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Safety of Windows and Prisms Used in FTIR

Spectroscopy Business Unit, Analytical & Measuring Instruments Division Kiyoshi Wada

A variety of windows and prisms are used in FTIR analysis. They are selected as appropriate for the sample and measurement method on the basis of their solubility with respect to the sample (particularly in the case of liquid samples), the transmission wavenumber range, and refractive index. In light of recent environmental problems, it is also important to consider the ease and safety with which windows and prisms can be used, stored, and disposed of.
Here, from the perspective of safety and environmental issues, I will describe some points to consider in the selection of windows and prisms.

Window and Prism Materials

The window and prism materials mainly used in FTIR analysis include those given in Table 1. Here, we will take a look at KRS-5, zinc selenide (ZnSe), and barium fluoride (BaF_2), materials that require particular care.

KRS-5

KRS-5 is a mixed crystal consisting of thallium bromide (TlBr) and thallium iodide (TlI).
As KRS-5 contains thallium, inhaling the powder produced when a KRS-5 window or prism is polished may cause intoxication. Users must not attempt to polish KRS-5 by themselves.
It is specified as a Class 2 Designated Chemical Substance by Japan's Law for Pollutant Release and Transfer Register (PRTR).

Zinc Selenide (ZnSe)

Zinc selenide is often used as a prism material. It reacts with acidic samples to produce toxic hydrogen selenide and it should only be used in the analysis of samples with pH values in the range of 6.5 to 9.5. Also, if ignited by fire or some other means, it decomposes to produce harmful fumes of selenium oxides.
It is designated as a poisonous substance (selenium compound) by Japan's Poisonous and Deleterious Substances Control Law and it is specified as a Class 1 Designated Chemical Substance by the PRTR Law.

Barium Fluoride (BaF_2)

Barium fluoride is often used as the window material in analysis performed with a microscope. If it is heated or comes in contact with acid, it produces harmful hydrogen fluoride gas.
It is designated as a deleterious substance (barium compound) by the Poisonous and Deleterious Substances Control Law and it is specified as a Class 1 Designated Chemical Substance by the PRTR Law.

Poisonous and Deleterious Substances Control Law (Japan)

Among the materials listed in Table 1, zinc selenide (poisonous substance) and barium fluoride (deleterious substance) are subject to control. I will leave interpretations of the law to more specialized documents. Here, I will describe some points related to purchase, storage management, use, and disposal that users must be careful to observe.

[Purchase Control]

- Be sure to create registers for purchased chemicals, and clearly indicate the current amounts and usage status.

[Handling of Poisonous and Deleterious Substances]

- Ascertain the physical and chemical properties, particularly the toxicity, of poisonous and deleterious substances. Regarding items that require immediate action in the event of an accident, obtain all the relevant information in advance, and maintain a state of readiness.
- Store poisonous and deleterious substances in robust medicine cabinets and chemical closets, keep these containers locked, and take any steps necessary to ensure that the substances are not stolen or lost.
- In places where stored poisonous or deleterious substances are on display, label them "not for medicinal purposes". Additionally, label poisonous substances "poisonous substances" with white letters on a red background and label deleterious substances "deleterious substances" with red letters on a white background.

[Storage Control of Chemicals]

- Store chemicals in clearly visible locations.
- Store poisonous or deleterious substances in locked containers specifically designed for this purpose.
- Clearly identify the administrators of keys, periodically check the numbers of keys, and take any other steps necessary to ensure comprehensive key management.
- Create an administrative ledger, and periodically check stocks. Perform the storage management required to prevent loss.

[Disposal Control of Poisonous and Deleterious Substances]

- Poisonous and deleterious substances cannot be disposed of without being treated.
- Either dispose of poisonous or deleterious substances using the legally specified method, such as decomposition, combustion, or neutralization, or have them disposed of by a disposal subcontractor authorized by the local authority.

[Management of Training for Handling Poisonous and Deleterious Substances]

- Periodically train personnel handling poisonous and deleterious substances with regard to the handling methods used.

Although crystalline materials such as windows and prisms are themselves subject to the Poisonous and Deleterious Substances Control Law, in cases where they are incorporated into holders or form part of the equipment in some other way, they are not. There is still the same level of danger, however, so handle such parts with due care.

