Instrumentation

Applications of FT-IR spectroscopy

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During the past decade, Fourier transform-infrared spectroscopy (FT-IR) has become extremely popular among IR spectroscopists. Although the basic technology for this instrument was developed around the turn of the century (1-3), the commercial availability of the instrument and its popularity are relatively recent phenomena.

Instrumentation

The essential component of an FT-IR spectrometer is the interferometer, used in place of the monochromator found in dispersive infrared instruments. The interferometers most commonly used today are based on the interferometer originally designed by Michelson in 1897.

TABLE 1

Different Types of Beam Splitters for Michelson's Interferometer

	Region in CM^{-1}	Materials	Coating
NIR	20,000-3,000	Quartz	MgO
NIR	10,000-2,000	CaF_2	Si
MIR	4,000- 400	KBr	Ge
MIR	800- 200	CsI	
FIR	650- 100	Mylar	
FIR	300- 30	Wire mesh	

TABLE 2

Detectors for FT-IR

Detector	Operating temperature	Detection range in CM^{-1}
TGS[a]	Room Temperature	5,000- 30
DTGS	Room Temperature	5,000- 30
MCT[b]	Liquid Nitrogen	4,000- 750
PbS	Liquid Nitrogen	20,000-3,000
PbSe	Liquid Nitrogen	20,000-3,000

[a] TGS is triglycine sulfate.
[b] MCT is mercury-cadmium-tellurium.

TABLE 3

Spectral Resolution in FT-IR

Mirror travel in CM	Retardation in CM[a]	Resolution in CM^{-1}
0.06	0.125	8.000
0.25	0.500	2.000
1.00	2.000	0.500
4.00	8.000	0.125
8.00	16.000	0.060

[a] Retardation is twice the distance mirror traveled (round-trip).

The interferometer basically consists of two mirrors and a beam splitter. One mirror is fixed and the other is movable. The beam splitter splits the infrared light beams and directs them to the mirrors (Fig. 1). Reflected beams then are recombined. Because one of the mirrors is movable, alternating constructive/destructive interference occurs, creating a modulated beam that interacts with the sample. A laser usually is used to control mirror position.

Although other types of interferometers have been designed, the Michelson interferometer still is the most commonly used in current commercial FT-IR instruments. The material and coating of the beam splitter (Table 1) determine the spectral regions in which the interferometer can be used. The type of detector (Table 2) determines the usable infrared regions and the sensitivity of the instrument. The distance traveled by the moving mirror determines the resolution of spectral bands (Table 3). The spectrum or interferogram thus obtained, however, is a time-domain spectrum (Fig. 2) and of very little use to IR spectroscopists.

Fourier, a 19th century French mathematician, provided a mathematical method necessary for transformation of time-domain spectra to frequency-domain spectra. Considering the large number of points necessary to obtain an IR spectra, calculations for this transformation are extremely tedious and time-consuming. The recent advances in computer technology and a specially developed version of this transformation—fast Fourier transform (FFT)—by Cooley and Tukey (4) make these calculations extremely rapid and the computer an integral part of the instrument.

Advantages of FT-IR instruments

There are a number of advantages offered by FT-IR over dispersive

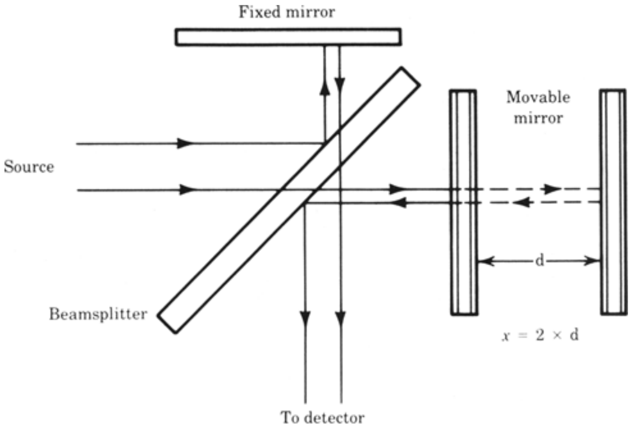


FIG. 1. Schematic diagram of a Michelson interferometer. X represents retardation.

