

Application News

No. A485

Spectrophotometric Analysis

Spectral Characteristics Dependent on ATR Crystal Selection – Differences in Properties (Shape, Hardness, Refractive Index) According to Sample –

ATR (Attenuated Total Reflectance) is a technique that is widely used in verification testing and contaminant analysis. With this technique, however, peak characteristics such as peak intensity and position, etc., vary depending on the shape of the sample and the type of crystal selected. Here, using a variety of samples

and three types of crystals (diamond, ZnSe, Ge), we conducted measurements and describe the typical ATR spectral characteristics associated with the contact status between the crystal and sample, as well as the shape of the sample.

■ ATR Crystal

A variety of materials are used as ATR crystals, including diamond, ZnSe, KRS-5 (thallium iodide and thallium bromide mixed optical crystal), Ge, etc., and depending on the type of crystal selected, differences in peak intensity and position may be observed.

Peak intensity is directly related to the principle underlying the ATR method. The penetration depth of infrared light into the sample using the ATR method can be calculated by expression (1) shown below.

$$dp = \frac{\lambda / n_1}{2\pi \sqrt{\sin^2\theta - (n_2 / n_1)^2}} \dots\dots\dots(1)$$

$$A = (\log_{10}e) \frac{n_2}{n_1} \frac{E_0^2}{\cos\theta} \frac{dp}{2} \alpha \dots\dots\dots(2)$$

Here, dp is the penetration depth of the infrared beam, λ is the wavelength in air, θ is the angle of incidence of the infrared beam, n_1 is the refractive index of the crystal, and n_2 is the refractive index of the sample.

It is clear from expression (1) that the penetration depth of the infrared light is proportional to the wavelength λ , and is also related to n_1 , the refractive index of the crystal (assuming a sample with a constant refractive index). In other words, as the refractive index of the crystal increases, the penetration depth of infrared light will decrease, thus generating weaker peak intensity.

For example, assuming a sample refractive index n_2 of 1.5, the calculated penetration depth of infrared light at a 45° angle of incidence is shown in Fig. 1.

The red trace shows the penetration depth obtained using a crystal consisting of diamond, ZnSe, or KRS-5 with a refractive index of about 2.4, and the green trace using a Ge crystal with a refractive index of about 4.0. Thus, from Fig. 1, it is clear that the depth of infrared light penetration differs greatly depending on the crystal used. In the case of the Ge crystal, as the penetration depth is shallow compared to that of diamond, etc., it is clear that more information pertaining to the sample surface can be obtained. On the other hand, the peak intensity of the obtained ATR spectrum is weaker with the Ge crystal.

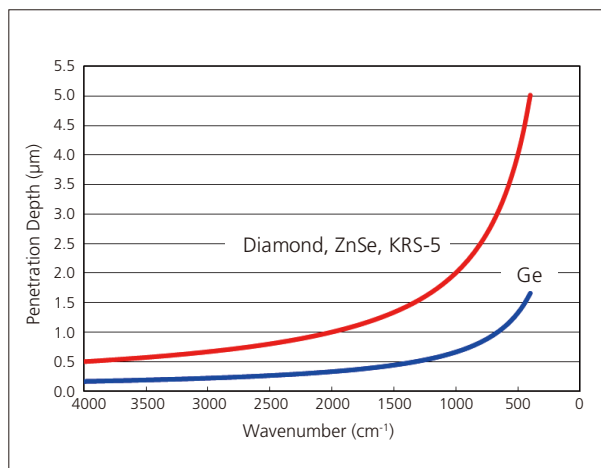


Fig. 1 Theoretical Calculation of Infrared Beam Penetration Depth

In addition, it is also known that in an ATR spectrum, the peak shape and its position change in accordance with expression (2).

Here, A expresses the absorbance, E_0 the evanescent wave electric field, and α the extinction coefficient corresponding to the sample thickness.