PRTR Law (Japan)

The Law for Pollutant Release and Transfer Register (the PRTR Law) was established "to promote businesses' voluntary improvements in the management of specific chemical substances and to prevent any impediment of environmental protection by requiring businesses handling such substances to report the release to the environment of chemical substances (PRTR) and to provide technical information on the properties and handling of such substances (MSDS)."
The applicable chemical substances are classified as either Class 1 or Class 2.

Class 1 Designated Chemical Substance	Class 2 Designated Chemical Substance
Subject to PRTR and MSDS	Subject to MSDS only
354 substances including the following: ● Zinc selenide (selenide and its compounds) ● Barium fluoride (barium and its water-soluble compounds)	81 substances including the following: ● KRS-5 (thallium and its water-soluble compounds)

Other Laws and Regulations

There are window and prism materials that are regulated by laws and regulations other than the Poisonous and Deleterious Substances Control Law and the PRTR Law. Be sure to use these materials safely with reference to the MSDSs described later and other appropriate documentation.

MSDS

An MSDS (Material Safety Data Sheet) is a document that summarizes information about a material that includes chemical and physical properties, dangers and hazards, emergency measures for dealing with intoxication, points to note in handling, storage, and disposal, and applicable laws and regulations. If you read this, you will know how to store, use, and dispose of the applicable material.
An MSDS for a material can be obtained from the place of purchase. It can also be searched for and accessed via the Internet.

Summary

Most of the window and prism materials used in FTIR analysis are crystalline, so they do not have an immediate effect on the human body. With some materials, however, swallowing a broken fragment or inhaling abrasion powder after polishing with deficient equipment may result in intoxication. In some cases, a material may react with a chemical to produce toxic gas. In addition, there are materials for which strict management of storage and disposal is demanded by laws and regulations.
We ask that you use materials properly with reference to the applicable MSDSs and other documentation.

Links to Relevant Information (Some of them are available in Japanese only.)

Poisonous and Deleterious Substances Control Law (Text)
http://law.e-gov.go.jp/htmldata/S25/S25H0303.html
Poisonous and Deleterious Substances Control Law (National Institute of Health Sciences)
http://www.nihs.go.jp/law/dokugeki/dokugeki.html
PRTR Information Plaza (Ministry of the Environment)
http://www.env.go.jp/chemi/prtr/risk0.html
Law Concerning Reporting, etc., of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management (Ministry of Economy, Trade and Industry)
http://www.meti.go.jp/policy/chemical_management/law/index.html
National Institute of Technology and Evaluation
http://www.safe.nite.go.jp/index.html
Material Safety Data Sheet Power Search, Japan Reagent Association
http://www.j-shiyaku.or.jp/home/msds/
GHS Model MSDS Information, Japan Advanced Information Center of Safety and Health
http://www.jaish.gr.jp/anzen_pg/GHS_MSD_FND.aspx

