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CHROMATOGRAPHIC PERFORMANCE AND CAPILLARY GAS CHROMATOGRAPHY–FOURIER TRANSFORM INFRARED SPECTROSCOPY

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SUMMARY

In gas chromatography–infrared spectroscopy (GC–IR), the instrumental requirements of Fourier transform (FT) IR spectroscopy place special constraints on the interface between the gas chromatograph and spectrometer as well as on the chromatographic experiment. State-of-the-art capillary GC–FTIR reflects a necessary compromise between sensitivity and chromatographic performance to yield an analytically useful system. Some of the trade-offs between optimal IR performance and optimal GC performance are reviewed. Investigations of the chromatographic performance of a capillary GC–FTIR system are reported.

INTRODUCTION

A major challenge in analytical chemistry has always been the identification of organic compounds in complex mixtures. For mixtures separated by gas chromatography (GC), mass spectrometry (MS), owing to its sensitivity and selectivity, has been the method of choice up to now. However, recent developments in infrared (IR) instrumentation have made it possible to obtain qualitative information from Fourier transform (FT) IR spectroscopy and, in the last few years, capillary GC–FTIR has developed into a very powerful structural elucidation technique[1–4]. A most useful characteristic of FTIR is, of course, that functional group information can be readily obtained.

Developments in capillary column technology in the past few years have produced highly efficient glass and fused-silica columns that are chemically inert to a wide variety of compounds. For their greatest utility, it is important that chromatographic integrity not be lost in the detection process. For capillary application of GC–FTIR, excellent chromatographic performance must be maintained throughout the system. This is especially important for the analysis of isomers and closely related compounds, some of which can only be differentiated on the basis of their IR spectra.

From its outset, capillary GC–FTIR has been recognized as providing structural information that is often complementary to that obtained by capillary GC–MS, and it is likely that the information from capillary GC–FTIR and capillary GC–MS, combined into a single data base, will find increasing application to more difficult analytical problems[4–6]. For such a combined system to be most effective, both GC–IR and GC–MS must exhibit comparable chromatographic performance.

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In GC–FTIR, as in all combined analytical techniques, compromises have been made in each independent technology to develop a successfully unified system. The fundamental compromises in GC–IR have been reviewed in part by Griffiths[7], Erickson[8] and Hirschfeld[9]. To a great extent, it is the design of the interface between the two instruments that limits both the sensitivity and chromatographic performance in GC–IR.

Most GC–IR interfaces in use today are designed to perform as low-volume, flow-through gas cells. These cells are incorporated into the optical path of the FTIR interferometer. Important design features of the cell, commonly referred to as a light-pipe, are the materials of construction and the size and geometry of the cell. These features greatly influence both the IR and GC performance.

The cells are constructed of materials specifically selected to satisfy FTIR requirements and to be chromatographically compatible. Windows are typically made of salt plates for optical transparency. The flow cells are gold-coated on their inner walls to enhance their optical throughput characteristics. These materials are generally assumed to be chromatographically inert. However, the surface interaction of the windows and the gold-coated glass with nanogram amounts of chromatographic solutes has not been investigated. In practice, solute adsorption may be affected by the temperature at the surfaces. Finally, solute interaction with the large surface area in the cell may vary with the quality and uniformity of the gold surface.

The size and geometry of the light-pipe affect a multitude of parameters, and many of the relationships between them are not fully understood. The length, inner diameter and the length-to-inner diameter ratio are all considered critical factors in achieving good signal-to-noise ratios in the resulting IR spectra[7]. These dimensions influence parameters such as the effective path length, the number of optical reflections and the total optical throughput of the cell. Although the size and geometry of a light-pipe are generally compromised to keep the volume small enough for chromatographic considerations, the volume is still larger than one would consider optimal for a capillary column detector, mainly because the cell volume is larger than a normal capillary GC peak.

In the studies on the chromatographic performance of capillary GC–FTIR reported here, a sample from the polymer industry and selected test mixtures were investigated.