E_0 and dp are functions of n_2 . n_2 changes greatly (phenomenon referred to as anomalous dispersion) in the presence of strong absorption. This, therefore, causes changes in the shape of the ATR spectrum as well as the peak positions. When a crystal having a low refractive index is used for measurement, there is greater susceptibility to the effects of anomalous dispersion, resulting in peak position fluctuation. But the effects of this abnormal dispersion can be mitigated by using a crystal with a higher refractive index $n_1^{(1), 2)}$.

Thus, fluctuation of peak intensity and peak position occur in the ATR spectrum depending on the refractive index of the crystal, but by approximating the transmission spectrum and utilizing an advanced ATR correction feature, it is possible to compare the ATR spectra measured using different crystals. For more information on the correction feature and its effectiveness, please refer to Application News A476.

■ ATR Measurement of Various Samples

This section describes the characteristics of ATR spectra obtained according to the sample properties (shape, hardness, refractive index) and type of crystal used. Measurements were conducted by single-reflection ATR measurement using three types of crystals, including diamond (with a ZnSe support element), ZnSe, and Ge. The measurement conditions are shown in Table 1.

Table 1 Instruments and Analytical Conditions

Instruments	:IRTracer -100, MIRacle 10
Resolution	: 4 cm ⁻¹
Accumulation	: 20
Apodization	: Happ-Genzel
Detector	: DLATGS

■ ATR Measurement of Liquid

As a very good contact can be achieved between a liquid sample and crystal, there is no need to apply pressure. The measurement results using a silicone oil sample are shown in Fig. 2.

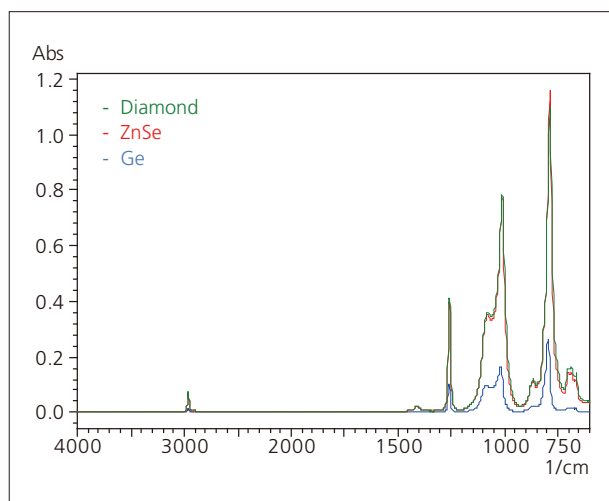


Fig. 2 ATR Spectra of Silicone Oil

Measurement using a diamond and ZnSe provide about the same degree of intensity, but the intensity obtained using Ge is only about one-fourth of that peak intensity. Fig. 3 shows an enlarged view of the peaks in the vicinity of 1,000 cm⁻¹, which are generated due to a Si-O stretching vibration in a silicone oil sample. The peak intensities in this vicinity of 1,000 cm⁻¹ match closely.

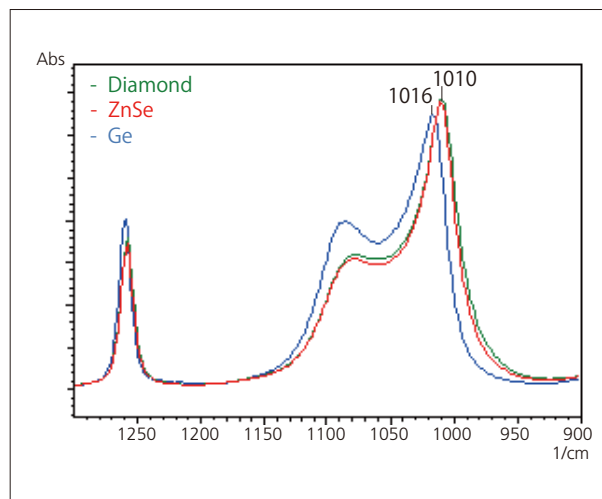


Fig. 3 Enlarged Spectra in Vicinity from 1,300 to 900 cm⁻¹

From Fig. 3, it is evident when comparing these with the Ge crystal, with its large refractive index, that the peak positions using the diamond and ZnSe crystals are shifted to the lower wavelength side by about 6 cm⁻¹. In this way, a peak wavenumber shift generally occurs prominently when using a crystal having a low refractive index.

