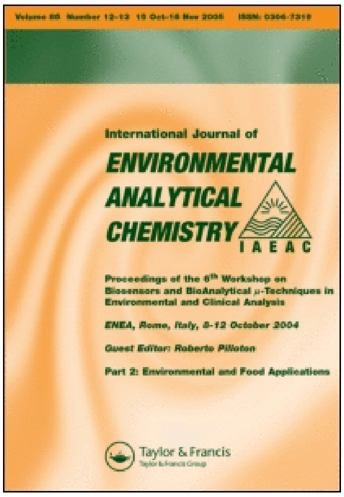

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GC/FTIR POTENTIAL FOR STRUCTURAL ANALYSIS OF MARINE ORIGIN COMPLEX MIXTURES*

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In this paper, we show the GC/FTIR contribution to the structural elucidation of marine origin complex mixtures. Three examples are given concerning aromatic hydrocarbons, fatty acid methyl esters and polychlorobiphenyls. These examples show the capability of GC/FTIR to differentiate isomers of aromatic hydrocarbons and polychlorobiphenyls and to rapidly characterize the different classes of fatty acid methyl esters (ramification, insaturation, cis/trans isomerism, hydroxyl group, cyclopropane ring).

KEY WORDS: GC/FTIR, Aromatic hydrocarbons, fatty acid methyl esters, polychlorobiphenyls, isomers.

INTRODUCTION

The organic compounds found in the marine environment (water, sediments, organisms) make up in most cases complex mixtures of many molecules with different molecular weights, structures and polarities. Generally, the components of these mixtures are only partially and incompletely identified by the currently available analytical techniques. This is particularly true in the case of isomer differentiation (ortho, para, meta benzene derivatives, cis-trans isomerism, relative position of various substituents on a benzene ring or position of a substituent on a carbon chain). Gas chromatography coupled to mass spectroscopy (GC/MS) is a prime technique for the analysis of complex mixtures, but it does not always make it possible to propose a definite structure for most of the compounds. On the contrary, in some cases, gas chromatography coupled to Fourier Transform infrared spectroscopy (GC/FTIR) turns out to be very useful to complement and precise the information obtained by GC/MS analysis.[1–6]

In this article we present some selected examples of the results obtained with GC/FTIR in the case of marine origin complex mixtures. They will illustrate the

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capabilities and limits of this technique as well as a possible GC/MS–GC/FTIR complementarity.

EXPERIMENTAL

In GC/MS analysis, a Delsi 700 GC connected to a Ribermag 1010C mass spectrometer was used (electron energy 70 eV, filament current 200 μA, source temperature 120 °C). Data were stored and processed with a SIDAR system. The 30000 EPA/NIH mass spectral library was used. The samples were chromatographed on a 50 m CPSIL 5 fused silica capillary column, programmed from 100 to 290 °C at 4 °C/min.

GC/FTIR was performed on a 20 SXB Nicolet spectrometer interfaced to a Vega 6180 Carlo-Erba chromatograph fitted with an on-column injection. The GC/IR light-pipe is a gold coated borosilicate glass cylinder (diameter: 1.2 mm; length: 16 cm) with KBr windows. A medium range Hg-Cd-Te liquid-nitrogen-cooled detector was used. A SE 52 fused silica capillary column (30 m × 0.32 mm) with a 0.4 μm film thickness was utilized for the separation. The flow rate of the helium carrier gas in the column was about 2 ml/min. The column was then directed to the GC/IR light-pipe through an inlet stainless-steel glass-lined transfer line. To preserve chromatographic resolution and to maintain positive pressure in the light-pipe a helium make-up was added to the column into the inlet transfer line (1 ml/min). The eluents from the light-pipe were then directed to the FID detector (320 °C) of the gas chromatograph through a fused silica capillary column and an outlet transfer line. In a standard GC/FTIR run the GC oven was initially set at 70 °C and was programmed at 5 °C/min until the temperature reached 270 °C and then maintained at this temperature until the last component has eluted. Transfer lines were heated to 270 °C and the GC/IR light-pipe to 275 °C.

