C103-E152

SHIMADZU
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FTIR TALK LETTER

Vol. 43

A tranquil autumn day in the historic capital of Kyoto.
Visitors travel from all corners of Japan and the world to view the autumnal foliage.

Spectrum Advisor Feature

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On December 7, 2023, Shimadzu released version 2.33 of the LabSolutions IR control software for its IRSpirit-X series of Fourier transform infrared spectrometers. This article describes the Spectrum Advisor feature that was added to this version of LabSolutions IR.

1. Introduction

FTIR spectrometers offer advantages such as rapid analysis and minimal sample damage due to the use of an infrared light source. However, they also typically require an experienced specialist to obtain and interpret high-quality spectra. Analysts with minimal experience in FTIR analysis have difficulty achieving and interpreting these high-quality spectra. When FTIR analysis does not produce useful spectroscopic data, it is the task of the analyst to identify the dominant issue from a range of potential causes, including sample pretreatment, analytical conditions, and environmental influences. This task poses a major barrier to the adoption of FTIR analysis.

To overcome this barrier, Shimadzu Corporation has equipped this version of LabSolutions IR with the Spectrum Advisor feature as standard to give less experienced analysts the ability to acquire high-quality spectra. The Spectrum Advisor feature can be used on all Shimadzu FTIR systems controlled by LabSolutions IR.

This article presents details of the Spectrum Advisor feature and its practical operation.

2. What is Spectrum Advisor?

After an infrared spectrum is acquired, Spectrum Advisor presents analysts with interactive prompts that allow it to verify the quality of the spectroscopic data and identify potential causes of poor-quality data. When potential causes of poor-quality data are identified, Spectrum Advisor then shows the analyst poor-quality and good-quality spectra to compare against their own spectrum and identify causes of poor spectroscopic data. Spectrum Advisor also offers detailed methods of resolving these causes of poor data. Spectrum Advisor was first launched as a standard feature in version 1.10 of AMsolution (released February 2023), the control software for Shimadzu's AIMsight infrared microscope and AIRsight infrared/Raman microscope. In AMsolution, Spectrum Advisor assists the analyst during transmission, reflection, and ATR measurements in IR microscopy. Now, Spectrum Advisor has been updated to also support transmission, reflection, and ATR sampling techniques in FTIR analysis. Spectrum Advisor identifies potential causes of poor data based on the unique conditions of each analysis and proposes methods of resolving these issues.

Table 1 shows the sampling techniques and corresponding measurement methods supported by Spectrum Advisor.

The next section of this article shows the process flow for using this feature.

Table 1: Sampling Techniques and Measurement Methods Supported by Spectrum Advisor

Technique	Measurement Methods
Transmission	Transmission measurements using a film holder, KBr pellet, liquid cell, sealed liquid cell, solid cell, or gas cell
Reflection	Specular reflectance measurements (SRM), reflection absorption spectroscopy (RAS), diffuse reflectance measurements (DRS)
ATR	Single reflection ATR measurements, multiple reflection ATR measurements

3. Using Spectrum Advisor

Spectrum Advisor is launched from the postrun analysis program window or the spectrum measurement program window of LabSolutions IR.

The analyst clicks the [Spectrum Advisor] button, shown in Figure 1, to launch the program while their spectral data is already open in the software.

