

# FTIR

## TALK LETTER

### Vol. 21



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# Optical Systems in Infrared Microscopes

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In recent years, a number of infrared microscopes have been introduced as FTIR accessories. They have become simpler to operate and are now a familiar piece of equipment. In this article, I will describe the structure of the Shimadzu AIM-8800 infrared microscope.

Infrared microscopes combine the functions of an optical microscope for observing microscopic regions with infrared spectroscopy.

Fig. 1 shows the Shimadzu AIM-8800 infrared microscope, and Fig. 2 shows its optical system. An infrared microscope consists mainly of (1) an infrared light inlet; (2) transmitted-light condenser mirrors; (3) a sample stage; (4) reflecting objective mirrors; (5) an aperture; (6) a condenser mirror (ellipsoidal mirror); (7) an MCT detector; and (8) a camera for visible-light observations.

I will now describe each part of the infrared microscope in more detail.

## (1) Infrared Light Inlet

With the Shimadzu AIM-8800 infrared microscope, the infrared light used for measurements enters from the FTIR unit. Depending on the selected measurement method (transmission/reflection), the infrared light entering the infrared microscope is directed by a light path switching mirror into either a transmitted-light path (red line in Fig. 2) or a reflected-light path (blue line in Fig. 2). The infrared light entering each light path is then condensed by parabolic mirrors. (The image point in the transmitted-light path is at the pinhole.)

## (2) Transmitted-Light Condenser Mirrors

The transmitted-light condenser mirrors are situated below the sample stage. They focus the infrared light passing through the transmitted-light path onto the sample stage. If a diamond cell or a KBr or BaF<sub>2</sub> window plate is used, the focal point of the transmitted-light condenser mirrors must be adjusted because the image point varies according to the refractive indices. To check that the light is condensed correctly, insert a pinhole in the light path and check the image point and focus of the pinhole image. This is because both the infrared light and visible light form an image at the pinhole position, sample stage, aperture, and detector. Accordingly, as in Fig. 3, if the pinhole image is correctly formed by the camera for visible-light observations, then the positions of the transmitted-light condenser mirrors have been accurately adjusted.



Fig. 1 Shimadzu AIM-8800 Infrared Microscope

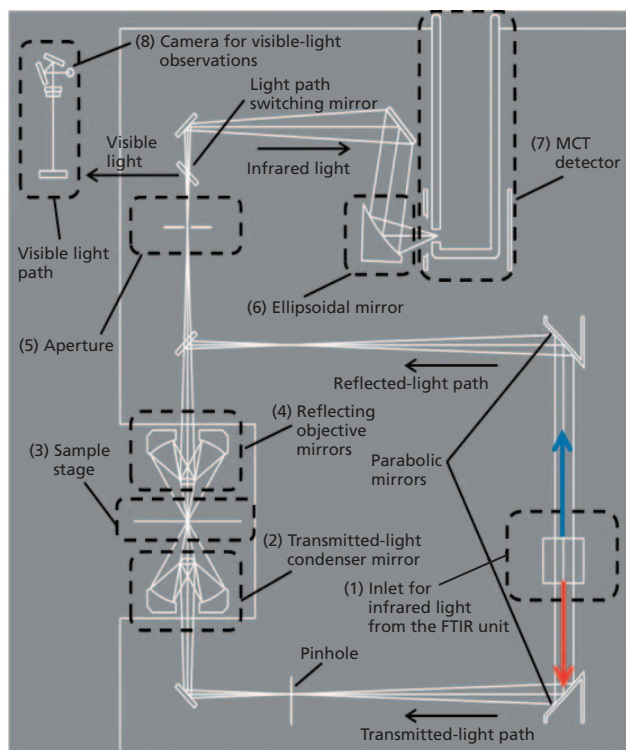


Fig. 2 Optical System in the Shimadzu AIM-8800 Infrared Microscope

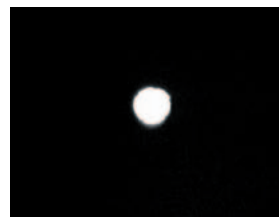


Fig. 3 Pinhole Image (Condenser Mirrors Adjusted Correctly)

### (3) Sample Stage

This is used to fasten and position the sample for measurement. The AIM-8800 sample stage can be moved in 1  $\mu\text{m}$  steps. In addition, a variety of accessories, such as a diamond cell to flatten the sample by applying pressure and a micro vice holder to keep the sample horizontal, can be installed.