In this work, using the Nicolet GC/FTIR software, spectra were collected with a resolution of 8 cm^{-1} over the range 4000–650 cm^{-1} and 4 to 16 interferograms co-added requiring a total measurement of 1.03 s to 2.03 s per each spectrum.

The IR reconstructed chromatograms were obtained using the Gram-Schmidt algorithm.[7] Computer spectral searches were performed with a Nicolet software utilizing the Aldrich vapor phase library which contained 5000 spectra and using a searching algorithm which involved the first derivative spectra.

RESULTS AND DISCUSSION

1. Aromatic Hydrocarbons

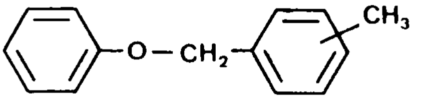
In a former study[8] we evidenced the usefulness of GC/FTIR in the analysis of complex mixtures of aromatic hydrocarbons. This technique allows to characterize compounds with up to 4 condensed rings for "minimum identifiable quantities" of 200 ng.[8] GC/FTIR turns out to be of particular interest for the distinction of isomers of aromatic hydrocarbons.

We shall develop only one example, resulting from the analysis of a marine sediment taken in the Arabian Gulf near Bahrain. After soxhlet extraction, the fraction obtained by elution with 25 ml of a toluene/hexane mixture (1:3) on a silica/alumina column exhibits an unusual FID chromatogram. When analyzed by GC/MS, the mass spectra corresponding to the 3 main peaks in the chromatogram are highly identical (molecular peak at m/z 198 and main fragment at m/z 91).

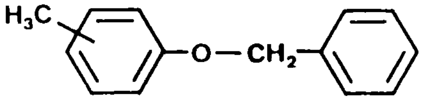
From these data, several aromatic skeletons can be considered for these compounds: Ar-Ar, Ar-O-Ar, Ar-CH_2-O-Ar, Ar-CH_2-Ar,... The various possible positions of the substituents on the aromatic rings increase dramatically the number of structures to be considered.

Three well resolved chromatographic peaks can be obtained by GC/FTIR. The three corresponding IR spectra present acceptable signal to noise ratios (Figure 1a–c). Computer spectral searches directs the structure elucidation towards aromatic compounds with CH_3 or OCH_3 groups and with an aryl-oxygen bond, and very often reveals an ortho, meta or para, substitution respectively for the compounds 1, 2 and 3.

Taking into account this method, the various observations made on the GC/FTIR spectra (mentioned on the Figure 1a–c) and the mass spectroscopy data, two structures remain to be considered.



A



B

In the case of an aryl-O-C pattern the νC-O vibration is always observed at frequency higher than $1200\,cm^{-1}$.[9] In the case of an electron donor group such as CH_3,[9] owing to resonance effects, the νC-O band is found at a higher frequency for a meta derivative than for its ortho and para homologs. This νC-O band—easily identified from its high intensity—can be observed at $1235\,cm^{-1}$ for compound 1, $1234\,cm^{-1}$ for compound 3 and $1257\,cm^{-1}$ for compound 2.

For an **A** type structure , there should not be any shift of the νC-O band in any of the 3 isomer spectra. On the contrary, for a **B** type structure, it is logical to find the C-O band at a higher frequency in the spectrum of compound 2 (meta) than in the spectra of compounds 1 and 3 (ortho and para). This **B** type skeleton is therefore the one to be considered.

2. *Fatty Acid Methyl Esters*

Esterification (BF3) followed by ether extraction of the aqueous phase obtained by extraction of a marine sediment results in a complex mixture of fatty acid methyl esters.[10] This mixture contains principally linear or branched saturated esters, hydroxylated esters, cyclopropane esters and unsaturated esters.[11] Among the latter, in the case of mono or diunsaturated derivatives, the cis and trans isomers