Figure 1: [Spectrum Advisor] Button

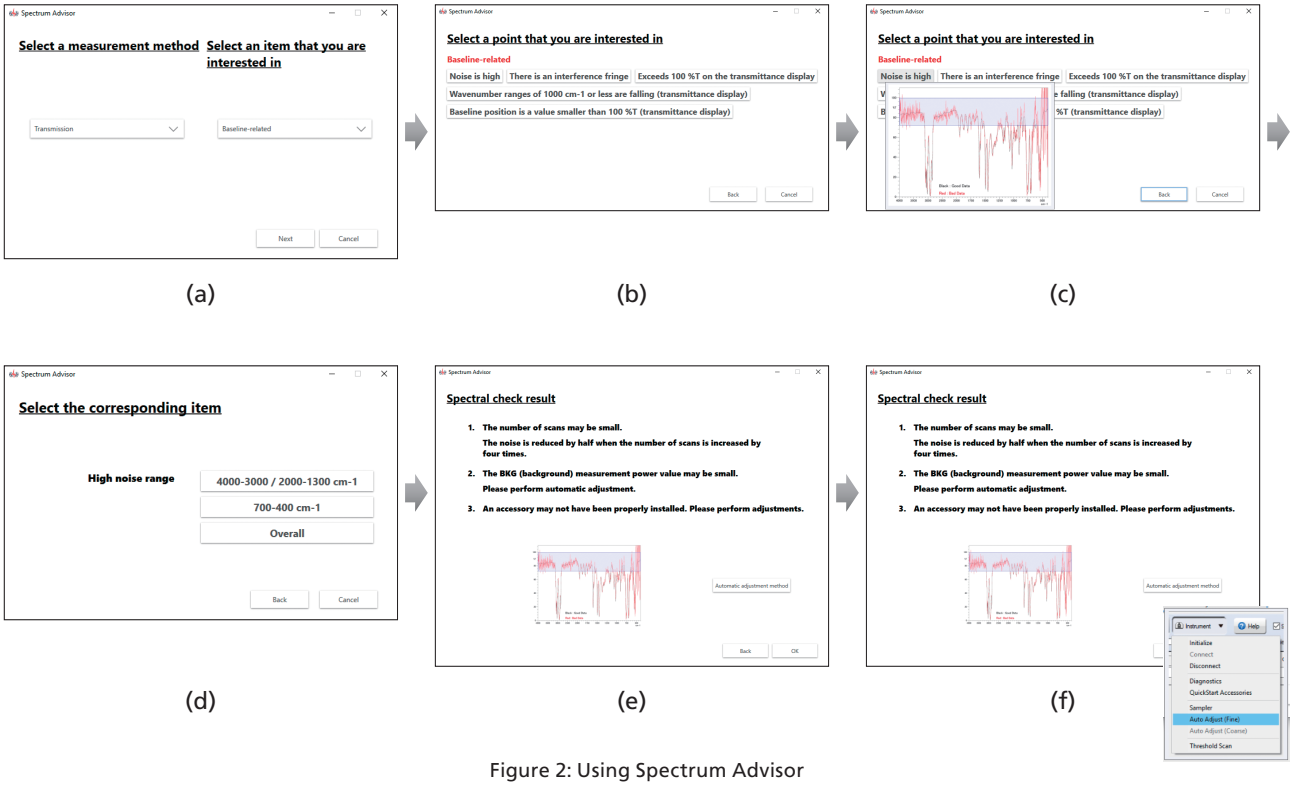

Figure 2: Using Spectrum Advisor

In Figure 2 (a), which shows the window that opens at program launch, the analyst selects the measurement method from transmission, reflection, and ATR. These options are set automatically based on the data (active data) currently open in LabSolutions IR. In the same window, the analyst selects the spectral feature of interest, whether a feature related to the spectrum baseline or related to the spectrum peaks, then clicks the [OK] button to proceed to the next window. In Figure 2 (a), the measurement method [Transmission] and the feature of concern [Baseline-related] have been selected. Clicking [Next] transitions to the window in Figure 2 (b).

If [Baseline-related] was selected in the previous window, various baseline-related causes of poor data are listed under [Select a point that you are interested in], as shown in Figure 2 (b). Some of the features listed may be unfamiliar to the analyst. Moving the cursor over a button displays a specific example of each feature over the button, as shown in Figure 2 (c). (In this example, the cursor is placed over the [Noise is high] button and Spectrum Advisor is displaying an example of a good spectrum superimposed over a poor spectrum.) Clicking [Next] transitions to the window shown in Figure 2 (d).

In Figure 2 (d), the analyst selects the wavenumber region affected by the high level of noise. In this example, [Overall] is selected.

Spectrum Advisor now examines the spectral data left open in the software based on the selected options (measurement by transmission sampling and a high level of baseline noise that is present throughout the wavenumber range) and displays potential causes (refer to Figure (e)) and solutions (refer to Figure 2 (f)).

As shown in Figure 2 (e), Spectrum Advisor notes three possible causes of a high level of noise: "Number of measurements is too low;" "Power value of background measurement is too low;" and "Attachments are not installed correctly." Also, it presents methods for resolving each of these possible causes. The analyst can acquire good spectral data by implementing the solutions presented by Spectrum Advisor and then repeating the analysis.

In Figure 2 (e), "Power value of background measurement is too low" is one of the possible causes and performing an auto-adjustment is shown as a solution. In case the analyst does not know how to perform the auto-adjustment, the [Automatic adjustment method] button is also located in the same window of Figure 2 (e). When the cursor is placed over this button, as shown in Figure 2 (f), Spectrum Advisor shows the analyst how to perform an auto-adjustment in LabSolutions IR software.

4. Conclusion

This article describes the Spectrum Advisor feature, which uses interactive prompts to identify causes and offer solutions to poor-quality spectroscopic data, thereby allowing analysts with minimal experience in FTIR analysis to obtain high-quality spectra. An example analysis performed using Spectrum Advisor is also detailed in Shimadzu's Application News bulletin and offers a useful reference point [1].

While this article describes a feature that checks spectroscopic data quality after the spectrum is acquired, Shimadzu also offers the IR Pilot analysis navigation program that assists with spectrum acquisition. Using IR Pilot and Spectrum Advisor together offers analysts with minimal experience in FTIR analysis the ability to acquire and analyze spectra with a high level of efficiency.

Reference

[1] Xu Yan, Karen Maruyama, "FTIR Analysis of Recycled Plastics Using the Spectrum Advisor Function," Shimadzu Application News 01-00653-EN (First Edition: Dec. 2023)

Notes on Infrared Spectral Analysis – Aliphatic Unsaturated Hydrocarbons (Olefins) and Aromatics –

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1. Introduction

The previous issue of FTIR TALK LETTER (Vol. 42) included an article that presented notes on the infrared spectral analysis of aliphatic saturated hydrocarbons (paraffins). The article presented some examples of infrared spectral analysis by discussing different crystallinities (densities) of polyethylene (PE) and the effect of molecular vibration modes on the orientation of molecules in polypropylene (PP).

This article describes how to analyze the infrared spectra of aliphatic unsaturated hydrocarbons (olefins) that contain carbon-carbon double bonds and aromatic compounds that contain benzene rings.

2. Using Infrared Spectra to Classify Olefins and Aromatics

Figure 1 shows the positions of major peaks in the infrared spectra of hydrocarbons that contain only carbon and hydrogen atoms and describes a method for classifying these hydrocarbons. Three hydrocarbon types (paraffins, olefins, and aromatics) can be classified simply by moving from the higher to lower end of the wavenumber spectrum and checking for the presence of certain peaks.

