Fourier Transform and Apodization

Spectroscopy Business Unit, Analytical & Measuring Instruments Div. Yasushi Nakata

Interferograms

When analyzing a sample by a Fourier transform infrared (FTIR) spectrophotometer, the measurement mode is normally set to transmittance or absorbance. However, unlike a dispersive spectrophotometer, the FTIR instrument does not measure these spectra directly.
In FTIR analyses, Infrared light from the light source passes through
a Michelson interferometer along the optical path.
The Michelson interferometer comprises a beam splitter, moving mirror, and fixed mirror. The light beam split into two by the beam splitter is reflected from the moving mirror and fixed mirror, before being recombined by the beam splitter. As the moving mirror makes reciprocating movements, the optical path difference to the fixed mirror changes, such that the phase difference changes with time. The light beams are recombined in the Michelson interferometer to produce interference light. The intensity of the interference light is recorded in an interferogram, with the optical path difference recorded along the horizontal axis.
The data directly acquired by the FTIR instrument is in the form of an interferogram of the infrared light that passed through the sample. Looking at the interferogram does not give an understanding of the sample characteristics. To get a normal spectrum with the wavenumber (wavelength) along the horizontal axis requires Fourier transform by a computer. This is the major characteristic of the FTIR instrument and differentiates it from a dispersive spectrophotometer, which measures spectra directly.

Principle of Fourier Transform Spectrophotometry

The final data required from sample measurements has the wavenumber along the horizontal axis, as described above. A spectrum shows the light separated into its component wavelengths and the intensity plotted at each wavelength. This separation process is called "spectroscopy."
When the infrared light at wavelength λ enters the Michelson interferometer, if the optical path difference is an integer multiple, the peaks and valleys superimpose, increasing the light intensity. Conversely, when the optical path difference is a half-integer multiple (integer + 1/2), the light becomes weaker. If the original light intensity is denoted as $P(\lambda)$, the intensity $I(x)$ at the optical path difference x can be expressed as

$$I(x)=\frac{1}{2}P(\lambda)\left(1+\cos\frac{2\pi x}{\lambda}\right)$$

In actual Fourier transform, the AC component (cos) in the above expression forms the interferogram with respect to infrared light at wavelength λ.
As the light actually emitted by the light source combines light at various wavelengths, the interferogram obtained is the sum of the expression above at various wavelengths λ.
If the optical path difference is zero (0), the light is reinforced at all wavelengths, such that the interferogram exhibits high intensity. This is called "center burst."
Fourier transform is the process of calculating the wave intensity at each period from the sum at all wave periods. Applying Fourier transform to an interferogram obtains the intensity at each period, that is, at each wavelength.
If an interferogram $I(x)$ for infrared light at continuous wavenumbers can be created using the wavenumber v instead of the wavelength λ, $I(x)$ can be expressed as

$$I(x)=\int_0^\infty S(v)\cos 2\pi vx\,dv$$

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Where, $S(v)$ is the infrared light intensity at wavenumber v. $S(v)$ can be calculated by Fourier transform.
The data obtained is a power spectrum. The ratio between the background and the sample power spectrum produces a spectrum expressed as transmittance.

Apodization

As described above, a transmittance spectrum (or a spectrum converted to an absorbance spectrum) is obtained when Fourier transform is applied to the measured interferogram.
However, the description above applies to a theoretical situation. Actual measurements differ from the ideal state. In particular, the integration range for the expression above is from 0 to infinity. This supports an infinite range of movement of the moving mirror. However, such a movement is impossible. The moving mirror reciprocates through a finite distance, such that in practice this integration has to be cut off in a finite range.
For example, if the integration range is restricted to [$-L$, L], such that the contributions outside this range are not calculated, the Fourier transform expression can be written as

