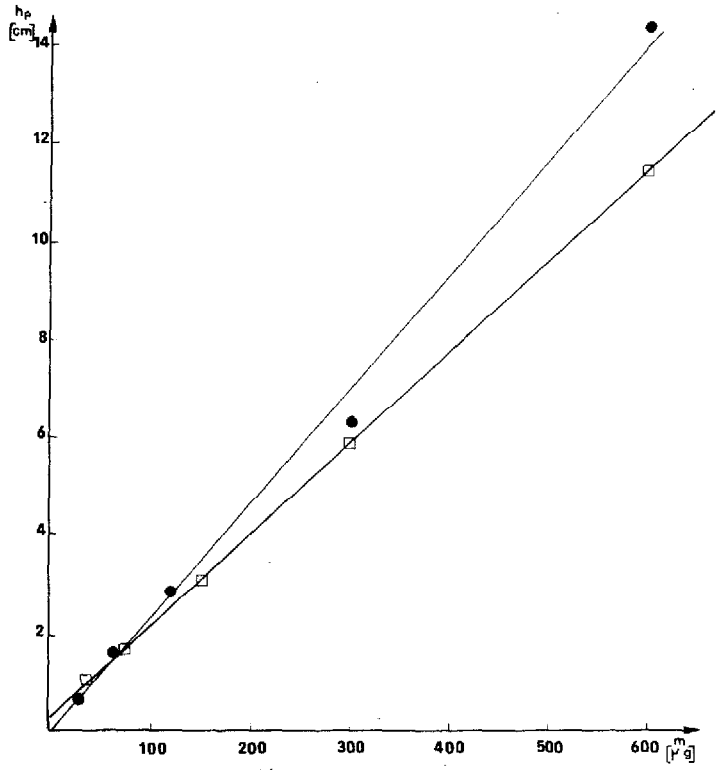

Fig. 3. Variation of the peak height (h_p) with the mass of solute injected (m). Column: 15 cm × 4.8 mm ($\frac{1}{4}$ in.) I.D. Stationary phase: LiChrosorb Si 60 silica, d_p 5 μm. Flow-rate: 1 ml min^{-1}. FTIR detection (0.2 mm KBr flow cell). For acetophenone (●): mobile phase, chloroform with 10 ppm of water; k' = 0.1. For *o*-methylanisole (□): mobile phase, carbon tetrachloride with 50 ppm of water; k' = 3.

can be used to determine the detection limit of a solute. The first consists in finding which smallest injected amount gives a detectable peak on the chromatogram. This is not the best method because, if the detection spectral region is not centred on the absorption maximum of the solute, the detectability found is too high. The second method consists in considering a characteristic band of the solute on an IR spectrum obtained during elution. It is then easy to determine which smallest amount injected provides a detectable band. With carbon tetrachloride, the preferred eluent for IR detection, the detectabilities are about 1 μg injected for all the solutes investigated (nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, anisole, *o*-methylanisole, *p*-methylanisole, cyclohexane, allyl bromide, diethyl ether, nitroethane, nitromethane and dioxan) (k' = 0.4–6 with a 5 cm × 4.8 mm I.D. column and a flow-rate of 1 ml min^{-1}).

Comparison with other detection methods

The detection limits for *o*-methylanisole obtained with different detection methods are as follows (k' = 3; column 5 cm × 4.8 mm I.D.): UV absorptiometry (LDC Spectromonitor III, 280 nm), 1 ng; refractometry (Waters R401), 1 μg; and FTIR (Nicolet 7199, 1 mm KBr flow cell), 1 μg. The sensitivity of FTIR detection