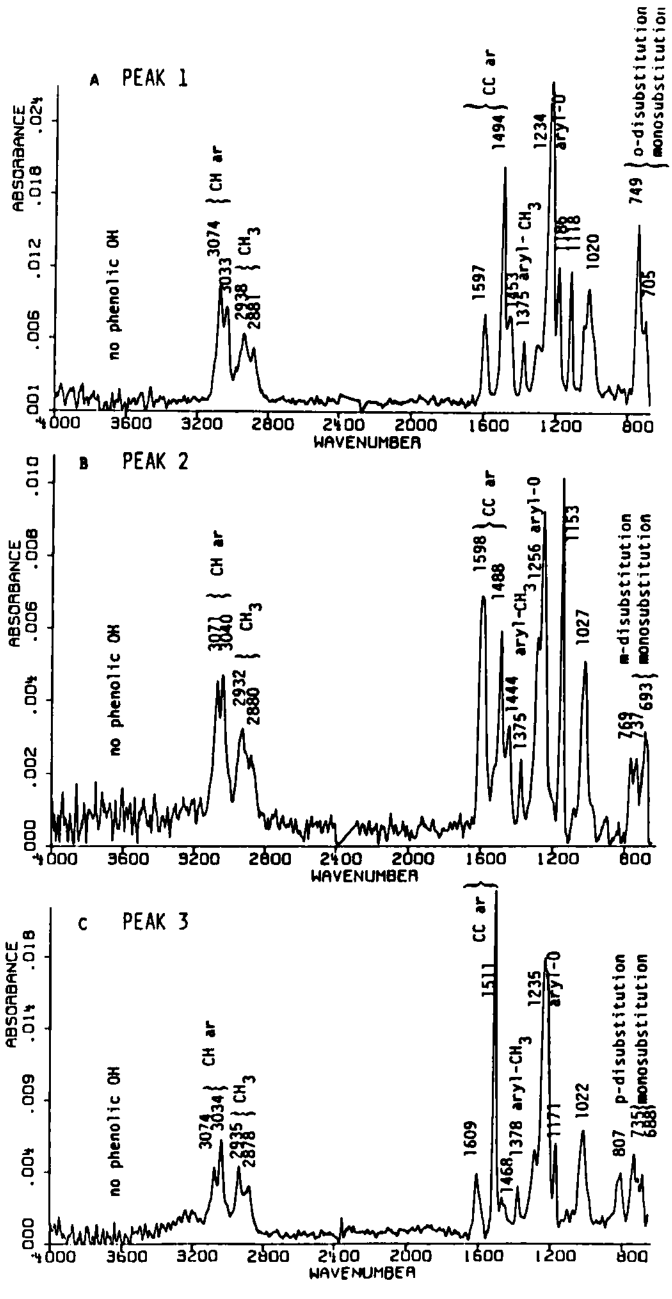


Figure 1 GC/FTIR spectra between 4000 and 650 cm^{-1} of A: peak 1; B: peak 2; C: peak 3.