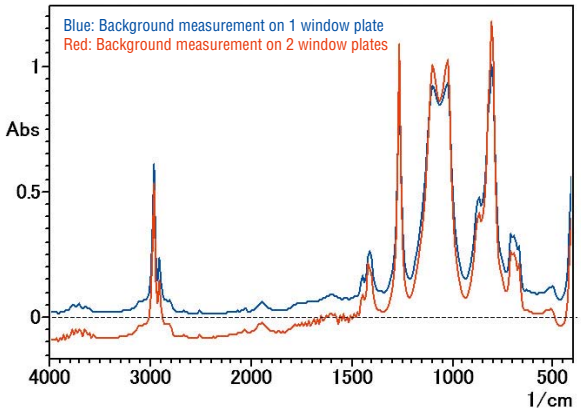


Fig. 5 Transmission Spectrum of Silicone Oil

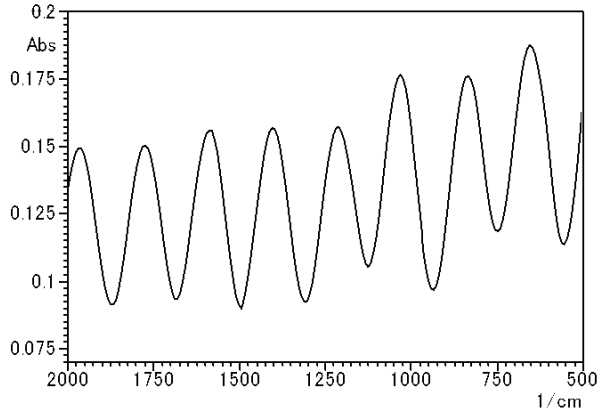


Fig. 6 Interference Fringes from a 0.025 mm KBr Fixed Cell

By measuring the background with one window plate only, the baseline absorbance value is close to zero and the noise due to water vapor is reduced.

4. Precautions During Quantitative Analysis – Determining the Cell Thickness –

When performing quantitative analysis, the same cell is used to measure a sample of known concentration to create the calibration curve and to measure the unknown sample. As only a single cell is used, any effects due to differences in cell thickness are eliminated. However, it may be impossible to maintain a constant cell thickness if multiple fixed cells are used to efficiently analyze a number of unknown samples or if an air-tight cell must be reassembled during the measurements. Correcting for cell thickness by plotting [absorbance value/cell thickness] on the vertical axis of the calibration curve allows the same calibration curve to be used with different cells.
The cell thickness can be accurately determined by using the interference fringes that occur between the two window plates.

If the refractive index between the window plates is n (as the cell normally contains air, this value is n = 1.0) and the angle of incidence is θ, the cell thickness d is given by Expression (1) below.

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2\theta}} \times \frac{1}{(\nu_1 - \nu_2)} \quad \text{Expression (1)}$$

Where, ν_1 and ν_2 are two wavenumbers in the interference fringe (normally selected at peaks or valleys) and Δm is the number of waves between ν_1 and ν_2.
In practical situations, the background measurement is performed with the FTIR sample compartment empty. Next, the empty cell for which the thickness is to be determined is inserted in the sample compartment and sample measurement performed. Fig. 6 shows the interference fringes measured for a KBr fixed cell marked as 0.025 mm cell thickness.

The thickness was calculated by selecting two appropriate wavelengths in the spectrum (2000 cm^{-1} and 1000 cm^{-1}) and substituting refractive index n = 1.0 and angle of incidence θ = 0. The calculated cell thickness was approximately 0.027 mm, which is an error of approximately 8 % with respect to the indicated thickness.
Calculations using the interference fringes are the most commonly used for determining the cell thickness.

5. Analysis Examples

5-1 Deterioration of Mineral Oil

Mineral oils are widely used as machine oils in the automobile, steel, and other industries. There are concerns that the quality may deteriorate over long-term use due to contamination and oxidative degradation. Therefore, periodic inspection or replacement is normally required.
We performed transmission measurements on used and unused machine oil in a 0.5 mm-thick fixed cell with KBr window plates to determine the differences between the oils. Fig. 7 shows the two transmission spectra overlaid.
The red line shows the results for the unused machine oil and the blue line shows the used oil.

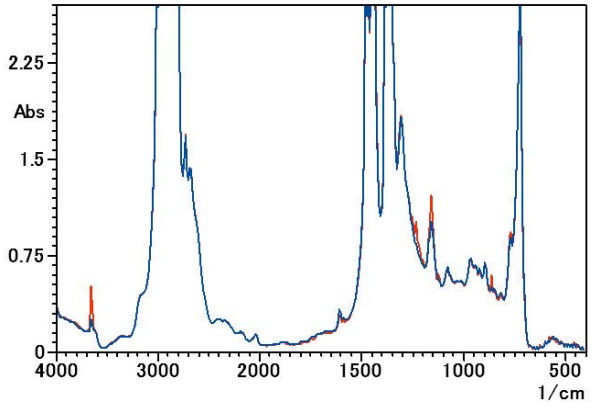


Fig. 7 Transmission Spectra of Used and Unused Machine Oil

Fig. 7 confirms differences near 3650 cm^{-1}, 1155 cm^{-1}, and 1260 to 1190 cm^{-1}. The differential spectrum was determined for the used and unused machine oil and a spectrum search performed using the Sadtler database (polymer additives) from Bio-Rad Laboratories, Inc.
Fig. 8 shows the results. The green line is the differential spectrum. The red line is the infrared spectrum for a phenolic antioxidant produced by the search.

