C103-E098

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FTIR
TALK LETTER
Vol. 22

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Semi-Custom FTIR Systems

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Three techniques are available for analyzing samples using a Fourier transform infrared spectrophotometer (FTIR) or infrared microscope. These involve measuring either transmittance, reflectance, or attenuated total reflectance (ATR). Various standard accessories are available for each of these techniques. However, in many cases, analytical objectives cannot be accomplished using only these standard accessories. Furthermore, even if satisfactory spectra can be obtained, the resulting data may be difficult to analyze. For these situations, Shimadzu can offer semi-custom products that may more closely fit customer needs.
This article features some of the semi-custom FTIR, infrared microscope, and software products that Shimadzu has created in order to satisfy particular analytical objectives.

1. TG-FTIR Gas Measurement System

1-1. Overview

The TG-FTIR gas measurement system measures gas using a combination of thermogravimetric (TG) and FTIR analysis. The system is able to quantitatively measure the change in sample mass due to decomposition, evaporation, etc., as the temperature changes on the TG side and, at the same time, qualitatively analyze the gases generated from the TG side by injecting the gases into the FTIR side.

1-2. System Configuration

Fig. 1 shows how the TG-FTIR system is configured. Generated gases discharged from the TG side pass through the TG-FTIR connector parts (injection tube) and enter a temperature-controlled gas cell installed in the FTIR sample compartment.

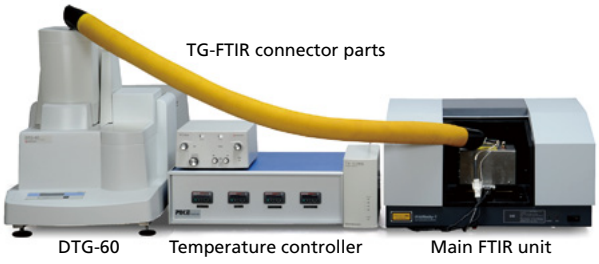

Fig. 1 Appearance of TG-FTIR System

1-3. Application[1)]

In this application, the TG-FTIR system was used to analyze a thermoplastic polyimide prepreg, which is used in carbon fiber reinforced plastic (CFRP) composites that contain heat-resistant polyimide resin, and then measure the generated gases.
Fig. 2 and Fig. 3 show a TG-DTA curve and 3D infrared red spectra results, respectively.
The DTA curve in Fig. 2 shows a glass transition near 250 °C and the TG curve shows a slight decrease in mass between 200 and 400 °C (between about 500 and 1000 seconds). Furthermore, though not shown here, results from the qualitative analysis of gases generated during the slight mass loss indicated above suggest that the gas was probably phthalate esters.

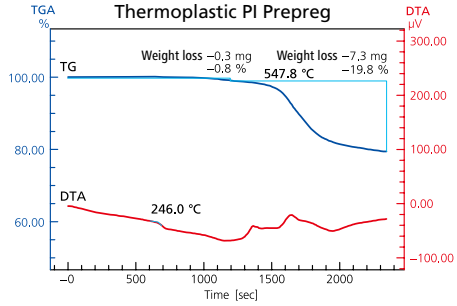

Fig. 2 TG-DTA Curve of Thermoplastic Polyimide Prepreg

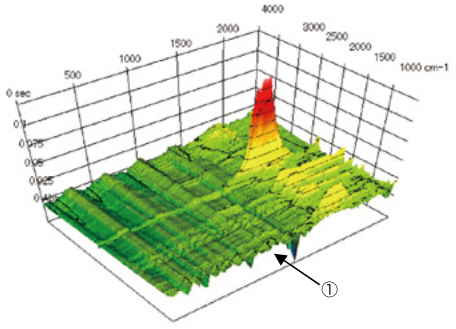

Fig. 3 3D Display of Infrared Spectra of Thermoplastic Polyimide Prepreg

2. UV Ray Irradiation Measurement System (Reflectance)

2-1. Overview

This system is used to track the reaction process during the curing of resins or other materials by UV irradiation. It tracks reactions by using a special specular reflectance attachment for measuring reflectance. Fast reactions that finish in a second or less are measured using an FTIR system capable of rapid scanning.