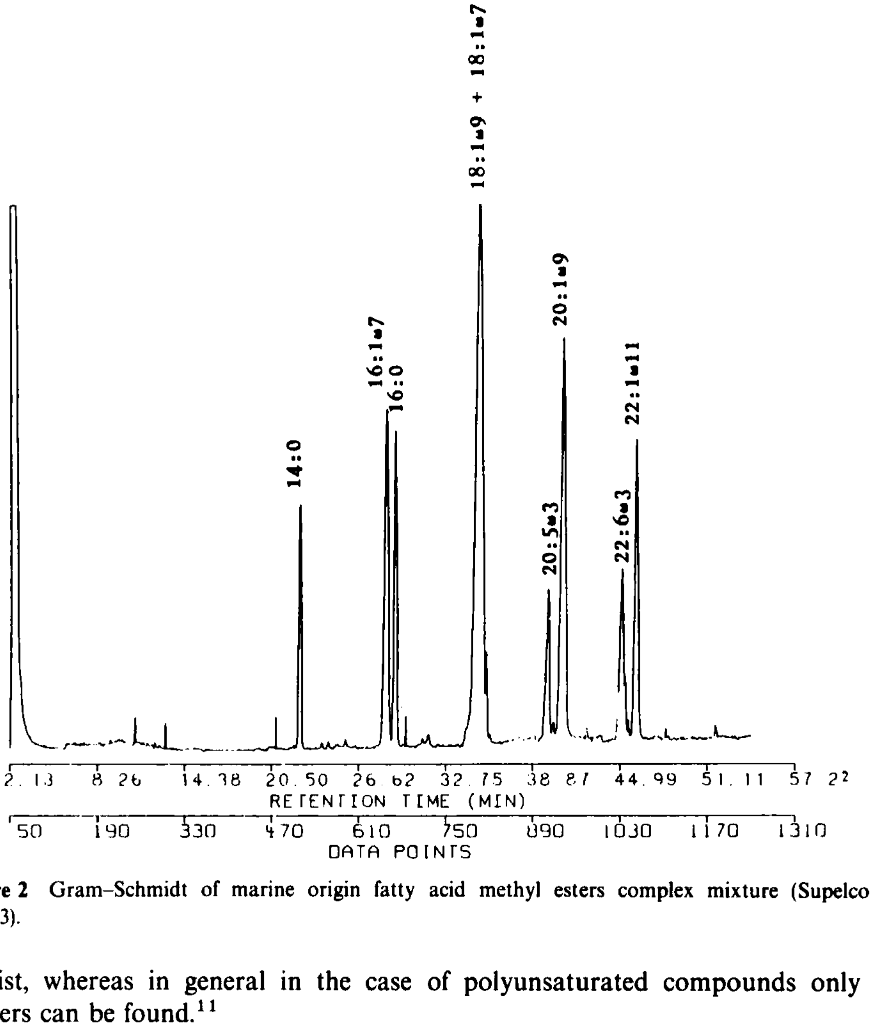


Figure 2 Gram-Schmidt of marine origin fatty acid methyl esters complex mixture (Supelco ref: 4.7033).

coexist, whereas in general in the case of polyunsaturated compounds only cis isomers can be found.[11]

Within the frame of a very general study on fatty acid methyl esters, we tried to underline how GC/FTIR complements and precises chromatography and GC/MS. For that purpose, we analyzed by GC/FTIR a great number of fatty acid methyl esters: pure standards, synthetic mixtures, commercial mixtures. An example of GC/FTIR analysis is given in Figure 2. Some other examples have already been given.[8] The preliminary results of this study clearly reveal the usefulness of GC/FTIR in this domain.

For example, a hydroxylated fatty acid methyl ester can rapidly be detected by the position of the band due to the ester group stretching vibration ($\nu C=O$). For a non-functionalized ester the band can be observed at $1759 \pm 1\,cm^{-1}$, whereas for an α or β hydroxylated ester, this band is shifted to lower frequencies ($1746 \pm 1\,cm^{-1}$) (Figure 3).

In the case of unsaturated esters, a trans isomer can be easily distinguished from its cis homolog by the position of the out-of-plane vibration (γCH) of the

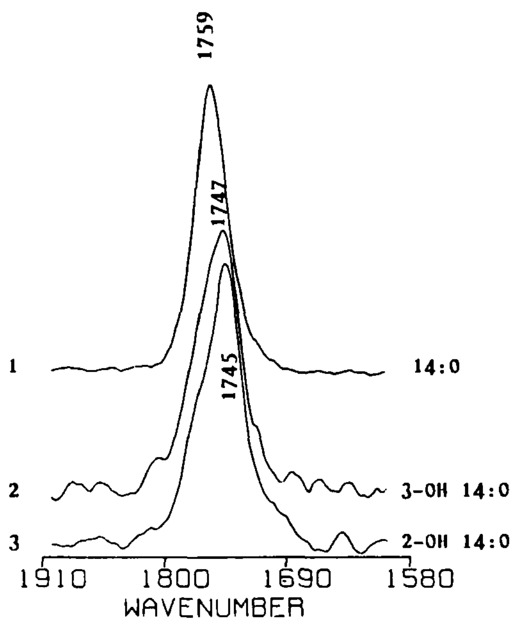


Figure 3 GC/FTIR spectra between 1900 and 1600 cm^{-1} of 1: methyl tetradecanoate (myristate); 2: methyl 3-hydroxytetradecanoate; 3: methyl 2-hydroxytetradecanoate.

ethylenic CH bond. Figure 4, shows the presence of this absorption near 960 cm^{-1} for trans isomers and near 700 cm^{-1} for cis isomers.

