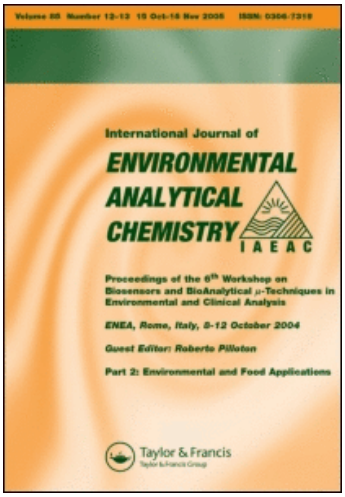

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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Maria M. Gomez-taylor[a]; Donald Kuehl[a]; Peter R. Griffiths[a]
[a] Department of Chemistry, Ohio University, Athens, Ohio, U.S.A.

To cite this Article Gomez-taylor, Maria M. , Kuehl, Donald and Griffiths, Peter R.(1978) 'Application of Fourier Transform Infrared Spectroscopy to the Identification of Trace Organics in Water', International Journal of Environmental Analytical Chemistry, 5: 2, 103 — 117
To link to this Article: DOI: 10.1080/03067317808071136
URL: http://dx.doi.org/10.1080/03067317808071136

Intern. J. Environ. Anal. Chem., 1978, Vol. 5, pp. 103–117

Printed in Great Britain

Application of Fourier Transform Infrared Spectroscopy to the Identification of Trace Organics in Water†

MARIA M. GOMEZ-TAYLOR, DONALD KUEHL and PETER R. GRIFFITHS‡

Department of Chemistry, Ohio University, Athens, Ohio 45701, U.S.A.

(*Received June 10, 1977*)

The application of dual-beam Fourier transform infrared spectroscopy to the on-line identification of organic water pollutants separated by gas chromatography and high performance liquid chromatography is described. The materials are concentrated using neutral polystyrene resins, eluted with diethyl ether, and chromatographed. For GC–IR measurements, readily identifiable spectra from compounds originally present at a level of 2 ppb may be obtained, and if procedures are optimized an increase in sensitivity of at least an order of magnitude is predicted. HPLC–IR measurements using conventional flow-through cells are less sensitive, and a procedure for solvent elimination is suggested which will yield submicrogram detection limits.

KEY WORDS: Fourier transform, IR spectroscopy, trace organics, water.

INTRODUCTION

In the past decade the number of chemical and analytical applications of Fourier transform infrared (FT–IR) spectroscopy has multiplied enormously. Ten years ago the number of chemists using mid infrared Fourier spectrometers could be counted on the fingers of one hand; today FT–IR spectroscopy is being used as a routine tool by many of the major analytical laboratories in this country. There are several reasons for the rapid increase in the popularity of FT–IR, the most important of which is undoubtedly the

†Paper presented at the 7th International Symposium on the Analytical Chemistry of Pollutants, Georgia, U.S.A., April 1977.

‡Author to whom all correspondence should be addressed.

increased sensitivity or decreased measurement time of a mid infrared Fourier transform spectrometer compared with a conventional grating spectrophotometer.

These advantages, which are due in part to the multiplexing of the spectral information and in part to the increased optical throughput of an interferometer compared with a scanning monochromator, are not as great as has been claimed by several spectroscopists in the past. On the average the sensitivity of a modern commercial FT–IR spectrometer operating from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution is about ten times that of a grating spectrometer operating under the same conditions.[1] However since an N-fold improvement in sensitivity translates into a reduction in the measurement time required to achieve a given signal-to-noise ratio (S/N) of a factor of N^2, any application where there is a limited time during which spectral data can be acquired is usually best performed using an FT–IR spectrometer. The experiments where the infrared spectrum of chromatographically separated components is measured as they elute from a gas chromatograph (GC) or high performance liquid chromatograph (HPLC), which will be described in this paper, certainly fall into this category.

There are other secondary factors which also account for the popularity of FT–IR spectroscopy, and of these the most important is the presence of a data system, which is an integral component of all contemporary FT–IR spectrometers. The data system is required for the acquisition of the infrared signal (or *interferogram*) and for performing the last Fourier transform (FFT) immediately after data acquisition has ended. However many other arithmetic operations may be performed on spectral arrays, in particular the scaled subtraction of absorbance spectra for spectral stripping experiments.[2] A large amount of mass memory, such as a magnetic tape or disc system, also allows the storage of many interferograms before they are computed, a feature which is again made use of extensively in the identification of chromatographically separated factions.

