Simple filter infrared analyzers have been designed around the same optical schematic, shown in Figure 11.8. Wavelength is selected through the use of .interchangeable, slide-mounted, fixed-wavelength interference filters Several filters may even be mounted on a-filter wheel for convenient selection:; Equipped with a micro flow-through cell designed for continuous monitoring' these infrared analyzers Can be coupled to liquid chromatographs for monitoring effluents ; or they can be used for; the quantitative determination of fiber finishes and Iubricating oils, or dissolved hydrocarbons in water after' extraction into CCTV or Freon solvent." Strongly 'absorbing-. liquids can be handled with a fixed-flow-through internal reflection cell, Such .*instrumentation is used for, the selective monitoring of compounds in on-line process control applications see Chapter 26).

Fourier Transform Infrared (FTIR) Spectrometer

Infrared radiation can be analyzed by means of a scanning Michelson interferometer (Figure 11.9). This consists of a moving mirror (4), a fixed mirror (3), And a beamsplitter (C). Radiation from the infrared source (B) is collimated by a mirror (2), and the resultant beam is divided at the beamsplitter ; half the beam passes to a fixed mirror (3) and half is reflected to the roving mirror. After reflection, the two beams recombine at the beamsplitter and, for any particular wavelength, constructively or destructively interfere, depending on the difference in optical paths between the two arms of the interferometer. With a constant mirror velocity, the intensity of the emerging radiation at any particular wavelength modulates in a regular sinusoidal manner. In the case of a broadband source the emerging beam is a complex mixture of modulation frequencies that, after passing through the sample compartment,. is focused onto the detector (G). This detector signal is sampled at precise intervals during the mirror scan. Both the sampling' rate and the mirror velocity are controlled by a reference signal incident upon a detector (E), which is produced by modulation of the beam from the helium-neon laser (A).

The resulting signal from detector 'G is known as an interferogram (stored in memory 1) and contains all the information required to reconstruct the spectrum via the mathematical process known as Fourier transformation (see; Section 2.6). For

11.8 Infrared analyzer, single-beam: (a) optical schematic and (b) circular interference filter drive system. (Courtesy of Foxboro/Wilks, Inc.)

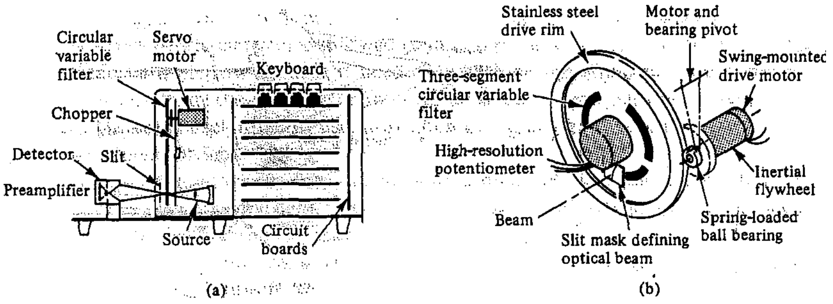
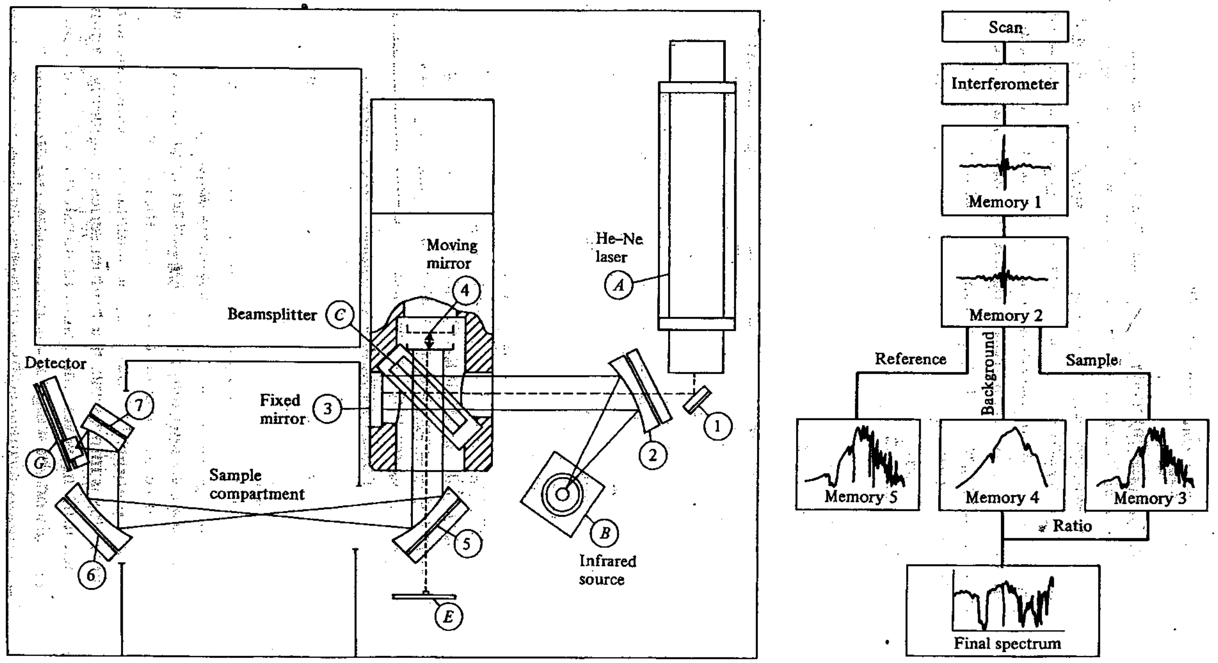


FIGURE 11.9 Infrared Fourier transform interferometric spectrometer: (a) optical path diagram and (b) block diagram of the instrument's functions. (Courtesy of Nicolet Instrument Corp.)