Table 1 Common Infrared Transmissive Materials

Material	Transmission Wavelength Range cm^{-1}(μm)	Refractive Index 1000cm^{-1}	Water-Solubility at 20ºC g/100 gH_2O	Properties
KBr (potassium bromide)	40,000 to 340 (0.25 to 29.4)	1.52	65	Inexpensive. Large wavelength range. Good workability (using absolute alcohol). Most frequently used. Relatively strong mechanically. Must be stored at humidity of 50% or less. Cleaning: Chloroform Carbon tetrachloride Use prohibited: Samples containing water Lower alcohol
NaCl (sodium chloride)	50,000 to 600 (0.2 to 16.6)	1.49	36	Most inexpensive material. Large wavelength range. Must be stored at humidity of 50% or less. Cleaning: Chloroform Carbon tetrachloride Use prohibited: Samples containing water Lower alcohol
KCl (potassium chloride)	40,000 to 500 (0.25 to 20.0)	1.46	34	Similar properties to NaCl and KBr. Not commonly used. Cleaning: Chloroform Carbon tetrachloride Use prohibited: Samples containing water Lower alcohol
CsI (cesium iodide)	33,000 to 200 (0.3 to 50.0)	1.74	44	Soft and easily damaged. Used in the far-infrared region. Extremely high deliquescence. Must be stored at humidity of 40% or less. Must be handled with care. Cleaning: Chloroform Carbon tetrachloride Use prohibited: Samples containing water Lower alcohol
KRS-5 (TlBr + TlI) (thallium bromide + thallium iodide)	16,600 to 250 (0.6 to 40.0)	2.37	0.05	Large wavelength range. High refractive index. Most commonly used material in ATR prisms. Almost completely insoluble in water. Tl is toxic and so special treatment equipment is required for fabrication. Cleaning: Chloroform Carbon tetrachloride Xylene Use prohibited: Acetone Ammonium salt Substances that form a complex with Tl, such as sulfuric acid, ammonia water, and EDTA
ZnS (zinc sulfide)	10,000 to 725 (1.0 to 13.3)	2.2	Insoluble	Highly resistant to water. Resistant to mechanical and thermal shocks. High refractive index. Effective for vapor deposition. Cleaning: Acetone Alcohol Use prohibited: Acidic liquids
ZnSe (zinc selenide)	10,000 to 550 (1.0 to 18.1)	2.4	Insoluble	Highly resistant to water. Highly resistant to organic solvents, weak acids, and alkalis. Can be used in a pH range of 6.5 to 9.5. High refractive index. Effective for ATR prisms. Specified as a poisonous substance by the Poisonous and Deleterious Substances Control Law (selenide compound). If used to analyze strongly acidic samples, toxic hydrogen selenide is produced. Cleaning: Acetone Water Use prohibited: Acidic liquids Strong alkalis Formates such as Ca $(HCOO)_2$ and NaHCOO that produce HCOO- in aqueous solutions

Material	Transmission Wavelength Range cm^{-1}(μm)	Refractive Index 1000cm^{-1}	Water-Solubility at 20ºC g/100 gH_2O	Properties
BaF_2 (barium fluoride)	50,000 to 770 (0.2 to 12.9)	1.42	0.004	Dissolves in acids and ammonia. Can be used at temperatures up to 500ºC. Almost completely insoluble in water. Specified as a deleterious substance by the Poisonous and Deleterious Substances Control Law (barium compound). Cleaning: Acetone Water Use prohibited: Acidic liquids Ammonium salts
CaF_2 (calcium fluoride)	50,000 to 1,100 (0.2 to 9.0)	1.39	Insoluble	Dissolves in ammonium salts. Highly resistant to acids and alkalis. Hard with good mechanical strength. Suitable for the windows of high-pressure cells. Cleaning: Acetone Water Use prohibited: Strongly acidic liquids Ammonium salts
Si (silicon)	8,000 to 660 (1.25 to 15.1)	3.4	Insoluble	Effective for semiconductors. Can be replaced with Ge as a window material. Not commonly used. Cleaning: Acetone Water Use prohibited: HF + HNO_3
Ge (germanium)	5,500 to 660 (1.8 to 16.6)	4	Insoluble	Effective for semiconductors. Effective for vapor deposition. Can be fabricated into lenses. High refractive index; suitable for use in ATR prisms in the analysis of substances with high refractive indices. Highly resistant to water. Cleaning: Toluene Water Use prohibited: Hot concentrated sulfuric acid
Type II diamond	40,000 to 12.5 (0.25 to 800)	2.38	Insoluble	The hardest substance. Brittle. Although there is a low level of absorption in the range of 3,000 to 1,500 cm^{-1} (in the case of Type II), it can be used in a range encompassing the ultraviolet and far-infrared regions. Natural diamonds can be classified as Type I or Type II. Type II is effective for infrared windows. Large-size materials are extremely expensive. Suitable for the windows of high-pressure cells. Cleaning: Ethanol Acetone
SiO_2 (fused silica)	50,000 to 2,500 (0.20 to 4.0)	1.42 (3,000 cm^{-1})	Insoluble	Effective for windows used in the ultraviolet and visible-light regions. In the infrared region, it only transmits wavelengths of up to 4 mm. In this range, however, it is stable, easy to fabricate, and an effective window material. Cleaning: Ethanol Acetone