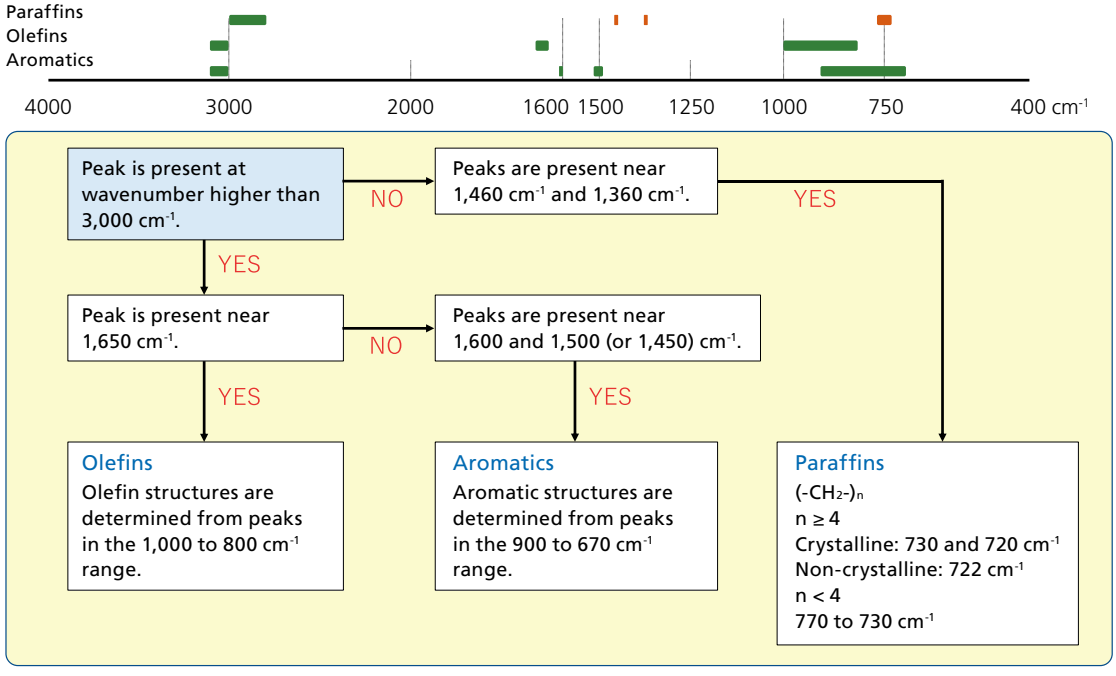


Figure 1: IR Spectra Peak Positions and Classification Flowchart for Paraffins, Olefins, and Aromatics

Figure 2 shows the peaks detected at around 3,000 cm^{-1} from a typical paraffin, olefin, and aromatic compound.