■ ATR Measurement of Film

Next, we show the measurement results for nylon 6 film in Fig. 4.

When measuring a solid sample, it is necessary to maintain close contact of the sample with the crystal by applying pressure from above. With samples such as film, which permit good contact due to their smooth surface, there is not much difference in the peak intensity obtained using either diamond or ZnSe.

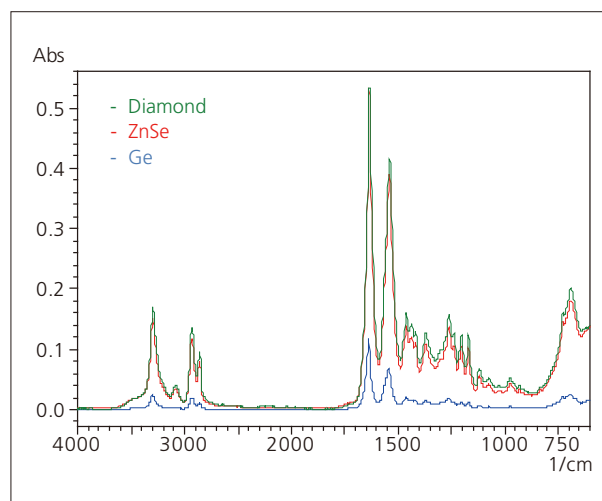


Fig. 4 ATR Spectra of Nylon 6 Film

■ ATR Measurement of Powder

Next, the measurement results for anhydrous caffeine powder are shown in Fig. 5.

As in the case of film, there is not much difference in the contact and peak intensity obtained using either diamond or ZnSe. In such a case, the contact can be improved by grinding the powdered sample more finely.

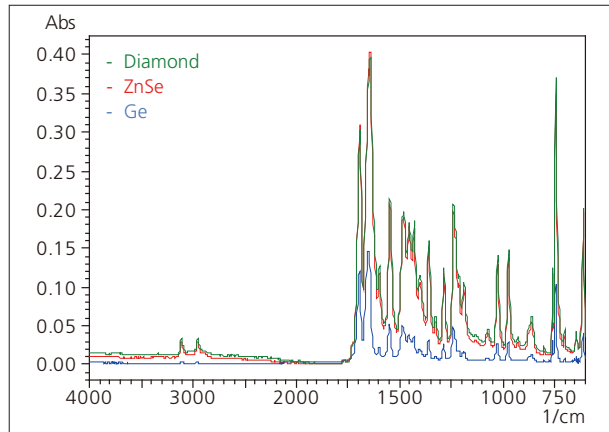


Fig. 5 ATR Spectra of Anhydrous Caffeine Powder

■ ATR Measurement of Resin Pellet

Resin pellets are generally cylindrical in shape, so the contact status can be expected to vary depending on how the sample is placed. Fig. 6 shows the results of measurement of an acrylonitrile butadiene styrene (ABS) resin pellet.

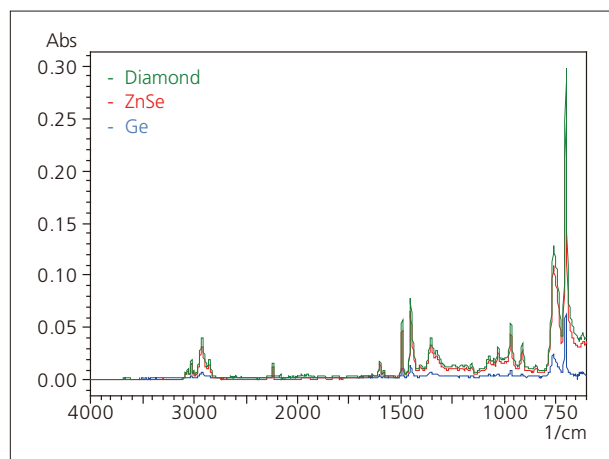


Fig. 6 ATR Spectra of ABS Resin

Comparing the results obtained using diamond and ZnSe crystals, it is diamond that clearly shows the stronger peak intensity. This may be attributed to stronger attachment using diamond, which presumably offers closer contact.