### (4) Reflecting Objective Mirrors

Fig. 4 shows the optical systems for the reflecting objective mirrors. The infrared light path in the area of the reflecting objective mirrors differs for the transmitted-light path and the reflected-light path. In the transmitted-light path, the infrared light transmitted by the sample passes through both sides of the reflecting objective mirror in the center and is condensed at the aperture position. In contrast, in the reflected-light path, half of the infrared light is reflected by the half mirror, and enters the reflecting objective mirror located in the center. The infrared light passes through one side of the reflectance objective mirror and shines on the sample surface. The infrared light that returns from the sample then passes through the opposite side of the reflecting objective mirror and is condensed at the aperture position. As a result, the light intensity in reflectance measurements is about half that in transmittance measurements.

### (5) Aperture

The aperture size is set to suit the region to measure. It blocks infrared light passing through other regions. Fig. 5 shows a sample aperture setting configured using AIMView infrared microscope measurement software. (The red frame is the configured aperture.) The aperture is determined by the size in the XY directions and by the rotation angle.

### (6) Condenser Mirror (Ellipsoidal Mirror)

The condenser mirror (ellipsoidal mirror) condenses the infrared light passing through the aperture onto the light receiving surface of the MCT detector. The ellipsoidal mirror has two focal points and allows infrared light shone from one focal point to be condensed onto the other. Accordingly, infrared light condensed at the aperture position is condensed again at the light receiving surface of the MCT detector.

### (7) MCT Detector

The high-sensitivity MCT detector demonstrates its worth in low-light-intensity measurements, such as microscopic measurements, or in gas analyses utilizing a gas cell with a long light path. It is more sensitive than the TGS detector, which is widely used in FTIR units, and so provides favorable spectra even

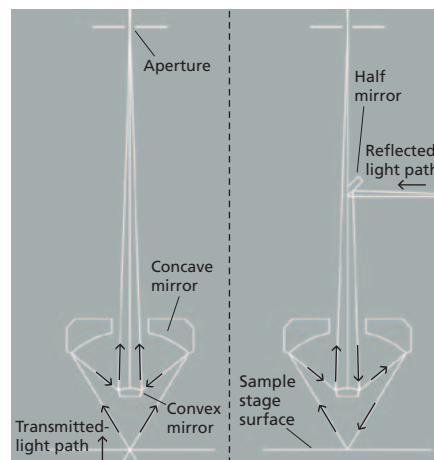


Fig. 4 Reflecting Objective Mirrors  
(Left: Transmitted-Light Path; Right: Reflected-Light Path)

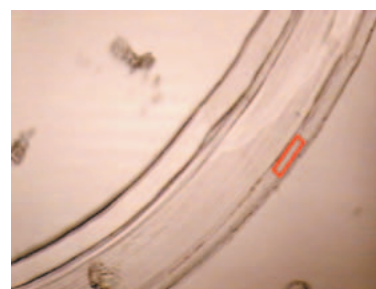


Fig. 5 Example of Aperture Set via AIMView

with a small number of scans. On the other hand, when an MCT detector is used, it must be cooled using liquid nitrogen. Also, it is insensitive to low wave numbers, so the measurable range of wave numbers is narrower than for TGS detectors. For details on TGS detectors, refer to FTIR TALK LETTER Vol. 12. For details on MCT detectors, refer to FTIR TALK LETTER Vol. 13. With the AIM-8800, the wave number measurement range is up to 720  $\text{cm}^{-1}$  (type 1), or up to 650  $\text{cm}^{-1}$  (type 2).

### (8) Camera for Visible-Light Observations

When the visible-light observation mode is set, a switching mirror is inserted just behind the aperture to switch the optical axis to the camera for visible-light observations. A CCD camera is adopted for visible-light observations, which enables observations of a region approximately 450  $\mu\text{m}$  by 330  $\mu\text{m}$ . In addition, a wider range can be observed or measured by using mapping software (optional).

### (9) AIM-8800 Accessories

Other accessories are also available for the AIM-8800 to suit a variety of needs, such as observations and measurements utilizing polarizers for visible or infrared light; measurements with an ATR prism objective mirror; or measurements using sample heating/cooling stages.

