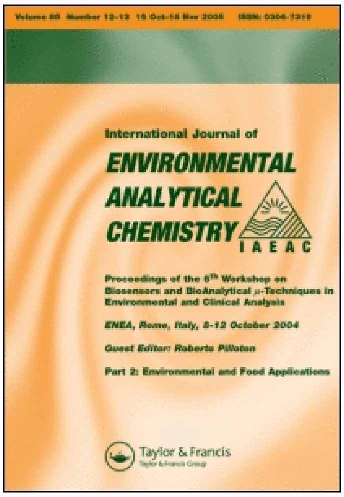

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Analysis of Hydrocarbons by Fourier Transform Infrared Spectroscopy

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This work presents the results of the determination of total hydrocarbons in marine samples using conventional infrared grating spectrometers and Fourier transform infrared spectrometers. These results given by the two methods are compared and discussed. Fourier transform infrared spectroscopy allows many difficult measurements to be made much more easily. The importance of this technique is pointed out as regards the detection threshold of the hydrocarbons, the accuracy, the sensitivity and the considerable time saving.

By Fourier transform spectroscopy using reflexion techniques (ATR: attenuated total reflectance or MIR: multiple internal reflexions) oil slicks on surface waters can also be analyzed directly without any previous chemical treatment. Other examples are also discussed and demonstrate the powerful tool of Fourier transform infrared spectroscopy for the analysis of hydrocarbons in the marine environment.

KEY WORDS: FTIR, hydrocarbons, reflexion techniques.

INTRODUCTION

Infrared spectroscopy is a widely used analytical technique for the identification and characterization of organic compounds. Several reasons may explain the power of this technique in analytical chemistry:

- ease of operation of IR spectrometers;
- ease of sampling;

— ease in which a sample may be classified according to its chemical class from its spectrum;
— variety of states in which a sample can be analyzed;
— availability of libraries of IR spectra;
— unique identification of compounds;
— accuracy to which quantitative analysis may be carried out.

In the field of the analysis of hydrocarbons the major problem being encountered is the sensitivity of the conventional grating spectrophotometer which is not adequate. We will begin with a brief outline of the FTIR technique and will discuss advantages and disadvantages of the FTIR technique with regard to dispersive IR spectroscopy. Then applications where FTIR is likely to make significant contributions will be presented.

FOURIER TRANSFORM INFRARED METHOD

With conventional spectrometers (dispersive instruments) each frequency of the polychromatic radiation after passing through the sample must be differentiated spatially (prism or grating), analyzed and detected (Figure 1).

A lot of disadvantages of dispersive IR instruments are inherent in the design of conventional instruments:

— many moving parts;
— no internal reference for frequency accuracy;
— stray light;
— only a small portion of total IR energy is used;
— a long time is needed to acquire the spectrum.

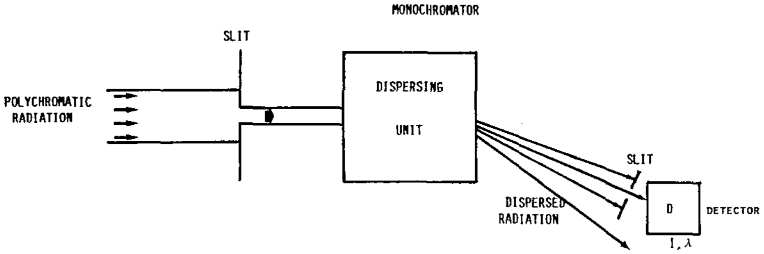

FIGURE 1 Schematic infrared dispersive instrument.

Consequently with conventional spectrometers (dispersive instruments) you can't measure IR spectra of trace components, transient species, strong absorbers, scatterers or samples having a low baseline transmittance (less than 1%).

A beam radiation can be examined spectroscopically either by passing it through a dispersive system (prism and, or grating) or by using interference techniques. The later way which needs the use of an interferometer instead of a monochromator shows important advantages for the measurement of infrared spectra. The optical system of a Fourier transform spectrometer is the Michelson interferometer which is shown schematically in Figure 2.

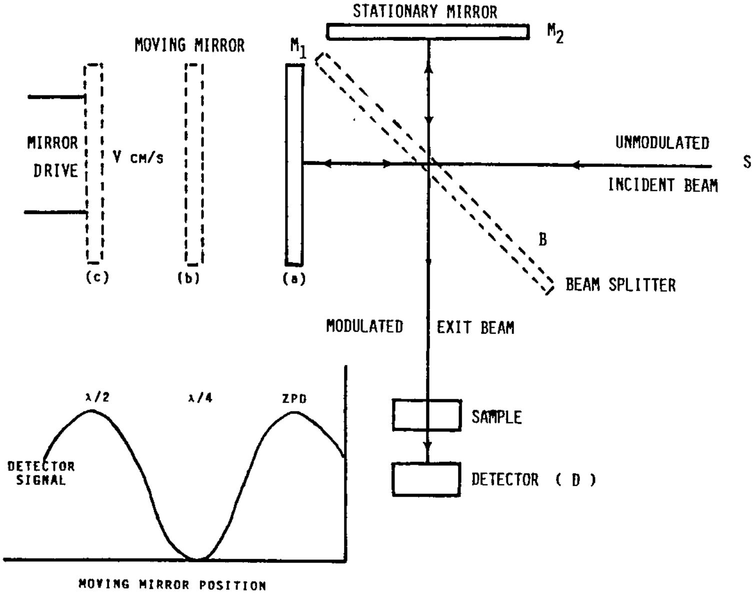

FIGURE 2 Schematic Michelson interferometer.

