

transforming IR spectroscopy

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FOURIER TRANSFORM SPECTROSCOPY is a viable analytical technique with a bright future and an illustrious past. As we know it today, the Fourier Transform spectrometer is the end product of a most successful mating, as A. J. Mittleldorf (1) puts it, "between an old optical instrument, somewhat older mathematical principles, and a new computer approach."

The optical instrument is the interferometer, which, at the time of its invention by A. Michelson in 1887, generated perhaps one of the most important experimental results ever obtained. The result, of course, was the Michelson-Morley experiment that later proved instrumental in shaping modern theories of light and matter. The mathematical principle is that of French mathematician, Baron Jean Baptiste Fourier, by which a complex summation of cosine waves, an interferogram, is transformed into an optical spectrum.

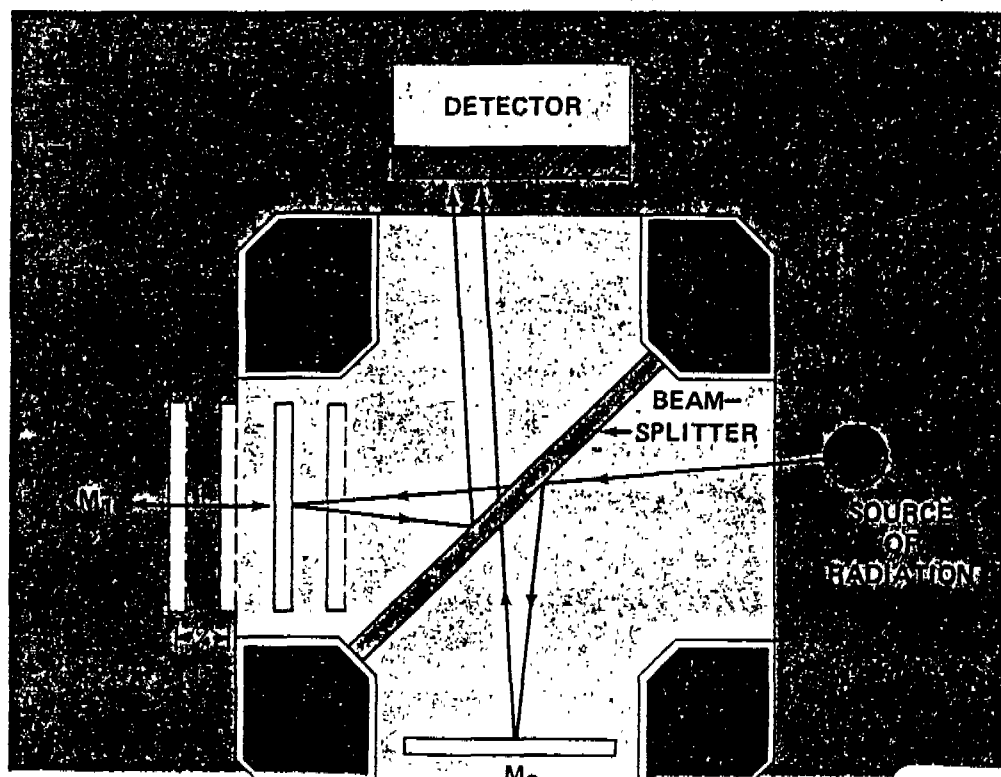
The mathematical manipulations are unwieldy, time consuming, and until the advent of small, fast digital computers presented a formidable barrier to most practical applica-

tions of the technique. Present day Fourier Transform systems use a dedicated digital computer to process the data. In real problem solving situations, there must be an immediate data display to adjust parameters, and in current systems spectra are either plotted or almost instantaneously displayed on an oscilloscope.

P. D. Fellgett is credited with introducing Fourier Transform spectroscopy with his 1951 dissertation at the University of Cambridge on the multiplex principle, the first numerically Fourier-transformed interferogram, and his work on infrared detectors. The high energy throughput of the interferometer was pointed out by P. Jacquinot and the results of these works were quickly exploited by H. A. Gebbie, G. A. Vanasse, and J. Strong who demonstrated the utility of the digital computer to Fourier Transform far infrared interferograms. These early developments are described in detail in an excellent account by Lowenstein (2).