EXPERIMENTAL

All GC–IR data were collected with an IBM IR-85 Fourier transform infrared spectrometer (IBM instruments, Danbury, CT, U.S.A.) equipped with an IBM GC-IR interface. The interface, described in detail elsewhere[1], consisted of a gold-coated Pyrex flow cell with potassium bromide windows. A scan rate of 5 scans/sec and a spectral resolution of 8 or 16 wavenumbers were used as the FTIR data acquisition parameters. The IR radiation transmitted through the interface was detected with a mercury–cadmium–telluride (MCT) detector, having a lower frequency cut-off of about 600 wavenumbers.

IBM fused-silica capillary columns were used for all separations. The chromatographic system consisted of a Hewlett-Packard 5880 gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.) with a capillary inlet system. The end of the capillary

column was connected directly to the GC–IR light-pipe entrance, obviating the need for an inlet transfer line. For the experiments with flame-ionization detection, (FID), the effluent from the light-pipe was connected to the capillary flame jet of the 5880 chromatograph with a short length of 0.5 mm I.D. fused-silica capillary, coated with a thin film of OV-101. The GC–IR light-pipe assembly and fused-silica lines were thermostated at a temperature set equal to the upper programmed temperature of the capillary column.

For the calculation of all Gram–Schmidt chromatograms, except for the data reported in Fig. 4, 30 data points offset 30 points from the interferogram centerburst, were abstracted from each successive interferogram during the data collection process. A background basis set consisting of 20 interferograms was established prior to each chromatographic experiment. For Fig. 4, 80 data points with an offset of 40 points and a 50-point basis set were used for the Gram–Schmidt calculation of the chlorinated hydrocarbons.

Silylated derivatives of the *n*-alkanols were prepared by reaction with N,O-bis-(trimethylsilyl)acetamide (BSA) (Pierce, Rockford, IL, U.S.A.) at room temperature for 30 min.

RESULTS AND DISCUSSION

In evaluating the GC–FTIR interface, the FTIR spectrometer served, in most instances, as the chromatographic detector. For the analysis of selected chromatographic solutes, an FID instrument was connected in series after the IR light-pipe.

Use of the FTIR spectrometer as a detector allows direct monitoring of the chromatography at the interface itself. The mathematical procedure used to calculate the Gram–Schmidt chromatograms has been described in detail by De Haseth and Isenhour[10]. Briefly, with this algorithm, IR absorbance information is abstracted in real time from the IR interferogram. In this way, the computationally time-consuming Fourier transform from the time to the frequency domain is avoided. In addition to the construction of a chromatogram, which is roughly proportional to the total IR absorbance, this procedure can be used for automatic spectral data collection. Scan rates of 5–10 scans per second permit the adequate definition of narrow capillary peaks having widths of the order of 0.5–1.0 sec.

The Gram–Schmidt chromatogram obtained during the analysis of a mixture of liquid impurities from a polypropylene extrusion process is shown in Fig. 1. Owing to the weak IR absorbance of the hydrocarbons in this sample, a capillary column with high solute capacity (1.0 μm film thickness) was used for the separation. A number of isomeric aliphatic hydrocarbons have been resolved. The IR spectra of the three components with an elution time of approximately 22 min indicate that they are probably structural isomers of a 1-alkene.

Fig. 2 shows a chromatogram of a test mixture of alcohols. The good peak shapes indicate the inertness of the interface or cell for the more polar compounds. It clearly is not necessary to derivatize the alcohols for chromatographic reasons. However, with FTIR, as with many GC detectors[11], sensitivity and/or selectivity can be altered by incorporating specific functionalities into the compounds being analyzed. The vapor-phase spectrum of dodecanol is shown in Fig. 3A. Both the O–H stretching band at 3600 wavenumbers and the C–O stretching band near 1100 wavenumbers are weak in