These experiments, which are commonly abbreviated to GC–IR (when the separation is performed on a GC) and LC–IR (when an HPLC is used), are becoming increasingly important for the identification of trace organic pollutants in water, and in this paper several recent developments in GC–IR and LC–IR will be described. GC–IR experiments are now at a fairly advanced stage and the application of these systems to water pollutant identification can be readily illustrated. LC–IR systems are at a much earlier stage in their development and in this paper we will attempt to summarize both the current state-of-the-art and to forecast future developments.

GC–IR

In most GC–IR systems the effluent from the chromatograph is continuously

passed through a light-pipe gas cell. Transmittance spectra of the contents of the light-pipe are measured either at regular intervals of approximately one second or during the time that each chromatographic peak is present in the light-pipe. Although systems for GC–IR measurements have been described for over a decade,[3–6] the first equipment capable of measuring spectra with detection limits of less than one microgram for common organic compounds was only described quite recently. The turning point in the development of sensitive GC–IR systems was the commercial availability of the liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Before this detector could be used, the only mid infrared detector readily compatible with medium resolution rapid-scanning interferometers, such as the one used in the Digilab FTS-14 FT–IR spectrometer, was the triglycine sulfate (TGS) pyroelectric bolometer, which is over an order of magnitude less sensitive than the MCT detector.

The MCT detector cannot be substituted for the TGS detector on commercial rapid-scanning FT–IR spectrometers and used for all types of measurements, however. If the S/N of the interferogram at zero retardation gets too large (greater than 6×10^4) it can exceed the dynamic range of the analog-to-digital converter (ADC), in which case no improvement in S/N is seen on signal-averaging interferograms[7] and the noise level of the spectrum is determined not by the noise of the detector but by the inability of the data system to extract all the useful spectral information from the signal.

Two approaches have been taken to get around the problem of this so-called *digitization noise* for GC–IR systems to allow the MCT detector to be used for the identification of very small quantities of samples. The first has been pioneered by Azarraga of the U.S. Environmental Protection Agency's Environmental Research Laboratory at Athens, Georgia.[8,9] Azarraga developed a method for coating the interior surface of glass tubes with a layer of gold, enabling light-pipes of almost any combination of length and internal diameter to be constructed. The dimensions of the light-pipe are chosen to provide the best comparison between the absorbing path (which should be as long as possible) and the reflection losses incurred when the beam is transmitted down the light-pipe (which should be as small as possible). In addition the volume of the cell should be no larger than the volume containing the GC peak between its half-height points. The maximum transmittance of the light-pipe to ensure that the spectrum is not digitization noise limited is approximately 7%, and the optimum light-pipe for GC–IR with this transmittance value has a length of approximately 50 cm and a diameter of 2 mm.

On the GC–IR systems of this type, a single-beam spectrum is measured when each GC peak is present in the light-pipe, and each spectrum so acquired is subsequently ratioed against a reference spectrum measured with no sample

in the beam to compute a transmittance spectrum of the sample. (In practice all data are stored as the interferograms and computed at the end of the chromatographic run). At the detection limits ordinate scale expansion in excess of 100× is often necessary to permit easy visualization of the absorption bands of the sample. Single-beam GC–IR systems based on Azarraga's model are commercially available from Digilab (Cambridge, MA) and Nicolet (Madison, WI).

A second approach to GC–IR by Fourier spectroscopy, which is being developed in our laboratory, is designed to permit light-pipes of higher transmittance than 7% to be interfaced with FT–IR spectrometers using intense continuous sources and MCT detectors without limiting the sensitivity by digitization noise. Such light-pipes are desirable since it can be shown[10] that in the absence of digitization noise the optimum light-pipe for GC–IR should have a transmittance slightly greater than 30%.

To get around the problem imposed by the dynamic range of the 15-bit ADC's used in all modern rapid-scanning FT–IR spectrometers, both beams emerging from the interferometer, see Figure 1, are measured. In the optical