# Introduction to Time Course Measurements, Which Are Effective for Reaction Analysis

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Real-time tracking of the synthesis or decomposition process for a chemical substance would enable obtaining extremely useful information for understanding the reaction mechanism. FTIR is one of only a few structural analysis methods capable of real-time measurements. If you are tracking processes with reaction times of a few minutes to a few hours, measurements can be performed with general FTIR. The LabSolutions IR FTIR control software provides an optional time course measurement program to track reactions. Here, I will introduce the functionality of the time course measurement program with several examples.

## 1. Overview of the Time Course Measurement Program

The time course measurement program measures a sample spectrum at regular time intervals. It then displays a time course graph showing changes in the shape of the overall spectrum and in peak intensity at a specific level, thus allowing you to analyze the sample reaction process. In addition to the peak height and area, it can track changes based on values calculated from them. After measurements are complete, the information can be saved as three-dimensional data, and displayed as either a bird's eye view or a contour map. In addition, the parameters can be changed and the time course graph recalculated.

Here is a brief description of the measurement procedure.

### 1) Select time course measurement

Select time course measurement on the menu shown in Fig. 1.

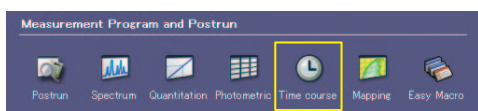


Fig. 1 Menu Selection Window

### 2) Initialize the instrument and set the instrument parameters

In the window shown in Fig. 2, click [Instrument] (1) to initialize the instrument. Next, click [Settings] (2) to display the [Instrument Parameters] window. Then configure the measurement parameters including the decomposition setting and the number of scans.

### 3) Configure the time settings

Next, click [Time Settings] (3) in Fig. 2 to display the [Time Setting] window shown in Fig. 3. Set the measurement time and measurement interval according to the reaction of interest. The measurement time is the time until the measurements finish. When you click [Obtain scan interval], shown in the red frame in Fig. 3, the software calculates the minimum interval possible under the conditions set at step 2). Use this as a reference when entering the measurement interval.

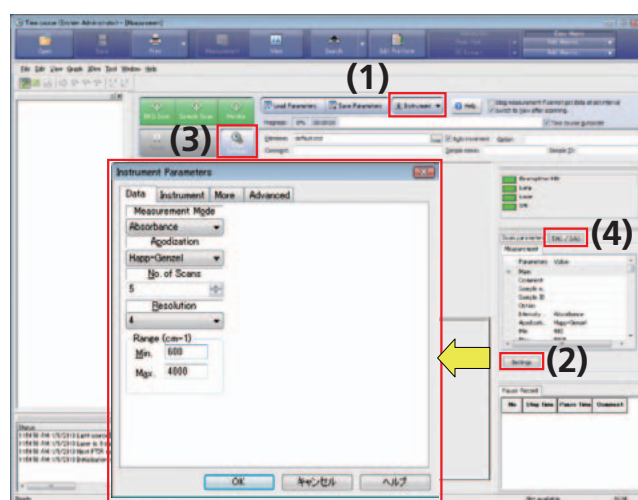


Fig. 2 Time Course Measurement Window

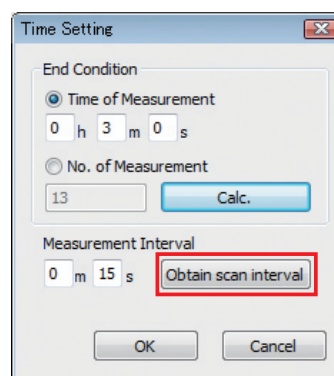


Fig. 3 Time Settings Window

### 4) Set the peak wave numbers of interest

If there are peaks you wish to monitor during the measurements, click [TAC/SAC] (4) in Fig. 2. Their evaluation items (peak height, area, etc.) and wave number information can now be set. At this point, a TAC (Total Absorption Curve) graph is displayed showing changes in absorption for all wave numbers. In addition, up to ten SAC (Selected Absorption Curve) graphs can be configured to show changes at other wave numbers.





Fig. 4 Window Displayed During Time Course Measurements

### 5) Start the measurements

Perform a BGK measurement before sample placement. Next, position the sample, and start the time course measurements. During the measurements, as shown in Fig. 4, the two-dimensional time course data based on the items configured at step 4) will be displayed at the top of the window, and the monitor spectrum will be displayed at the bottom.