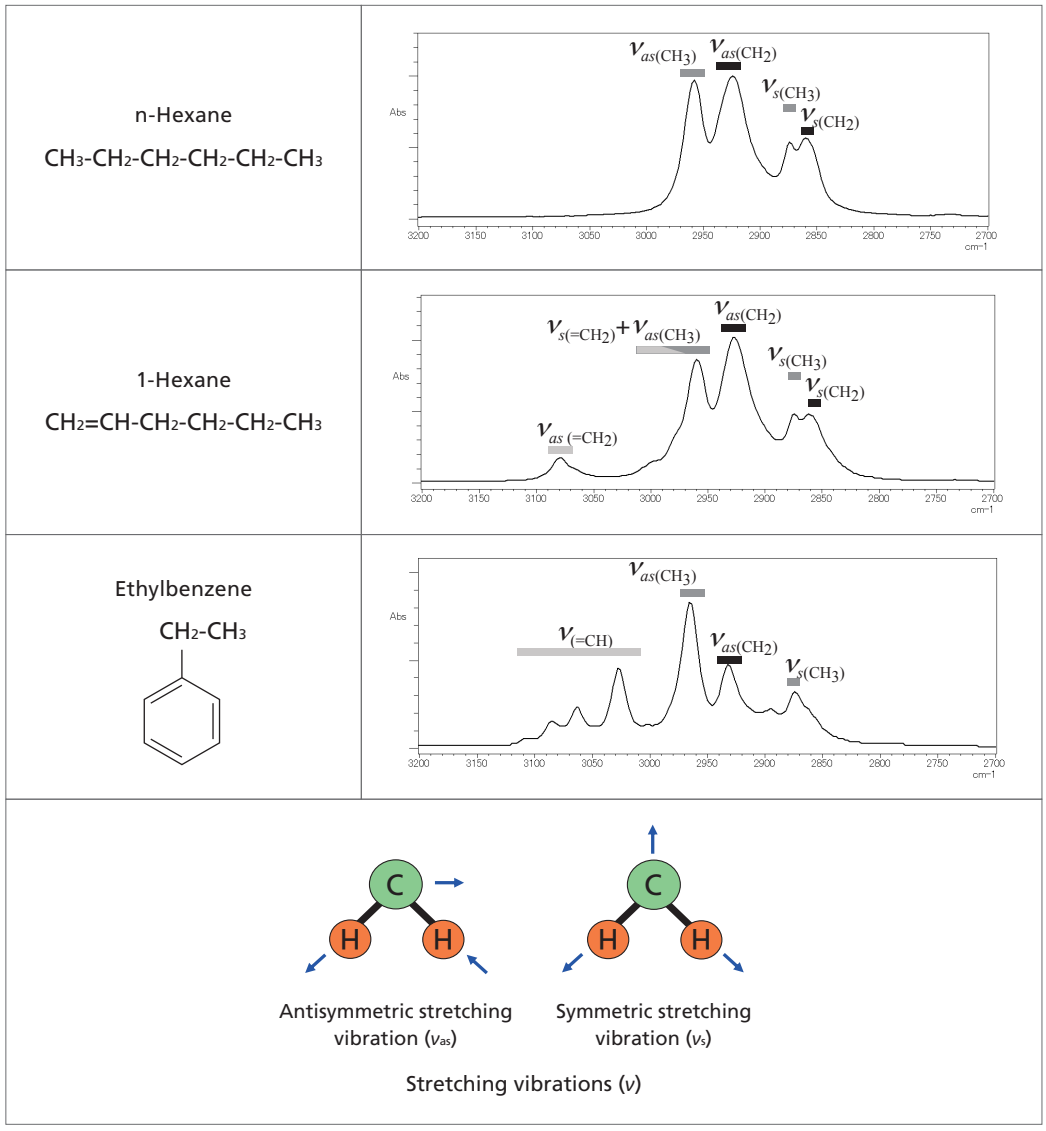


Figure 2: Attribution of Peaks Near 3,000 cm^{-1} [1]

Peaks in the 3,000 to 2,800 cm^{-1} region are caused by C-H stretching vibrations and appear with all paraffins, olefins, and aromatics. When there is a double or triple bond between the carbon in C-H and an adjacent carbon, such as the -C=C-H or -C≡C-H found in olefins and aromatics, the C-H stretching vibration shifts to a wavenumber above 3,000 cm^{-1}.

Next, we will discuss peaks caused by C=C stretching vibrations that appear at around 1,650 cm^{-1} and 1,600 cm^{-1} that can be used to distinguish between olefins and aromatics. Figure 3 shows the spectra of isoprene rubber (IR) and polystyrene (PS) in the 1,700 to 1,400 cm^{-1} region.

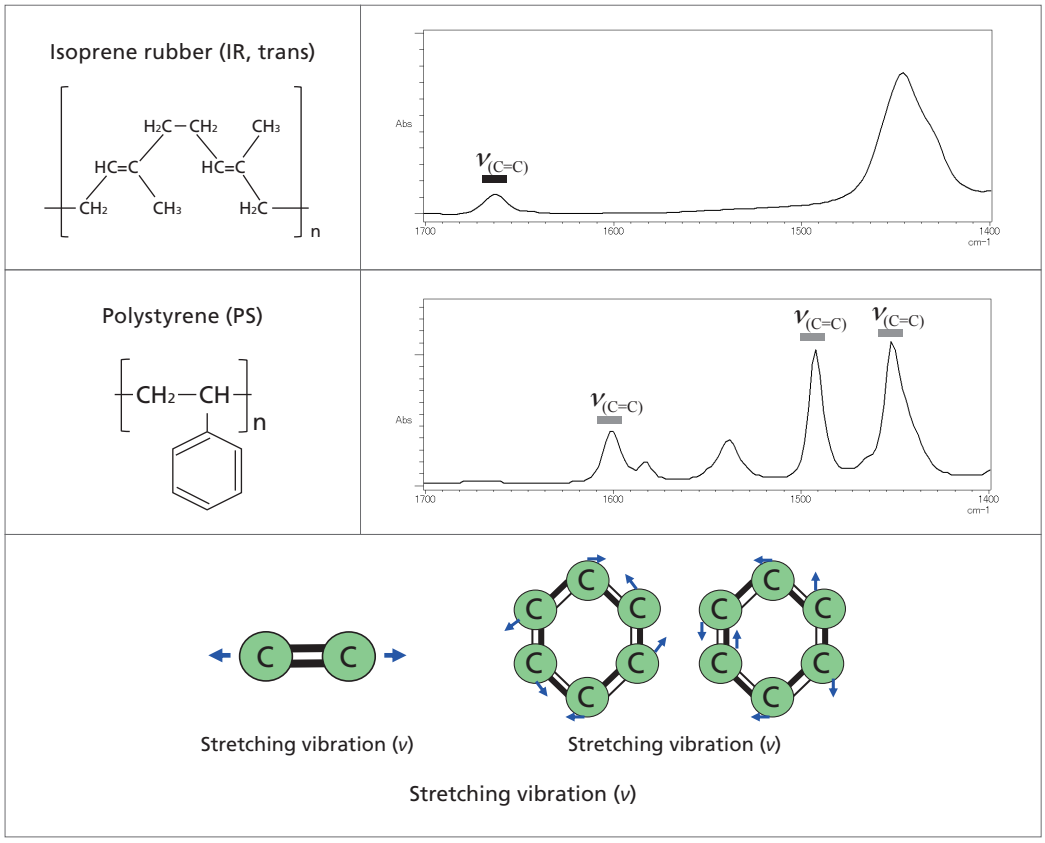


Figure 3: Peak Attributions in the 1,650 to 1,450 cm^{-1} Region [1]

The isoprene rubber peak at 1,665 cm^{-1} is caused by a C=C stretching vibration and the polystyrene peaks at around 1,600, 1,490, and 1,450 cm^{-1} are caused by C=C stretching vibrations in the benzene ring and vibration of the benzene ring caused by C-C stretching vibrations. Benzene rings demonstrate a phenomenon called resonance, whereby the alternating C=C and C-C bonds in the benzene ring switch places with each other. This resonance structure causes the C=C bonds in a benzene ring to be weaker than the C=C bonds in olefins, and lowers the wavenumber of the peak representing C=C bonds in benzene rings compared to the C=C bonds in olefins.