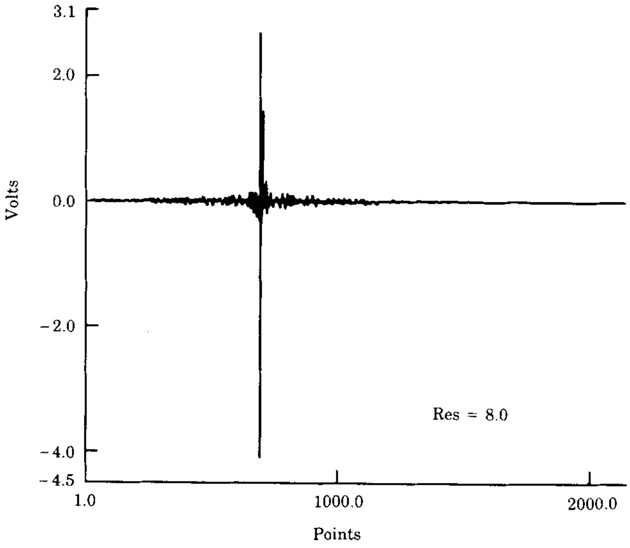


FIG. 2. Time-domain interferogram.

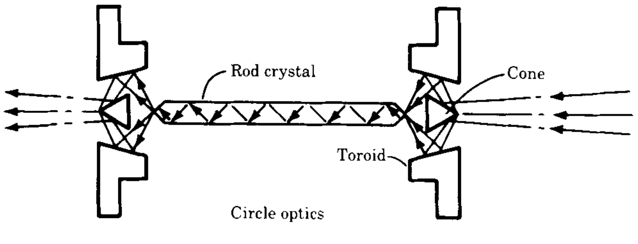


FIG. 3. Schematic diagram of a cylindrical internal reflectance cell. Rod crystal is ZnSe.

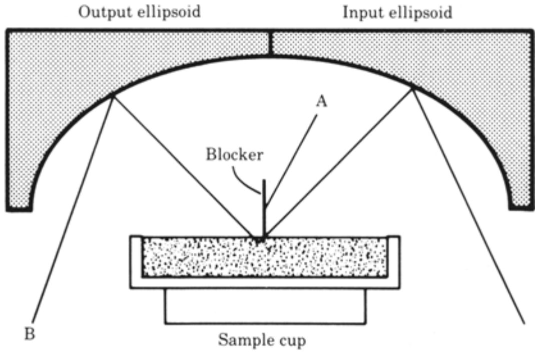


FIG. 4. Schematic diagram of diffuse reflectance accessory (DRIFTS).

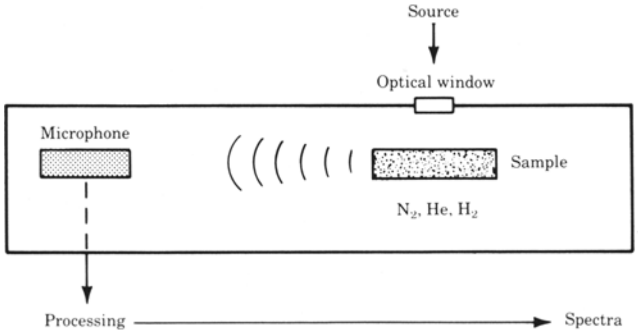


FIG. 5. Schematic diagram of photoacoustic chamber.

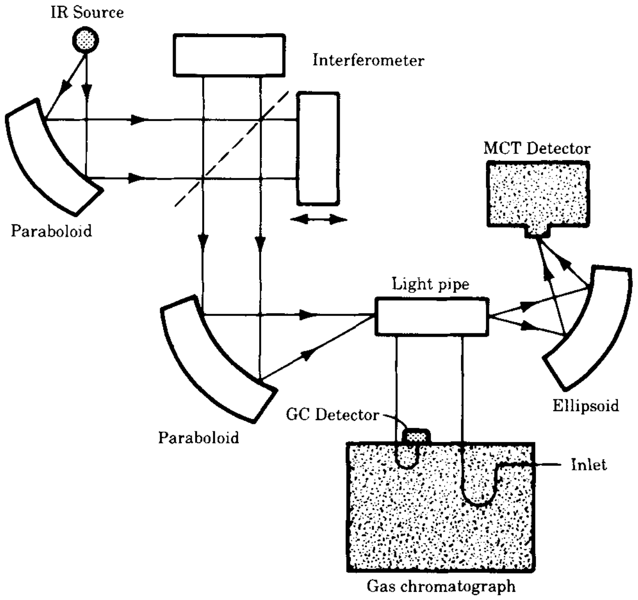


FIG. 6. Schematic diagram of capillary GC-FT-IR system.