### 6) Finish the measurements

After measurements are complete, the program switches from the [Measurement] window to the [Display] window, in which a three-dimensional graph is displayed.

### 7) Perform post-run analysis

Baseline correction and other batch data processing can be performed on the resulting spectrum. Spectral extraction and even reaction rate calculations utilizing data from peaks of interest are also possible.

Now, I will introduce examples of actual time course measurements.

## 2. Hardening of a Vinyl Chloride Resin Adhesive

The sample we used is an adhesive consisting of a thermoplastic vinyl chloride-vinyl acetate copolymer resin dissolved in an organic solvent (such as acetone or cyclohexanone), which is used as an adhesive for vinyl chloride pipes. Because of the volatility of the organic solvent, it hardens completely in about 20 minutes.

The Specac ATR accessory (Golden Gate Diamond ATR), shown in Fig. 5, was utilized for the measurements. This sample measurement unit is suitable for measuring adhesives because an ATR prism made of diamond is attached to the prism plate using



Fig. 5 Golden Gate Diamond ATR Accessory

Table 1 Instrument and Analysis Conditions

Instrument : IRAffinity-1,  
Golden Gate Diamond ATR  
Resolution : 4.0 cm<sup>-1</sup>  
Accumulation : 40  
Apodization : Happ-Genzel  
Detector : DLATGS

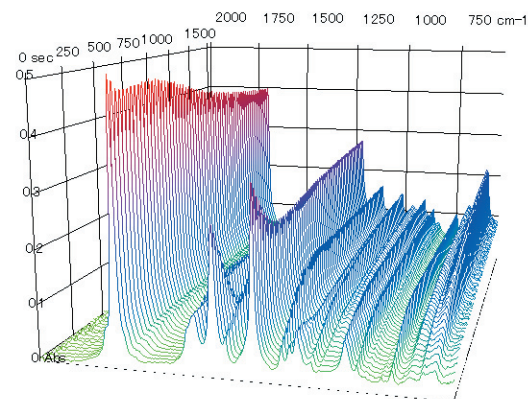


Fig. 6 Three-Dimensional Graph of Time Course Measurements

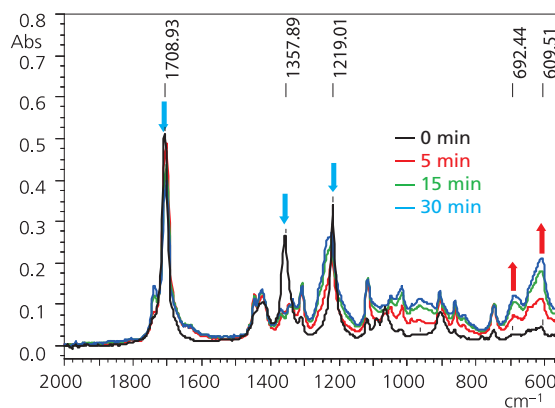


Fig. 7 ATR Spectral Overlap

high-temperature tungsten carbide disc soldering. Measurements were started when a drop of the sample was placed on the diamond disc, and were continued for 1,800 seconds (30 minutes) at 30-second intervals. The analysis conditions are shown in Table 1.

Fig. 6 shows the three-dimensional graph of the 2,000 cm<sup>-1</sup> to 550 cm<sup>-1</sup> region obtained from the time course measurements. The X and Y axes show time (sec) and wave number (cm<sup>-1</sup>), respectively. The Z axis shows the absorbance. The reaction process for this sample can thus be observed chronologically.

Fig. 7 shows an overlap of the infrared spectra sampled directly after the start of measurement (0 minutes), and after 5 minutes, 10 minutes, and 30 minutes. It can be seen that peaks in the vicinity of 1,708 cm<sup>-1</sup>, 1,357 cm<sup>-1</sup>, and 1,219 cm<sup>-1</sup> gradually diminish as the measurements continue. These are likely peaks for components originating from the acetone. In addition, it shows that peaks for the C-Cl stretching vibrations in the vicinity of 692 cm<sup>-1</sup> and 609 cm<sup>-1</sup>, originating from the vinyl chloride resin, gradually increase.