Next, we will discuss peaks caused by C=C-H out-of-plane bending vibrations that appear in the 1,000 to 800 cm^{-1} region in olefins and olefin structural isomers. Figure 4 shows a variety of olefin structures and the position of peaks caused by C=C-H out-of-plane bending vibrations in each of these structures.

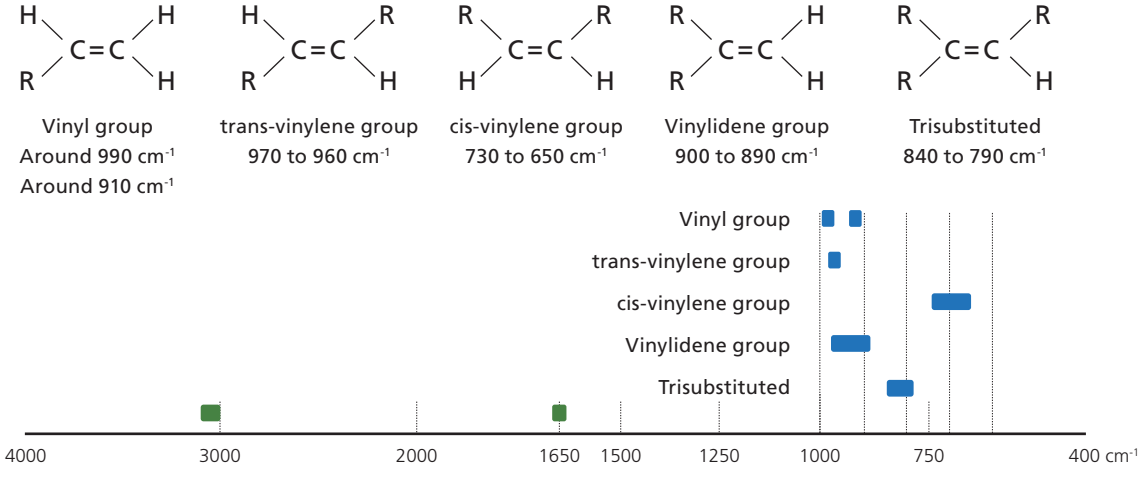


Figure 4: Various Olefin Structures and Peak Position of Corresponding C=C-H Out-of-Plane Bending Vibrations

Figure 5 shows the infrared spectra of 1,2-polybutadiene and isoprene rubber, which contain vinyl groups and trisubstituted structures, in the 1,100 to 600 cm^{-1} region where C=C-H out-of-plane bending vibrations appear.

