Infrared Fourier Transform Spectroscopy in Flavor Analysis. IV. Spectra of Gas Chromatography Fractions

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Infrared spectra of gas chromatography fractions were recorded using a modified Digilab, Inc., Model FTS-14 Fourier transform spectrometer. The sampling was carried out by means of a modified Wilks Scientific vapor phase gc–ir analyzer fitted with a carrier gas eliminator. It was possible to record good spectra of trapped 0.01 to 0.001-μl samples.

The utility of infrared spectra for the identification of gas chromatography fractions had led to the development of a variety of techniques and instrumentation. The work in this area, mostly concerned with the use of dispersion spectrometers, has been reviewed by Welti (1970). Infrared Fourier transform spectrometers have also been used in single-beam (Low, 1966; Low and Freeman, 1968) and dual-beam modes (Low, 1968, 1971), but the gc–ir data were obtained with interferometers capable of only modest spectral resolution. As new and greatly improved instrumentation has now become available, some experiments were carried out to further explore the utility of infrared Fourier transform spectroscopy for the characterization of gc effluent.

INSTRUMENTATION

The instrument used was the Digilab, Inc., Model FTS-14 infrared Fourier transform spectrometer marketed by Sadtler Research Laboratories. The FTS-14 is described in detail elsewhere (Dunn and Block, 1969; Low, 1970a,b). Its salient features are as follows. The instrument is a completely automated infrared Fourier transform spectrometer incorporating a dedicated minicomputer having a 16K core memory. The computer is used not only for data acquisition, storage, and data reduction procedures required for Fourier transform spectroscopy, but also controls the entire instrument. The operator has access to the instrument *via* Teletype and, as the computer monitors instrument performance and maximizes all instrument parameters, high-quality spectra are obtained routinely. Some of the capabilities of the instrument system are described elsewhere (Low and Freeman, 1970).

The optical system of the FTS-14 was modified in order to improve instrument "sensitivity" and to permit various sampling attachments to be installed easily and quickly. The complete modifications will be described in detail elsewhere; changes pertinent to the present work involved the removal of various mirrors from the FTS-14 dual-beam sampling system so that a sampling attachment could be used in the manner shown schematically in Figure 1.

The sampling device used the main portions of the Model 41B gc–ir fraction collector marketed by Wilks Scientific Co. The use and operation of that device have been described in detail elsewhere (Gilby, 1970; Selander and Gilby, 1971). The modified device is shown schematically in Figure 1. The mirror T was a 90°-torroid used to deflect the beam coming from the FTS-14 through 90°, as shown in Figure 1. However, T was rotated 90° through its optical axis. This deliberately improper use of the torroid had a beneficial effect in "shaping" the infrared beam. The beam of the FTS-14 is circular in cross section and has a radius of about 10 cm at the normal sampling position of the spectrometer. The unmodified beam was consequently ill-matched to the rectangular cross section of the Wilks micro gas cell C. The torroid, used "improperly," distorted the beam and threw a roughly rectangular image onto the end of the micro cell. In this fashion, about one-half of the FTS-14 beam was passed into the cell. The beam emerging from the cell was passed to the detector D by means of an off-axis elliptical mirror E. Both D and E were mounted on a plate and could be moved so as to maximize the signal produced by D.

The following procedures were used to record spectra. The modified Wilks device (fitted with a heated line and

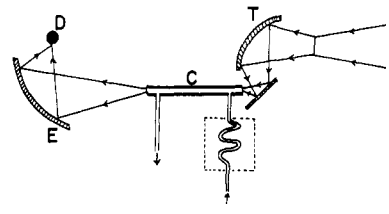

Figure 1. Experimental setup. T is a 90° torroid. C is a 0.6-ml volume Wilks Scientific Co. micro gas cell. D is a triglycine sulfate pyroelectric detector, and E is a 6:1 off-axis elliptical mirror. The area within the dashed line could be cooled with Freon or flash-heated. A flow-bypass valve of the Wilks Model 41B attachment is not shown