Next, the hardening reaction rate was calculated by

using the peak area value in the vicinity of  $609\text{ cm}^{-1}$ , assuming that the reaction rate at the start of the measurements was 0 % and that the hardening reaction time was 30 minutes. If  $A$  is the peak area for the C-Cl stretching vibrations in the vicinity of  $609\text{ cm}^{-1}$  during the hardening reaction,  $A_0$  is the peak area in the vicinity of  $609\text{ cm}^{-1}$  for the unhardened substance (0 minutes), and  $A_{30}$  is the peak area in the vicinity of  $609\text{ cm}^{-1}$  for the hardened substance (30 minutes), then the hardening reaction rate  $X$  (%) can be found from the following formula.

$$X (\%) = (A - A_0) / (A_{30} - A_0) * 100$$

Fig. 8 shows the calculation results. As noted above, with the two-dimensional time course data, not only peak height, peak area values, and peak ratios, but also reaction rates and other calculation results can be displayed.

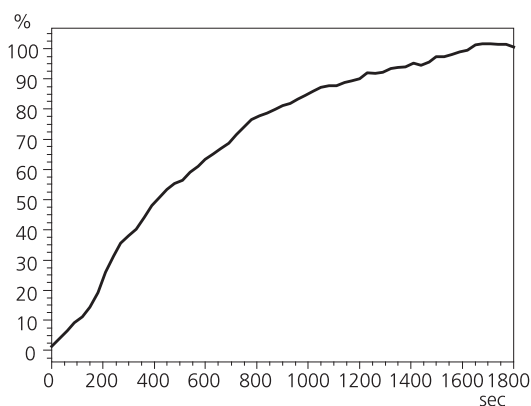


Fig. 8 Reaction Rate for the Hardening of a Vinyl Chloride Resin Adhesive

### 3. Measuring the Heating of Erasable Ink

Special inks that enable written characters to be erased using a rubber have become a focus of attention. With such inks, the frictional heat causes the ink components to react, making the colored components transparent. Observing the reaction during the heating process requires a temperature-controlled accessory. Here, I will introduce an example of time course measurements of the heating process utilizing a heating stage that can be attached to an infrared microscope.

Fig. 9 shows the heating stage used for the measurements. This heating stage can be thermally controlled across a range from room temperature to  $500\text{ }^{\circ}\text{C}$ , and can be used with either the transmittance or reflectance method. A sample of the special ink was applied to an aluminum plate, which was then set on the heating stage. The peak intensity of the infrared spectrum varies depending on the thickness of the ink layer, so a search was made for the position where the appropriate spectral intensity was obtained, and a  $30\text{-}\mu\text{m}$  square aperture was configured.

Fig. 10 shows the configured measurement area. The heating stage was set to heat from  $25\text{ }^{\circ}\text{C}$  to  $70\text{ }^{\circ}\text{C}$  with a rise of  $5\text{ }^{\circ}\text{C}/\text{min}$ . The analysis conditions are shown in

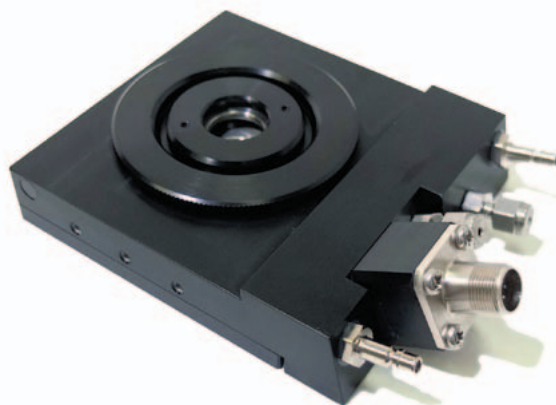


Fig. 9 Heating Stage

Table 2. Fig. 11 shows the overlapping total infrared spectra obtained from the measurements. Fig. 12 shows a three-dimensional graph of the infrared spectra in the range from  $2,000\text{ cm}^{-1}$  to  $750\text{ cm}^{-1}$ . It is evident that a number of peaks increase or decrease in intensity as a result of the temperature rise. The changes in the peak area in the vicinity of  $1,179\text{ cm}^{-1}$ , shown by the red arrow in Figs. 11 and 12, are shown with respect to the time axis in Fig. 13(a). It is evident that the spectral changes start about 300 seconds after the initial measurement.