Points to Note in Rubber Analysis: Black Rubber

Tokyo Applications Development Center, Analytical Applications Department, Analytical & Measuring Instruments Division
Sachio Murakami

There are many different types of rubber in the world. Broadly speaking, rubber can be classified as either natural rubber or synthetic rubber. A vast majority of the rubber that is sold commercially is classified as synthetic rubber. Synthetic rubbers usually contain many components other than rubber. The substances that are combined with rubber can be broadly classified by their effects as vulcanizing agents, vulcanization accelerators, vulcanization retarders, antioxidants, fillers, and plastics. The machining performance and product performance of rubber products can be altered by changing the combinations and the amounts of these substances. Rubber products appear in almost every aspect of daily life as, for example, the rubber parts used in automobile tires and wipers, raincoats and other types of clothing, the balls that are indispensable for sports such as soccer and rugby, and the packing for home appliances.
In order to obtain infrared spectra for these rubber products, the appropriate pretreatment and measurement methods must be selected in accordance with their color and shape. Here, using actual examples, I will present some points regarding the selection of prisms used to analyze black rubber with the ATR method.

Black rubber gets its color from the carbon black (hereafter referred to as "carbon") that is worked into it. The amount of carbon used varies with the application of the rubber. When analyzing black rubber with the ATR method, the prism must be selected in accordance with the amount of carbon. For example, if rubber containing a comparatively large amount of carbon is analyzed with a ZnSe prism or a diamond prism, the peaks are distorted, causing peaks to appear in incorrect positions and giving spectra for which qualitative analysis is not possible. I will not go into the details of why this happens, but the basic problem is a violation of the ATR principle that the material of the ATR prism used for analysis must have a higher refractive index than the sample. (Refer to Q&A in FTIR TALK LETTER Vol. 1 for details.) Usually, a Ge prism is used to analyze rubber containing large amounts of carbon, and a ZnSe prism or diamond prism is used to analyze rubber containing small amounts of carbon. There are no precise numerical criteria for prism selection, however, and the analyst usually makes judgments based on the spectra obtained. Here, spectra were obtained for samples containing carbon in amounts ranging from 1 to 50 wt% using three types of prisms, and the spectra were evaluated. NBR (acrylonitrile butadiene rubber) was used as the analyzed rubber material.
Fig. 1 shows an overlay of spectra obtained for NBR containing carbon in amounts ranging from 1 to 50 wt% using a diamond prism (refractive index, n = 2.4). From the bottom of Fig. 1, the respective amounts of carbon are 1, 3, 5, 10, 16, 20, 30, 40, and 50 wt%.

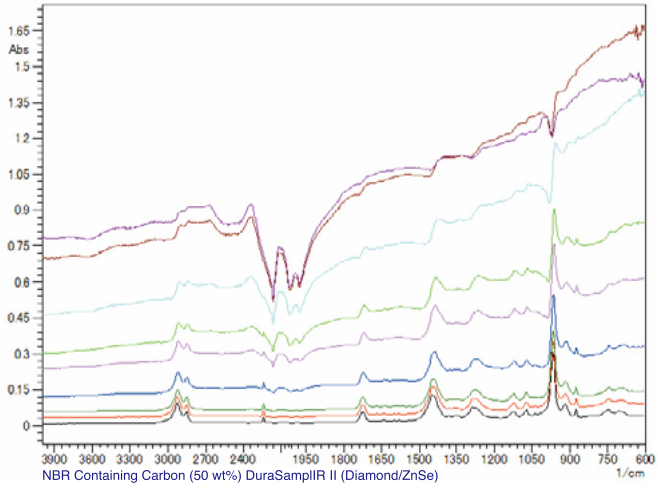

Fig. 1 Spectra of NBR Containing Carbon
Method: Single-Reflection ATR (Prism: Diamond)

It can be seen from Fig. 1 that, as the amount of carbon increases, the spectral baseline rises, particularly at the right end. This phenomenon occurs because carbon has absorbance throughout the entire infrared region and because, with the ATR method, light penetrates to a relatively large depth in the low wavenumber region. (Refer to Q&A in FTIR TALK LETTER Vol. 6 for details.) It can be seen that, if a diamond prism is used, the right end is particularly high for amounts of carbon of 10 wt% or more. Fig. 2 indicates the relationship between the peak position and the amount of carbon. The peak used for evaluation corresponds to the C=C-H out-of-plane bending vibration (trans-vinylene group) of polybutadiene that is representative of NBR and which exists at 966 cm^{-1}.