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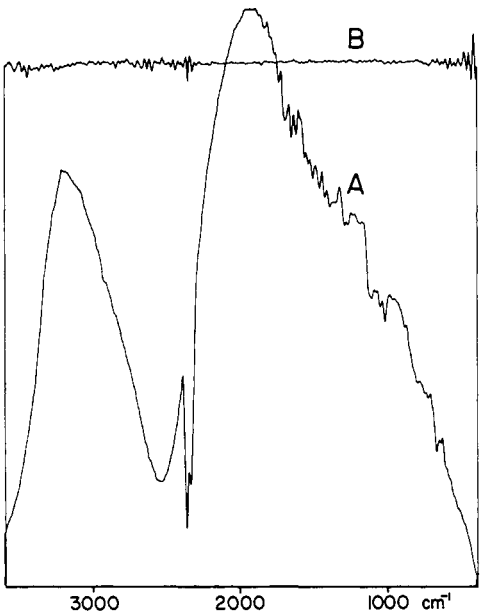

Figure 2. FTS-14 instrument profile. Trace A is a single-beam spectrum. When two such spectra are ratioed against each other, spectrum B results. The sensitivity falloff at each end and the dip near 2500 cm^{-1} of spectrum A were caused by the beam splitter

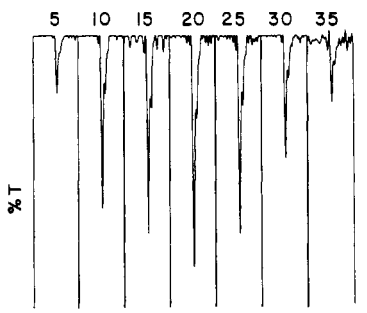

Figure 3. Calibration procedure. An eluted sample was allowed to flow through the cell and, after a certain time period had elapsed, the gas within the cell was trapped. A spectrum was then recorded and one segment of it was plotted. The procedure was then repeated. The number at the top of each segment indicates the time in seconds which had elapsed between the detection of the peak by the gc and the trapping of the gas, so that the series gives a concentration profile of gas within the cell as function of time

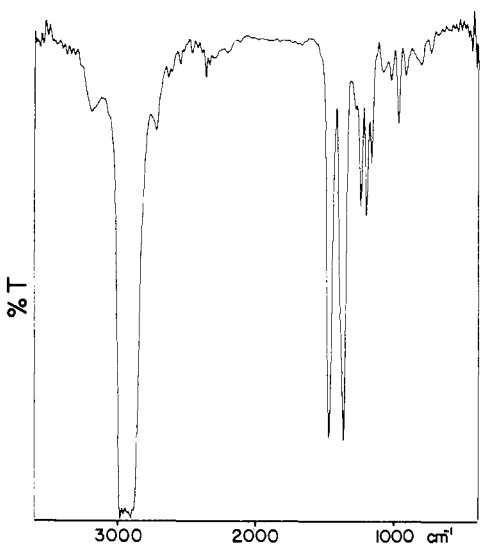

Figure 4. Spectrum of 2,2,4-trimethylpentane. Sample: 0.1 μl; trapped, 50 scans; 150° C

operated at 150–200° C) was installed and portions of the instrument were fitted with covers so that the system could be flushed with dry air. The various parts were then adjusted until the light passing through the cell and falling on the detector was maximized. A "background" spectrum was then recorded and stored in the computer's memory. Trace A of Figure 2 is an example of such a single-beam spectrum which would serve as background for a whole series of spectra. A "sample" spectrum, *i.e.*, the instrument profile such as Trace A of Figure 2 modified by the absorptions of the sample within the cell, was then recorded and ratioed against the stored spectrum and then plotted over a preset wavelength range using preset ordinate and abscissa scale expansion parameters. These various ratioing and scaling operations were carried out automatically. All spectra were recorded at a resolution of 16 cm^{-1} over the entire spectral range.