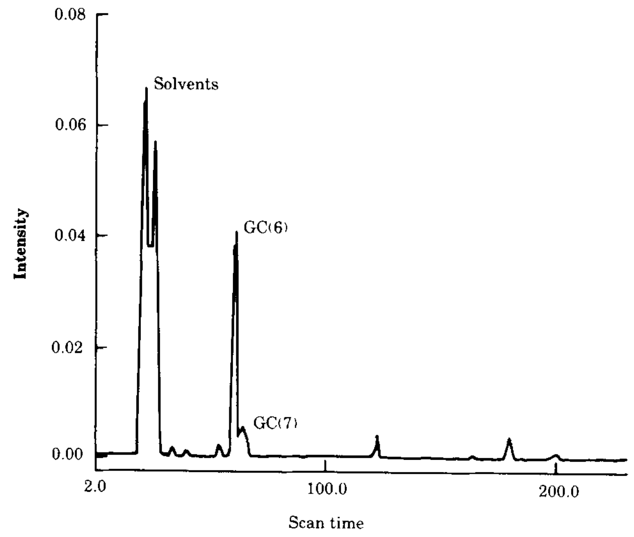


FIG. 7. Gram-Schmidt chromatogram of distillate from an ethoxylated fatty amine.

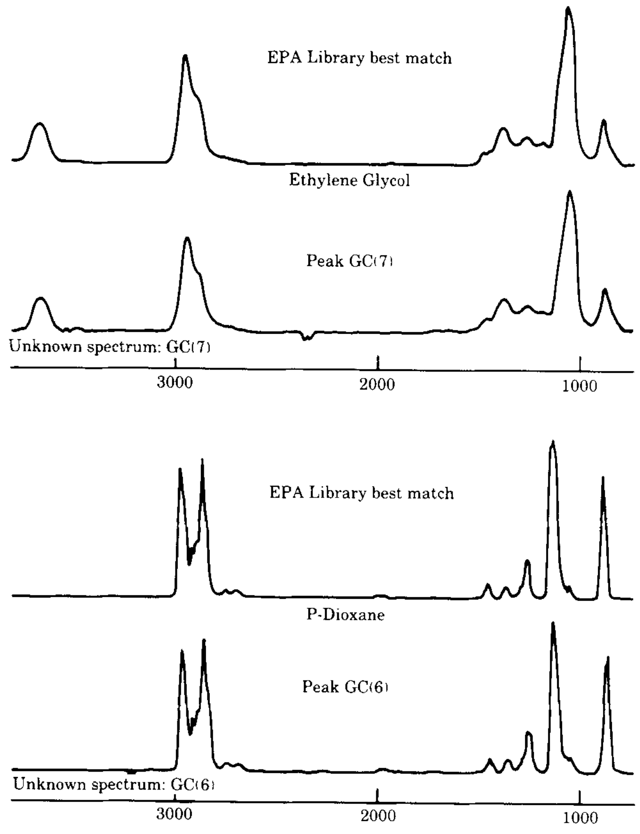


FIG. 8. IR spectra of GC(6) and GC(7) and their respective matches.