2-2. System Configuration

Fig. 4 shows an overview of the reflectance measurement system, which consists of an FTIR unit capable of rapid scanning with an MCT detector and a special specular reflectance attachment. UV rays are irradiated from above, with an external switch used to start the measurement at the same time as UV irradiation.

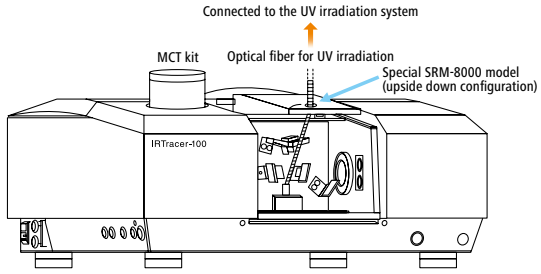

Fig. 4 Appearance of UV Irradiation System (Reflection System)

2-3. Application[2)]

A metal plate was coated with a commercial UV-curable acrylate-based resin and the curing reaction process was tracked using the specular reflectance method. The UV rays, which serve as the reaction trigger, were irradiated from above and the measurement was started at the same time as the UV irradiation. Fig. 5 shows three-dimensional measurement results, based on infrared spectra plotted at one-second intervals.

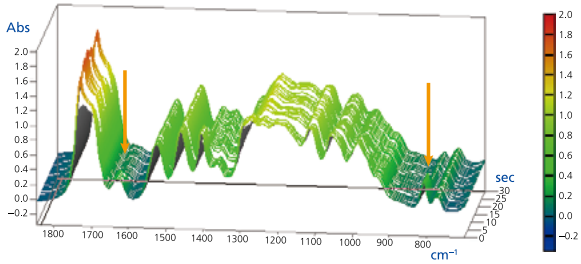

Fig. 5 3D Spectra of Rapid Scan Measurement Generated in Curing Reaction in UV-Irradiated Resin

It shows vinyl groups forming in a short time after UV irradiation. Note that the absorption at 1,635 cm^{-1} and 810 cm^{-1} is due to C=C stretching vibration and C–H out-of-plane bending vibration of the vinyl group.

3. UV Ray Irradiation Measurement System (Transmittance)

3-1. Overview

This is basically the same as the UV ray irradiation measurement system described in 2. above, but it measures samples based on transmittance. This system also starts measurements at the same time as UV irradiation.

3-2. System Configuration

A horizontally mounted sample transmittance measurement unit is installed in the sample compartment and UV rays are irradiated from above. (*See* Fig. 6.)

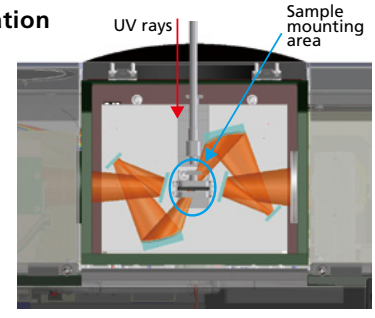

Fig. 6 Overview of UV Irradiation System (Transmission System)

4. Spectral Emissivity Measurement System[3)]

4-1. Overview

This system measures the intensity distribution of infrared radiation from a heated sample and from a black body furnace at the same temperature as the sample and then determines the emissivity (radiant emittance) at each wavelength based on their ratio.

4-2. System Configuration

Infrared light emitted from an external light source or heated sample enters via the parallel light output port on the side of the interferometer in the FTIR unit. The system then measures the intensity distribution of those light spectra. (*See* Fig. 7.) It can measure temperatures of 200 °C or higher. To stabilize the surface temperature of samples, flat plate shaped samples are recommended. For more details, refer to FTIR TALK LETTER Vol. 13.

If measurements at temperatures below 200 °C are desired, an integrating sphere can be used to perform theoretical calculations based on the assumption that the sum of transmittance, reflectance, and emissivity is equal to one.

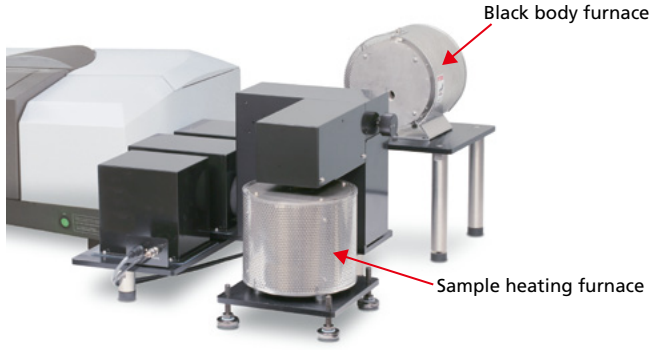

Fig. 7 Appearance of Spectral Emissivity Measurement System

4-3. Application

The spectral emissivity spectrum was measured from a 1 mm thick round flat alumina ceramic plate heated to 450 °C. (*See* Fig. 8.) It shows extremely high emissivity near wavelengths between 6 and 10 µm.