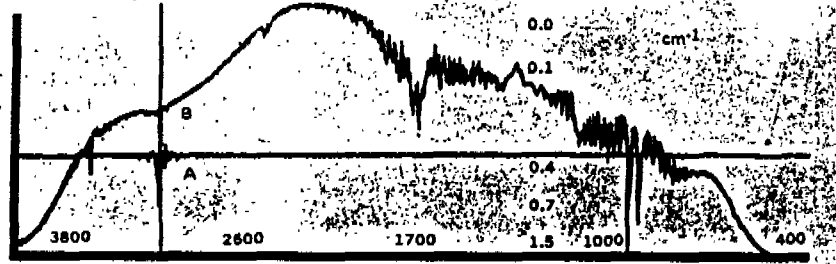
The theory of Fourier Transform spectroscopy has been treated in detail by many authors (3) and will be outlined here only

MICHELSON
Interferometer radiation is partially transmitted and partially reflected to the two mirrors M_1 and M_2 . The reflected beams will either constructively or destructively recombine at the beam splitter depending on the position of the moving mirror M_1 . For monochromatic radiation, the detector will see a cosine signal whose amplitude is a function of mirror position.

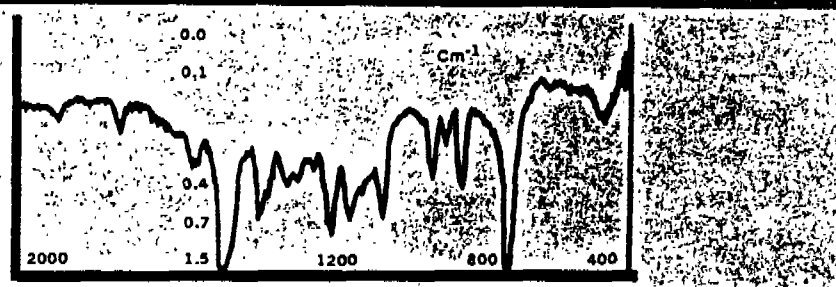


(A) Interferogram obtained from a scan at 4 cm resolution with a 10-cm cell containing NH_3 in the sample beam (the frequency scale does not pertain to the interferogram).

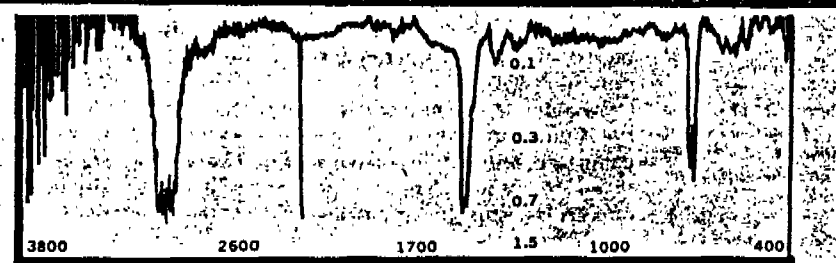
(B) Single beam plot of the Fourier Transform of A.



Spectrum of a 4-mm thick sheet of polyethylene foam obtained at 0.1 cm resolution by computer ratiointing 200 coadded against an equal number of reference scans. The ordinate is expanded 25 times. The major polyethylene bands are at 1460, 1370, and 720 cm^{-1} . Bands due to the blowing agent, Freon fluorocarbon gas, are observed at 1190, 1140, 1055, 924, and 850 cm^{-1} .



Spectrum of polyethylene film attenuated (with 0.05-mm aperture). About 40 ng of sample was in the beam path. The spectrum of 300 scans of the sample was ratiointed against 300 stored scans of the background of the 0.05-mm pinhole.



in a qualitative sense. The Michelson interferometer consists of two mirrors and a beam splitter. The beam splitter transmits half of all incident radiation from a source to a moving mirror and reflects half to a stationary mirror. Each component reflected by the two mirrors returns to the beam splitter, where the amplitudes of the waves are combined.

If the two mirrors are equidistant from the beam splitter, the amplitudes constructively combine. But if one mirror is moved a distance equal to $\lambda/4$ (assuming monochromatic incident radiation of wavelength λ), the emerging beam will be the result of two 180° out-of-phase beams that recombine destructively. Thus, for monochromatic incident radiation, the detector will see a cosine signal whose amplitude is a function of mirror position.