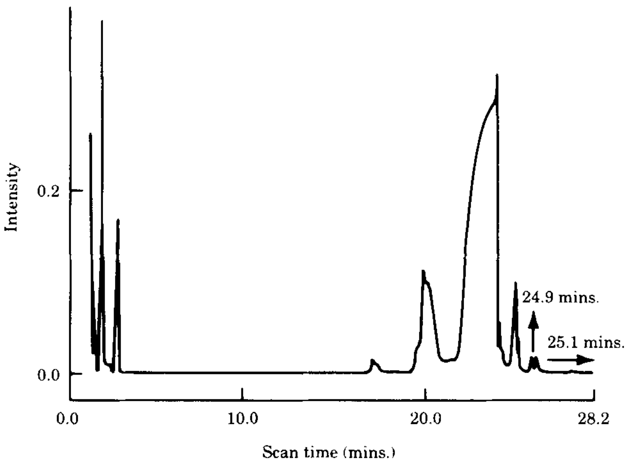


FIG. 9. G-S chromatogram of oleyl amine (bottom solid layer).

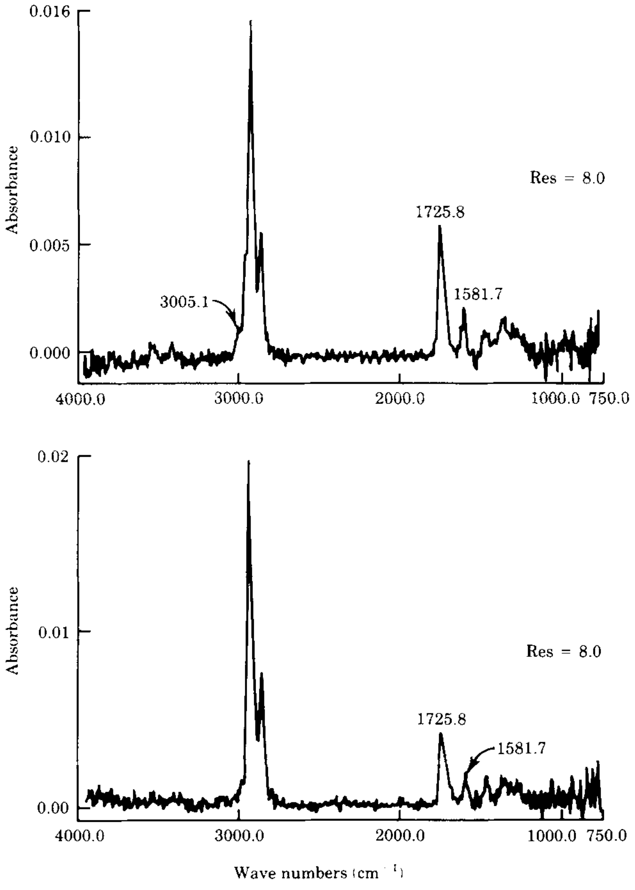


FIG. 10. Top: Vapor phase IR spectrum of the peak at 24.9 min. Bottom: IR spectrum of the peak at 25.1 min.

infrared instruments. The following summarizes some of these advantages.

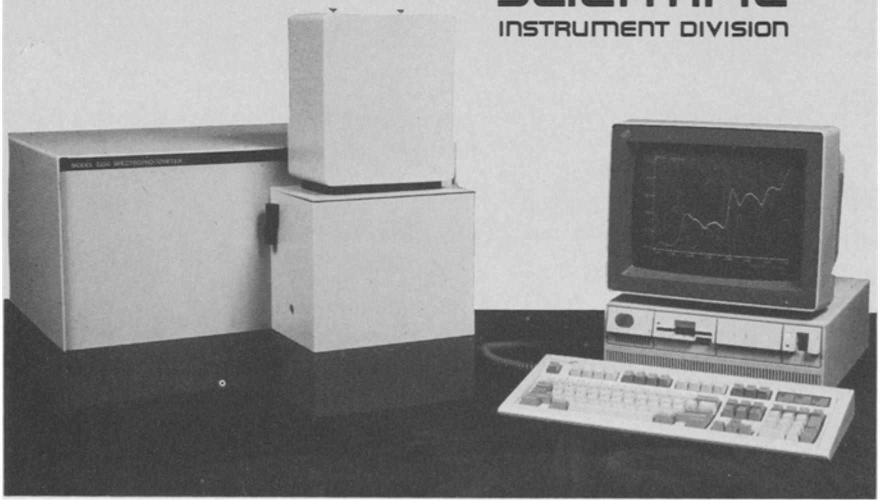
The Fellgett advantage, or multiplex advantage (5), is associated with the speed of data acquisition in the FT-IR instrument. The Jacquinot advantage (6) refers to the high-energy throughput in these instruments. The calculated values of Jacquinot advantage are 40-50 times more than a dispersive instrument. In practice, however, the number is not that high (7). Connes' advantage briefly refers to the high degree of wavelength accuracy obtained in the IR spectra due to the use of highly monochromatic laser light for precise mirror positioning. Finally, the stray light advantage, heat effect (sample is far removed from the IR radiation source) and mechanical simplicity of this instrument make FT-IR a far superior instrument to its dispersive predecessor.