The Wilks device permitted spectra to be recorded with samples which were flowing or were trapped. For either mode of operation it was necessary to measure the time required for

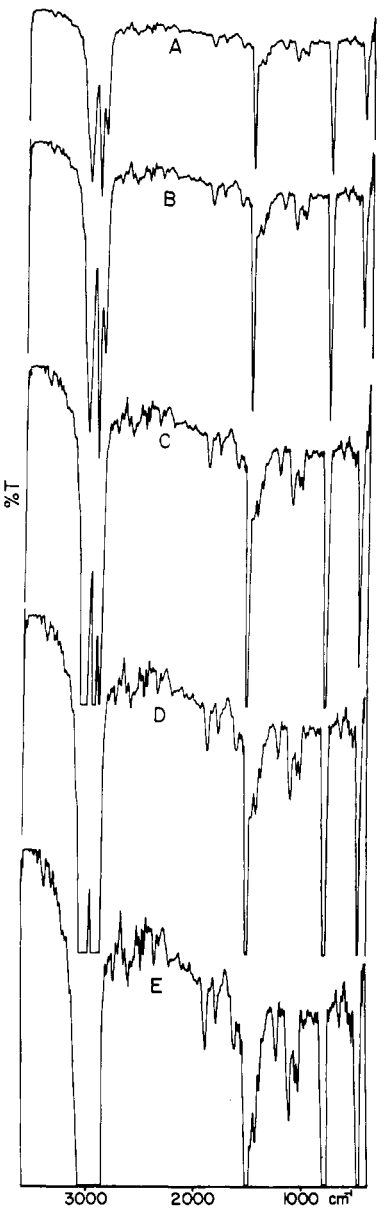

Figure 5. Spectra of *o*-xylene. Sample: 0.01 μl; trapped; 100 scans; 150° C. After spectrum A was recorded it was replotted using ordinate scale expansion to increasing extents (B–E)

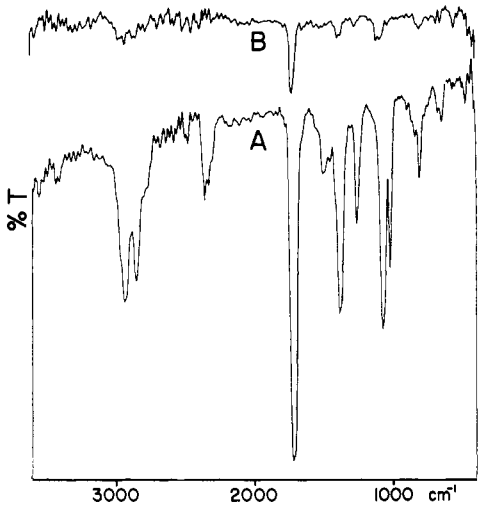

Figure 6. Spectra of dimethylformamide. A: approx. 0.005 μl; trapped; 120 scans; 150° C. B: approx. 0.0005 μl; trapped; 120 scans; 150° C

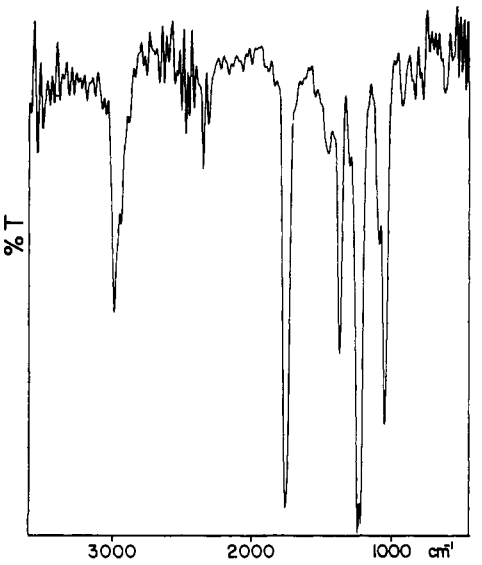

Figure 8. 1-Sec spectrum of ethyl acetate. The sample was flowing and is estimated to be 0.02–0.03 μl

an eluted sample to pass from the gc detector to the micro cell, and a series of such measurements was made at various carrier gas flow rates (10 to 30 ml/min). The valve of the Wilks device was set to pass all of the effluent stream through the cell. A sample was injected and eluted (usually, 1-μl volumes of dilute solutions of the sample proper dissolved in a suitable liquid were used; the gc peak of the solvent was bypassed). The valve was then reset a certain time after the breakthrough of the gc peak had been recorded by the gc plotter, so that the effluent stream bypassed the cell and the gas within the cell was trapped. The spectrum of the trapped gas was then recorded. A series of such measurements was made so that the gc-to-cell delay time and the concentration profile within the cell could be determined. The results of one such series are shown in Figure 3.