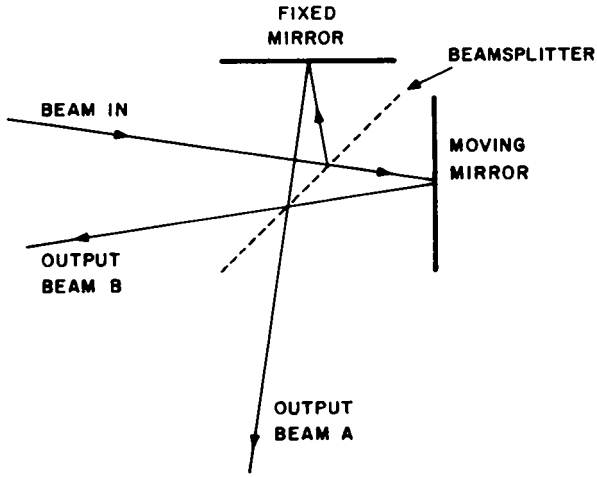

FIGURE 1 Schematic diagram of a Michelson interferometer with a skewed input beam, showing the two output beams, A and B.

configuration conventionally used for FT–IR spectroscopy, the beam from the source is at normal incidence to both mirrors in the interferometer, and only beam A (the "transmitted" beam) is measured since beam B (the "reflected" beam) returns to the source. If the input beam is skewed slightly, as shown in Figure 1, the interferogram from both output beams can be measured. The interferograms of the transmitted and reflected beams are 180° out-of-phase,

and if the two beams are passed through optically identical paths onto a single detector, the resultant a.c. interferogram should become zero. In practice the achievement of a perfect optical null appears to be impossible, but the magnitude of the signal at zero path difference may be reduced to the point that the S/N is less than the dynamic range of the ADC even when an MCT detector is used for the measurement, see Figure 2.

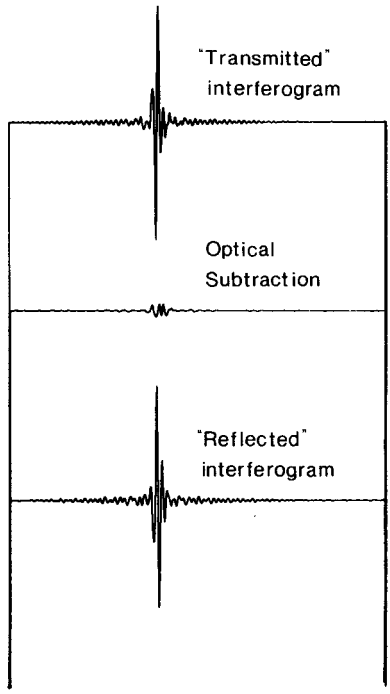

FIGURE 2 Measured interferograms from a practical dual-beam FT–IR system. The "transmitted interferogram" is measured if beam B is blocked, the "reflected interferogram" is measured if beam A is blocked, and optical subtraction occurs if neither beam A nor beam B is blocked.

If a sample of transmittance $T(v)$ is placed in beam B the resultant a.c. interferogram is given by the sum of the interferogram of beam A, $I(\delta)_A$:

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

and that of beam B, $I(\delta)_B$:

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

where δ is the optical path difference, in cm, ν is the wavenumber, in cm^{-1}; $B(\nu)$ is the signal due to radiation of wavenumber ν; and θ_ν is a small frequency-dependent phase angle giving rise to the asymmetry of the interferograms seen in Figure 2.

Therefore:

$$I(\delta)_A + I(\delta)_B = \int_{-\infty}^{+\infty} [1 - T(\nu)]\ B(\nu) \cos(2\pi\nu\delta + \theta_\nu) d\nu.$$

The smaller the quantity of sample in the beam the closer its transmittance is to unity at all wavenumbers and the smaller is the amplitude of this *dual-beam* interferogram. It can be seen that the FFT of this interferogram is the