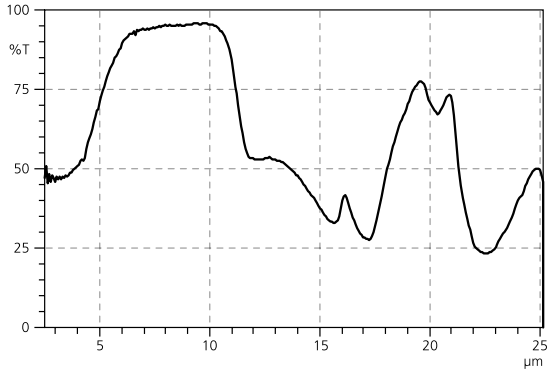

Fig. 8 Spectral Emissivity Spectrum of Alumina Ceramic

5. Liquid Nitrogen-Free Detector for Infrared Microscopes

5-1. Overview

This liquid nitrogen-free system features a TGS detector, capable of measuring samples at room temperatures, installed on an infrared microscope. It is especially useful for measurements in environments where liquid nitrogen cannot be used or in wavenumber regions that cannot be measured using MCT detectors that require liquid nitrogen.

5-2. System Configuration

To switch between MCT and TGS detectors as necessary, the TGS detector is mounted in the optical path switching area of the infrared microscope. (*See* Fig. 9.)

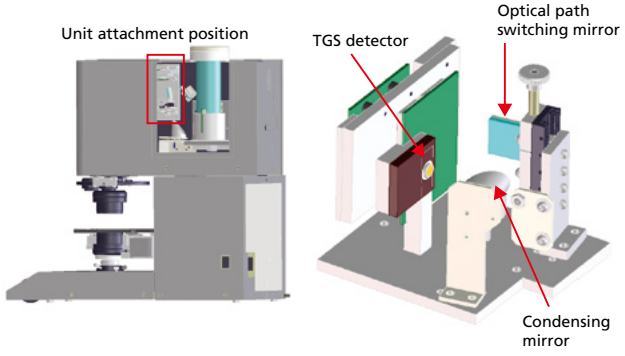

Fig. 9 Detector Unit Overview and Mounting Position for Shimadzu AIM-8800 Infrared Microscopes

5-3. Application

Fig. 10 shows a resinoid contaminant measurement example. In the infrared spectra, the red line indicates measurement by an MCT detector, whereas the blue line indicates measurement using a TGS detector.

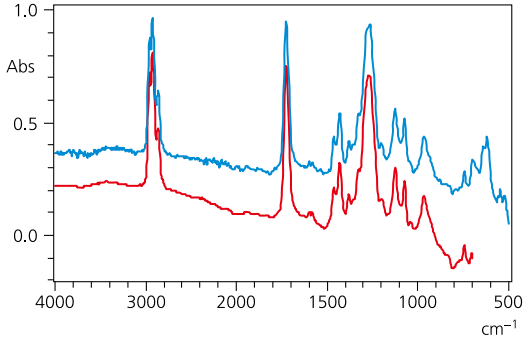

Fig. 10 Infrared Spectra of Resinoid Contaminant (Red line: MCT detector; Blue line: TGS detector)

Though not shown here, a search for the red spectrum indicated three similar candidate substances (alkyd resin, phthalate ester, and PVC), but it is not possible to determine which search result is correct. In contrast, the blue spectrum shows absorption near 600 cm^{-1}, which allows you to determine that the contaminant is PVC. (The absorption near 600 cm^{-1} is due to C–Cl stretching vibration.)

6. Program for Calculating the Concentrations of Light Elements in Silicon Wafers

6-1. Overview

This software is used to automatically quantify the substitutional atomic carbon content and interstitial atomic oxygen content in silicon crystals and the hydrogen content from N–H and Si–H in SiN films.