EXPERIMENTS AND RESULTS

The Wilks device was fitted with a helium eliminator. Freon-22 was sprayed onto a short length of tubing; the temperature dropped to −50° C within a few seconds and the sample conveyed by the carrier gas was condensed. The tubing was then flash-heated, the vaporized sample was passed into the cell, and spectra was recorded of the concentrated sample (Gilby, 1970; Selander and Gilby, 1971). This procedure was used in examining some samples. An alternative trapping procedure usable with large samples consisted of simply closing the cell, while an eluted peak was flowing through it. The sample concentration within the cell could be estimated by means of concentration profiles such as that shown in Figure 3.

Samples in the 1–0.1 μl range did not lead to useful results because it was very difficult to trap all of the sample and, if an appreciable fraction of a large sample were trapped, some prominent absorption bands would "bottom out" and some spectral detail was lost. An example is given in Figure 4, showing the spectrum obtained with 0.1 μl of 2,2,4-trimethylpentane.

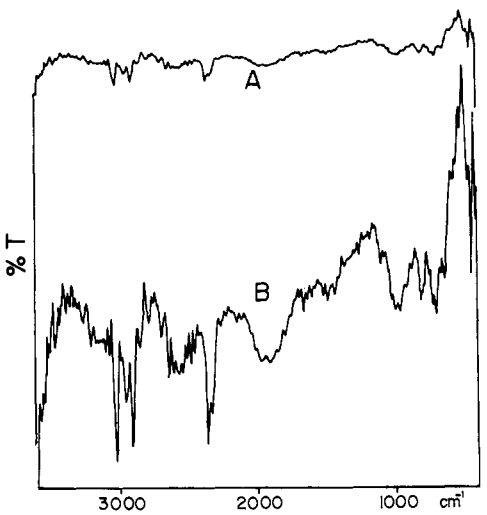

Figure 7. Spectra of 1,5-cyclooctadiene. Sample: approx. 0.0001 μl; trapped; 120 scans; 150° C. After spectrum A was recorded it was scale expanded (B)

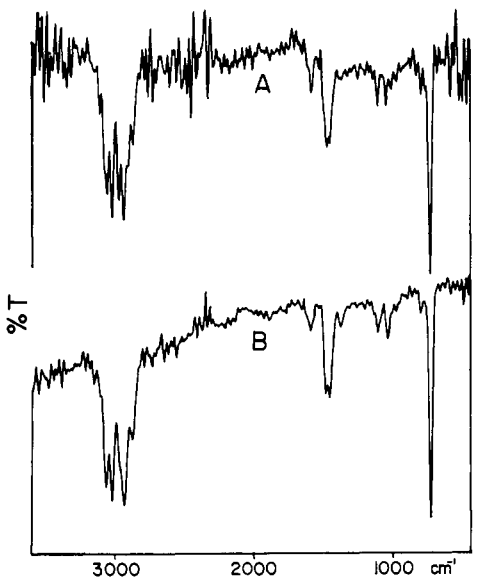

Figure 9. Spectra of toluene. A: The sample was flowing and is estimated to be 0.01–0.02 μl; 1 scan. B: 0.01 μl; trapped; 10 scans