We can extend this simple treatment to the case where polychromatic radiation enters the interferometer. The signal received at the detector is a 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 (energy) as a function of distance traveled by the mirror. The relationship between the intensity of the interferogram as a function of mirror travel, $I(x)$, and the

intensity of the source as a function of optical frequency, $I(\nu)$, is given by a cosine Fourier Transform,

$$I(x) = \int_{-\infty}^{\infty} I(\nu) \cos(2\pi x\nu) d\nu$$

and the inverse transform

$$I(\nu) = \int_{-\infty}^{\infty} I(x) \cos(2\pi \nu x) dx$$

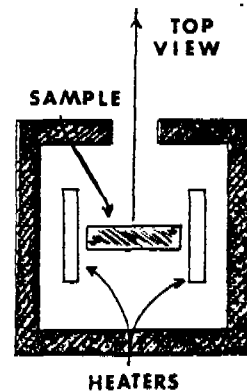
relates the interferogram to the optical spectrum.

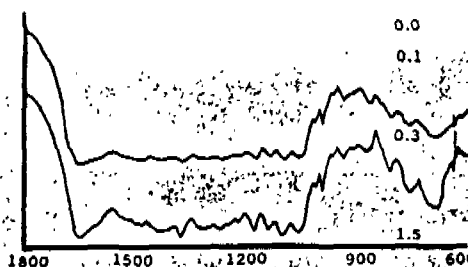
Taking advantage of Fellgett and Jacquinot

There are two major advantages of Fourier Transform systems over conventional dispersive spectrometers and these advantages are based on the speed and the throughput of the two instruments. The multiplex, Fellgett's advantage, has to do with the fact that all wavelengths of light simultaneously reach the detector. The interferometric signal (S) is directly proportional to the observation time (T) while the noise (N) is proportional to $T^{1/2}$. The signal-to-noise ratio is, therefore, proportional to $T^{1/2}$.

In a dispersive instrument each resolution element (M) is observed sequentially for an average time, T/M . The noise is proportional to $(T/M)^{1/2}$ and the signal-to-noise ratio, to

THE BASIC experimental arrangement for emission experiments is quite simple. Solid samples are mounted on a metal stand between two vertical heaters and contained in an insulated bird-house enclosure. The sample temperature is monitored by a calibrated thermistor readable to $\sim 0.25^\circ\text{C}$.





SPECTRUM
of a black speck
(0.25-mm dia)
found in molded plastic
sample, 300 scans, top.
Spectrum of portion
from dead insect
found in storage bin
of granulated polymer
feed stock, 300 scans,
lower. Photo shows
dead insects found in bin.

(T/M)^{1/2}. Thus, an advantage of $M^{1/2}$ is realized for the interferometer over the dispersive instrument operated at an equivalent signal-to-noise ratio.

Jacquinot's advantage is concerned with the light throughput of the interferometer compared with a dispersive instrument at a given resolution. The interferometer has a circular aperture of approximately 50 mm in diameter and has no slits. The slit area for a