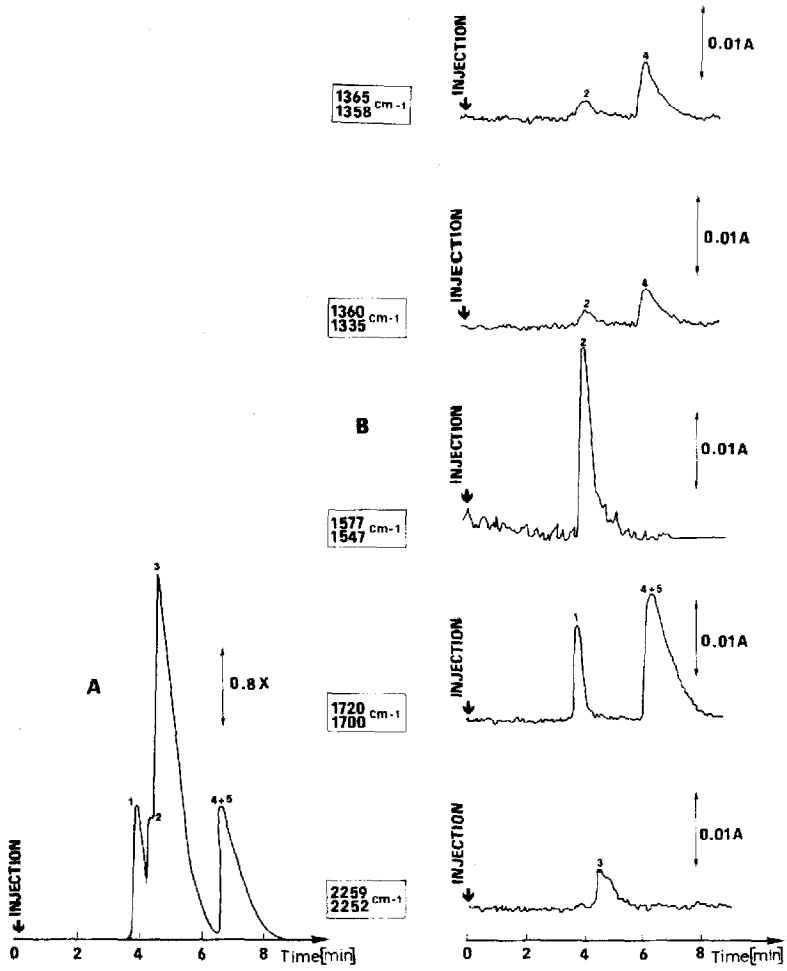

Fig. 4. Comparison of (A) refractometric and (B) FTIR (0.2 mm KBr flow cell) detection. Column: 15 cm × 4.8 mm (¾ in.) I.D. Stationary phase: Woelm N alumina, d_p 3–6 μm. Mobile phase: chloroform with 100 ppm of water; flow-rate, 1 ml min^{-1}. Solutes: 1 = ethyl formate; 2 = nitromethane; 3 = acetonitrile; 4 = acetone; 5 = cyclohexanone.

is therefore very similar to that of classical differential refractometry. The efficiency is the same for the three detection systems, with similar flow cell volumes.

The chromatograms obtained with refractometric and FTIR detection can be compared in Fig. 4. The FTIR spectrometer can be seen to be a useful separation device because, depending on the detection spectral region chosen, solutes are detected or not.

INFLUENCE OF THE NATURE OF THE MOBILE PHASE

The performances of FTIR detector in reversed-phase and adsorption HPLC differ, as discussed below.

In reversed-phase HPLC

Most of common eluents used in reversed-phase chromatography, especially alcohols and water, show intense IR absorption bands, which preclude the identification of unknown solutes, and limit the detection to solutes with an absorption band located in the transparent region of the solvent. Moreover, there is generally an intense solvent absorption level even in the transparent region, which results in poor sensitivity for the solutes. With IR detection, reversed-phase HPLC can be applied readily only when using eluents that do not contain water or alcohols. For example, separations of hydrocarbons and glycerides can be achieved by reversed-phase HPLC and monitored by IR detection with eluents such as methylene chloride, tetrahydrofuran and acetonitrile[2,3]. With acetonitrile, identification at different wavenumbers is possible, and the detection limits are about 20 μg for *tert.*-butyl chloride, methyl iodide, ethyl bromide and butyl bromide (k' = 0.1–0.2; column 15 cm × 4.8 mm I.D.).

In adsorption HPLC

FTIR detection is well adapted to adsorption chromatography and the worst case studied (diisopropyl ether) is similar to acetonitrile (which was the best case in reversed-phase HPLC).