The 3200–2700 cm^{-1} region is particularly rich in structural information. The existence fo infrared bands near 3060 and 3000 cm^{-1} reveals the presence of cyclopropane esters (νCH_2 stretching vibrations of the three-carbon ring). A cis-unsaturated ester gives rise to an absorption near 3011 cm^{-1} (νCH). The intensity of this band increases according to the unsaturation number and will allow to determine the number of cis double bonds in the case of polyunsaturated esters. The infrared bands due to the CH_2 and CH_3 aliphatic groups appearing in that region (near 2960, 2935 and 2863 cm^{-1}) turn out to be, owing to their intensities, very useful for the quick and easy detection of a branched chain and for the determination of the chain length in the case of saturated fatty acid methyl esters.

3. *Polychlorobiphenyls*

Polychlorobiphenyls (PCB) are now considered as major polluting substances in our industrial environment, because of their potential toxicity and stability. They are industrially synthetized by direct biphenyl chloration. The non-selectivity of the substitutions leads to a complex mixture at the end of the reaction. This mixture may theoretically contain 209 congeners,[12] out of which only 103 can be

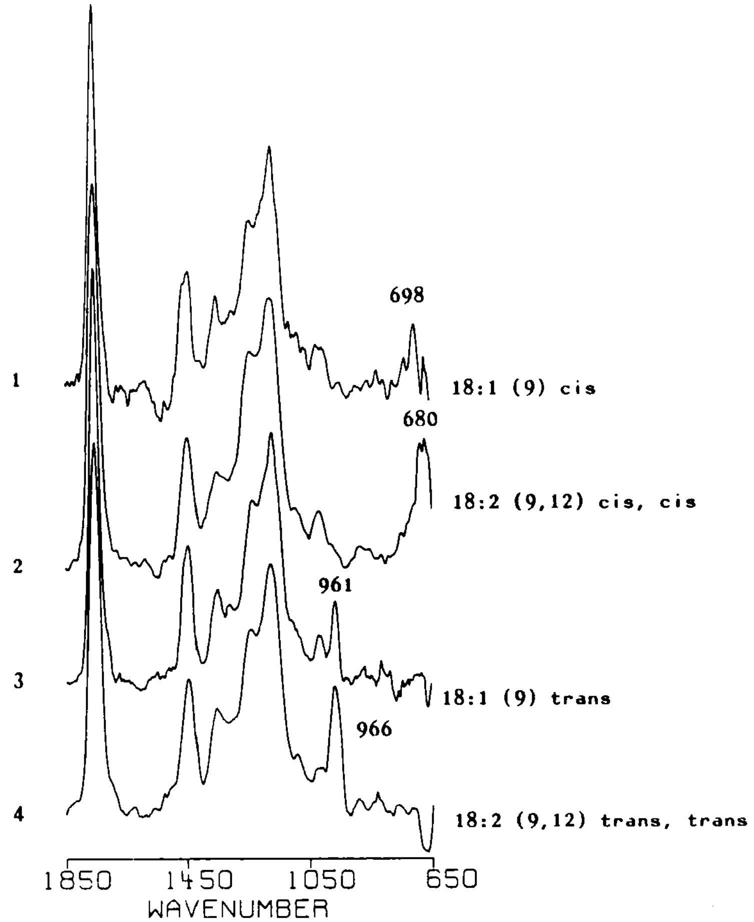


Figure 4 GC/FTIR spectra between 1850 and 650 cm^{-1} of 1: methyl cis-9-octadecenoate (oleate); 2: methyl cis-9,12-octadecadienoate (linoleate); 3: methyl trans-9-octadecenoate (elaïdate); 4: methyl trans-9,12-octodecadienoate (linoelaïdate).

considered as sterically "possible". As an example, 69 different PCB can be found in the Aroclor 1254 mixture, very often used in industry.

It is easy to understand the usefulness of an analytical method which allows detection and identification of such compounds. In this repect, GC/FTIR is able to combine the separation capability of gas chromatography and the differentiation and characterization power of infrared spectroscopy in the case of aromatic isomers.