In the heating measurements, it is necessary to check spectral changes with respect to the temperature axis. However, if the temperature information with respect to the time axis is already known, it is possible to convert the horizontal axis in the time course data to a temperature axis. Fig. 13(b) shows the horizontal axis converted to a temperature axis. It reveals that the spectrum changes significantly in the vicinity of  $60\text{ }^{\circ}\text{C}$ .

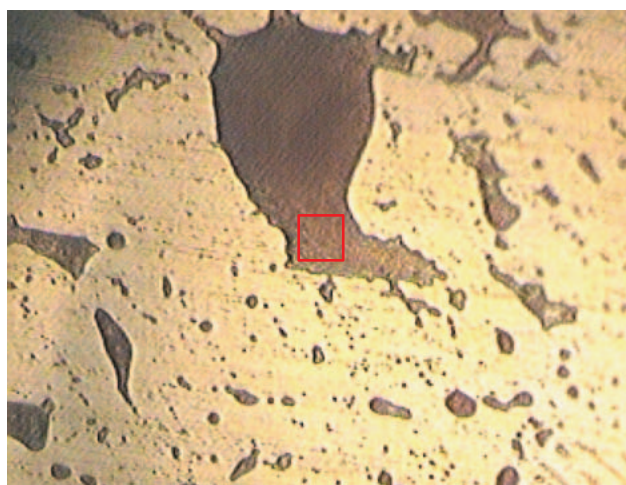


Fig. 10 Photograph of the Measurement Area

Table 2 Instrument and Analysis Conditions

Instrument : IRAffinity-1, AIM-8800
Resolution : $8.0\text{ cm}^{-1}$
Accumulation : 20
Apodization : Sqr Triangle
Detector : MCT