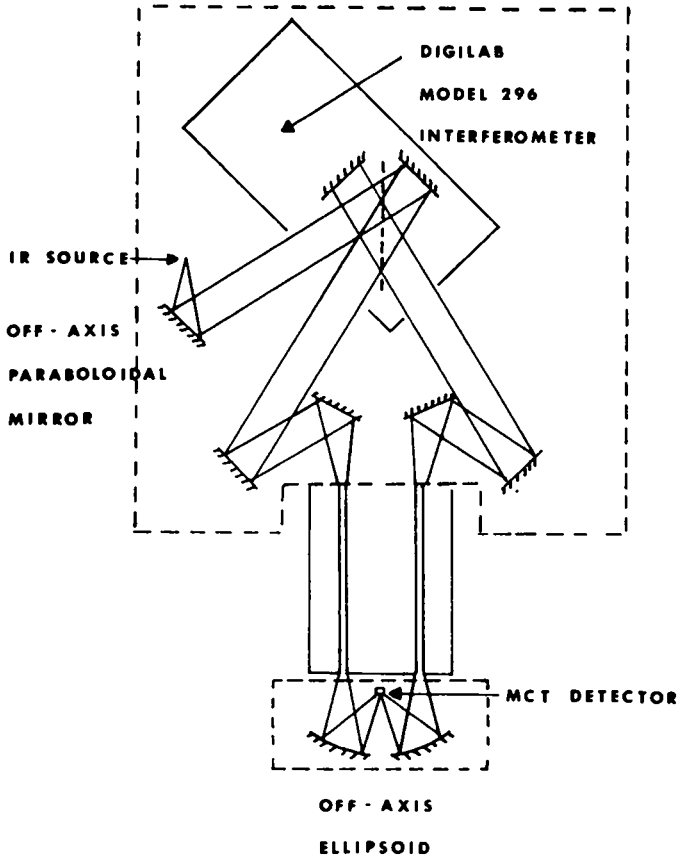

FIGURE 3 The optical layout of the dual-beam FT-IR system for GC–IR used to obtain the spectra shown in Figures 4 and 5.

difference between the spectra which would be found if $I(\delta)_A$ and $I(\delta)_B$ were measured individually and transformed separately. To obtain the transmittance spectrum, $T(\nu)$, the difference spectrum must be divided by $B(\nu)$ and subtracted from unity, a procedure which can be readily achieved in practice.

To apply this technique to GC–IR measurements, the optical system shown in Figure 3 is used. We have interfaced a Digilab FTS-14 spectrometer with dual parallel light-pipes 30 cm in length and 4 mm square in cross section (Norcon Instruments, S. Norwalk, CT) and an MCT detector (Texas Instruments, Dallas, TX) using custom-built optics (Special Optics, Little Falls, N.J.).[11] The effluent from a gas chromatograph fitted with 6′ long × $\frac{1}{8}$″ o.d. columns is passed through one light-pipe, and when a peak enters the interferograms are averaged until the sample leaves the light-pipe; typical