6-2. System Configuration

With respect to substitutional atomic carbon content and interstitial atomic oxygen content, the software is compliant with standards established by the Japan Electronics and Information Technology Industries Association (JEITA). However, compliance with JEITA standards requires respective blank samples, which must be prepared by the customer. For more details regarding blank samples, refer to the JEITA standards or the Shimadzu FTIR Custom Products Handbook (C103-E097).

6-3. Application[4)]

The transmittance was measured for three types of 2 mm thick monocrystalline silicon samples with different interstitial atomic oxygen content levels. Fig. 11 shows the automatic quantitation results.

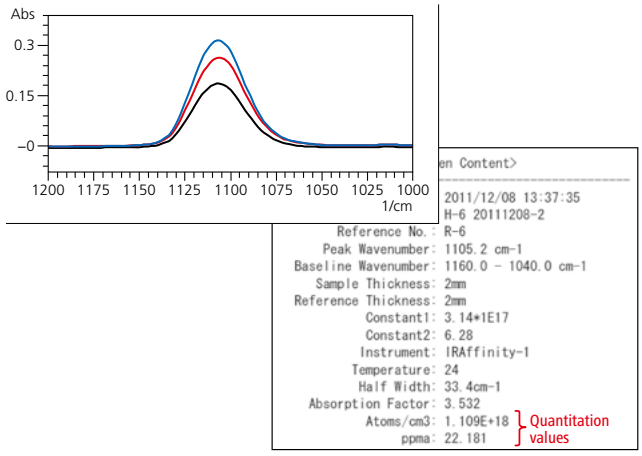

Fig. 11 Infrared Spectra of Samples with Differing Interstitial Atomic Oxygen Levels and Automatic Quantitation Results for the Blue Line Sample

Conclusion

This article features a few semi-custom products that have been customized to customer needs (five hardware products and one software product). However, Shimadzu offers many other semi-custom products and additional ones can be prepared according to customer requirements. To request additional information, please contact your Shimadzu sales representative.

References

1) SHIMADZU Application News No. A474
2) SHIMADZU Application News No. A457
3) FTIR TALK LETTER Vol. 13
4) SHIMADZU Application News No. A445

Using Difference Spectra

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One spectral data processing function allows performing arithmetic operations (addition, subtraction, multiplication, or division) on spectra. In particular, subtraction between spectra (to obtain a difference spectrum) is especially useful and widely used for detecting substances other than the primary components or changes in components. This article discusses the effectiveness of using difference spectra and some key considerations for actually calculating and using them.

1. Introduction

On occasion, customer who use FTIR systems contact us for advice on contaminant analysis. In most cases, they are able to measure the infrared spectrum of the contaminant, but are frustrated with analyzing the data. We often hear that a library search for the infrared spectra obtained does not result in any perfect matches or that they are able to determine the areas that differ between the spectra, but cannot interpret what specifically is different and how.
In such cases, we recommend using difference spectra to analyze the spectral data. This article features examples and discusses some key points for using difference spectra.

2. Measuring Contaminants and Calculating Difference Spectra

Fig. 1 shows an infrared spectrum obtained from measuring a white fibrous contaminant by single reflection ATR, along with the top matching cellulose spectrum from library search results, which are shown offset. The contaminant spectrum is very similar to the cellulose spectrum from the library, which indicates that cellulose is a primary component of the contaminant.

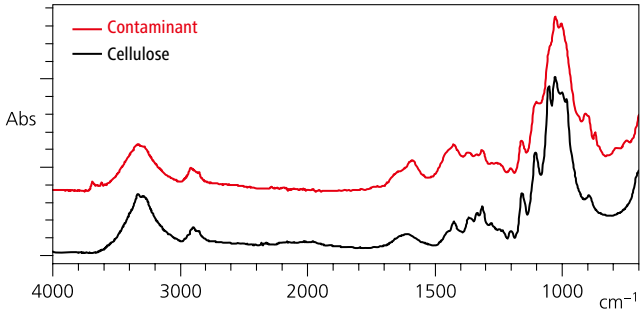

Fig. 1 Contaminant Spectrum and Cellulose Spectrum from Library

Based on the search results and external appearance of the white fiber, the substance may be from a paper towel. Therefore, an infrared spectrum obtained from measuring the paper towel and a spectrum of the contaminant are overlaid, as shown in Fig. 2.