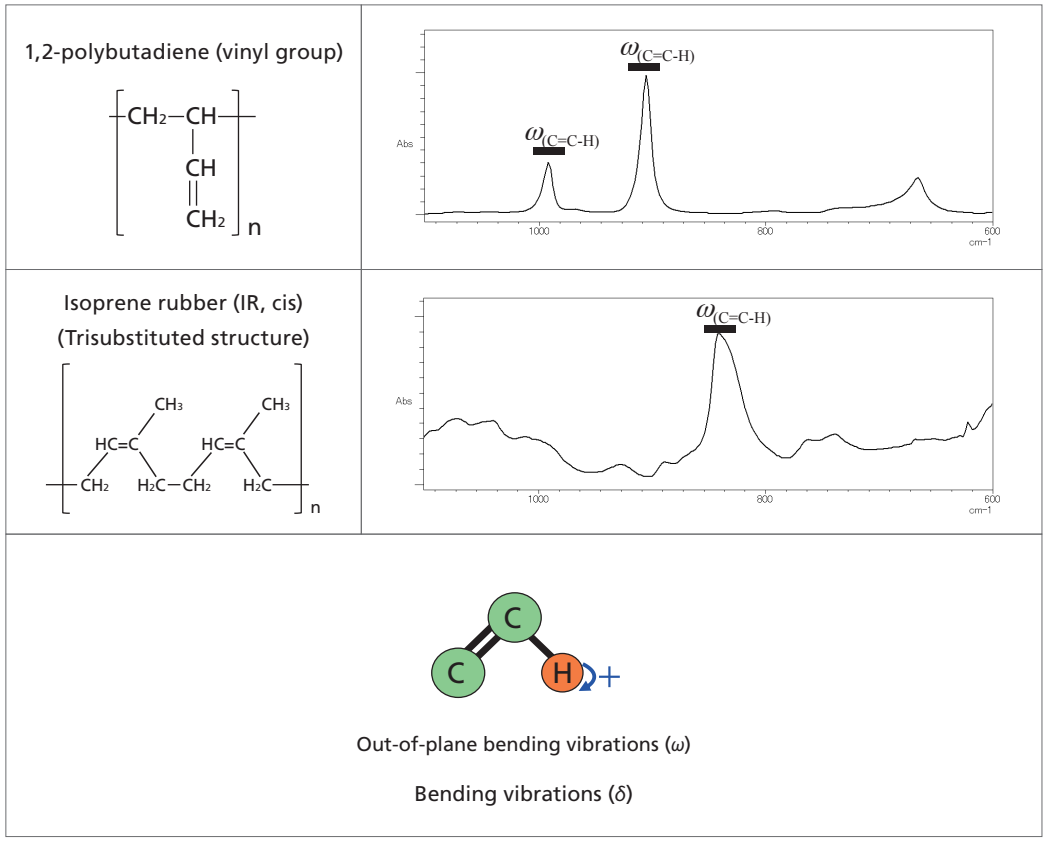
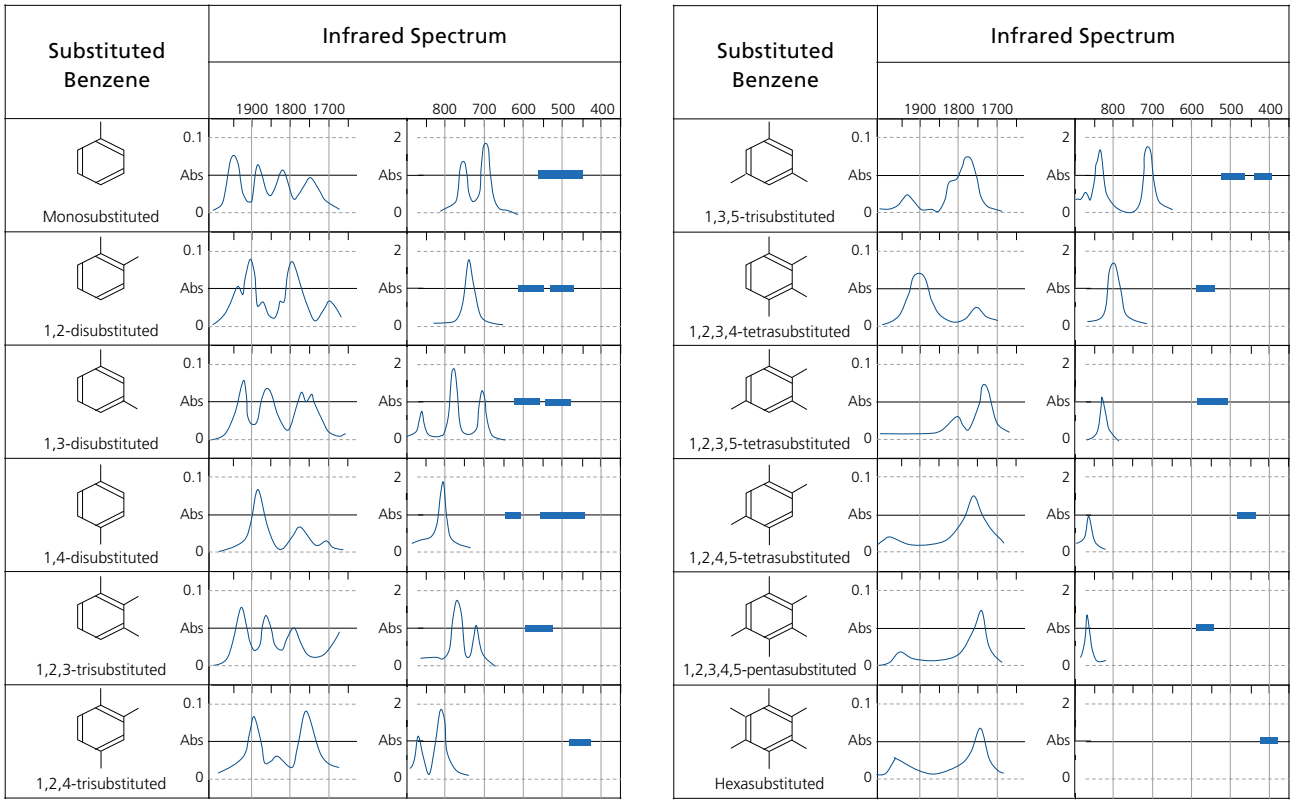


Figure 5: Peak Attributions around 990 cm^{-1}, 910 cm^{-1}, and 840 cm^{-1} [1]

1,2-polybutadiene that contains vinyl groups shows two peaks at around 990 cm^{-1} and 910 cm^{-1} each, while isoprene rubber that contains a trisubstituted structure shows just one peak at around 840 cm^{-1}. Peak positions in the 1,000 to 800 cm^{-1} region can be used to estimate the position of substituted groups in olefin structures. Further information on correlations between the position of substituted groups and the peaks in infrared spectra (number and position) can be found in the paper by Colthup [2]. Estimating the position of substituted groups becomes difficult when the substituted group is a highly polar functional group or when the substituted group forms a conjugate system. For example, the presence of a highly polar halogen such as Cl or Br in the molecular structure causes a significant shift in the peak positions shown in Figure 4 to lower wavenumbers [1].

This article has discussed how C=C-H out-of-plane bending vibrations can be used to distinguish between olefin structures, but peaks from C=C-H out-of-plane bending vibrations can also be used to estimate the position of substituted groups in aromatic compounds.

Figure 6 lists correlations between the position of substituted groups and the position and number of peaks in aromatics. As shown in Figure 6, for aromatic compounds, peaks derived from C=C-H out-of-plane bending vibrations appear in the 900 to 670 cm^{-1} region, while peaks derived from overtones and combination tones of C=C-H out-of-plane bending vibrations also appear in the 2,000 to 1,660 cm^{-1} region.



Vertical axis shows relative intensity in high wavenumber region and low wavenumber region as a reference.
Peaks sometimes appear in the blue areas in the low wavenumber region.

Figure 6: Correlations between Substitution Positions in Aromatics and Position and Number of Peaks

Figure 7 shows the infrared spectra of m-xylene (1,3-disubstituted) and p-xylene (1,4-disubstituted) in an example of structural isomers of an aromatic compound.