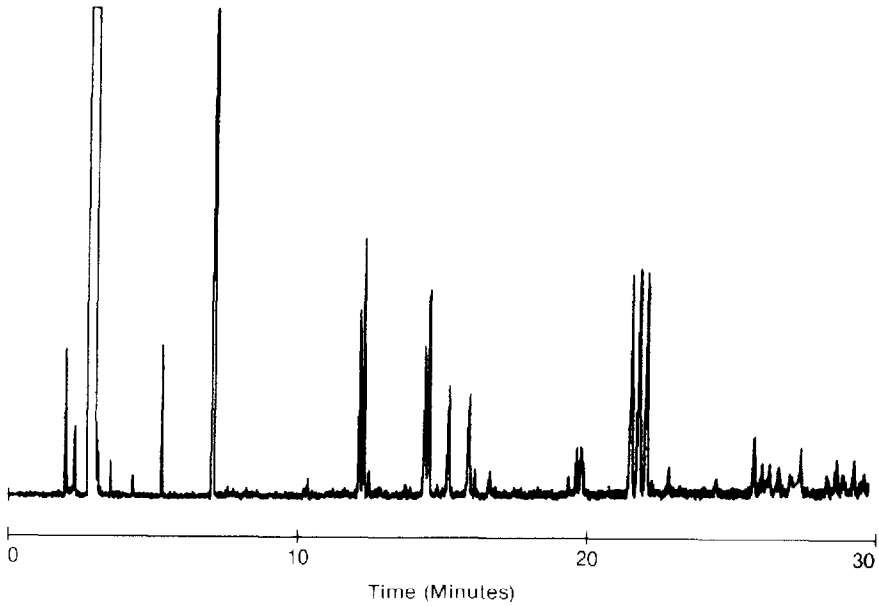

Fig. 1. Gram–Schmidt chromatogram of a mixture of hydrocarbon impurities, obtained from a polymer extrusion process. Optical resolution, 8 wavenumbers. Chromatographic conditions: 30 m × 0.33 mm I.D. fused-silica column, coated with a 1.0-μm film of DB-1. Injection 1.0 μl; splitting ratio, 1:5; temperature, programmed from 60 to 190°C at 5°C/min; carrier gas helium, at 1.5 ml/min.

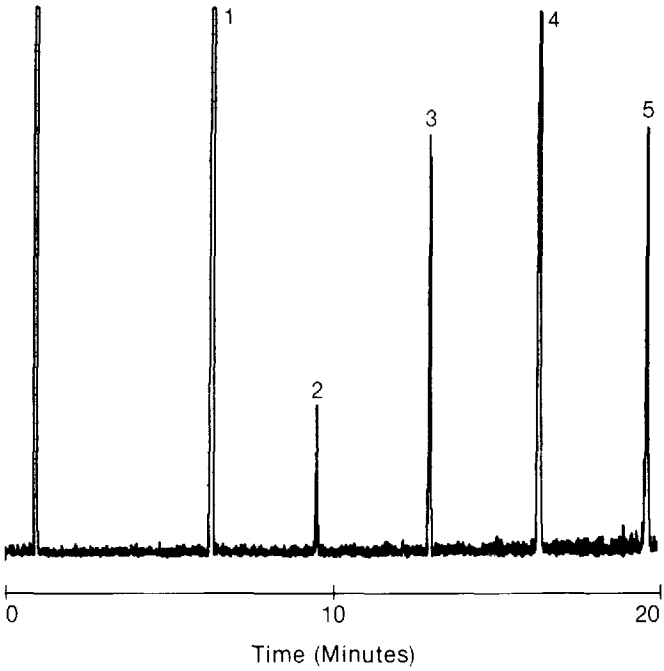

Fig. 2. Gram-Schmidt test chromatogram, of a standard C_{12}–C_{20} alcohol mixture. Optical resolution, 8 wave numbers. Chromatographic conditions: column, as in Fig. 1; injection 1.0 μl; splitting ratio 1:10; temperature, programmed from 140° to 250°C at 6°C/min; carrier gas helium, at 3.0 ml/min. Peaks: 1 = 1-dodecanol; 2 = 1-tetradecanol; 3 = 1-hexadecanol; 4 = 1-octadecanol; 5 = 1-eicosanol.