This commonly used Michelson arrangement includes a source (*S*), a detector (*D*) , a beam splitter (*B*) and two mirrors (M_1 and M_2).

The beam splitter is a crystal of potassium bromide (KBr) coated with germanium (Ge) it can transmit 50% of the light to the mirror M_1 and reflect 50% of the light to the mirror M_2. The two mirrors are perpendicular, M_2 is stationary while M_1 moves at a constant velocity V cm/s. When the two mirrors are equidistant from the beam splitter if a monochromatic radiation of wavelength λ enters the interferometer, the radiation will be split into two components at the beam splitter, then it will be reflected at each of the mirrors and finally it will be recombined at the beam splitter. The resulting rays are in phase, their amplitudes are additive and the signal given by the detector will be maximum. If the mirror M_1 is moved by $\lambda/4$ to position (b) the pathlength difference between the two rays reaching the detector is $\delta = 2(\lambda/4) = \lambda/2$ and the two rays are exactly out of phase and the detector signal is zero. Such constructitive or destructive interference occurs at positive or negative mirror displacements of $\lambda/4$ equivalent to pathlength differences of $\lambda/2$ with intermediaire values in between. So that the detector output signal, or, interferogram varies cosinusoidally with a frequency $f = (V/(\lambda/2)) = 2V/\lambda$. For a monochromatic radiation the intensity of the light reaching the detector $I(\delta)$ can be expressed as:

$$I(\delta) = B(\bar{v}) \cos 2\pi\bar{v}\delta.$$

$B(\bar{v})$:Product of the incident intensity of light of frequency $\bar{v}$, by a factor for beam splitter efficiency, detector response, amplifier characteristics.

(δ) :Retardation or optical path difference.

For a polychromatic radiation the output of the interferometer is the summation of all the interferences as each wavelength component interacts constructively or destructively with every other component. The resulting signal is an interferogram which is a complex pattern of light amplitude as a function of distance travelled by the moving mirror. The relationship between the intensity of the interferogram as a function of mirror travel $I(\delta)$ and the intensity of the source as a function of optical frequency $B(\bar{v})$ is given by a cosine Fourier transform

$$I(\delta) = \int_{-\infty}^{+\infty} B(\bar{v}) \cos 2\pi\bar{v}\delta dv$$

and the inverse transform

$$B(\bar{v}) = \int_{-\infty}^{+\infty} I(\delta) \cos 2\pi\bar{v}\delta d\delta$$

or

$$B(\bar{\nu}) = 2\int_{0}^{+\infty} I(\delta)\cos 2\pi\bar{\nu}\delta\, d\delta$$

relates the interferogram $I(\delta)$ to the optical spectrum $B(\bar{\nu})$.

So, by passing the light of a polychromatic source through a Michelson interferometer an interferogram $I(\delta)$ is produced which is characteristic of the source and the beam splitter. If the output signal is passed through a sample, the sample will absorb certain radiations from $I(\delta)$ depending on its chemical nature. The signal that emerges from the sample is an interferogram $I(\delta)$ which is characteristic of the sample, the source and the beam splitter (Figure 3).

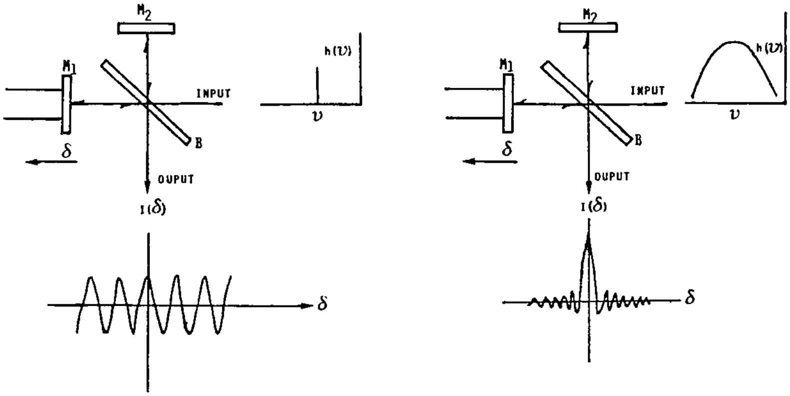

FIGURE 3 Interferograms of mono and polychromatic sources.

Figures 4 through 8 show the evolution of the infrared transmittance spectrum of No. 2 fuel oil taken at 2 cm^{-1} resolution using an FTIR system (Nicolet 5DX). Figure 4 is the interferogram $I(\delta)$ of the background (no sample in the beam) and Figure 5 shows the interferogram obtained with a No. 2 fuel oil sample. Fourier transform of these two interferograms produces the energy spectra $B(\nu)$ of the background (Figure 6) and the sample (Figure 7). The transmittance of the sample (Figure 8) is obtained by rationing the two single beam transmission spectra. The difference in principles operation between a Fourier transform spectrometer and a conventional grating instrument results in several advantages of Fourier transform spectroscopy (Figure 9).

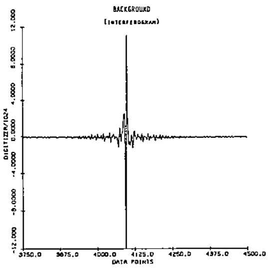

FIGURE 4 Interferogram of the background.