With GC/MS, it is not always possible to distinguish 2 PCB isomers by their mass spectra only. For example that is the case for 2-chlorobiphenyl and 4-chlorobiphenyl as well as for 2,2′,4,4′-tetrachlorobiphenyl and 2,2′,5,5′-tetrachlorobiphenyl. On the contrary, these compounds can easily be distinguished by their GC/FTIR spectra, as shown in Figures 5a, b and 6a, b.

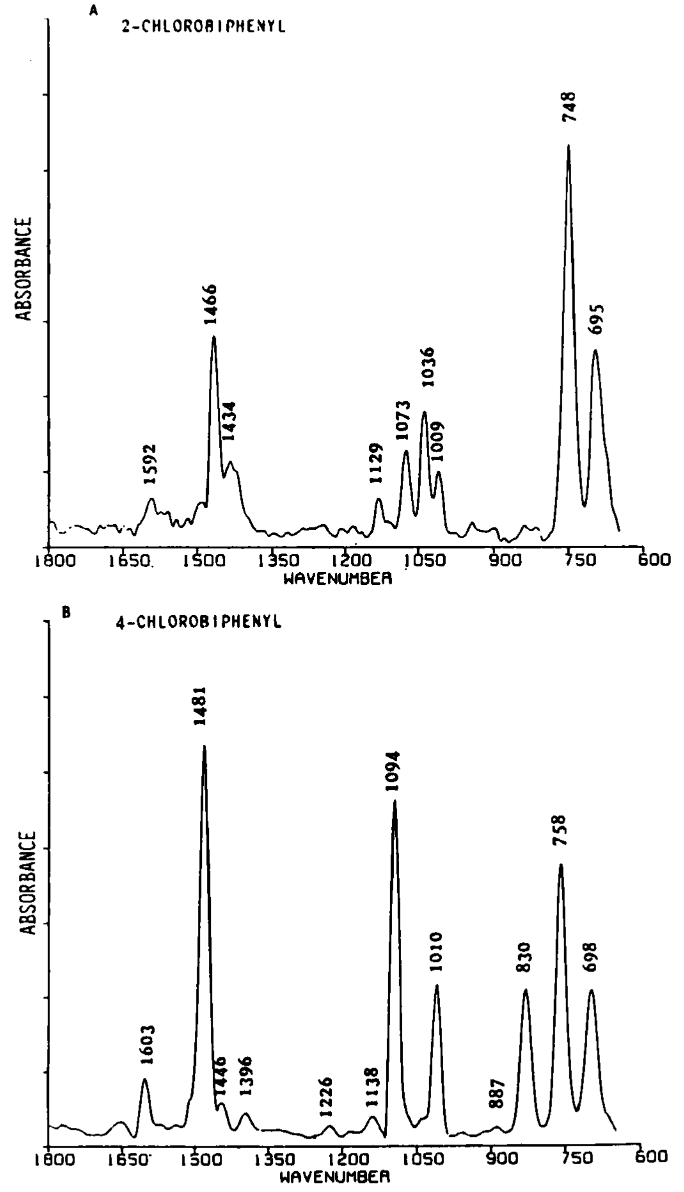


Figure 5 GC/FTIR spectra between 1800 and 650 cm^{-1} of A: 2-chlorobiphenyl; B: 4-chlorobiphenyl.