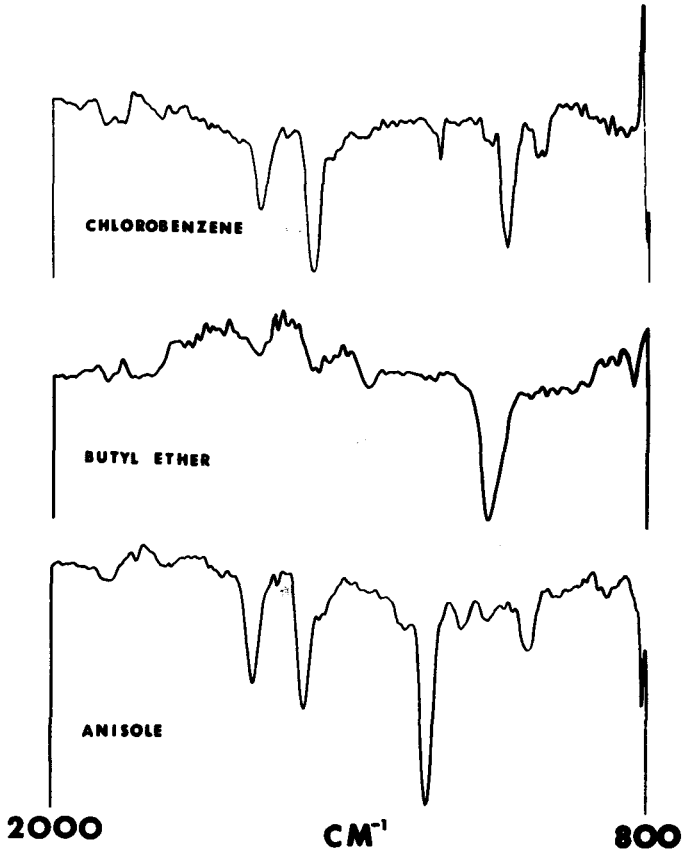

FIGURE 4A

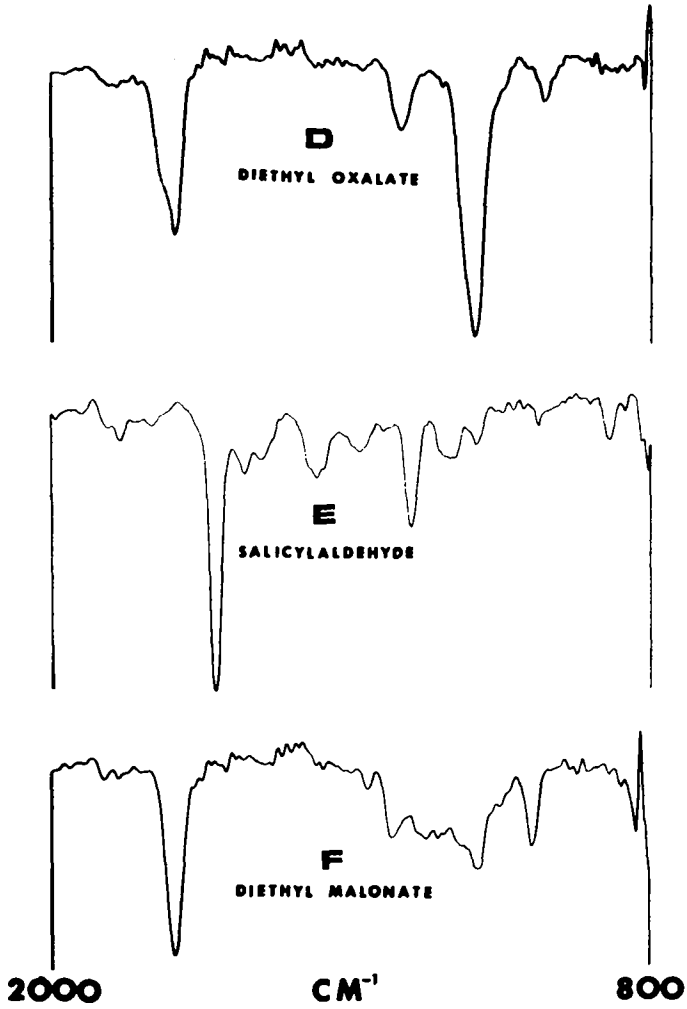

FIGURE 4 On-line GC–IR spectra measured from a water sample spiked at the 2 ppb level with (in order of elution) chlorobenzene, butyl ether, anisole, diethyl oxalate, salicylaldehyde, and diethyl malonate; assuming 100% recovery, 500 ng of each compound was injected into the chromatograph. GC conditions were as follows: Column: 6′ × ⅛″ stainless steel column with 3% OV 17 on 80–100 mesh Chromsorb W; Temperature program: 70°C for 2 min, increased at 8°C/min to a final temperature of 110°C; the injection port, FID and interface were all held at 200°C.

measurement times are of the order of 10 seconds. At the end of the chromatogram, a dual-beam interferogram of the empty cell (averaged over an extended period of time) is subtracted from the dual-beam interferogram corresponding to each GC peak to remove any residual background due to

imperfect matching of the two beams, and the FFT of each interferogram is then computed.

This system has been applied to the identification of trace quantities of organic compounds in water at the part per billion level. To illustrate the feasibility of GC–IR for this application, 25 liters of distilled water were spiked with 50 μg of several organic chemicals readily available "off-the-shelf" in our laboratory (anisole, butyl ether, chlorobenzene, diethyl malonate, diethyl