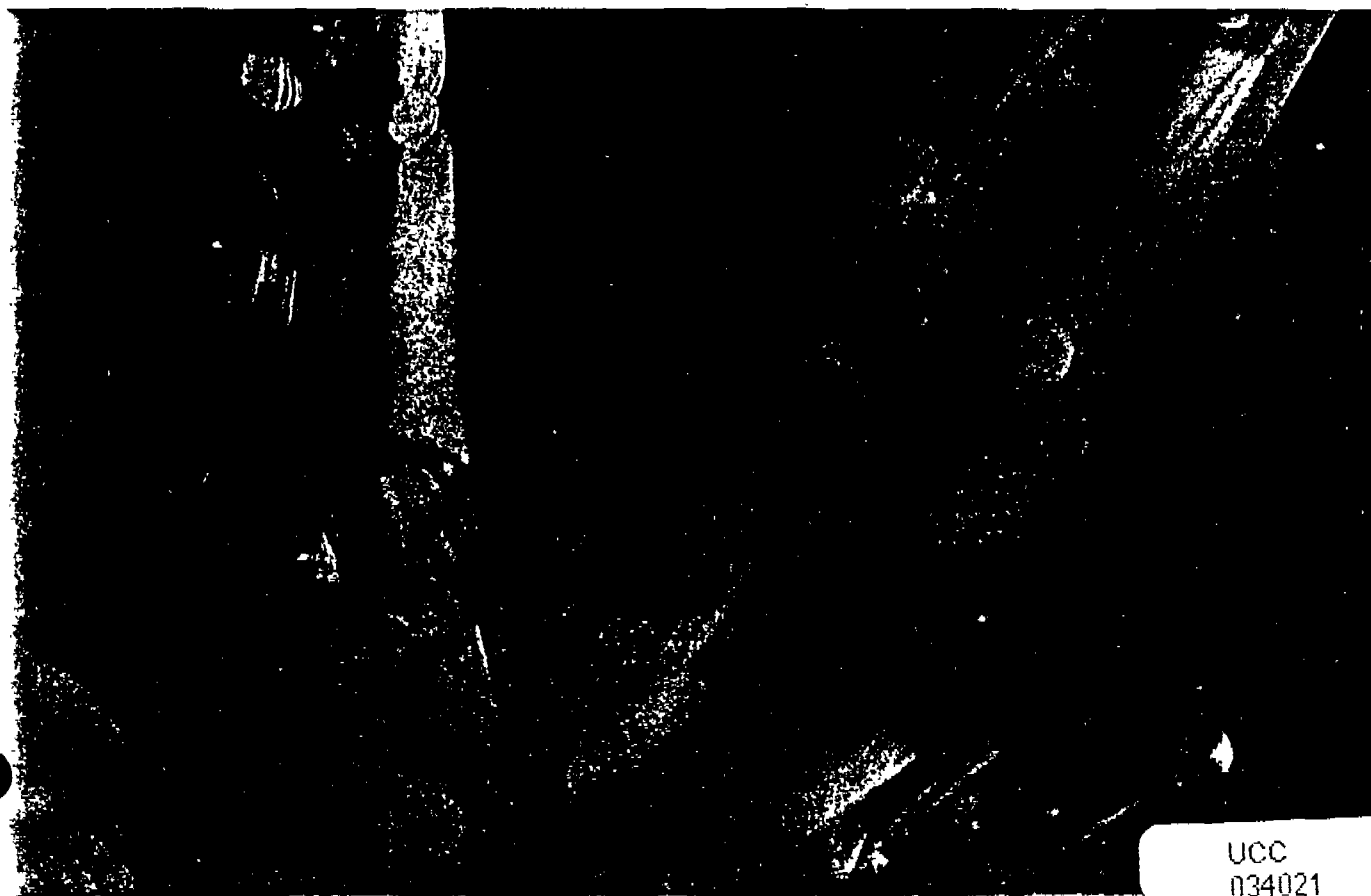
dispersive instrument operating at 1 cm⁻¹ resolution is approximately 1 mm².

Comparing these figures, one arrives at a throughput advantage of about 2000 for the interferometer over the dispersive instrument. However, in practice, this figure is never realized because the solid angle of view is about 50 times greater for the dispersive instrument than for the interferometer. A realistic estimate of the throughput advantage is closer to 40 times greater for the interferometer.

Many applications of Fourier Transform spectroscopy take advantage of the capacity of the instrument to produce spectra in energy-limited situations and conditions under which conventional dispersive instruments fail to function satisfactorily.

A big emphasis on the small view

The analysis of micro samples is perhaps one of the most important applications of Fourier Transform techniques. Here, both Fellgett's and Jacquinot's advantages are extremely important, because when working with the minimum amount of sample that will still give a usable spectrum, one sacrifices more than 99% of the incident radiation in some cases. This is truly an energy limited situation. Using a 6X beam condenser and a mask with a 0.05 mm diameter hole in it with Fourier Transform techniques, however, we



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can obtain acceptable spectra of polyethylene film with an estimated 40 nanograms of sample in the beam.

A combination of microscopy-micro infrared techniques has been successfully applied to the identification of microscopic particles isolated from a variety of substrates, including molded plastics, paper, and integrated circuits. The cause of delamination in plastic laminates is easily traced to specific substances by examining microscopic chips from the delaminated regions.

Similar techniques have been applied to micro potassium bromide pellets containing nanogram quantities of sample, to dilute solutions containing sample in the sub-microgram range, and to minor components isolated by the various chromatographic methods.

Another application that illustrates the ability of Fourier Transform spectroscopy to cope with energy limitations deals with the detection of minor additives, blowing agent residues, plasticizers, and so forth, in thick plastic films and foams. No sample preparation is necessary with this type of sample other than to cut the material physically and mount it in a sample holder.