All of these advantages, particularly Fellgett, contribute to a more sensitive, higher signal-to-noise ratio (S/N) and, in general, better quality infrared spectra. IR spectroscopists now are able to use many new accessories that were not applicable to the dispersive instrument. For example, the recent advances in interfacing the gas liquid chromatograph (GC), microscopes and the thermo gravimetric system (TGS) with FT-IR mainly are due to these advantages.

FT-IR accessories

Accessories for FT-IR instruments include the following:

- Attenuated total reflectance (ATR)—Even though this accessory has been used extensively by spectroscopists with dispersive IR instruments, FT-IR provides much better resolution and higher S/N spectra. The quality of IR spectra obtained from the Germanium crystal (depth of infrared light penetration 2-4 micron), for example, is superior to any spectra obtained from a dispersive IR instrument.
- Cylindrical internal reflection (Circle Cell)—This cell (Fig. 3) permits IR spectra of a sample diluted (1 to 5%) in a solvent such as water, or other solvents that have high infrared adsorption.
- Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)—This particular accessory (Fig. 4), with its micro sampling capability, allows IR analysis of minute amounts of solid samples and, in most cases, eliminates the need for making a potassium bromine (KBr) disk for IR analysis of solid samples.
- Photoacoustic spectroscopy (PAS)—This accessory (Fig. 5) is uniquely innovative and has been adapted to FT-IR technology. In this accessory, sound waves are detected by a focused and powerful microphone from the heat waves generated from the sample that has been exposed to infrared light. The advantage of PAS is that the shape



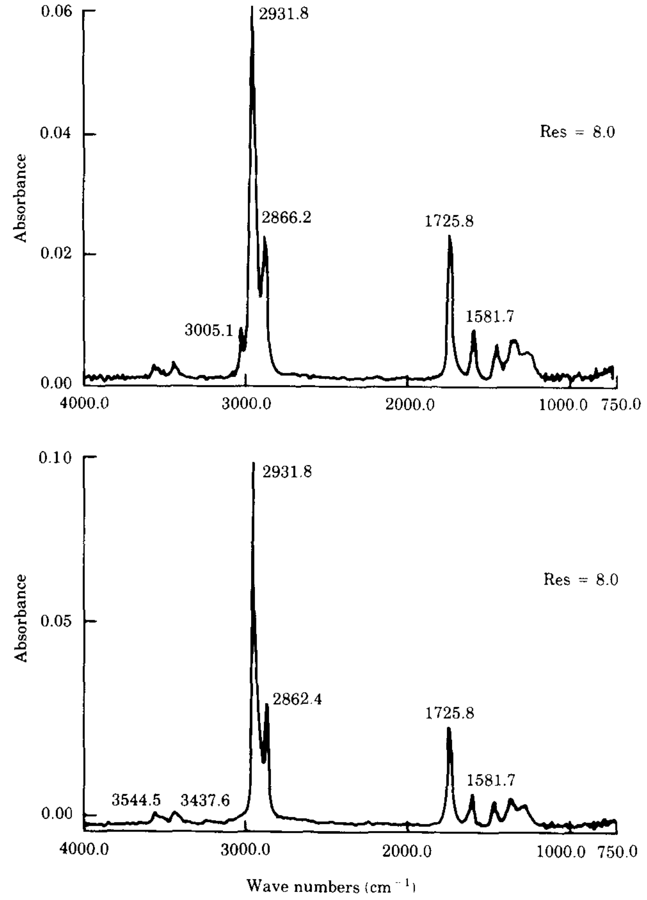


FIG. 11. Top: Standard vapor phase IR spectrum of unsaturated primary amide. Bottom: IR spectrum of saturated amide.