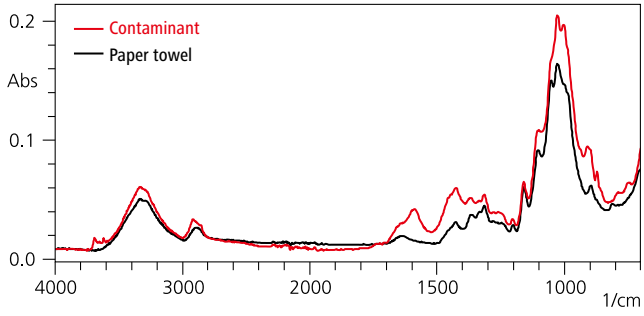

Fig. 2 Infrared Spectra of Contaminant and Paper Towel

Since the overall intensity of these two spectra differs, displaying the spectra with their overall intensity levels aligned is a convenient way to compare them in detail to determine whether or not their shapes match. In LabSolutions IR software, this is accomplished by right-clicking on the screen and clicking [Y-Expand To Fit] on the right-click menu. Using this function, the peak near 1028 cm^{-1} is used as a reference for aligning intensity, as shown in Fig. 3.

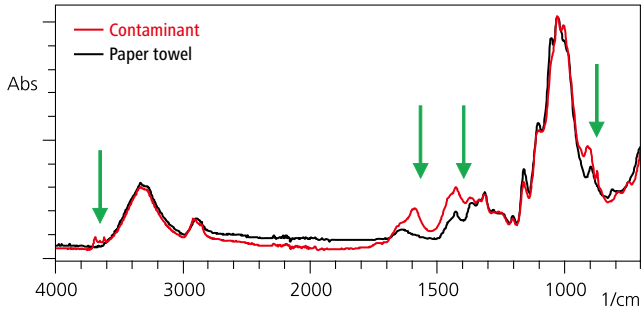

Fig. 3 Infrared Spectra of Contaminant and Paper Towel (with Intensity Levels Aligned)

The shapes of the contaminant and paper towel spectra are very similar. However, the areas indicated with arrows include peaks unique to the contaminant, making it somewhat difficult to conclude that the contaminant is the same substance as the paper towel.

So what is the component causing the contaminant-specific peaks? The top candidates listed in the spectral search results for the contaminant are cellulose-based substances and successively investigating each small difference in spectra is not an easy task. However, using difference spectra provides a very effective way to identify these small differences. In general, this involves overlaying the spectra to determine which spectrum has more peaks and then subtracting the spectrum with fewer peaks from the spectrum with more peaks. In this case, we subtracted the paper towel spectrum from the contaminant spectrum. Spectral search results for the difference spectrum obtained did not include any components that perfectly matched the entire difference spectrum, but included kaolin, an inorganic compound, at the top of the list. Fig. 4 shows the difference spectrum and library spectrum for kaolin. It indicates how the characteristic peak profile shape for kaolin is similar to part of the difference spectrum.

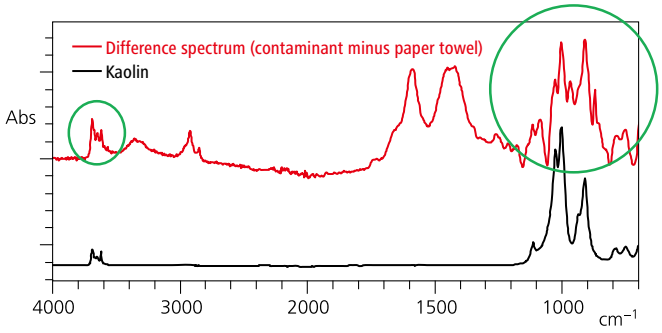

Fig. 4 Difference Spectrum and Library Spectrum for Kaolin

Furthermore, by focusing on the peaks between 3000 and 1200 cm^{-1} in the difference spectrum and comparing the peak profile to listed library spectra for that interval, it was determined that the library spectrum for carboxylate was very close. Fig. 5 shows the difference spectrum and library spectrum for magnesium stearate.