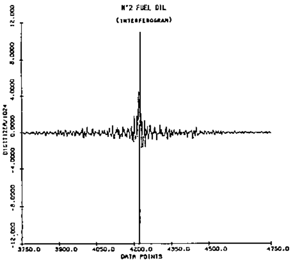

FIGURE 5 Interferogram of No. fuel oil.

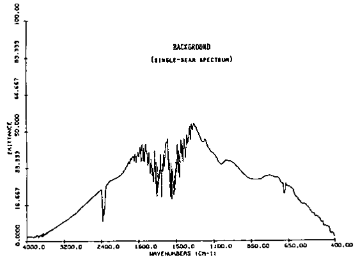

FIGURE 6 Single beam spectrum of the background.

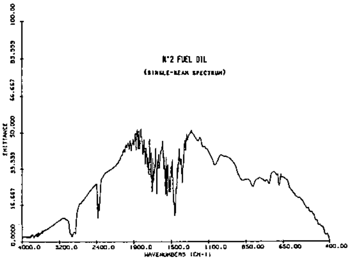

FIGURE 7 Single beam spectrum of No. 2 fuel oil.

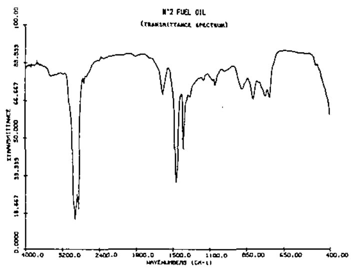

FIGURE 8 Transmittance spectrum of No. 2 fuel oil.

Felgett's advantage or multiplex advantage

An interferometric system measures all wavelength at once, and a dispersive instrument picks off one wavelength interval at a time. Since the interferometer detects and measures all wavelengths elements simultaneously it is able to measure a complete spectrum in the same time it takes a dispersive system to measure one resolution element. So for equivalent experiments interferometric systems are N times faster (N: number of resolution elements in the spectrum) or have $\sqrt{N}$ more analytical sensitivity than the dispersive spectrometer. For example:

$$\text{resolution } \Delta\nu = 2\,\text{cm}^{-1}.$$

$$\text{spectral range: } 4{,}000\text{–}400\,\text{cm}^{-1}\ \nu_R = 3{,}600\,\text{cm}^{-1}$$

$$N = \nu_R/\Delta\nu = 3{,}600/2 = 1{,}800 \quad \sqrt{N} \simeq 42.$$

Jacquinot's advantage

An interferometric system has no energy limiting slits and allows more energy to reach the sample and subsequently the detector.

More energy at the detector yields higher analytical sensitivity. The calculated numerical value of the Jacquinot's advantage is the order of 40 × to 50 × over dispersive system. Consequently a higher S/N and a better precision and accuracy is obtained with interferometric systems.

Conne's advantage

In interferometric systems a helium–neon laser is used to calibrate the wavelength of each scan, thus ensuring extremely high accuracy of wavelength calibration. This is a requirement for spectral manipulation of data.

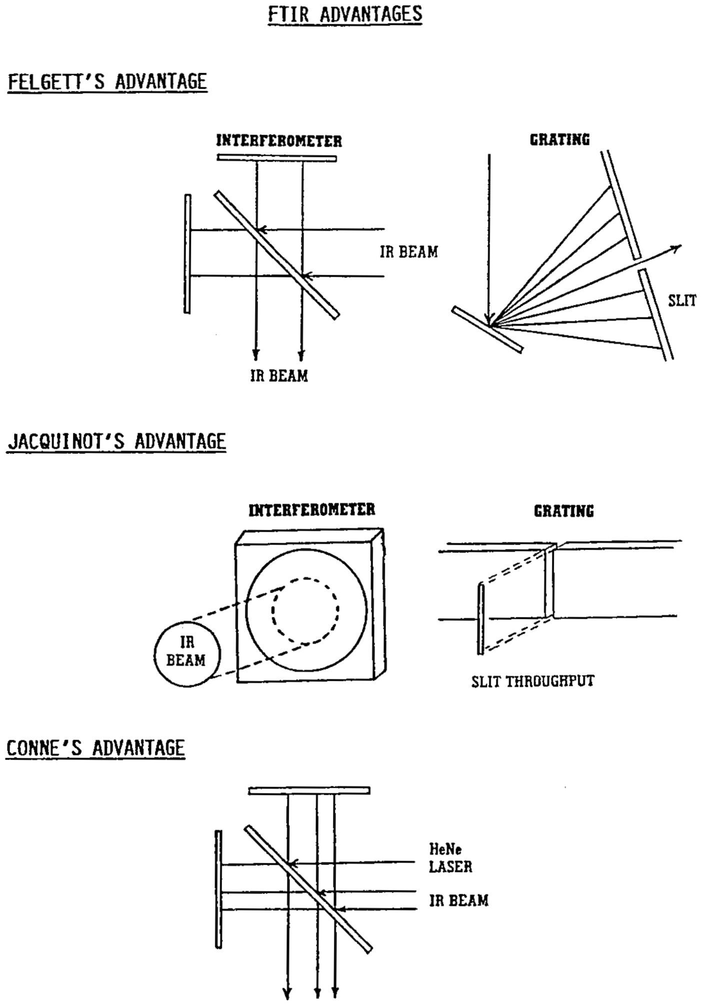

FIGURE 9 Schematic representation of FTIR advantages (from Nicolet S.A.).