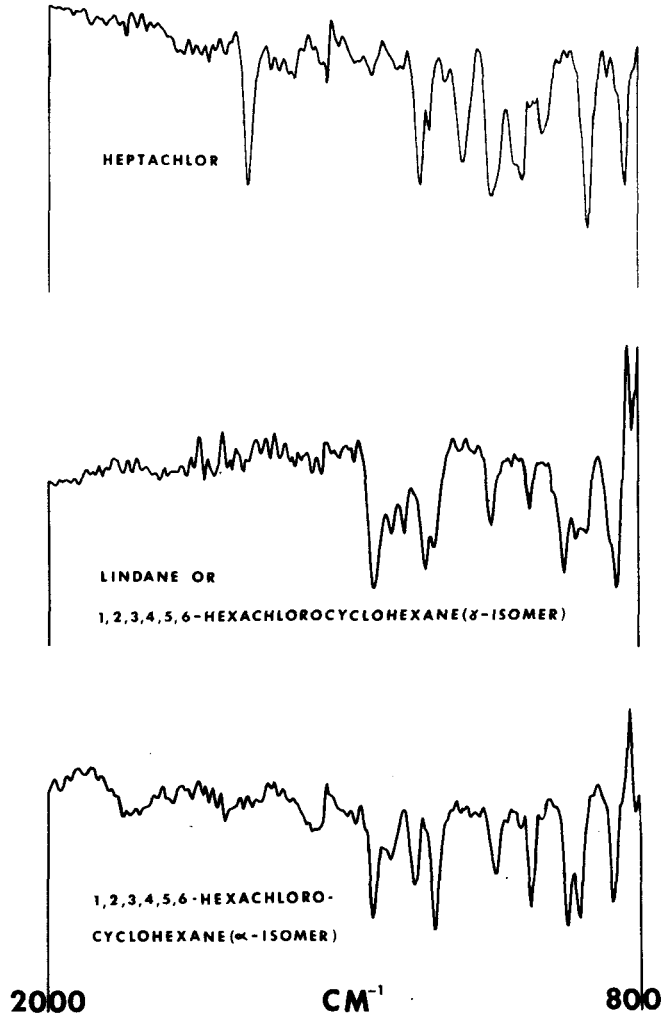

FIGURE 5A

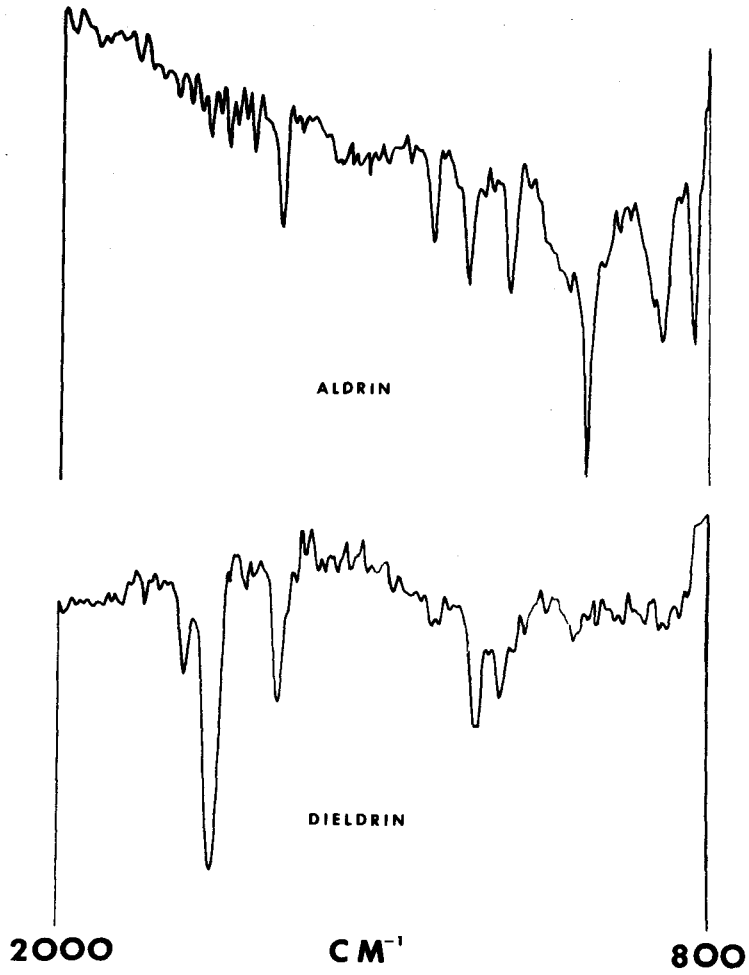

FIGURE 5 On-line GC–IR spectra of chlorinated pesticides from spiked water samples: assuming 100% recovery, 1 μg of each compound was injected into the chromatograph. GC conditions were as follows: Column: 6′ × 2 mm i.d. glass column with 0.10% OV-17 on 100–120 mesh textured glass beads; Temperature program: 175°C for 4 min, increased at 8°C/min to a final temperature of 200°C; the injection port, FID and interface were all held at 250°C. The strong carbonyl peak in the spectrum of Dieldrin suggests that this compound decomposes in the stainless steel transfer line to the light-pipe, indicating the need for all glass transfer lines in pesticide analysis.

oxalate and salicylaldehyde). The water sample was then passed through a column of Amberlite XAD-2 macroreticular neutral polystyrene resin[11] (Malinkrodt Chemical Co., St. Louis, MO) onto which the organic solutes were sorbed. They were subsequently eluted using 100 ml of diethyl ether and

the resultant solution was evaporated to 1 ml. A 10 μl aliquot was injected into the chromatograph and the spectra of each component are shown in Figure 4. Each component is present at a maximum level of 500 ng (assuming 100% sample recovery).