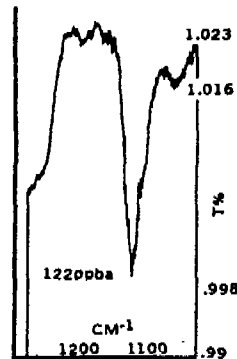
Polyethylene foam has a relatively simple infrared spectrum and lends itself rather nicely to this kind of study. Bands due to Freon fluorocarbon gas, a blowing agent, entrapped in the foam are easily observed in the



SMALL FLAKES
(<0.2 mm) in a delaminated plastic can be examined by micro Fourier Transform techniques. The cause of the delamination can be quickly identified. Scale: 1 mm/div.

polyethylene matrix as long as several hours after foaming. Trace amounts of blowing agent residues, such as cyanuric acid, a decomposition product of azobisformamide, are also easily observed by this technique.

The effect of antioxidant on foam was studied by computer ratioing spectra of the foam before and after exposure to UV light. The spectrum of the foam before exposure was stored in the computer's memory (disc) and retrieved as necessary during the study which spanned several days. Since essentially no sample preparation is necessary in these cases, the data are collected in a few minutes as opposed to work-up times as long as an hour associated with conventional techniques.



SCALE EXPANDED
spectrum (4 cm^{-1} res.) of 2-cm-thick St slug containing 122 ppba oxygen. Based on S/N, estimated lower limit of detection is 8 ppba.

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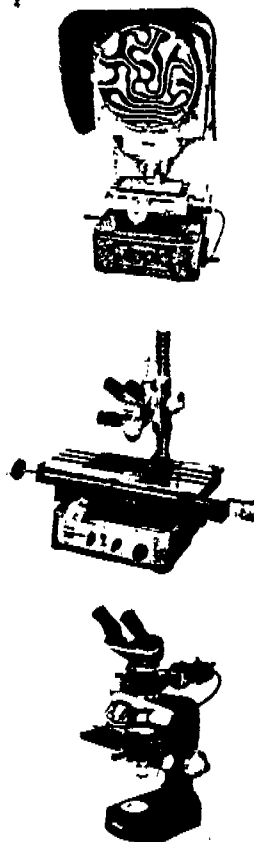
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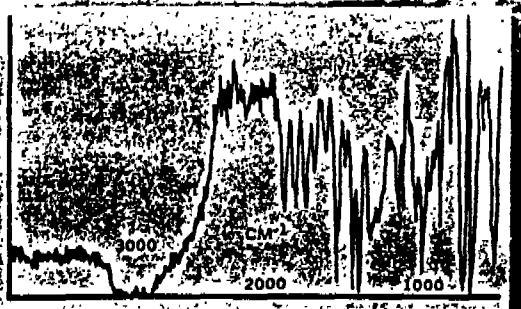
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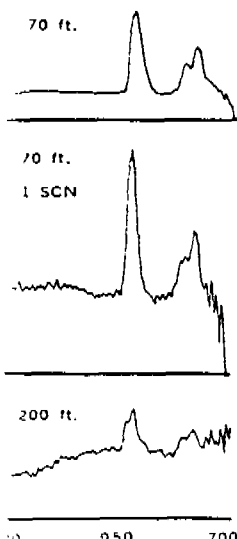
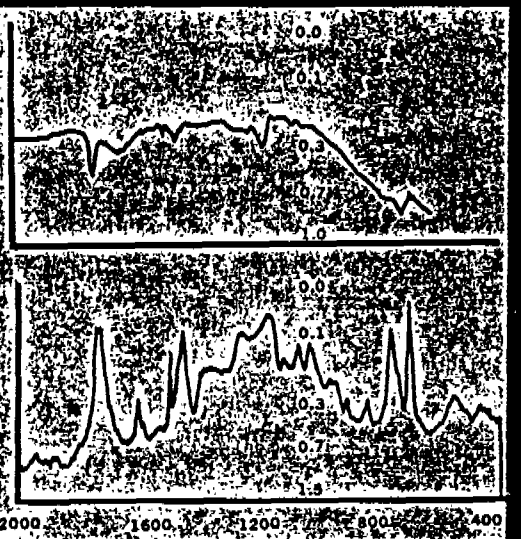
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Spectrum of a sheet of polystyrene obtained with a resolution of 2.40 cm⁻¹ and 20 scans. The original was expanded 100 times so that the (700 cm⁻¹) band played full scale. The infrared spectrum is much more revealing than the reflectance spectrum.



Multiple internal reflection (MIR) and emission (bottom) spectra of a rigid polystyrene strip. The MIR spectrum is a plot of the ratio of the sample to a clear polystyrene detail. The emission spectrum is a plot of the ratio of the sample to a black body emitter. The MIR spectrum is much more revealing than the reflectance spectrum.