(a)

(b)

spectroscopy, Equation 2.7 may be written as

$$P_{(x)} = \int_{-\infty}^{+\infty} P_{0(\bar{v})} \cos(2\pi x\bar{v})\, d\bar{v} \tag{11.1}$$

where $P_{(x)}$ is the intensity of the total beam at the detector, $P_{0(v)}$ is the intensity of the source at frequency v (in cm^{-1}), x is the mirror displacement (in cm), and the summation is overall frequencies or as many as are in the radiation that reaches the detector' Only cosine waves are needed since x is measured from the position where both arms of the interferometer are equal, at which point all waves constructively interfere; that is, all wave intensities are at al maximum at x = 0. The Fourier transform or spectrum as a. function of frequency is then given by the equivalent of Equation 2.6, or

$$P_{(\bar{v})} = \int_{-\infty}^{+\infty} P_{(x)} \cos(2\pi x\bar{v})\, dx \tag{11.2}$$

The transform is carried out by a computer which is an essential part of the spectrometer, by an appropriate algorithm such as the Cooley-Tukey transform algorithm.

This technique has several distinct advantages over the conventional dispersive techniques. There is only one moving part involved, mirror 4, mounted on a frictionless air bearing. Dispersion or filtering is not required so that energy-wasting slits are not needed. This is a major advantage, particularly with energy at a premium in the far-infrared. The use of a helium-neon laser as a reference results in near absolute frequency accuracy, better than 0.01 cm^{-1} over the range 4800-400 cm^{-1}. Because all wavelengths are simultaneously detected throughout the scan, the scanning interferometer achieves the same spectral signal-to-noise ratio as a dispersive spectrometer in a fraction of the time (Felgett's advantage).

The automatic process between the initiation of the scan and the final plot is shown in Figure 11.9b. The interferogram recorded with each scan is stored in memory l. This interferogram is then automatically aligned with, and added to, the averaged interferograms in memory 2. At the same time annotation of the plot is begun in preparation for the final spectrum. After a number of scans, often 32 (approximately 60 sec), this averaged interferogram is Fourier transformed to produce a single-beam spectrum, which, in the standard sample mode, is stored in memory 3. This single-beam spectrum is then ratioed against the stored background (run once a day) in memory 4 and the resulting "double-beam" spectrum is plotted on the high speed digital plotter. Memory 5 is additional space available for storage of a reference spectrum that would be used in the Spectral subtraction technique. This memory is also used to store a newly measured spectrum while maintaining the sample and background spectra for further manipulation. The time from insertion of the sample to the completed plot is about 2 min.

In Equations 11.1 and 11.2, the summation should extend from -oo to +oo. Of course, this is impossible. If a Fourier series is suddenly terminated (i.e., a "boxcar" truncation), however, the resulting transform will have some wiggles or "ringing" especially on the wings of an intense peak. To minimize these effects the series may be gradually terminated by multiplying the data by some apodizing function such as a triangular function, trapezoidal function, or the Norton Beer function. Resolution is, however, decreased somewhat by the use of an apodizing function.

Resolution of a Fourier transform ;spectrometer is given by.

$$R = \frac{1}{\Delta_{max}}\ \text{cm}^{-1} \qquad (1.3)$$

where R is the maximum attainable resolution in wavenumbers and D_{max} is the maximum retardation-that is, twice the distance of the mirror movement in centimeters. Besides the decrease in resolution due to the application of an apodizing function, resolution-is adversely affected by divergence of the beam and instability of the mirror motion, in either speed or alignment, resulting in poorer resolution than that predicted by Equation 11.3.

Since the computer uses digital data, the photodetector signal must be converted to digital form by an analog-to-digital converter. The data must be sampled at precise points and the resultant data stored. The data must be sampled, at least twice every wavelength, so the sampling interval must be half the minimum wavelength to be observed; that is, v_{max} $1/2Dx = 1/l_{min}$. If the sampling intervals are longer than this value, the high-frequency, waves will be "aliased" or folded back into the spectrum.

Felgett's advantage , mentioned earlier, results because an interferometer measures all wavelengths simultaneously. Thus an interferometer-spectrometer, when compared with a sequential dispersive spectrometer, carries out N measurements, where N is the number of resolution elements of the dispersive spectrometer, in the same time as one complete scan on the sequential dispersive spectrometer. The signal is N times as strong and the noise is N^ advantage (Felgett's advantage) is N^ instruments is known as Jacquinot's advantage., This is due to the increased energy throughput. The interferometer has a large circular entrance aperture. rather than smaller entrance slits like a dispersive instrument but the interferometer does lose half the radiation at the beamsplitter.

Fourier transform infrared spectrometers are still more expensive than sequential dispersive instruments due to the precision needed for mirror movement and the computer that is also required. However, dispersive instruments are now often equipped with computers that can record and remember spectra, plot absorbance, transmittance, or some function of absorbance, subtract one spectrum from another, and do other functions, and this adds to their price. The power of FTIR instruments has led to much competition in the instrumentation industry, resulting in an increased availability of commercial instruments and a decrease in price.. Low-cost FTIR instruments are, beginning to appear., Fourier transform spectrometers are faster than dispersive instruments and therefore are especially useful in situations that require fast, repetitive scanning. They are used in recording the output of gas or liquid chromatographs or obtaining kinetic data.

11.3 SAMPLE HANDLING

Infrared instrumentation has reached a remarkable degree of standardization as far as the.. sample compartment of various spectrometers, is concerned. Sample handling itself, however, presents a number of problems in the infrared region. There is no rugged window material for cuvettes that is transparent and also inert over this