Chlorinated pesticides are much weaker infrared absorbers than the materials used in the study above and probably represent a "worst case" for the identification of environmentally important water pollutants by GC–IR. A series of solutions containing chlorinated pesticides at levels of 50 ppb (100 μg of each in 2 liters of water) were analyzed in a similar fashion to the method described above and representative spectra, each of which are caused by a maximum of 1 μg of the pesticide assuming 100% recovery, are shown in Figure 5. Table I shows the percent recovery from 20–50 mesh XAD-2 for each pesticide studied when acetonitrile, diethyl ether and hexane were used as the eluting solvent. The water flow rate was 20 ml/min and the flow rate for the eluting solvent was 2 ml/min; in each case 100 ml of the eluting solvent was used.

TABLE I

Effect of varying the eluting solvent and the water flow rate on the recovery of some chlorinated pesticides using 20–50 mesh XAD-2 resin

	Percent Recovery			
Pesticide	Acetonitrile (20 ml/min)	Hexane (20 ml/min)	Diethyl Ether (20 ml/min)	Diethyl Ether (100 ml/min)
Aldrin	50	43	94	83
Lindane	73	69	100	88
DDD	78	74	93	79
p,p'-DDT	69	72	93	80
Perthane	85	71	96	85
Dieldrin	89	65	95	83
Heptachlor	76	59	87	68
Hexachlorobenzene	83	65	89	78

Assuming that 25 liters of the water sample are available and that the diethyl ether extract can be evaporated down to 100 μl, it can be seen from these results that identification of the principal organic components in drinking water can be identified at levels less than 1 ppb. However the sorption of the organics onto the XAD-2 resin will take almost a day if the water flow rate is only 20 ml/min. We also studied the effect of increasing the flow rate to 100 ml/min on the recovery and it appears that even this high flow rate does not seriously deteriorate the recovery of chlorinated pesticides, see Table I. With the impressive rate at which developments in GC–IR are taking place at this time,

it is not difficult to forecast that identifiable spectra of organic compounds present in water at levels of 0.1 to 0.01 ppb will be able to be measured in the near future.

LC–IR

HPLC is becoming a progressively more popular technique for separating the components of complex mixtures, particularly for compounds of low volatility or thermal lability which cannot be readily separated by gas chromatography. However the on-line identification of species separated by HPLC, either by mass spectrometry or by FT–IR spectroscopy, is considerably more difficult than for GC. We have been attempting to develop new methods for measuring the infrared spectra of HPLC peaks at higher sensitivity than has been previously achieved using FT–IR spectrometers. The philosophy governing our choice of methods will be described, some preliminary results will be shown and a forecast as to future developments in LC–IR will be made.

The most significant problem associated with the measurement of LC–IR spectra occurs because of the infrared absorption of the mobile phase. Whereas for GC–IR the optimum sensitivity is found when the volume of the cell is equal to the volume between the half-width points of the GC peak, for LC–IR flow cells the pathlength must be about 100 μm or less in order that sufficient radiation is transmitted over at least 95% of the spectrum to allow solvent-compensated spectra to be measured with an adequate S/N. Since the aperture of a liquid cell need be no larger than 3 mm, the volume of the cell will usually be less than 8 μl, a value which is a small fraction of the volume of typical HPLC peaks. Therefore even though absorption features of less than one microgram of a solute *in the cell* may be observed with short measurement times, the total amount of solute in the peak may be of the order of a milligram.

To improve the sensitivity of LC–IR measurements using Fourier spectrometers one cannot increase the pathlength of the flow cell and compensate for the energy absorbed by the solvent by using an MCT detector because the absorption by the solvent is not uniform. Most organic solvents have a high transmittance between about 2800 cm^{-1} and 1800 cm^{-1} but have several strong bands outside of this region. It is generally in the region where the solvent absorbs strongly that the characteristic absorption bands of solutes will also occur. Thus if an MCT detector is used for the measurement of infrared interferograms it is possible that the S/N of the signal may exceed the dynamic range of the ADC even though much of the useful "fingerprint region" of the spectrum is effectively blacked out.