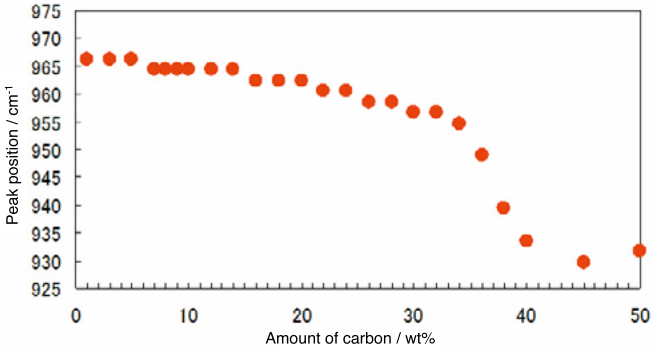

Fig. 2 Peak Shift of C=C-H Out-of-Plane Bending Vibration (Trans-vinylene Group)
(Prism: Diamond)

It can be seen in Fig. 2 that, when the amount of carbon exceeds 30 wt%, the peak starts to distort, and its position is shifted greatly toward the low wavenumber region. In addition, it can be seen that, if a diamond prism is used, there is a downward peak in the neighborhood of the range of 2,400 to 2,000 cm^{-1}. (Refer to the neighborhood of the range of 2,400 to 2,000 cm^{-1} in Fig. 1.) This downward peak represents a reversal of the absorbance of diamond itself (absorbance residue). Although NBR, which was used for analysis on this occasion, has a characteristic nitrile-group peak near 2240 cm^{-1}, if a diamond prism is used, when the amount of carbon exceeds 20 wt%, it becomes difficult to distinguish between the peak and the absorbance residue of the prism, and for amounts of carbon exceeding 40 wt%, the nitrile group is completely hidden by the absorbance residue. (Refer to Fig. 3.)

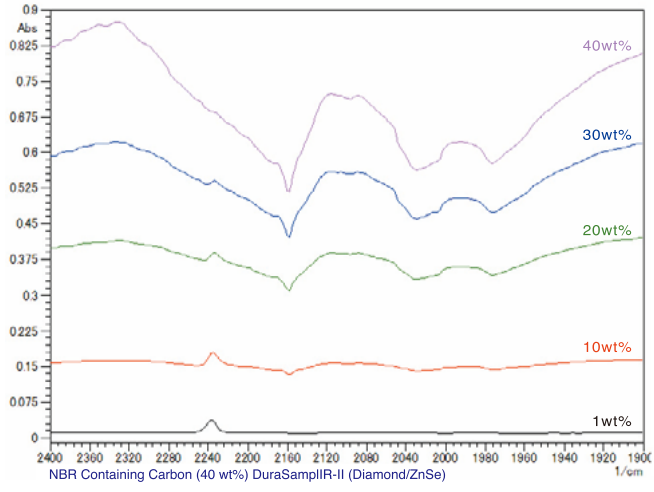

Fig. 3 Absorbance Residue of Diamond Prism

As reference, Fig. 4 shows the results (i.e., the hit positions) of a search for spectra of NBR samples containing different amounts of carbon performed with the Sadtler Database (polymer ATR library). The amounts of carbon contained in NBR that were used in the search were 1, 5, 10, 16, 20, 24, 30, 40, and 50 wt%. (Note that the search algorithm varies with the company. The hit positions should only be used as guidelines.)
It can be seen from this graph that, when the amount of carbon exceeds 10 wt%, the hit position starts to decrease,