For chloroform and carbon tetrachloride, which present few absorption bands,

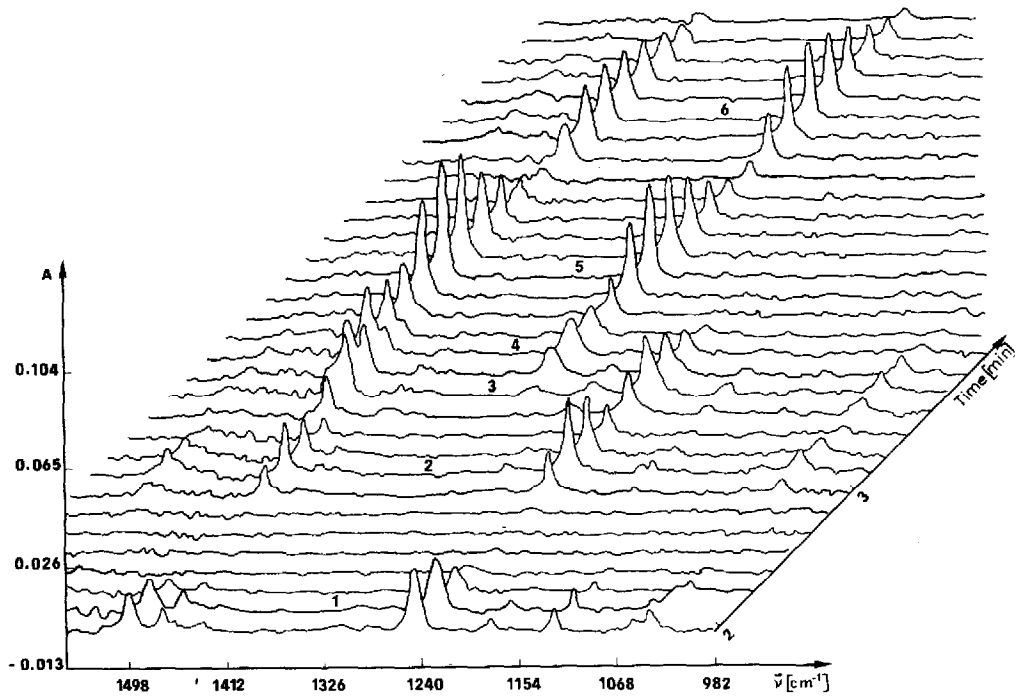

Fig. 5. Example of a three-dimensional chromatogram. Column: 5 cm × 4.8 mm (¼ in.) I.D. Stationary phase: LiChrosorb Si 60 silica, d_p 5 μm. Mobile phase: carbon tetrachloride with 30 ppm of water; flow-rate, 1 ml min^{-1}. FTIR detection (0.2 mm KBr flow cell). Solutes: 1 = *o*-methylanisole; 2 = anisole; 3 = *p*-methylanisole; 4 = *o*-nitrotoluene; 5 = nitrobenzene; 6 = *p*-nitrotoluene.

identification of unknown solutes is possible. The detection limit is about 1 μg injected. With such solvents, chromatograms can be represented in three dimensions (Fig. 5): absorbance, wavenumber and time. A section perpendicular to the wavenumber axis provides a chromatogram in any IR spectral region.

These results can be transposed to normal partition chromatography, because the eluents involved in these two techniques are similar.

FTIR SPECTROSCOPY AS AN IDENTIFICATION METHOD

Quality of the spectrum

For a given separation, the spectra obtained during elution do not all present the same information, depending on the nature of the eluent and the amount of solute injected. First, identification is possible only with eluents with few absorption bands, such as chlorinated compounds. Second, the number of IR bands detected depends on the amount injected. This number was studied for anisole in carbon tetrachloride, under the same experimental conditions as in Fig. 5. Table II shows that the number of IR bands decreases with decreasing amount injected.

Identification of nitrobenzene and o- and p-nitrotoluene

In adsorption chromatography, with carbon tetrachloride as eluent, *o*- and *p*-nitrotoluene and nitrobenzene can be separated (Fig. 5). These chemically similar solutes show two intense absorption bands corresponding to NO_2 vibrations. The characteristic wavenumber of the symmetric vibration is 1348 cm^{-1} for all three compounds, but the antisymmetric vibration wavenumbers differ slightly, being 1525 1529 and 1531 cm^{-1} for *o*-nitrotoluene, nitrobenzene and *p*-nitrotoluene, respectively. These solutes can be identified from the spectra obtained during elution by comparing their absorption maxima wavenumbers with those of antisymmetric NO_2 vibrations of the pure solutes, which are stored in a memory (Fig. 6).

This method was also used for the identification of six carbonyl derivatives eluted by chloroform on Woelm N alumina. These solutes were identified using the CO valence vibration (acetophenone 1682, cyclohexanone 1703, acetone 1710, ethylbenzoate 1714, dibutyl phthalate 1718 and ethyl formate 1720 cm^{-1}).