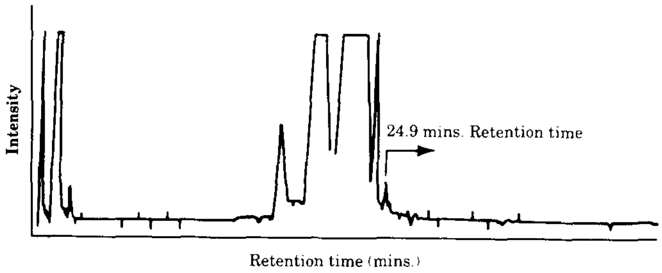


FIG. 12. FID chromatogram of oleyl amide (top layer liquid).

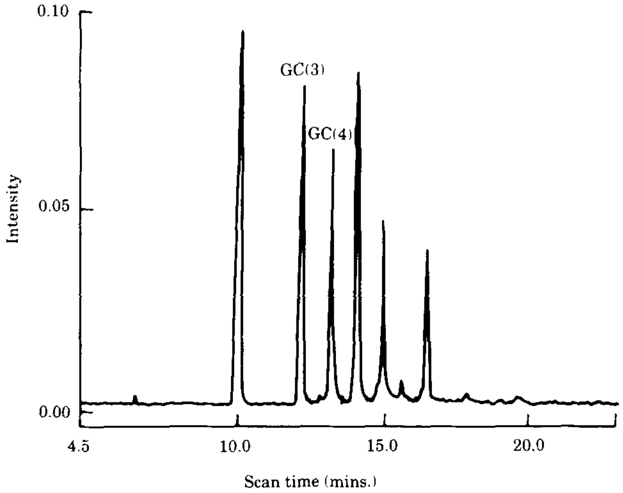


FIG. 13. G-S chromatogram of coconut oil-based dimethyl amine oxide.

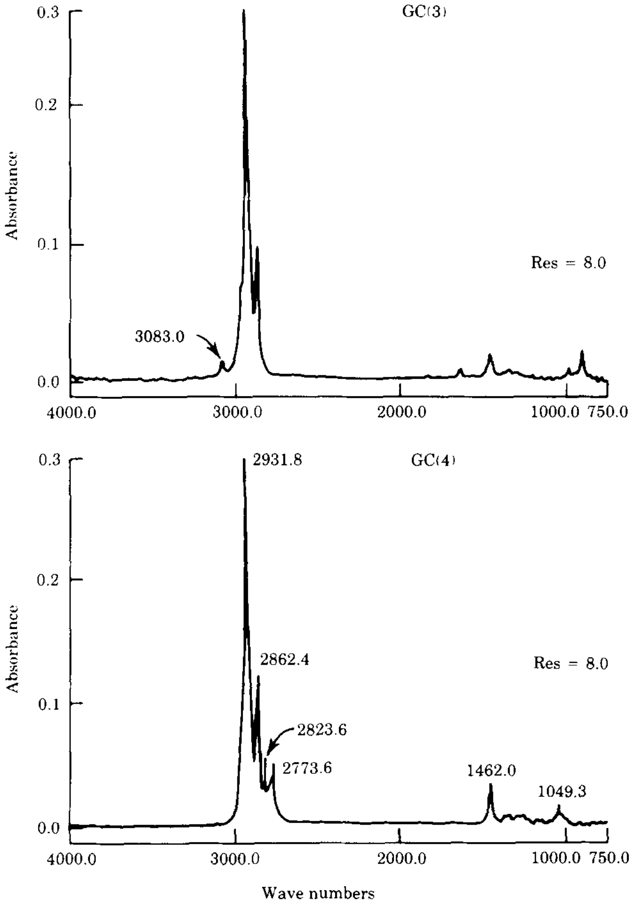


FIG. 14. Vapor phase IR spectrum of the olefin [peak GC(3)] and of coconut oil-based dimethyl amine [peak GC(4)].

of the solid sample does not pose any problem for IR analysis; as a result, PAS can be used for surface analysis of different shapes and types of solid samples.