■ ATR measurement of Internal Coating of Aluminium Can

Aluminium cans are coated both internally and externally, but it is the inner surface coating that must meet the more stringent criteria as specified by the Food Sanitation Law, due to the direct contact of that surface with beverages. Fig. 7 shows the results of measurement of epoxy resin coated on the inner surface of a can in order to prevent corrosion. The measurement sample was prepared by cutting off a piece of the aluminium can, and then flattening the excised piece for measurement.

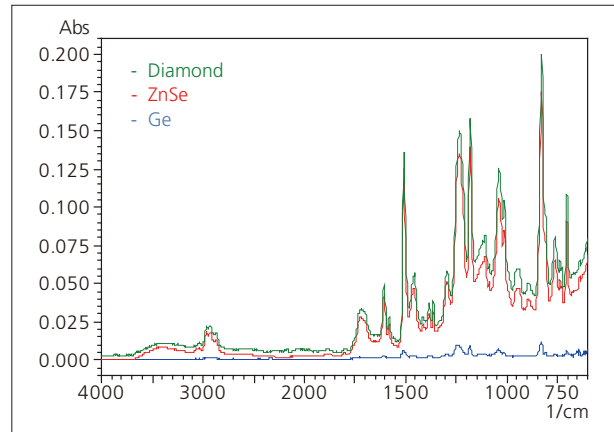


Fig. 7 ATR Spectra of Internal Coating of Aluminium Can

In Fig. 7, the difference in peak intensity between that obtained with the diamond and ZnSe crystals is clearly evident. As for Ge, a bigger difference in peak intensity occurs than the expectations from the difference in theoretically-derived penetration depth. It is presumed that this might be attributable to insufficient flattening of the piece of can used as the specimen, which resulted in imperfect contact between the sample and crystal. Thus, when conducting measurement of a sample whose properties prevent close contact with the crystal, care is required due to large differences in peak intensity depending on the selected crystal.

■ ATR Measurement of Black Rubber

Carbon black is often added to rubber as an augmentation agent, but as the amount of added carbon black increases, the greater becomes the refractive index of the rubber sample. Also, carbon exhibits absorption throughout the infrared region, and in accordance with ATR principle (penetration depth dependence on wavelength), the baseline rises in the lower the wavenumber region, with greater light penetration. The results of measurement of acrylonitrile butadiene rubber (NBR) containing carbon 10 wt% using three types of crystals are shown in Fig. 8.

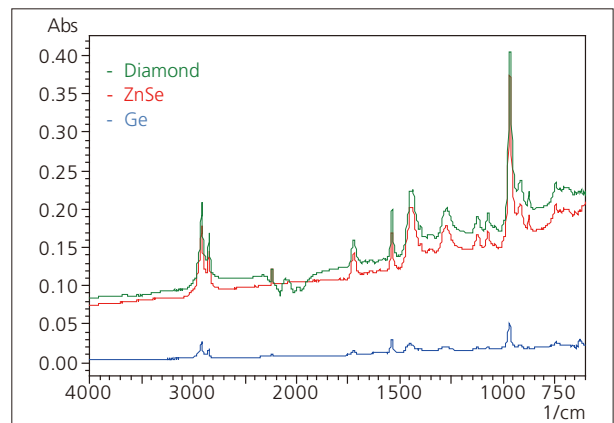


Fig. 8 ATR Spectra of NBR Containing 10 wt% Carbon

Regarding the results using the diamond and ZnSe crystal, compared to that using Ge, there is clearly a large rise in the baseline. Further, comparing the results using the diamond and ZnSe crystals, there is an evident dip in the vicinity from 2,400 to 2,000 cm^{-1} with the diamond crystal. This is due to absorption by the crystal itself (residual absorption by the diamond), and because this phenomenon is commonly seen in measurement of elastic samples such as rubber in which a diamond crystal is used, caution is necessary. In addition, to check the ATR spectrum of a high-carbon content sample, we conducted measurement of NBR rubber with a carbon content of 30 wt% using three types of crystals. The measurement results are shown in Fig. 9 to 11.