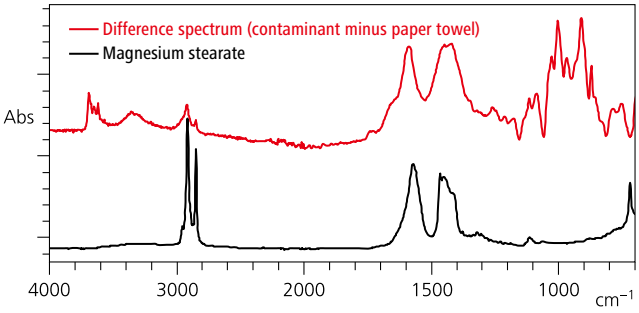

Fig. 5 Difference Spectrum and Library Spectrum for Magnesium Stearate

Kaolin and magnesium stearate are widely used as additives in plastic products. It is typical for such additive peaks to result in only small differences overlapping with peaks for primary components, so utilizing difference spectra can be especially effective for identifying such peaks.

3. Key Considerations for Calculating Difference Spectra

Spectra A and B are subtracted by calculating A minus B over the entire spectra. However, with actual measurement results, spectra A and B typically have different overall intensity levels and the peak intensity levels for the components in A and B are also inconsistent. Therefore, simply subtracting spectrum B from spectrum A will leave some peaks remaining that ideally should be eliminated or will cause inverted peaks due to subtracting too much. Consequently, in actual calculations, results are adjusted by multiplying one of the spectra by a coefficient that results in eliminating certain target peaks, in the form A – kB, where k is the coefficient. The data calculation (spectral calculation) function used to calculate difference spectra includes a function for adjusting this k value.
Fig. 6 shows calculation results using significantly different k values for the difference spectrum in Fig. 4. The k value was somewhat small for the upper difference spectrum, resulting in a spectrum similar to the original contaminant spectrum, which reduces the benefit of calculating a difference spectrum. This gives the impression that not enough was subtracted. In contrast, the k value was too big in the lower difference spectrum, which resulted in prominent inverted peaks. Therefore, it gives the impression that too much was subtracted.

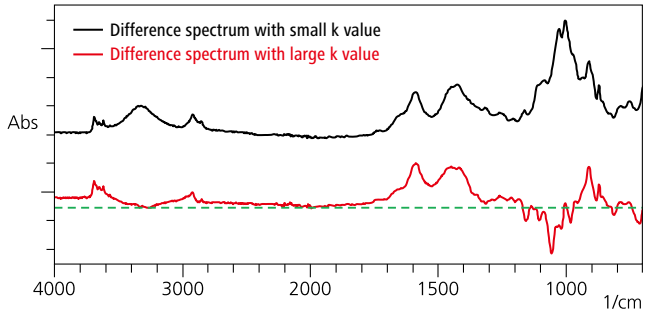

Fig. 6 Comparison of Difference Spectra Calculated Using Large and Small k Values

In many cases there are no clear criteria for judging whether too little or too much was subtracted. Therefore, it is often useful to quickly calculate trial difference spectra at several levels. As a general guideline, k values are set so that certain target peaks are cancelled out. However, if too much is subtracted, resulting in prominent inverted peaks, such as when assuming a baseline like the one indicated with a dashed green line in Fig. 6, then fine adjustments should be made to the k value until the inverted peaks are eliminated.
Since the peak near 1028 cm^{-1} was used as a reference for aligning the intensity level in Fig. 3, when calculating the difference spectrum in Fig. 4, the k value was tentatively set so that the intensity of that peak would be cancelled out. However, doing so resulted in exceeding the baseline for other wavenumber regions,

which caused significant inverted peaks. Therefore, the k value was readjusted until the inverted peaks no longer appeared. Table 1 summarizes the procedure for calculating difference spectra.

Table 1 Procedure for Calculating Difference Spectra

1	**Overlay the two spectra to be subtracted.**
2	**Display spectra with overall intensity adjusted to the same level. Then compare the spectra in more detail to decide which peak to eliminate.**
3	**Set a k value that results in cancelling out those peaks and then subtract the spectra.**
4	**Check the calculation results. If there are significant peaks that exceed the baseline (the peak points downward when displaying absorbance or upward when displaying transmittance), then adjust the k value slightly to eliminate these peaks.**

Note that subtracting spectra with overall intensity levels that are as close as possible will provide the best difference spectra. Adjusting the concentration or thickness of the sample will vary overall spectral intensity when using the transmittance method. Similarly, the intensity will vary depending on how tightly the sample contacts the prism when using the ATR method. If adjustable, subtract the spectra using measurement results with intensity adjusted as close as possible.