There also are other accessories, such as microscopes and TGS, that have been designed to take advantage of FT-IR capabilities. GC-FT-IR is one such accessory.

In 1966, Low and Freeman (8) demonstrated the potential importance of the GC-FT-IR-interfaced instrument. Even though this demonstration lacked the sensitivity and sophistication available today, it was considered a major breakthrough in the field of IR technology. In 1969, Digilab Co. (now Bio-Rad Digilab Div.) manufactured the first commercial GC-FT-IR instrument. The rapid advancement in this field was due to two major developments: introduction of the MCT (mercury-cadmium-tellurium) detector, which has brought the limit of detection to the nanogram level, and construction of gold-coated borosilicate glass "light-pipe" (7).

Today, however, the availability of cryogenic freezing of GC column eluent in solid argon matrices has lowered the detection limit of this instrument to the GC-mass spectrometer level.

Figure 6 shows the diagram of the commercially available GC-FT-IR instrument. The analysis is done as different fractions are eluted from the GC column into the light-pipe "on the fly." The chromatogram (9) thus generated, called Gram-Schmidt (G-S), is computer-reconstructed and is qualitatively similar to a flame ionization detector (FID) chromatogram. Quantitatively, however, a G-S chromatogram is different than an FID one, due to the sensitivity of infrared light to molar adsorbence of different classes of organic compounds. In general, a G-S chromatogram is a means for computer assignment of each fraction to a specific IR spectrum.

Experiments reported in this article were carried out on a Digilab Model FTS-60/GS-FT-IR (light-pipe) instrument. The GC instrument interfaced with this instrument was Hewlett-Packard Model 5890, equipped with a fused-silica capillary column (DB1-30 meter 0.25 micron film thickness from J&W Scientific Inc.). The carrier gas was helium at 3 ml per minute flow.

Example 1

Figure 7 is a G-S chromatogram of distillate from an ethoxylated fatty-based amine. The peaks assigned as GC(6) and GC(7) are not well resolved. The lack of resolution is due to the capability of the column used. However, the IR spectrum of each of these peaks, as shown in Figure 8, is well-matched with the IR spectrum of such pure compounds from the U.S. Environmental Protection Agency library as p-dioxane and ethylene glycol.

Example 2

One impurity commonly present in the fatty-based amine is an amide. Primary amides are the main cause of coprecipitation of the fatty amine products. Figure 9 shows a G-S chromatogram of the bottom solid layer of oleylamine. The two peaks at 24.9 and 25.1 minutes of retention time are of special interest. Figure 10 shows the IR spectrum of each peak.

In comparing this with the standard vapor phase spectra of a saturated and an unsaturated primary amide (Fig. 11), it becomes clear that the peaks are due to the presence of primary amides in the bottom solid layer of the sample.

Furthermore, the FID chromatograph of the top liquid layer of the same sample mainly shows the presence (Fig. 12) of the peak at 24.9 minutes of retention time (due to unsaturated primary amide). This suggests that the saturated primary amide is the main cause of coprecipitation in the sample.

Example 3

One of the most common tasks performed by GC in the analysis of various fatty amines is the determination of alkyl chain length distribution. In some cases, however, the peaks observed in the FID chromatogram are due not only to the chain length distribution, but also to decomposition of the product. For example, the oxide form of coconut oil-based dimethyl amine (10-11), without any prior sample preparation, decomposes only partially to its olefinic hydrocarbons.

Figure 13 shows a G-S chromatogram of coconut oil-based dimethyl amine oxide. However, the IR spectrum of each peak reveals the nature of this partial decomposition. Figure 14 shows the IR spectra of two of these peaks. The bottom spectrum, with IR bands at 2823 and 2773 cm^{-1}, shows the presence of dimethyl amine; the top spectrum shows the corresponding olefin (IR band at 3083 cm^{-1} and none at 2823 and 2773 cm^{-1}).

Conclusions

The field of FT-IR technology has been extremely active in recent years. FT-IR instrument prices have been reduced to the price level of dispersive IR instruments and innovations or improvements of old techniques have been introduced. The ease of data manipulation and the addition of many valuable accessories will foster the use of this technology in years to come.

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