Resolution

With FTIR spectrometers the spectrum is measured at a constant resolution over the entire spectral region, as opposed to grating instruments in which the resolution varies with frequency.

Stray light advantage

In an interferometric system each infrared frequency is chopped by the interferometer at a different frequency (proportional to ν). The result is that stray light is eliminated from the interferometer experiment.

Heat effects

Heat transfers from the source to the sample in a dispersive system can cause decomposition of labile or heat sensitive samples because of the close proximity of the two. In an interferometric system the sample is far removed from the source of radiation, after the interferometer and next to the detector. So heat transfers do not occur.

Mechanical simplicity

In conventional dispersive spectrometers there are many moving components: grating, cams, filters, slits, mirrors, choppers,.... In an interferometric system there is only the moving mirror.

Fourier Transform Infrared spectroscopy presents also some disadvantages, such as:

— the price of the apparatus;
— the necessity of well qualified people to run the spectra and to do the maintenance of the apparatus;
— Fourier transform infrared spectrometers are generally single-beam apparatus;
— Fourier transform infrared reference spectra are still less numerous.

APPLICATIONS OF FTIR SPECTROSCOPY TO HYDROCARBON ANALYSIS

Quantitative analysis of hydrocarbons in water

Infrared spectroscopy is a widely used tool in the world for the identification of organic compounds. It is the most commonly used spectroscopic technique for the quantitative analysis of water dispersed oils.

Several methods for isolation and determination of oil are described in the literature. Following the work of Simard and coworkers[1] the determination of oil in water by extraction into carbon tetrachloride and measurement of the infrared absorbance in the region 3,200 cm^{-1} (3.12 μm) to 2,800 cm^{-1} (3.57 μm) has become a widely used method. Standard methods based on this procedure have been published. Four methods of calculation are described in the literature:

(i) Simard and co-workers[1] used the sum of the absorbances at 2,925, 2,860 and 2,960 cm^{-1} which they assigned to CH_2, CH_3 and CH groups respectively.

(ii) Coles and co-workers[2] also used the sum of three absorbances but they used the absorptions at 2,930, 2,960 and 3,030 cm^{-1} attributing the peak at 3,030 cm^{-1} to CH aromatic groups, the peak at 2,960 cm^{-1} to CH_3 groups and the peak at 2,930 cm^{-1} to CH_2 groups.

(iii) Method API 733-58[3] uses the sum of the absorbances of the two peaks at 2,930 and 3,030 cm^{-1}.

(iv) Other authors use only a single peak at 2,930 cm^{-1}.[4-7]

Whatever the calculations the major problem is the choice of an oil for calibration. Generally when a sample of the oil actually being measured is not available, the use of a synthetic oil, a mixture of hexadecane (37.5%), iso-octane (37.5%) and toluene (25%) appears to have been accepted. Method API 733-58 quotes the accuracy of the method as ±10% when using the authentic oil for calibration and ±20% if the synthetic oil is used except when oils of high aromatic content are determined.

All the methods based on a CCl_4 extraction of one liter sample followed by an IR measurement have shown a detectability of 0.05 ppm.

A detectability of 0.001 ppm can be reached with a three liter sample, a 5 cm pathlength cell and a scale expansion spectrometer.

In the field of the analysis of hydrocarbons the major problem being encountered is the sensitivity of the conventional dispersive infrared spectrometers.

Comparison between dispersive and interferometric systems has never been done in the field of the analysis of hydrocarbons in sea-water. We have conducted this comparison in two ranges of concentrations:

$$0.05 < [C] < 4\,\text{ppm}$$

$$[C] < 0.05\,\text{ppm}.$$

For the first range of concentrations $0.05 < [C] < 4$ ppm the comparison has been made with three calibration oils: No. 1 fuel oil, synthetic oil (mixture of 37.5% hexadecane, 37.5% iso-octane and 25% toluene) and No. 2 fuel oil. No major difference has been found (Figures 10 and 11).

Instead of plotting the absorbance versus the concentration for the calibration curves, we have plotted with the interferometric system the area of the absorptions between 3,000 and 2,820 cm^{-1} versus the concentrations. Several reasons may explain this choice:

- firstly, with computers it is easier to measure the area of the absorptions between 3,000 and 2,820 cm^{-1} than the absorbances of the three bands at 2,960, 2,925 and 2,860 cm^{-1};
- secondly, it is faster;
- thirdly, for very low concentrations, after having rationing the two single beam transmission spectra (sample and background), it may happen a negative baseline and consequently a wrong determination of the absorbances. On the contrary, the area of the absorptions between two wavelengths does not depend on the position of the baseline;
- finally, the determination of the area is more precise, particularly in the case of complex mixtures such as hydrocarbons. By this method the intensities, the shapes and the widths of the different absorptions are taken into account. For the calibration curves, when the absorbance of the absorptions is plotted versus the concentrations only the intensities of the bands are considered.