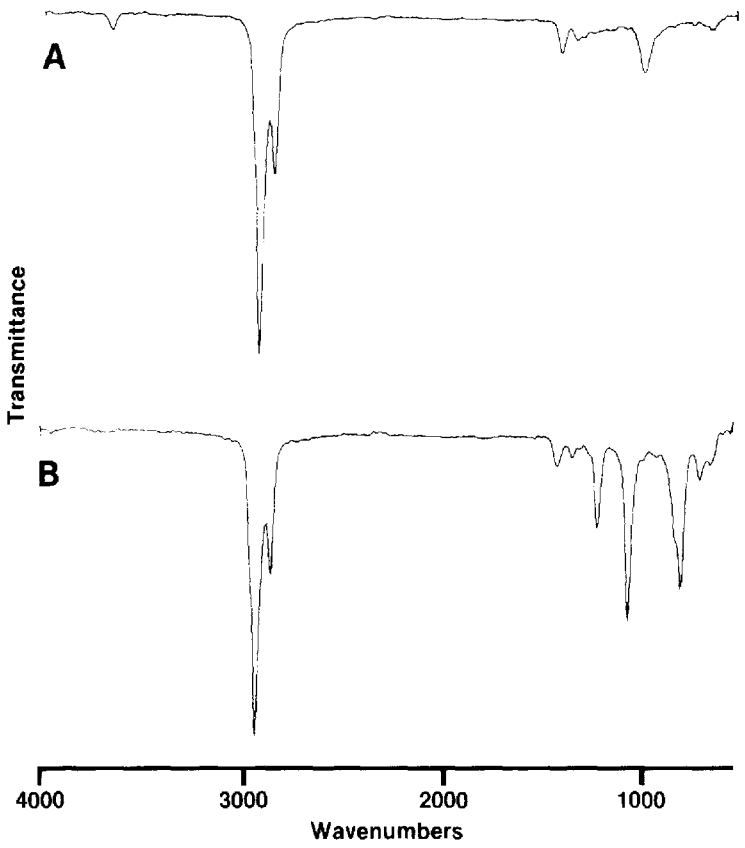

Fig. 3. Vapor-phase spectra, in transmittance, of dodecanol (A) and the trimethylsilyl derivative of dodecanol (B). Spectral resolution, 8 wavenumbers.

the vapor phase owing to the absence of hydrogen bonding. Derivatization to incorporate a trimethylsilyl group introduces a strong IR-absorbing group into the molecule. The frequencies of two absorption bands associated with the trimethylsilyl groups are not very dependent on the rest of the molecule. These bands occur around 1250 and 850 wavenumbers[12]. As expected, the frequency associated with the silicon–oxygen–carbon linkage of silylated hydroxy compounds is influenced by the nature of the group attacched to the oxygen. For *n*-alcohols and other aliphatic alcohols, this band occurs at around 1100 wavenumbers, as shown for the trimethylsilyl derivative of dodecanol in Fig. 3B. In the phenolic compounds thus analyzed, this band occurs at around 920 wavenumbers. In this way, derivatization may be used to improve detection capabilities and provide additional structural information and to improve chromatographic performance.

GC–IR has found recent application in the analysis of complex mixtures of chlorinated hydrocarbons[13]. This type of sample is of both industrial and environmental importance. Some of the compounds of interest, such as the chlorinated butadienes and cyclopentadienes, are moderately polar and may show adsorption during the chromatographic analysis. The GC–IR analysis of a standard mixture of chlorinated hydro-