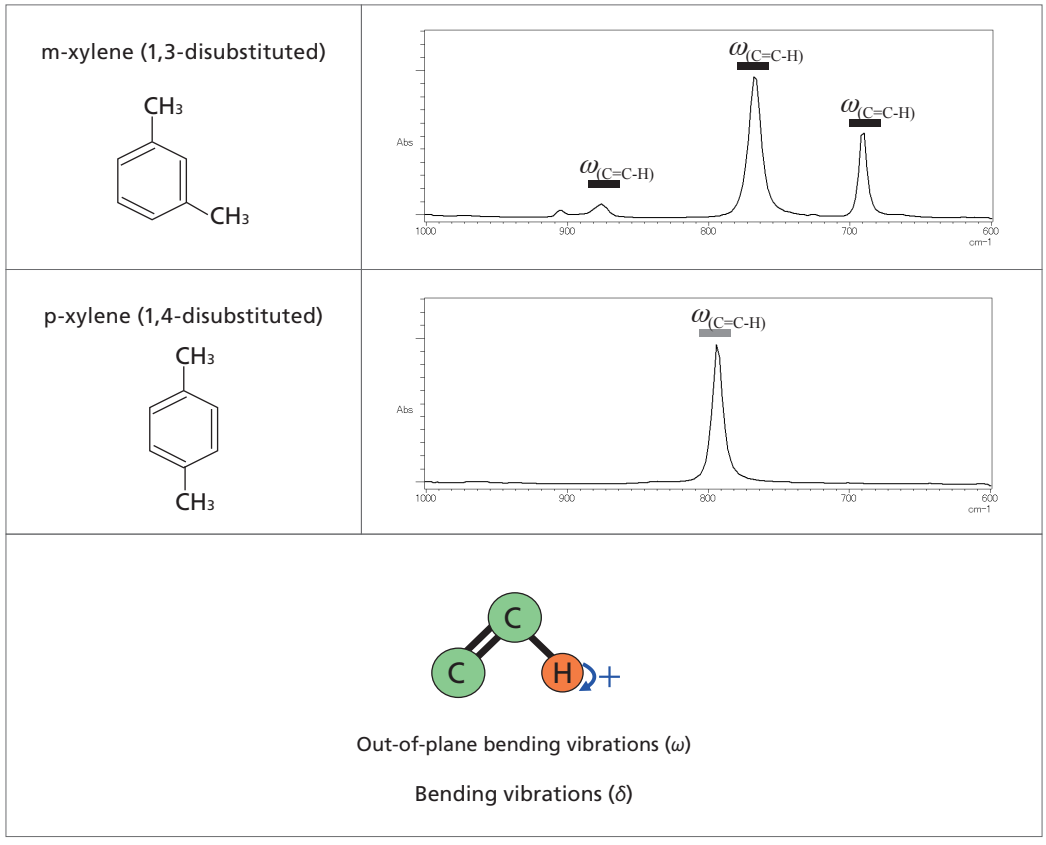


Figure 7: Peak Attributions at around 900 cm^{-1}, 800 cm^{-1}, 780 cm^{-1}, and 680 cm^{-1} [1]

Because the position and number of peaks derived from C=C-H out-of-plane bending vibrations in aromatics differ depending on the position and number of substitutions, the structure of aromatic compounds can be estimated based on the position and number of these peaks. Overtones and combination tones of C=C-H out-of-plane bending vibrations also appear as low intensity peaks in the 2,000 to 1,660 cm^{-1} region as shown in Figure 6. Because these peaks are in a wavenumber region where very few other functional groups exhibit infrared absorption, the accuracy of estimations can be improved by checking for peaks in this region as well as in the 900 to 670 cm^{-1} region.

Note that many aromatic compounds contain highly polar substituents such as nitro groups and carboxy groups*. The presence of highly polar substituents eliminates the correlations between substituent position and peaks in the 900 to 670 cm^{-1} region, either by shifting the peaks to lower wavenumbers or by creating peaks that overlap the substituent peaks shown in Figure 6, making it difficult to estimate the aromatic compound structure [1], [3].

* The -COOH substituent group is called a carboxy group according to the IUPAC recommendations on nomenclature.

3. Distinguishing between Trans and Cis Butadiene Rubber

One group of polyolefins in widespread use are polyolefin rubbers. Butadiene rubber (BR) is a popular general-purpose polyolefin rubber, along with styrene butadiene rubber (SBR) and natural rubber (NR). Butadiene rubber is synthesized by linking 1,3-butadiene monomers into a long polymer chain.

The resulting butadiene rubber contains a mixture of three geometric isomers: the vinyl isomer (1,2-polybutadiene) shown in Figure 5, a trans isomer (trans-1,4-polybutadiene), and a cis isomer (cis-1,4-polybutadiene). The proportion of each isomer present in butadiene rubber can be controlled to an extent by adjusting the method of polymerization and solvents used [4]. Butadiene rubbers containing 90 % or more of the cis isomer are called high-cis butadiene rubbers and butadiene rubbers containing 40 % or less of this cis isomer are called low-cis butadiene rubbers. Each has different applications. In the case of automobile tires, high-cis butadiene rubber exhibits excellent tensile elasticity and is used in sidewalls, while low-cis butadiene rubber exhibits excellent wear resistance and is used in tire tread (the surface in contact with the ground).

C=C-H out-of-plane bending vibrations (1,000 to 800 cm^{-1} region) can be used to differentiate between the infrared spectra of high-cis butadiene rubber and low-cis butadiene rubber due to the different proportion of vinyl groups, trans-vinylene groups, and cis-vinylene groups in each. Figure 8 shows the infrared spectra of a high-cis butadiene rubber, low-cis butadiene rubber, and a high-trans butadiene rubber. Because spectral profiles in the 1,000 to 800 cm^{-1} region vary significantly based on isomer content, infrared spectra can be used to distinguish between different types of butadiene rubber.