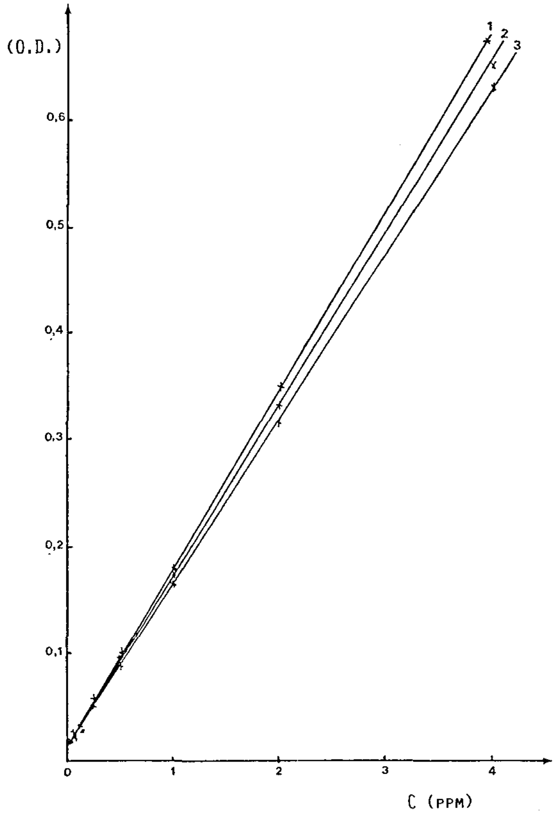

FIGURE 10 Calibration curves (dispersive instrument). $0.05 < [C] < 4$ ppm. (1) No. 1 fuel oil. (2) Standard mixture. (3) No. 2 fuel oil.

When the concentrations of hydrocarbons are less than 0.05 ppm, dispersive instruments cannot be used anymore because their sensitivities are not high enough. 0.05 ppm is the detection limit for routine analysis of hydrocarbons with dispersive systems. With interferometric systems the energy reaching the detector is more important and allows a higher analytical sensitivity.

Without changing the analytical conditions (2 cm pathlength cell and 25 scans) the detection limit is close to 0.0004 ppm (Figure 12). The choice of the number of scans is not critical. We have tried several numbers of scans (from 1 to 100) and have found results

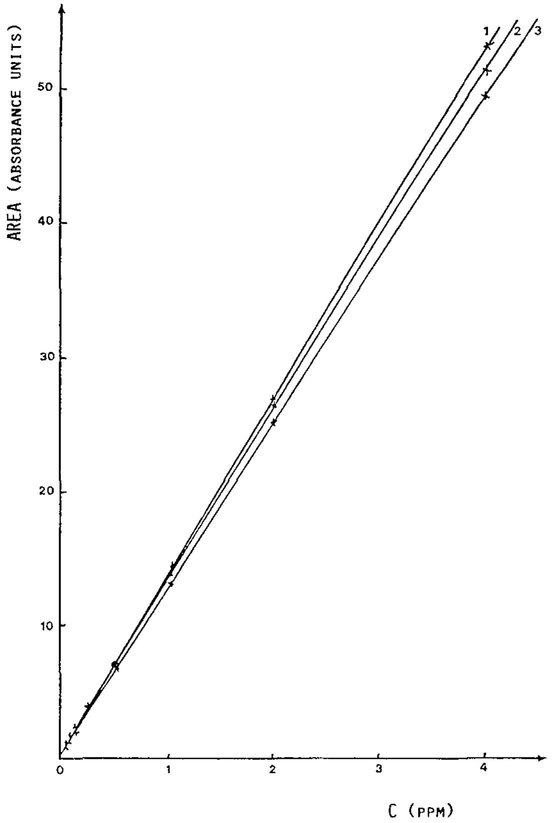

FIGURE 11 Calibration curves (interferometric instrument) $0.05<[C]<4$ ppm. (1) No. 1 fuel oil. (2) Standard mixture. (3) No. 2 fuel oil.

within an error less than 10%. We have chosen 25 scans in order to have both, a good signal to noise ratio and a reasonable time to run the analysis (20 to 30 s). Figure 13 shows the infrared spectra between 3,200 and 2,700 cm^{-1}, of 0.0005 mg of hydrocarbons extracted from one liter of sea water. By using a 5 cm pathlength cell the detection limit of the FTIR method can be lower to 0.0002 ppm. This threshold detectivity has been obtained with a Nicolet 5DX FTIR instrument equipped with a DTGS (deuterated triglycine sulfate) detector. More sensitive detectors are now available such as liquid nitrogen cooled mercury/cadmium/telluride (MCT) detectors.

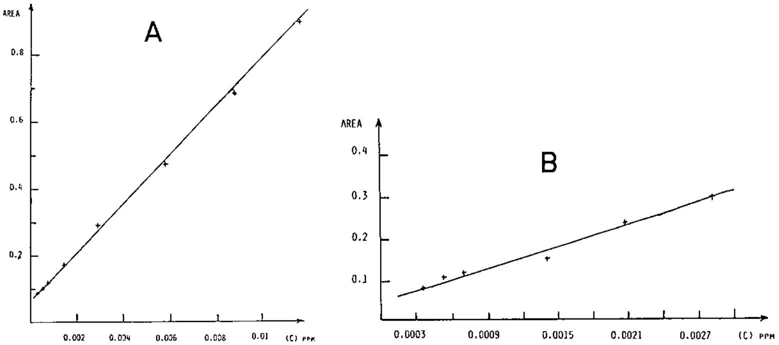

FIGURE 12 Calibration curves (interferometric instrument). No. 2 fuel oil. (a) $0.002 < [C] < 0.01$ ppm. (b) $0.0003 < [C] < 0.03$ ppm.