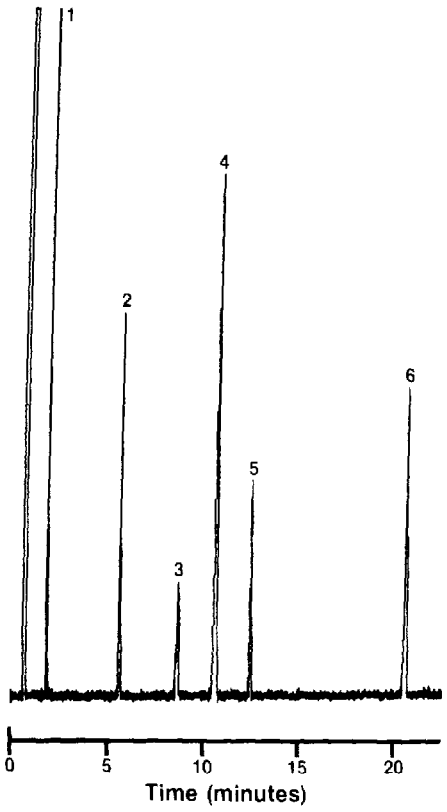

Fig. 4. Gram-Schmidt chromatogram of a mixture of chlorinated hydrocarbons. Optical resolution, 8 wave numbers. Chromatographic conditions: column, as in Fig. 1; injection 1 μl; splitting ratio, 1:30; temperature, programmed from 35 to 200°C at 5°C/min; carrier gas, helium at 2.0 ml/min. Peaks: 1 = 1-chlorobutane; 2 = tetrachlorethylene; 3 = 1,2,3-trichloropropane; 4 = *p*-chlorotoluene; 5 = *p*-dichlorotoluene; 6 = hexachloro-1,3-butadiene.

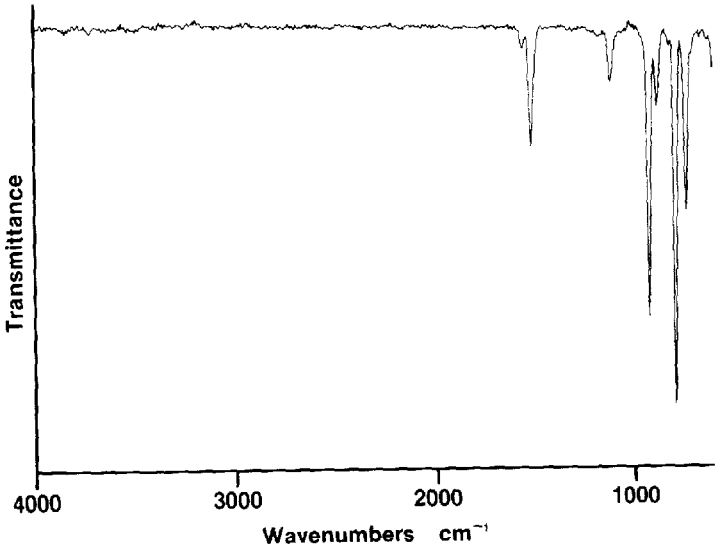

Fig. 5. Vapor-phase spectrum, in transmittance, of hexachloro-1,3-butadiene (component 6 in Fig. 4). Optical resolution, 8 wavenumbers.

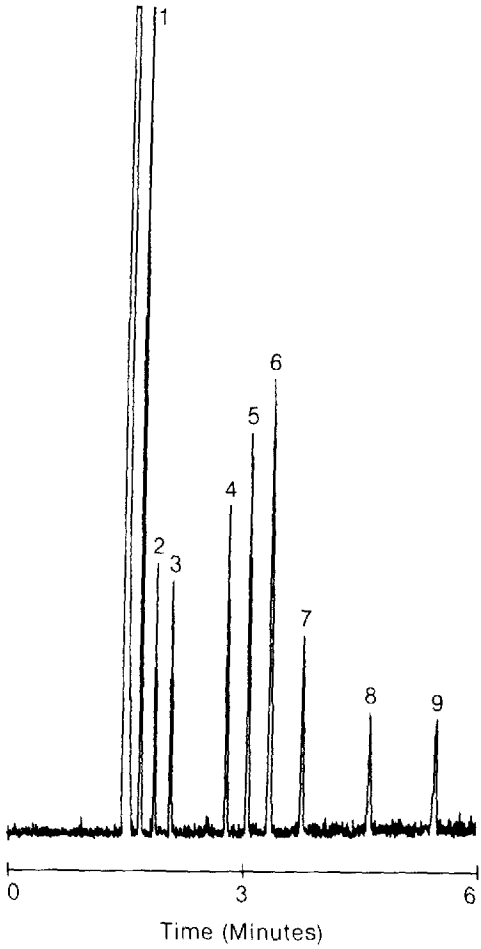

Fig. 6. Gram–Schmidt test chromatogram of a standard polarity mixture. Optical resolution, 16 wavenumbers. Chromatographic conditions: 30 m x 0.33 mm I.D. fused-silica column, coated with a 0.25-μm film thickness of SE-30; injection, 0.5 μl; splitting ratio, 1:50; temperature, programmed from 50 to 160°C at 6°C/min; carrier gas, helium, at 2.0 ml/min. Peaks: 1 = ethyl acetate; 2 = 1-butanol; 3 = 1,4-dioxane; 4 = ethyl butyrate; 5 = 2-methoxyethyl acetate; 6 = N,N-dimethylacetamide; 7 = 2-heptanone; 8 = benzaldehyde; 9 = 2-octanol.

carbons is shown in Fig. 4. The vapor-phase IR spectrum of hexachloro-1,3-butadiene, shown in Fig. 5 was automatically collected during the GC run.