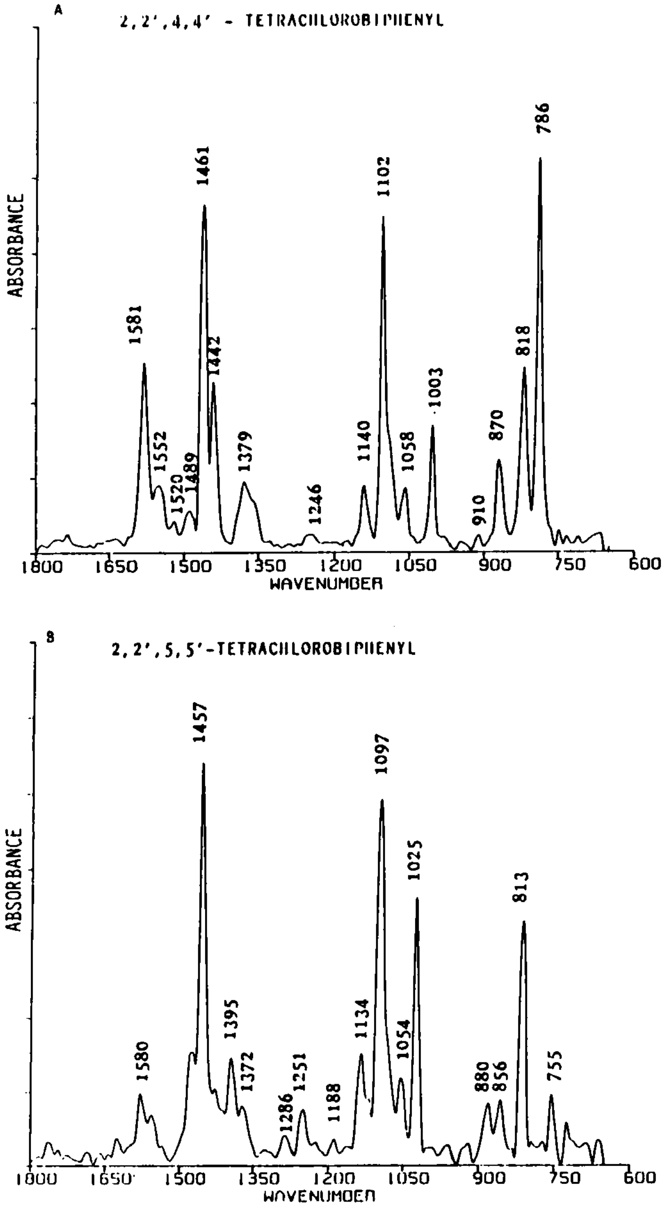


Figure 6 GC/FTIR spectra between 1800 and 650 cm^{-1} of A: 2,2',4,4'-tetrachlorobiphenyl; B: 2,2',5,5'-tetrachlorobiphenyl.

CONCLUSION

The results of the analysis of several marine origin complex mixtures made by GC/FTIR reveal the usefulness of this technique as well as its complementarity with the GC/MS technique for the structural study of complex mixtures. The complementarity between the two techniques is presently materialized in new devices coming out which allow simultaneous coupling of the three techniques: gas chromatography, Fourier transform infrared spectroscopy and mass spectroscopy.[13] With such equipment, it will now be possible to study more precisely complex mixtures down to smaller details.

References

1. K. S. Chiu, K. Biemann, K. Krishnan and S. L. Hill, *Anal. Chem.* **56,** 1610 (1984).
2. K. S. Kalasinsky, *J. Chrom. Sci.* **21,** 246 (1983).
3. D. F. Gurka and L. D. Betowski, *Anal. Chem.* **54,** 1819 (1982).
4. P. R. Griffiths, J. A. De Haseth and L. V. Azarraga, *Anal. Chem.* **55,** 1361 (1983).
5. K. H. Shafer, T. L. Hayes, J. W. Brasch and R. J. Jakobsen, *Anal. Chem.* **56,** 237 (1984).
6. M. Guiliano, P. Doumenq, G. Mille, H. Monti, C. Viskov and G. Leandri, *J. Mol. Struct.* **189,** 279 (1988).
7. J. A. De Haseth and T. L. Isenhour, *Anal. Chem.* **53,** 1977 (1977).
8. P. Doumenq, M. Guiliano and G. Mille, *Analusis,* **17,** 39 (1988).
9. N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1975), 2nd ed., Chap. 5, p. 226 and Chap. 10, p. 313.
10. J. W. Farrington and J. G. Quinn, *Geochim. Cosmochim. Acta.* **35,** 735 (1971).
11. J. W. Farrington and J. G. Quinn, *Geochim. Cosmochim. Acta.* **37,** 259 (1973).
12. K. Ballschmitter and M. Zell, *Z. Anal. Chem.* **302,** 20 (1980).
13. D. F. Gurka and R. Titus, *Anal. Chem.* **58,** 2189 (1986).