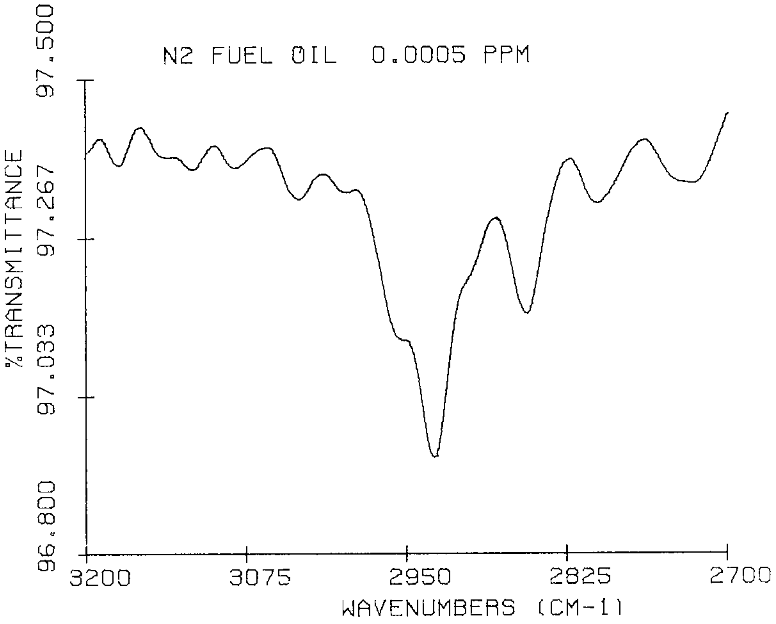

FIGURE 13 Infrared spectrum (3,200–2,700 cm^{-1}) of No. 2 fuel oil. $C = 0.0005$ ppm.

Narrow range or medium range MCT detectors have specific detectivity values ten times greater than DTGS detectors. With these kinds of detectors the threshold detectivity for the analysis of hydrocarbons may still be lower by an order of magnitude.

The main conclusions from the comparative study: dispersive system/interferometric system concerning the determination of amounts of oil in water, are:

(i) FTIR spectroscopy has almost reached the sensitivity of other analytical techniques and becomes a valuable tool in the field of the analysis of hydrocarbons. Very small amounts (0.0005 mg) of hydrocarbons in one liter of sea water can be detected by FTIR spectroscopy in a routine way;

(ii) to obtain the same sensibility with dispersive system 1001 of water must be sampled and extracted. So the number of samples which can be studied is limited (storage, transport,...) (Table I).

(iii) using an interferometric system and if a detectability of 0.05 ppm is sufficient only 10 ml of water have to be sampled. This is very important when many samples have to be taken specially as regards handling, storage, transport, conservation....

TABLE I

Results of the comparative study: dispersive system/interferometric system.

	Dispersive system	Interometric system
Detectability PPM	0.05	0.0005
Volume of sample	1 L	1 L
Volume of sample for the same detectability given by the other method	100 L	10 mL

Analysis of fuel oils by multiple internal reflectance FTIR spectroscopy

The higher sensibility of interferometric system can be applied for multiple internal reflexion studies. Multiple internal reflectance (MIR) spectra are obtained from a thin film of oil spread on the surface of a special crystal (Zn Sr or KRS-5). This approach can be used for thin oil films on water or very heavy oils (Figure 14).

The method consists in dipping a MIR crystal through the oil film several times. Then the crystal is gently shaken to remove water droplets. The sample is now conditioned for IR spectral analysis. This procedure presents some advantages:

—no chemical treatment of the sample is required before the analysis, so no residual compounds, generally used for the extraction (solvents or dehydrating reagents), may interfere;

—the MIR technique eliminates the extraction procedure necessary with other techniques and thus bypasses the possibility of chemical degradation of the sample;

—spectra of optically opaque materials are easily measured;

—the cleaning of the IR accessories (crystal) is every easy;

—the cost of the analysis is low.

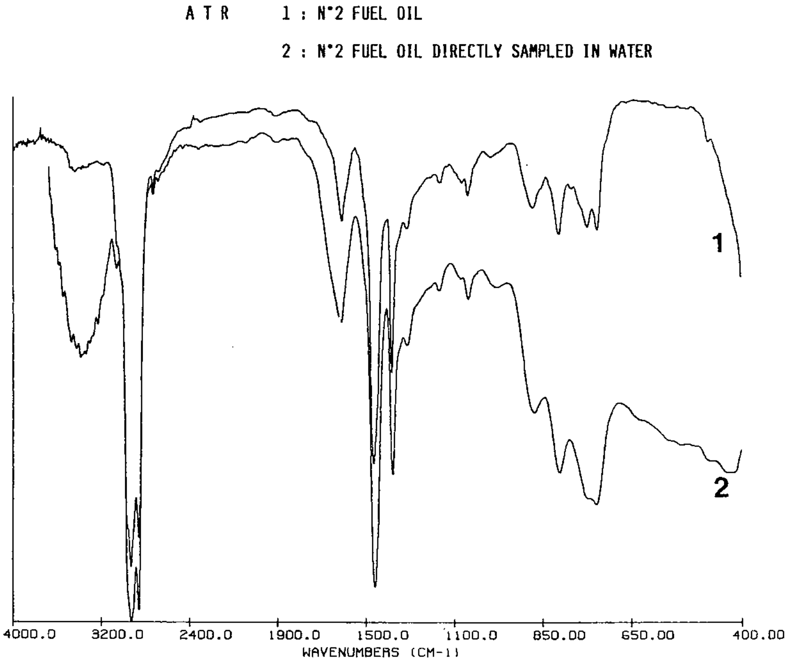

FIGURE 14 Multiple internal reflexion spectrum of: (1) No. 2 fuel oil. (2) No. 2 fuel oil directly sampled on surface water.