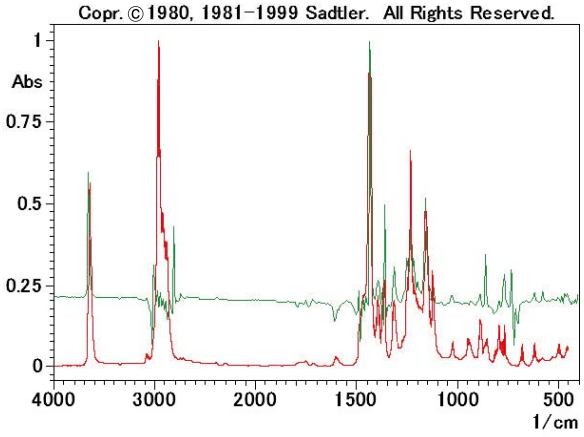


Fig. 8 Search Results for the Differential Spectrum

5-2 Quantitative Analysis of Biodiesel
Biodiesel is produced by methyl esterification of a vegetable oil to remove the glycerin, and then converting the oil to fatty acid methyl esters (FAME). European standards (BS EN 14214: 2003) [1] prescribe a maximum limit of 5 % FAME mixed in automobile fuel. Japanese standards [2] also comply with this limit.
We performed transmission measurements on a FAME standard sample diluted to 0.1 to 0.7 % in accordance with BS EN 14078: 2003 [3].
A 0.5 mm-thick fixed cell was used for the measurements. A calibration curve was created using the carbonyl group peak heights in the measured infrared spectra. Fig. 9 shows the carbonyl group peaks in the FAME standard sample. Fig. 10 shows the calibration curve. An excellent 0.9998 coefficient of correlation was obtained.

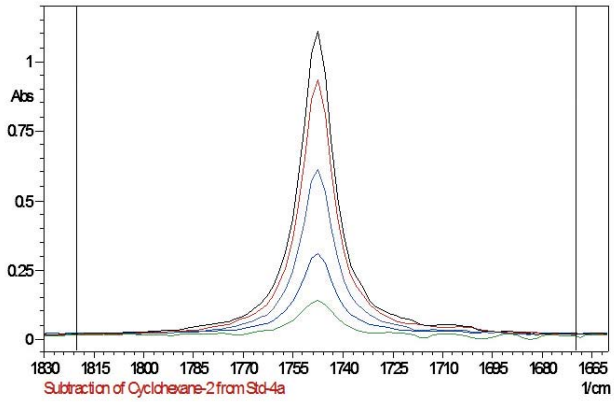


Fig. 9 Carbonyl Group Peaks in FAME Standard Sample

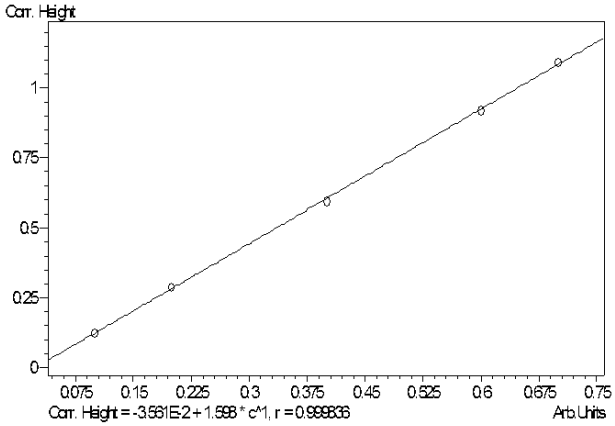


Fig. 10 Calibration Curve for FAME

6. Summary

The liquid film method described above is widely used for quantitative analysis, as well as qualitative analysis. However, the optimal cell type, cell thickness, and window plate material must be selected to suit the purpose of the measurement and the target sample.

References

1) Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods
2) Japanese Agency for Natural Resources and Energy website: Ministerial ordinance concerning partial revisions to the Act on the Quality Control of Gasoline and Other Fuels http://www.enecho.meti.go.jp/info/event/data/077115a.pdf
3) Liquid petroleum products. Determination of fatty acid methyl esters (FAME) in middle distillates. Infrared spectroscopy method

Q&A

Question

Why are ripples in the baseline of the infrared spectrum? What are interference fringes?