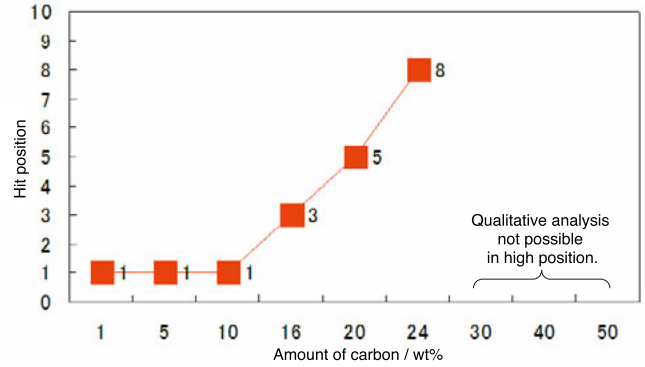

Fig. 4 Hit Positions in Spectral Search
(Prism: Diamond)

and for carbon contents of 30 wt% or more, there are hardly any hits at all. (For a carbon content of 30 wt%, there were no hits in the top 200 positions.) Possible reasons for this are (1) the baseline rises at the right end, (2) the peak position is shifted toward the low wavenumber region, and (3) the nitrile group is hidden by the absorbance residue of diamond.
Next, the same samples were analyzed using a ZnSe prism with the same refractive index as the diamond prism, 2.4. Fig. 5 shows the spectra obtained. From the bottom of Fig. 5, the respective amounts of carbon are 1, 5, 10, 16, 20, 30, 40, and 50 wt%.

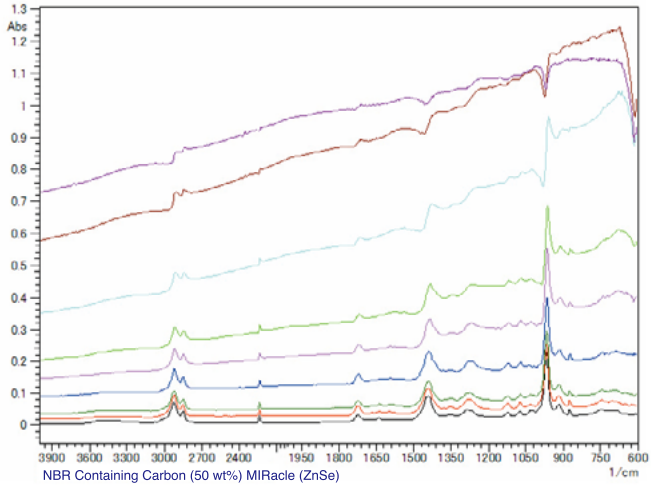

Fig. 5 Spectra of NBR Containing Carbon
Method: Single-Reflection ATR (Prism: ZnSe)

It can be seen from Fig. 5 that, although there is no diamond absorption residue in the neighborhood of the range of 2,400 to 2,000 cm-1, the spectra exhibit the same tendencies as those obtained with a diamond prism, i.e., the rise of the baseline at the right, the shift of the peak position toward the low wavenumber region, and the peak distortion. This is because the refractive indices of the diamond and the ZnSe are almost the same. Therefore, even with a ZnSe prism, accurate qualitative analysis based on searches is possible for amounts of carbon of up to approximately 20 wt%.
Finally, Fig. 6 shows examples of spectra obtained with a Ge prism. From the bottom of Fig. 6, the respective amounts of carbon are 1, 3, 5, 10, 16, 20, 30, 40, and 50 wt%.

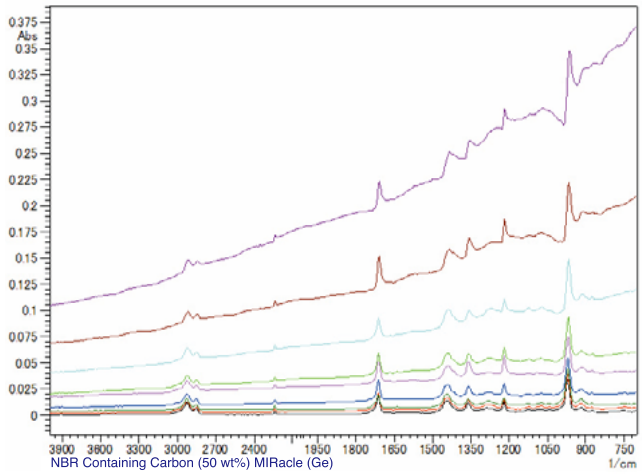

Fig. 6 Spectra of NBR Containing Carbon
Method: Single-Reflection ATR (Prism: Ge)