Nevertheless the disadvantage of multiple internal reflectance spectroscopy is that no reference spectra are available.

Qualitative analysis of fuel oils by FTIR spectroscopy

Infrared spectra of fuel oils are generally very similar. Only small differences do exist between two fuel oils. The higher sensibility of interferometric systems can be used for fingerprinting and to detect differences between several fuel oils more easily. The most important region generally used for this fingerprinting is 950–650 cm^{-1}. In this spectral range are found aromatic CH out of plane vibrations γCH and CH_2 rocking vibrations $r CH_2$. Between 950 and 700 cm^{-1} each fuel oil generally shows seven absorptions at 870, 847, 810, 780, 767, 743 and 724 cm^{-1} those relative intensities vary with the nature of the oil. For light oils the most intense absorptions are at 810, 767, 743 and 724 cm^{-1} and for heavy oils at 870, 810 and 743 cm^{-1} (Figure 15). Within the same class of fuel oils (light oils for example) differences can also be detected (Figure 16) and can be used to characterize fuel oils or to study the weathering of an oil.

Several works have already be done in this field[8-12] with dispersive instruments. Using Fourier transform spectrometers this kind of work will certainly be easier and more accurate.

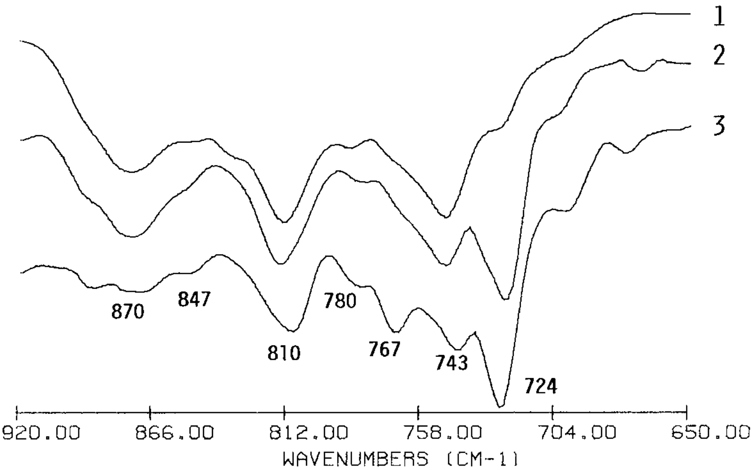

FIGURE 15 Infrared spectra (920–650 cm^{-1}) of fuel oils. (1) Bunker C. (2) No 2 fuel oil. (3) Irak.

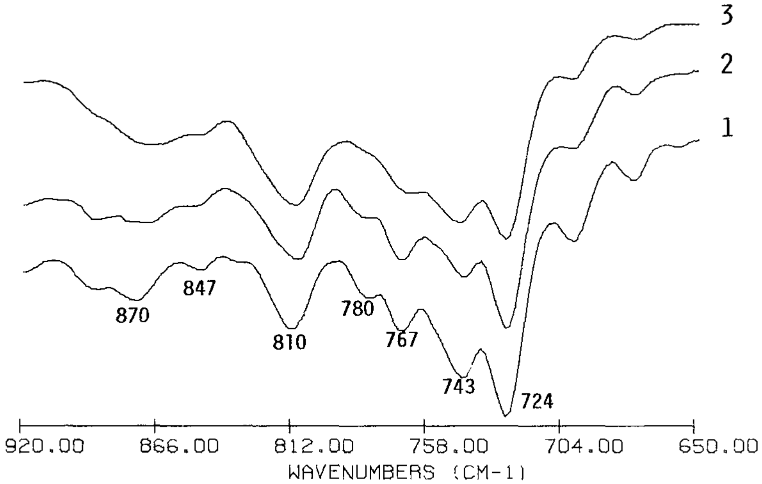

FIGURE 16 Infrared spectra (920–650 cm^{-1}) of light fuel oils: (1) South Lousiana. (2) Irak. (3) Souedie.

Analysis of polycyclic aromatic hydrocarbons (PAH) separated by thin layer chromatography (TLC)

After having been separated by thin layer chromatography, polycyclic aromatic hydrocarbons can be analysed by FTIR spectroscopy. The adsorbent (alumina gel or silica gel) containing the compound is scraped from the TLC plate and transferred to a glass vial containing a Wick Stick (porous triangle of pressed potassium bromide).[13] The Wick Stick concentrates most of the sample at the apex of the KBr triangle. One or 2 mm of the tip is cut off, mixed with KBr powder and incorporated into a 3 mm microdisk and then analysed. Figure 17 shows the infrared spectra of 0.5 μg of benzo(a)pyrene separated from a mixture of several polycyclic aromatic hydrocarbons by thin layers chromatography. The sensitivity of this method depends on the nature of the samples, but in most cases 200 to 500 ng of a specific compound can be easily detected.