Subtraction technique

Classical FTIR subtraction techniques are useful for separating two badly re-

TABLE II

VARIATION OF THE NUMBER OF DETECTED BANDS WITH THE AMOUNT INJECTED

Amount injected (μg)	*No. of IR bands detected*
300	15
150	10
75	6
30	4
10	2
0.5	1

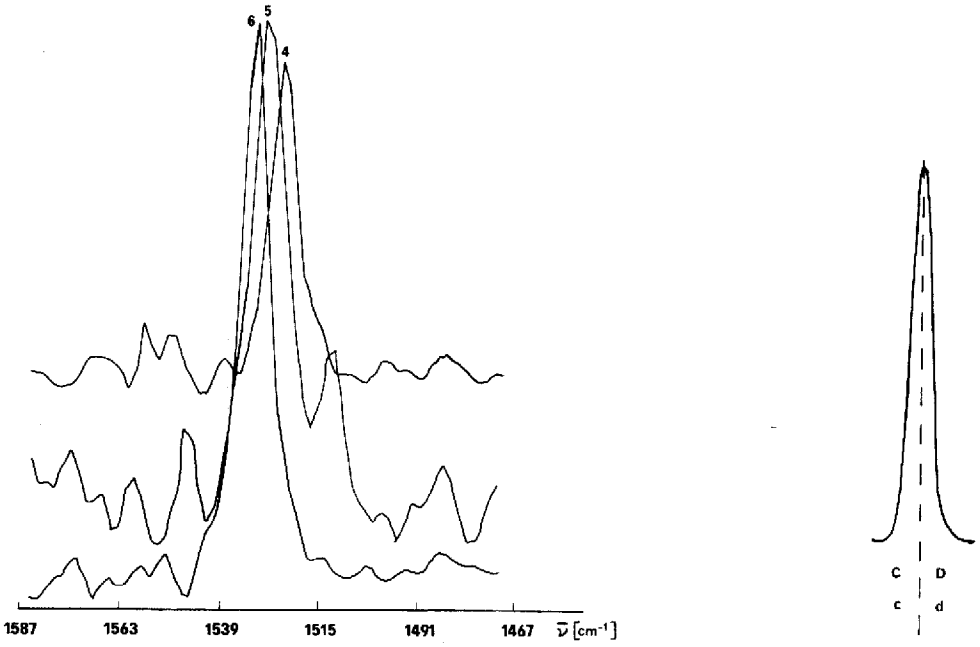

Fig. 6. NO_2 IR absorption bands of nitro derivatives separated by adsorption chromatography. Experimental conditions as in Fig. 5.

Fig. 7. Basic principle of the subtraction technique.

solved solutes. A simple method consists in separating the chromatographic peak of the two solutes, γ and δ, into two parts, C and D, with IR spectra c and d (Fig. 7). The solutes γ and δ are assumed to be characterized by two absorption bands at different wavenumbers $\bar{\nu}_\gamma$ and $\bar{\nu}_\delta$, respectively.

Subtractions $| c - kd |$, where k is a variable, are then calculated in order to cancel absorbance at $\bar{\nu}_\gamma$, for example. The spectrum of γ is then deleted, and the spectrum of pure δ can be obtained. If $k < 1$, the main compound in D is γ; if $k > 1$, the main compound in C is γ. The IR spectra of pure γ and δ and the elution order can therefore be obtained.

This method is illustrated by the separation by adsorption chromatography of acetone and cyclohexanone with chloroform as eluent (Fig. 4). The characteristic IR absorption band wavenumbers of acetone and cyclohexanone are 1350 and 2850 cm^{-1}, respectively. With the subtraction technique, the spectra of pure acetone and cyclohexanone can be obtained, and the elution order (acetone before cyclohexanone) can be found.

APPLICATION TO THE SEPARATION AND THE IDENTIFICATION OF MINERAL OIL ADDITIVES

Nature of the additives

The problem was to characterize and separate six additives in a mineral oil. Each additive and the mineral oil, while possessing a specific function, are composed

TABLE III

IR CHARACTERISTICS OF THE ADDITIVES AND THE MINERAL OIL

Compound	*Characteristic function*	*Detection spectral region (cm^{-1})*	*Wavenumber of maximum absorption (cm^{-1})*
Mineral oil	Alkane	2930–2920	2925
1			
2			
3	Alcohol	3650–3640	3645
4	Aromatic amine	1505–1490	1498
5	Ester	1740–1730	1735
6	Phosphoric ester	965– 955	960

of numerous compounds. For each additive and the mineral oil, a characteristic IR band can be determined (Table III).

Separation of very polar additives

The four most polar additives can be separated by adsorption chromatography on silica with carbon tetrachloride containing 50 ppm of water as eluent. The most retained additive is eluted by the backflushing technique. The two less polar additives and the mineral oil are unretained.

The chromatograms for the six additives are shown in Figs. 8 (refractometric detection) and 9 (FTIR detection) as full lines, and the change caused by the addition of the oil is shown by the broken lines. With refractometric detection, the mineral oil peak cancels the first three additive peaks, especially the badly resolved third one (alcohol function). In contrast, with FTIR detection, additive No. 3 is separated in its characteristic spectral region (3650–3640 cm^{-1}) in which the oil is transparent.