EMISSION SPECTRA of perchloroethylene vapors above a beaker placed at 23 and 66 m from the instrument. Top and bottom spectra show 20 coadded scans computer ratioed against black body emitter. Center spectrum is single 1-sec scan taken at 23 m.

In the case of "Styrofoam" brand polystyrene foam and similar products, the rich polystyrene spectrum masks much of the usable fingerprint region of spectrum. With the exception of carbonyl-containing compounds, identification of minor additives would be difficult.

Paper is another example of a poor medium for the detection of low level additives. The spectrum of paper is dominated by intense cellulose absorption bands and a characteristically high level of scattered radiation. However, some additives that have absorption bands in regions where cellulose is transparent have been identified directly by applying Fourier Transform techniques. In many of these cases, the additive could not be isolated by conventional extraction and separation methods.

Eliminating the cold look

Special low temperature techniques and conventional dispersive spectrometers have been used extensively to measure oxygen as an impurity in silicon down to the detector limit of about 50 parts per billion atomic (ppba). Since the oxygen content of many gas float-zoned crystals ranges from less than 50 ppba to 300 ppba, an improvement in the lower limit of detection for oxygen would be most desirable.

The measurement itself is not straightforward since the absorption band due to the Si-O stretching vibration lies beneath a strong Si-Si lattice band. One must, therefore, first compensate or ratio out the lattice band to observe and measure the Si-O band. Through Fourier Transform techniques, it has been recently shown that a lower limit of detection for oxygen of about 8 ppba can be achieved with the sample at ambient temperature. This eliminates the need for cryogenic equipment and special handling of the samples, all of which contribute substantially to the overall time of analysis.

During the last ten years, many of the so-called inherent limitations shrouding various spectroscopic techniques have fallen by the wayside. This is particularly true of infrared emission techniques in which most chemical spectroscopists showed little interest. Sensitivity limitations on existing dispersive instrumentation partially justified this attitude, but there was also a mistaken belief on the part of many that good emission spectra could not be obtained at temperatures much below a few hundred degrees centigrade. This, of course, spells instant disaster for the organic chemist, who visualizes months of synthesis work going up in smoke.

In fact, this is not the case at all, for emission spectra have been obtained using dispersive instrumentation at temperatures well below 100 C, but the techniques are exceedingly tedious and time consuming and certainly not amenable to practical applications work.

But the infrared emission picture has changed dramatically during the past few years since the introduction of Fourier Transform systems. Usable emission spectra can be obtained in a reasonable length of time (minutes) with the sample at near-ambient temperatures using Fourier Transform techniques.

In the emission experiment, the source unit of the Fourier Transform spectrometer is replaced by an attachment designed to pass external radiation through the system to the detector. The sample, mounted on a specular mirror that is a poor emitter, is heated in an external "bird house" like enclosure.

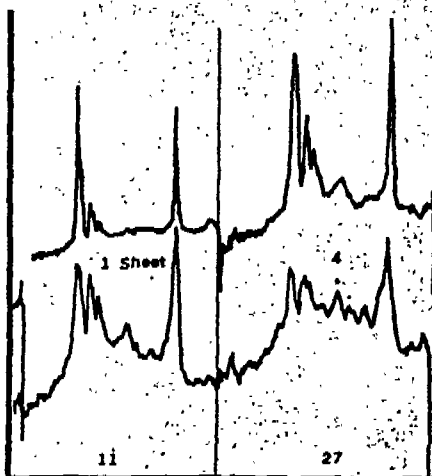
One of the major shortcomings of infrared emission spectroscopy is the effect of sample thickness on the spectrum. The spectrum of thin, uniform samples, 10 μ m to 0.1 mm in thickness, clearly shows discrete emission bands. As the sample thickness is increased beyond 0.5 mm, the band structure is no longer discernible and the recorded spectrum resembles that of a gray body.