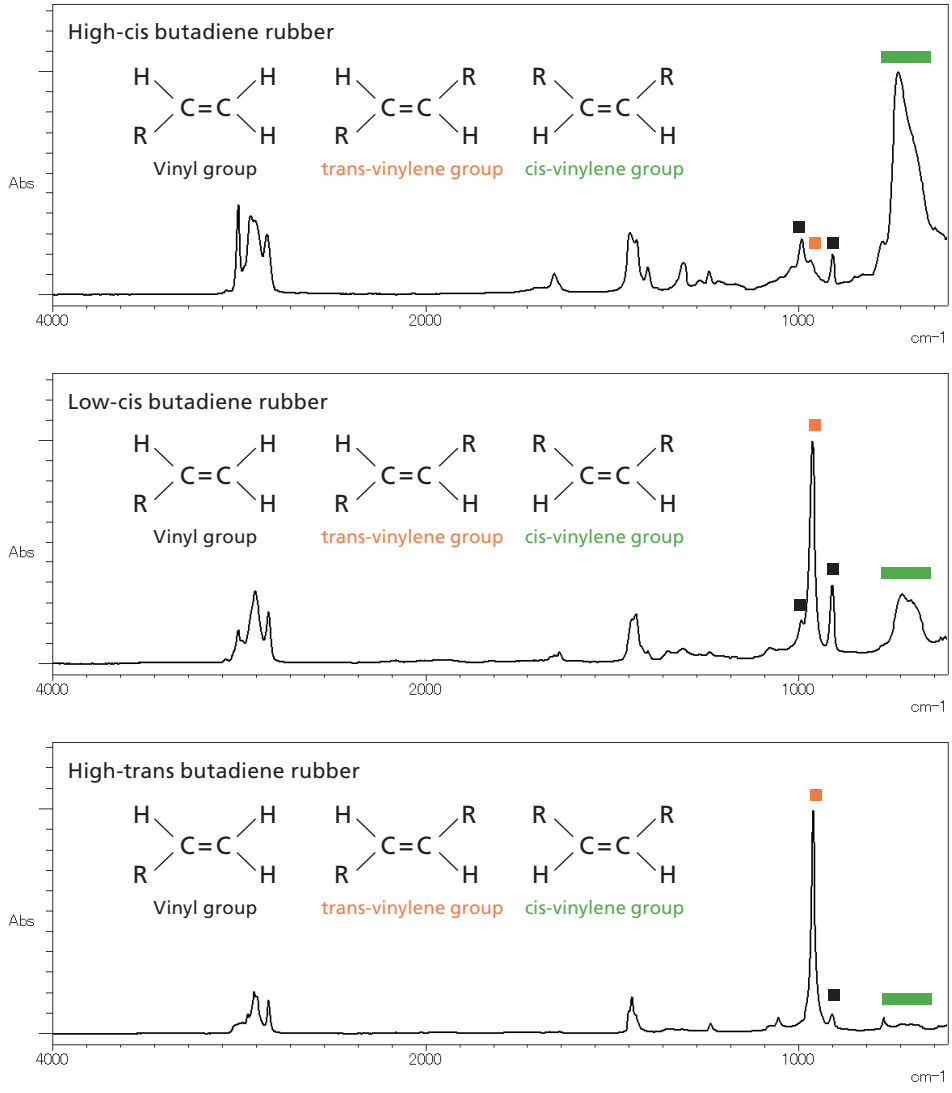


Figure 8: Infrared Spectra of High-Cis, Low-Cis, and High-Trans Butadiene Rubber

4. Conclusion

The information on infrared spectral analysis presented in this article is summarized below.

- Paraffins, olefins, and aromatics can be differentiated by checking for the presence of C-H stretching vibration peaks at wavenumbers above 3,000 cm^{-1}.
- Olefins and aromatics can be differentiated based on C=C stretching vibrations. A C=C stretching vibration peak at around 1,650 cm^{-1} indicates an olefin compound and peaks at around 1,600 cm^{-1} and 1,500 cm^{-1} indicate an aromatic compound.
- Olefin geometric isomers and structures can be differentiated based on C=C-H out-of-plane bending vibrations (1,000 to 800 cm^{-1} region). This method can also be used to differentiate between butadiene rubbers with different structures (high-cis and low-cis).
- The position of substituted groups in aromatics can be estimated based on C=C-H out-of-plane bending vibrations (900 to 670 cm^{-1} region). Low intensity peaks derived from overtones and combination tones of C-H out-of-plane stretching vibrations (2,000 to 1,660 cm^{-1} region) can also help in differentiating between compounds.

The next article will present notes on the analysis of carbonyl groups.

References

[1] Shigeyuki Tanaka and Norio Teramae, Infrared Spectroscopy, Kyoritsu Shuppan (1993)

[2] N. B. Colthup: J. Opt. Soc. Am. 40, 397 (1950)

[3] P. J. Larkin: "Infrared and Raman Spectroscopy: Principles and Spectral Interpretation, Second Edition", Elsevier (2017)

[4] Takuo Sone, Journal of the Society of Rubber Science and Technology, Japan, 88, 178 (2015)

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Shimadzu offers a variety of instruments to meet customer needs at every step of microplastics analysis, from sample pretreatment to sample observation, particle analysis, and component analysis. This product line includes an automatic pretreatment unit for isolating microplastics from surface water samples in the environment and a Fourier transform infrared spectrometer and infrared microscopes for simple and nondestructive component analysis.

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