4. Measuring a Film Coating and Calculating the Difference Spectrum

To investigate a silicone polymer coating on polyethylene terephthalate (PET) film, two samples were prepared, with and without the coating, and then the surface of each was measured by single reflection ATR. Fig. 7 shows an overlay of the infrared spectra obtained .

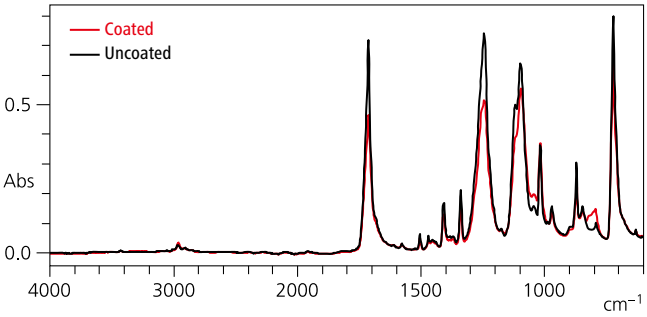

Fig. 7 Comparison of Coated and Uncoated PET Film

Spectra are overlaid with the overall intensity level aligned and observed to compare in more detail how well peaks align. Fig. 8 shows the spectra with intensity matched at the peak near 1714 cm^{-1}. Differences in the peak shape below 1300 cm^{-1} are presumably due to the silicone coating.

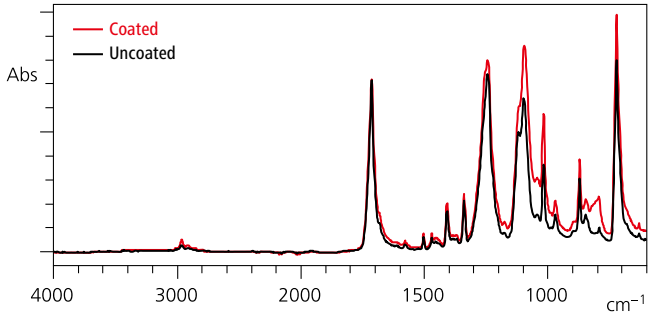

Fig. 8 Comparison of Coated and Uncoated PET Film (with Intensity Levels Aligned)

Fig. 9 shows the difference spectrum (coated minus uncoated) and uncoated samples and the spectrum measured separately from the silicone polymer.

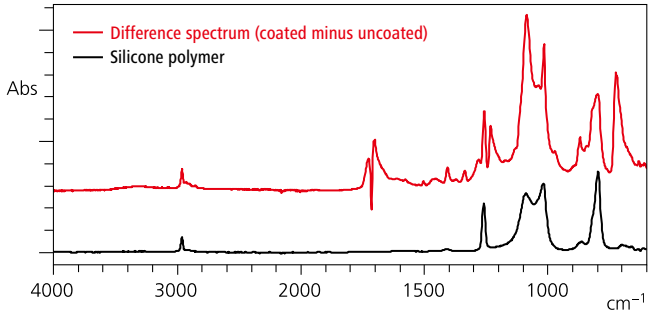

Fig. 9 Difference Spectrum (Coated Minus Uncoated) and Silicone Polymer Spectrum

In Fig. 8, the PET substrate material results in a large number of peaks with relatively high intensity, which makes it difficult to identify peaks from the coating. Based on these differences, even those familiar with the spectra of silicone polymers would have difficulty imagining that the spectra are from a silicone polymer. The difference spectrum includes residual PET peaks (remaining after subtraction) near 1714 cm^{-1}, however it clearly shows the peaks for silicone polymer.

5. Conclusion

Most difference spectra displayed are the result of trial-and-error adjustments to the k value. However, we recommend simply trying some difference spectra calculations, without thinking too hard about it. Since the substance being analyzed is a contaminant, in other words an unknown substance, there are no rigid procedures or standards involved. Therefore, it is acceptable to keep trying difference spectra calculations as you try to predict results. Therefore, try utilizing difference spectra for comparing small differences in spectral data or for identifying contaminants.

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