It can be seen from Fig. 6 that, although the baseline rises at the right as it does with diamond and ZnSe prisms, there is little peak distortion right up to a carbon content of 50 %wt. This is because the refractive index of Ge (n = 4.0) is bigger than that of diamond and ZnSe (n = 2.4). If a Ge prism is used, however, light only penetrates to a relatively small depth compared to diamond and ZnSe prisms, so the intensity of the peaks obtained is lower. (Refer to the vertical axes of Fig. 1 and Fig. 6.)
I also investigated peak shift and the search hit order for the spectra obtained with the Ge prism. The results are shown in Fig. 7 and Fig. 8.

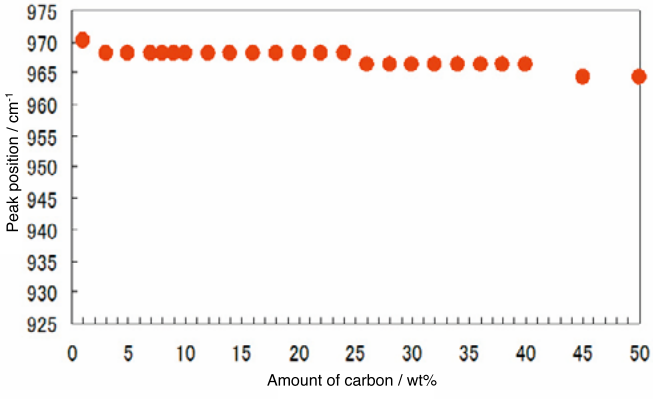

Fig. 7 Peak Shift of C=C-H Out-of-Plane Bending Vibration (Trans-vinylene Group)
(Prism: Ge)

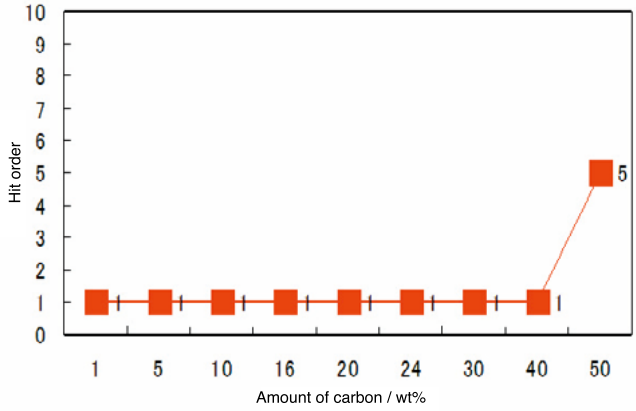

Fig. 8 Hit Positions in Spectral Search
(Prism: Ge)

It can be seen that, if a Ge prism is used for analysis, there is hardly any change in peak position. Also, it can be seen from Fig. 8 that, in comparison with analysis performed using a diamond prism, it is easier to get hits.
I performed a search for the Ge prism spectrum obtained for NBR with a carbon content of 50 wt% after subjecting it to multipoint baseline correction. As a result, I got a hit in the first position.
It can be seen, then, that using a Ge prism makes it possible to obtain ATR spectra that are effective for the qualitative analysis of NBR with a carbon content of 50 wt%.
Incidentally, NBR with high concentrations of carbon (i.e., 60 wt% or more) cannot be made because it is impossible to maintain the rubber shapes.

Finally, I would like to thank Orion Inc. for their help in making the rubber materials used in the analysis described here.

Question

I analyze film using a single-reflection ATR instrument. Why does the peak intensity vary with the film thickness?

Answer

It can be said that, among solid samples, film samples are the easiest to analyze using a single-reflection ATR instrument. The analysis procedure consists of simply performing BKG measurement without any sample, placing the film on the prism surface, and restraining it with a pressure rod. It is easy for anyone to obtain spectra. The spectral intensity, however, varies with the material and shape of the sample and with the size of the pressure; therefore, in order to increase the peak intensity, it is necessary to implement measures appropriate for the sample. Here, I will describe the influence of thickness on the analysis of film samples.