As with IR spectroscopy in general, the sensitivity in GC–IR depends on the nature of the compounds investigated. It is possible to analyze low-nanogram levels of many compounds by capillary GC–FTIR. Here, chromatographic performance, both efficiency and inertness, become very important. A chromatogram of a polarity mixture is shown in Fig. 6. These compounds were separated on a 30-m column, coated with a 0.25-μm film of SE-30. Again, good peak shapes were observed for the more polar compounds such as 1-butanol.

By using the FID instrument in series with the light-pipe, test compounds can be investigated at low levels, regardless of their IR-absorbing properties. However, this approach may introduce some chromatographic degradation owing to the transfer line and connections made between the two detectors. A typical test chromatogram for standard alkenes is shown in Fig. 7.

In summary, the current instrumental configuration for GC–FTIR has been de-

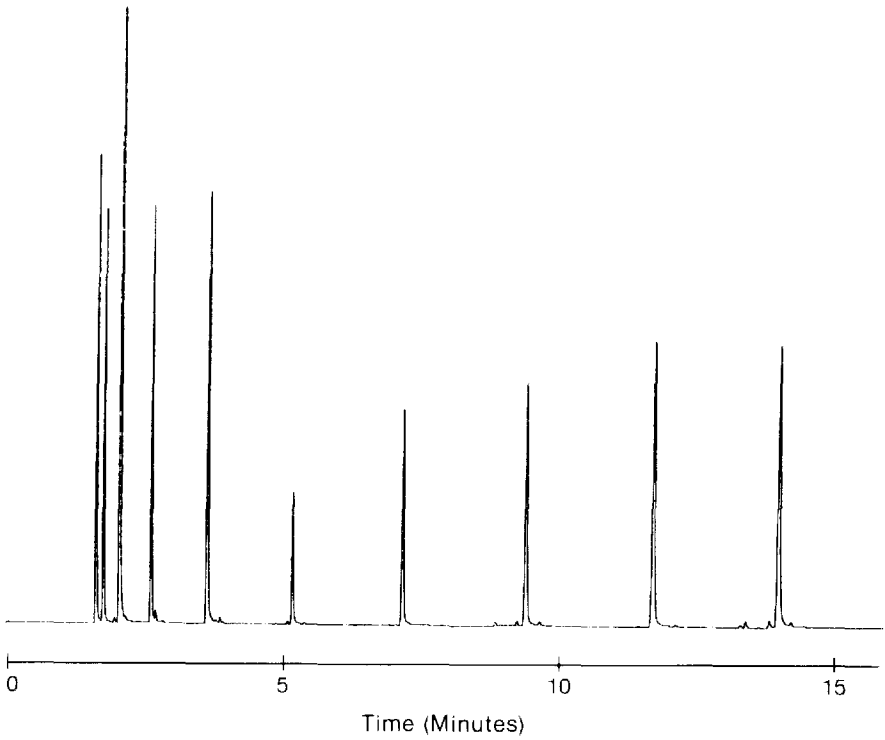

Fig. 7. Test chromatogram of a standard alkene mixture with a flame-ionization detector connected in series after the GC–IR light-pipe. Chromatographic conditions: column, as in Fig. 6; splitting ratio, 1:100; temperature, programmed from 60 to 180°C at 6°C/min. Peaks: C_5–C_{14} 1-alkenes.

signed to optimize the sensitivity of the system while, at the same time, preserving the separation. In the work outlined above for the non-polar and moderately polar solutes analyzed qualitatively thus far, the capillary GC–FTIR system showed good chromatographic performance. Work is in progress to apply the GC–FTIR–FID instrumental configuration to the analysis of more chromatographically demanding test mixtures.

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