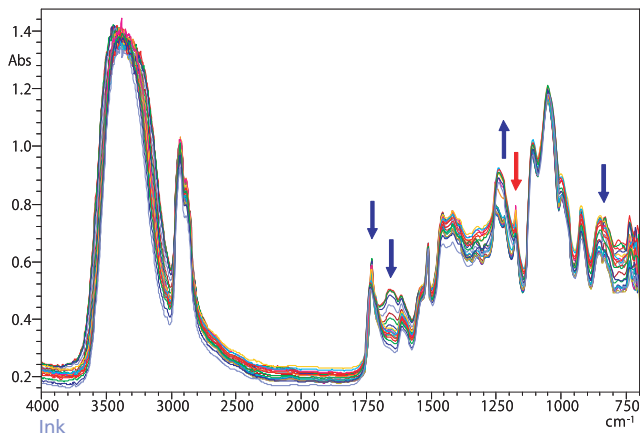


Fig. 11 Overlap of the Total Spectra from the Time Course Measurements

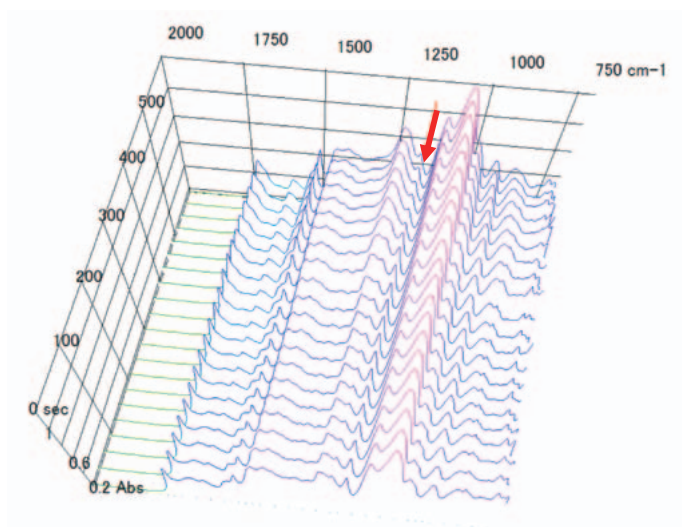


Fig. 12 Three-Dimensional Graph from the Time Course Measurements

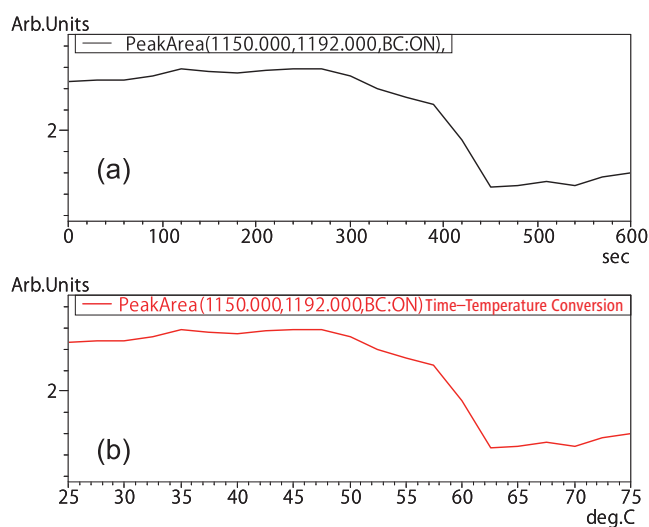


Fig. 13 Changes in Peak Area in the Vicinity of 1,179  $\text{cm}^{-1}$

## 4. Conclusion

This article has introduced measurement examples of the hardening of an adhesive and the loss of color of an ink, utilizing the time course measurement program. The time course measurement program introduced here not only provides the continuous data sampling functionality required for reaction analyses, but also includes functions to meet the detailed requirements of everything from the display of data after measurement to post-run analysis.

In measuring the reaction processes of actual samples, it is necessary to select the optimal measurement methods and accessories according to the form of the samples and the measurement objectives. In addition to the accessories introduced here, a variety of heating measurement instruments is commercially available. For inquiries about measurement methods, please contact your Shimadzu representative.



# IRTracer-100

Fourier Transform Infrared Spectrophotometer



## Features

### Superior Sensitivity and Reliability

- High sensitivity, high resolution, and high speed
- Interferometer optimization and stabilization technology support high sensitivity
  - The dehumidifier and Advanced Dynamic Alignment enable easy interferometer maintenance.
  - Self-diagnostics and monitoring technology ensure fast, easy instrument control.

### Next-Generation Workstation Designed for the Future

- LabSolutions IR provides network compatibility, a wealth of libraries, and advanced search functions as standard. Macro functions provide for automation and labor savings.

### Applications Play an Active Role in a Variety of Situations

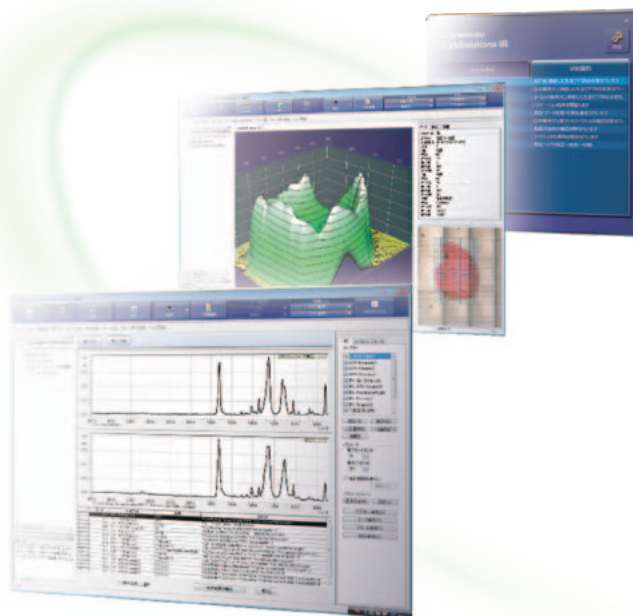
- Supports analysis with two key applications for contaminant analysis and identification tests.
- A wealth of options enhance expandability.

# LabSolutions IR

Analytical Data System for FTIR

## Features

- In addition to improved search functions, libraries containing approx. 12,000 spectra are included as standard.
- An "Easy Macro" program is included to easily create macros for routine work, everything from measurement to data processing, searches, and printing.
- Special programs are included as standard to simplify contaminant analysis (analysis of mixtures) and pharmacopoeia analysis (identification testing).
- As part of the LabSolutions family, this software provides advanced security and user administration functionality.
- Complies with FDA 21 CFR Part 11, PIC/S, and other ER/ES regulations.
- Enables centralized management of valuable FTIR data, as well as LC and GC data, using network servers.
- Security and backup procedures are easy.



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