Answer

Sometimes the infrared spectrum baseline appears to have ripples or to be superimposed on a regularly fluctuating wave, like a sine wave.

Fig. 1 shows the results of transmission measurements using an infrared microscope on a polypropylene (PP) fragment squashed onto a diamond cell. The baseline measured for the red frame in the photograph exhibits waves similar to sine waves.

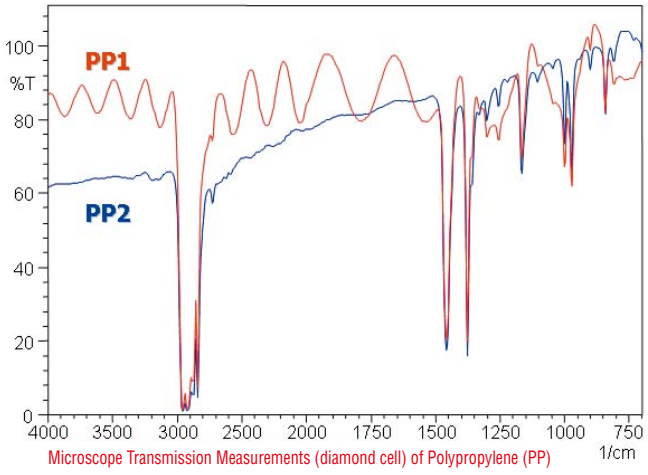
These waves are called "interference fringes." They are caused by multiple internal reflections of the light inside the sample. As shown in Fig. 2, some of the infrared light shone onto the sample passes through the sample (A), some undergoes specular reflection from the sample front surface (B), some undergoes specular reflection from the sample rear surface (C), some undergoes double specular reflections between the front and rear surfaces (D), and some undergoes three or more specular reflections between the front and rear surfaces (E). If the sample is a plastic film, the reflected light (B) to (E) is weaker than the transmitted light (A) because the difference in refractive index at the boundary with the air is 10 % maximum. Light components (A) and (D) move toward the detector. However, due to the multiple reflections in the film, the phase of (D) differs from (A).

The mixture of these two different phases produces the interference fringes.

The interference fringes affect the peak positions and intensities. In addition, interference fringes can hinder both the quantitative analysis and the identification and qualification of unknown substances.

To prevent interference fringes, avoid positions on the sample surface that appear relatively smooth, as shown in Fig. 1. Perform the measurements at rough positions on the sample. Interference fringes can also be prevented by sample pretreatment. Actual examples of this are introduced in "Pretreatment Method for Eliminating Interference Fringes" in Application News A350.

Note, however, that interference fringes can be used to measure the sample's thickness. For details, see ABC of the FTIR Measurement Methods above.



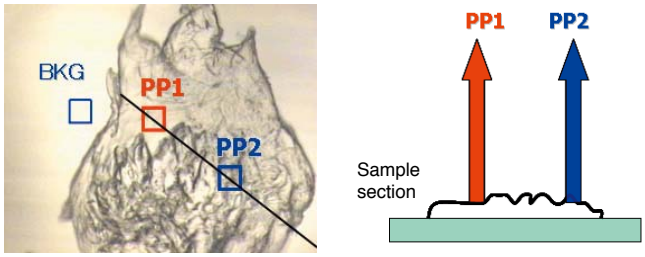


Fig. 1 Transmission Spectrum of Polypropylene (PP)
Appearance of Interference Fringes Due to Measured Position

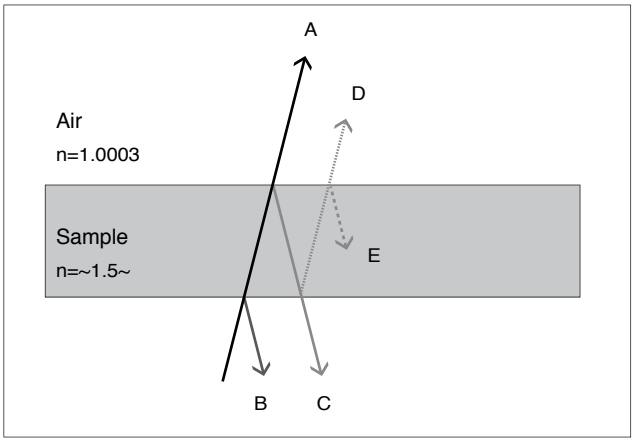


Fig. 2 Overview of Transmission Method

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SHIMADZU CORPORATION. International Marketing Division
3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan
Phone: 81(3)3219-5641 Fax. 81(3)3219-5710
URL http://www.shimadzu.com

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