A situation such as this is obviously well suited to the application of dual-beam FT–IR techniques, where relatively short pathlengths can be used for the

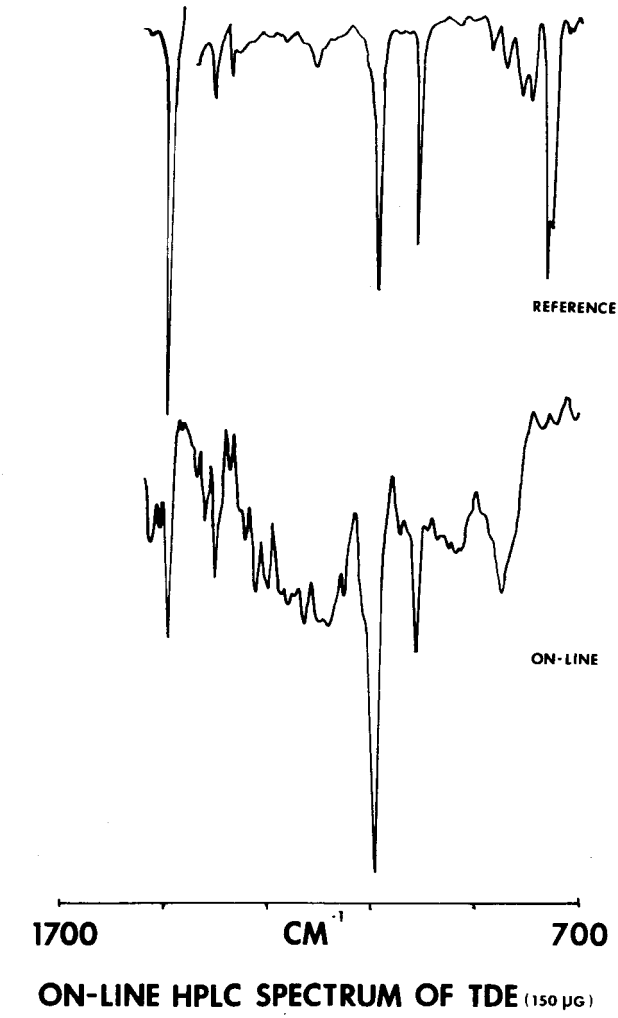

FIGURE 6 On-line LC–IR spectrum of 150 μg of TDE eluted from a μ-Porasil column with *n*-hexane measured using a dual-beam optical configuration with a reference cell containing pure *n*-hexane; both cells had a pathlength of approximately 90 μm.

flow cell and weak solute bands can be measured at high sensitivity provided that a reference cell containing an equal thickness of solvent is placed in the other beam. We have shown[12] that the application of dual-beam FT–IR spectroscopy with an MCT detector gives an advantage over corresponding single-beam measurements made using a TGS detector of at least an order of magnitude, and allows identifiable spectra of solutes to be measured from

solutions at levels of about 100 ppm using 100 μm pathlength cells with data acquisition times of less than 10 seconds.

However with an optical system such as this applied to the measurement of LC–IR spectra, we have been able to obtain barely recognizable spectra of strongly absorbing samples separated by HPLC when injected into the chromatograph in quantities of about 10 μg. However for weak absorbers, such as the chlorinated pesticides, these detection limits may be an order of magnitude greater than this, as shown in Figure 6.

These rather disappointing results suggested that the only way to measure LC–IR spectra with submicrogram sample quantities is to eliminate the solvent in some way and measure the spectrum of the total sample instead of just a small fraction. After a couple of false starts, we believe that we have developed a concept which will form the basis of an LC–IR system with submicrogram detection limits. In this device the effluent from the chromatograph is sprayed into a light-pipe which is heated (usually to a temperature of less than 100°C) and held vertically in a carousel with three other "identical" light-pipes. The solvent evaporates and is flushed out of the light-pipe while the solute is deposited on the walls. After the HPLC peak has eluted the carousel is rotated through 90° and the next HPLC peak is deposited into a second light-pipe while the spectrum of the first peak is measured. The process is repeated for all subsequent peaks, with the other two quadrants of the carousel being used for washing and reheating the light-pipes after the sample deposition and measurement steps. Although construction of this system has not yet been completed, off-line feasibility studies suggest that submicrogram sensitivity will be achievable even when a TGS detector is used.

SUMMARY

With techniques such as GC–IR and LC–IR available, the analyst possesses two important tools for the identification of trace water pollutants. However it must be stated that no single spectroscopic method will be able to be used for the unequivocal identification of a high proportion of all unknown GC or HPLC peaks. A combination of two rapid-scanning spectroscopic methods giving complementary information will be of far greater usefulness than either technique used individually. In this respect it is quite possible that a combination of FT–IR and mass spectroscopy will allow a very high proportion of all chromatographically separated peaks to be identified. Such a system, although it would undoubtedly be very expensive, will be of tremendous value for the rapid identification of water pollutants.

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