Miscellaneous applications of FTIR spectroscopy

In the field of the analysis of environmental pollutants or complex organic mixtures a lot of examples show the power of the FTIR technique.

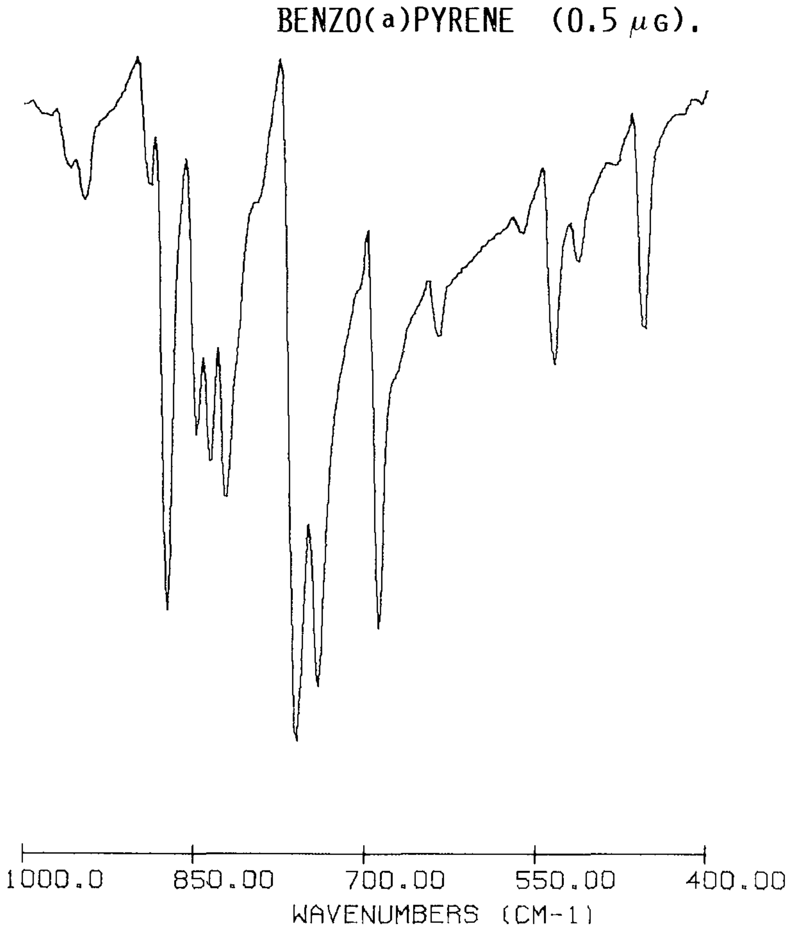

FIGURE 17 Infrared spectrum (1,000–400 cm^{-1}) of benzo(a)pyrene (0.5 μg) separated by thin layer chromatography.

—Detection of atmospheric pollutants:[14] infrared detection of air pollutants has been extended to the parts-per-billion sensitivity range (acetylene 0.02 ppb; carbon monoxide, ethylene, propylene 1 ppb; methane 0.6 ppb....). The increased detection sensitivity results from the use of the scanning Michelson interferometer, cooled solid state detectors, the fast minicomputer and the multiple pass long path cell.

- Coal and coal products structures.[15–23]
- Identification of chlorobiphenyl isomers.[24]
- Polycyclic aromatic hydrocarbon analysis by matrix isolation.[25,26]

Matrix isolation Fourier transform infrared spectroscopy is a technique highly suited to the identification of polycyclic aromatic hydrocarbons (naphthalene, anthracene...) and nitrogen or oxygen-containing aromatic hydrocarbons (pyrole, carbazole, indoles, quinolines, acridine, phenazine, phenols, naphtols...). Isomeric compounds can be easily distinguished by this technique.

CONCLUSION

FTIR spectroscopy is now a valuable technique for the analysis of environmental pollutants and complex organic mixtures. This technique has both proved to be a very sensitive one (0.0004 ppm for hydrocarbons in sea water) and a fast analytical method. Fourier transform infrared spectroscopy allows many difficult measurements to be made much more easily: oil slicks on surface waters by multiple internal reflexions, fuel oils, polycyclic aromatic hydrocarbons separated by thin layer chromatography, polycyclic aromatic hydrocarbons or N or O-containing aromatic hydrocarbons by matrix isolation....

FTIR spectrometers can be coupled to gas chromatography or to liquid chromatography. GC/FTIR and GC/MS are two complementary techniques, especially in the field of environmental samples such as hydrocarbon mixtures. In this case GC/MS will give more information if the sample contains largely non-aromatic compounds and GC/FTIR will be advantageous in the case of predominant aromatic compounds. In the case of isomer mixtures, particularly aromatic isomers, the MS fragmentation patterns of isomers are frequently very similar and they cannot be identified whereas the infrared spectra can often allow a complete identification and an unambiguous differenciation between several isomers.[27] Moreover, FTIR spectroscopy is actually used in doubly hyphenated technique such as GC/FTIR/MS. Preliminary results[28] suggest a promising role for this technique in real world sample analysis and it is reasonable to predict that more and more laboratories will soon be equipped. They will have an easier, a more complete and a more precise analytical tool for the identification, the quantification and the structural determination of complex mixture components.

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