The identification of the separated additives can be achieved by comparing the absorption maxima wavenumbers of the spectra obtained during elution with those in Table III.

Separation of less polar additives

The separation of the mineral oil and additives 1 and 2 is carried out on silica with heptane containing 1 ppm of water. As these three compounds belong to the same organic family (alkanes) as the eluent, only refractometric detection can be used.

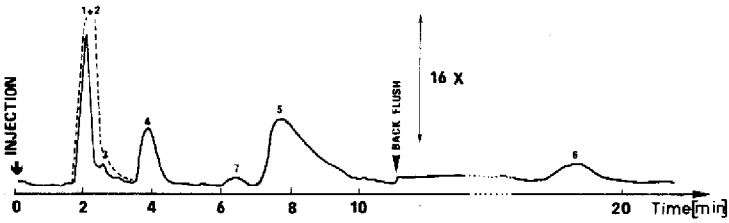

Fig. 8. Separation of additives in a mineral oil by adsorption chromatography with refractometric detection. ———, Chromatogram of additive separation; – – –, change in chromatogram caused by the presence of the mineral oil. Column: 15 cm × 4.8 mm (¼ in.) I.D. Stationary phase: LiChrosorb Si 60 silica, d_p 5 μm. Mobile phase: carbon tetrachloride with 50 ppm of water; flow-rate, 1 ml min^{-1}. Solutes: 1–6, see Table III; 7 = unidentified compound.

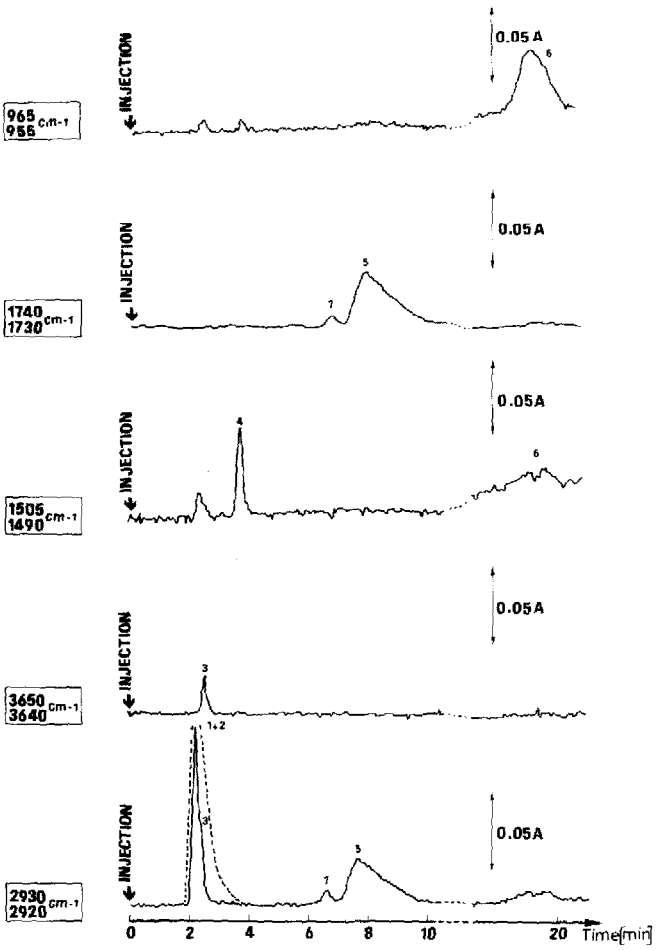

Fig. 9. Separation of additives in a mineral oil by adsorption chromatography with FTIR detection (0.2 mm KBr flow cell). ———, Chromatogram of additive separation; — — —, change in chromatogram caused by the presence of the mineral oil. Experimental conditions as in Fig. 8.

Compared with classical IR spectroscopy, FTIR spectroscopy has two main advantages: the signal-to-noise ratio is about 150 times greater and the throughout energy per unit time is 100–200 times higher.

We use on-line coupling. Five simultaneous chromatograms are plotted in different IR spectral regions and the spectra of the eluted solutes can be acquired at any elution time.

Common eluents in reversed-phase chromatography (water, methanol, acetonitrile and their mixtures) are hardly compatible with IR detection. Nevertheless, FTIR spectroscopy is well adapted to adsorption chromatography, especially with chlorinated eluents, because most of the spectral range of such eluents is usable. The

detection limits (*ca.* 1 μg injected) are similar to those obtained in classical differential refractometry. FTIR detection is a powerful means of identification in adsorption chromatography. Solutes with functional groups can easily be identified. With badly resolved chromatographic peaks, the subtraction technique makes FTIR spectroscopy an interesting separation method.

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