This is indeed a limitation but it applies only to emission from thick samples. Thin coatings of such things as plastic, grease, and paint, on metal surfaces can sometimes be more easily characterized by emission spectra than by multiple internal reflection (MIR)

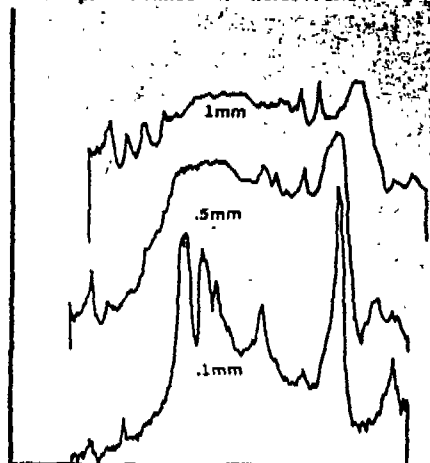
spectra, which is more or less the quick conventional technique applied in these cases. This is particularly true if the metal substrate is rigid and the coated surface rough so that good optical contact between the sample and MIR plate cannot be achieved.

Measuring into the wind

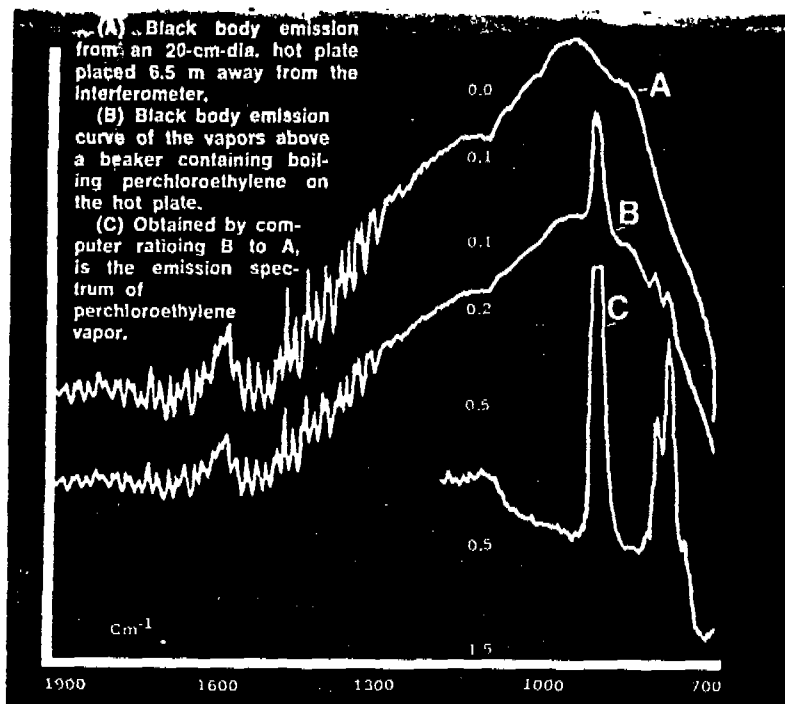
A most intriguing application of the Fourier Transform emission system is its use in detecting radiation emitted from a hot sample that is located some distance away from the instrument. In a simple laboratory set-up, emission spectra were recorded of hot vapors above a beaker of boiling perchloroethylene placed over 65 m away from the instrument. Similar spectra were recorded in field tests with the sample 33 m away from the instru-



Series of emission spectra obtained by successively stacking layers of 10-mil thick polyethylene sheets. The spectra, covering the range 2000-400 cm^{-1} , were obtained with the sample at 60 C and are ratioed against a black body emitter. The discrete emission bands due to polyethylene merge into a broad band centered around 1300 cm^{-1} as the sample thickness is increased.



The band structure no longer is discernible for a single sheet 0.5 mm thick.



ment but exposed to a 48 km/hr (30 mph) wind. Systems using cooled detectors and a Cassegrain telescope collector have been used to monitor hot gas emission from smoke stacks.

The advantages of Fourier Transform systems are real and significant, and the system offers problem solving capabilities previously not available to the spectroscopist. The examples cited only point to the great potential of this extremely sensitive instrument. There are obviously many analogous situations where the sensitivity and speed of a Fourier Transform spectrometer, as well as its flexibility to adapt to unusual experimental configurations, will prove this to be a valuable laboratory tool. ■

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THE AUTHORS

Dr. Ronald O. Kagel, right, below, is a senior analytical specialist in the instrument group of the Analytical Laboratories of Dow Chemical Co., Midland, Mich. His PhD in physical chemistry is from the Univ. of Minnesota. He presently is chairman of the Fourier Transform Users Group. Dr. Stanley S. T. King is an analytical specialist in the polymer group at Dow Midland. After undergraduate work in Taiwan, he also earned a PhD in physical chemistry at Univ. of Minnesota. In this photo they are using the Digilab FTS-14 system.



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