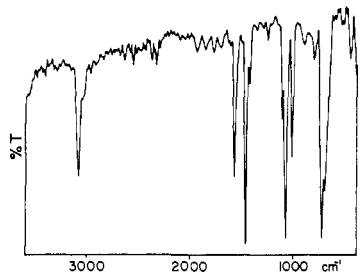

Figure 10. Spectrum of monochlorobenzene. Sample: 0.01 μl; flowing; 100 scans

Somewhat better results were obtained with smaller samples. Some examples are shown in Figures 5 and 6. Good quality spectra were frequently obtained with 0.01-μl samples, so that scale expansion was possible, *e.g.*, the sequence of spectra of Figure 5. It was occasionally possible to obtain good spectra with 0.005 and 0.001 μl samples, *e.g.*, Figure 6. However, attempts to record spectra of smaller samples usually were fruitless because the spectrum obtained showed no characteristic bands at all, was very noisy, as in spectrum B of Figure 6, or was extremely noisy and distorted, as in Figure 7. In the latter, the spectrum shows some C–H bands characteristic of the sample, but their relative intensities are altered, and the rest of the spectrum shows little but noise. In general, reproducibility was poor with small samples, and the frequency with which acceptable spectra would be obtained declined with decreasing sample size.

A few experiments were also carried out with flowing samples. However, as the available computer memory capacity and software permitted only one spectrum to be stored in addition to the background spectrum, the amount of work was not extensive. One procedure involved injecting and eluting samples ranging from 1 to 0.1 μl and using calibration plots such as that shown in Figure 3 to estimate the sample concentration within the cell; a single scan was then made at the appropriate predetermined time. Some examples of single-scan spectra are given in Figures 8 and 9; the spectra show characteristic absorptions but are rather noisy. Another technique involved scanning "across a peak," *i.e.*, scans were taken while an entire small eluted sample flowed through the cell. In this case, principally in order to improve the signal-to-noise ratio but also to avoid missing a part of the sample, the scanning was started 10–15 sec before the sample entered the cell and was continued after the sample had passed through the cell. An example is shown in Figure 10. A 0.02-μl sample was eluted and required approximately 30 sec to pass through the cell. A total of 100 1-sec scans was taken, so that the cell contained only the helium carrier for about two-thirds of the scanning periods.

DISCUSSION

The various results indicate that it was possible to record useful spectra of samples in the 0.01–0.001 μl range. However, the hit-or-miss nature of the results obtained with very small samples points to inadequate sampling and trapping techniques, these probably including the loss of sample due to gas leaks at the valve and cell, as well as improper cooling rates and temperatures of the helium eliminator (Selander, 1971). The experiments were thus limited by sample handling and not by the performance of the spectrometer. As it seems likely that the mechanics of sample handling can be improved and the signal-to-noise ratio can be enhanced by redesigning the optics, it seems not unlikely that it will be possible to obtain spectra of trapped samples at the 0.0001- and 0.00001-μl level with 50 to 200 scans. The spectral resolution can be changed, if required, to 8, 4, 2, 1, or 0.5 cm^{-1} without difficulty, because the scan length need only be increased, but then the time required for scanning will be longer. However, a greatly increased scan time would not be useful for examining gc peaks "on the fly." The present results obtained with flowing samples suggest that it would be possible to record spectra of flowing samples. If adequate computer memory capacity were available, it should be possible to record spectra of each of a series of gc peaks.

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LITERATURE CITED

Dunn, S. J., Block, M. J., American Laboratory (October 1969).
Gilby, A. C., Abstracts, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1970.
Low, M. J. D., *Chem. Commun.* 371 (1966).
Low, M. J. D., *Anal. Lett.* **1,** 819 (1968).
Low, M. J. D., *J. Chem. Educ.* **47,** A163, A255, A349, A415 (1970a).
Low, M. J. D., *Naturwissenschaften* **57,** 280 (1970b).
Low, M. J. D., *J. Paint Technol.* **43,** 31 (1971).
Low, M. J. D., Freeman, S. K., J. AGR. FOOD CHEM. **16,** 525 (1968).
Low, M. J. D., Freeman, S. K., J. AGR. FOOD CHEM. **18,** 600 (1970).
Selander, S.-E., Wilks Scientific Corp., South Norwalk, Conn., private communication, 1971.
Selander, S.-E., Gilby, A. C., Abstracts, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1971.
Welti, D., "Infrared Vapor Spectra," Sadtler Research Labs., Inc., Philadelphia, 1970.

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