Fig. 1 (a) shows the result obtained by analyzing a single nylon film with DuraSamplIR II (System I, High Pressure Device Type). The film thickness is approx. 15 μm. Fig. 1 (b) shows the result obtained by analyzing the film with a single sheet of paper placed on top of it and the same pressure applied. It can be seen that the intensity is at least twice as large. The peak intensity obtained with the ATR method depends greatly on the state of contact between the prism and the sample. With just a single film, the force that the bottom of the pressure rod exerts on the sample is probably dispersed to places other than the center of the prism, as shown in Fig. 2 (a). On the other hand, if an object that absorbs a certain amount of pressure is placed on the sample, a greater force is exerted on the prism surface, making it possible to improve the peak intensity, as shown in Fig. 2 (b). Although this effect depends on the hardness, surface roughness, and thickness of the sample, it is probably applicable to samples that are relatively hard and thin. In such cases, placing a single piece of paper on the film or piling multiple films on top of each other will increase the peak intensity.

With single-reflection ATR, then, the key is to restrain the sample so that it makes more effective contact with the prism. If necessary, try various measures, such as changing the way the sample is placed or piling multiple samples on top of each other.

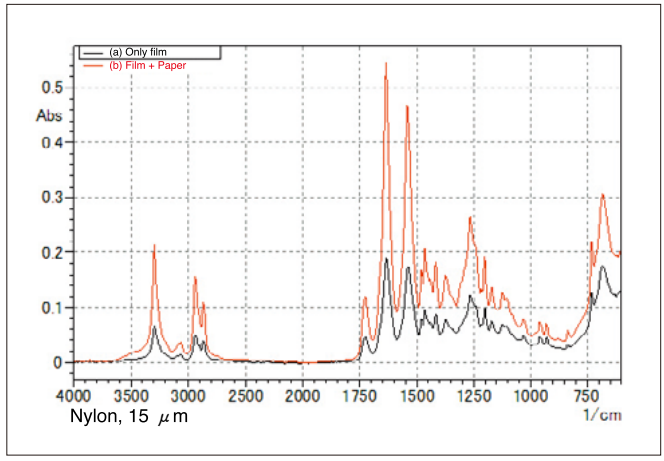

Fig. 1

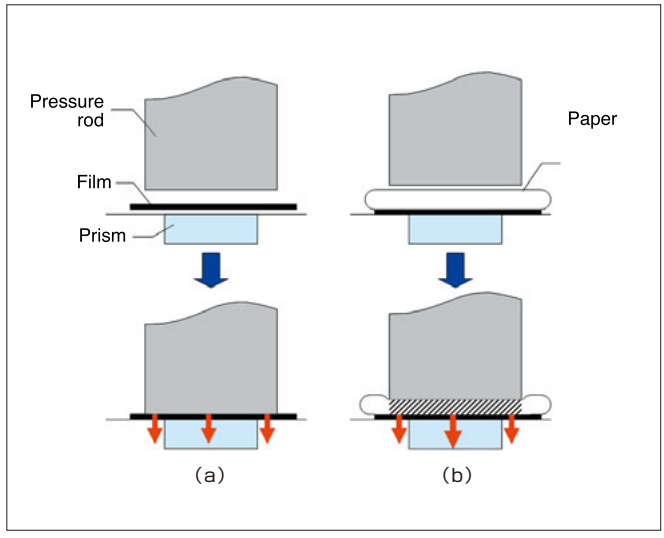

Fig. 2

NEW PRODUCTS

Shimadzu FTIR Microscope System

IRPrestige-21& AIM-8800

The AIM-8800 infrared microscope, which has established a good reputation for operability, and the IRPrestige-21, a high-sensitivity, high-performance FTIR spectrophotometer, combine to form a system that is highly effective for applications involving microscopic measurement, such as the analysis of foreign substances. The incorporation of a "Foreign Substance Analysis Program" as a standard feature provides powerful support for the qualitative analysis of mixtures that are difficult for beginners to analyze.

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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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