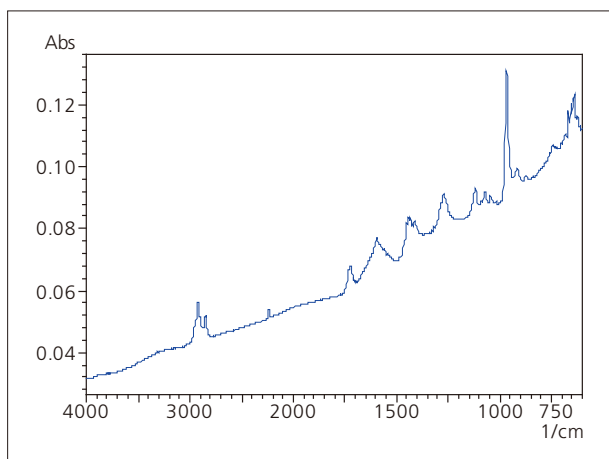


Fig. 9 ATR Spectrum of NBR Rubber Containing 30 wt% Carbon (ATR Crystal: Ge)

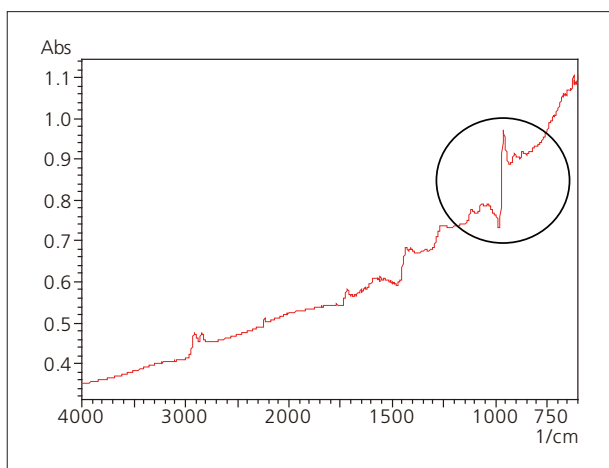


Fig. 10 ATR Spectrum of NBR Rubber Containing 30 wt% Carbon (ATR Crystal: ZnSe)

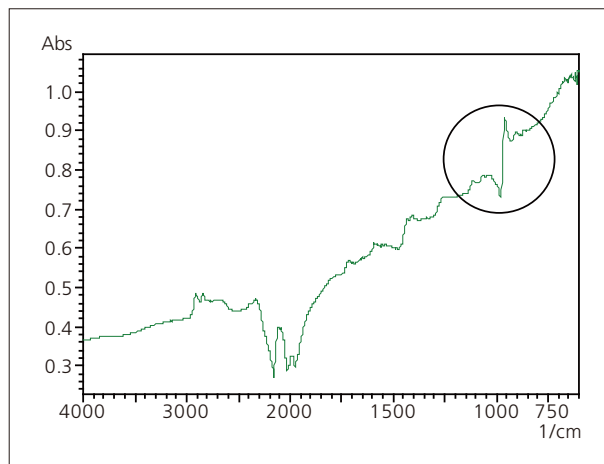


Fig. 11 ATR Spectrum of NBR Rubber Containing 30 wt% Carbon (ATR Crystal: Diamond / ZnSe)

Comparing Fig. 8 and figures from Fig. 9 to 11, the baseline rise increases further as the carbon content increases.

Also, peak distortion is noticeable (circled areas in figures) in the spectra generated using the diamond and ZnSe crystals, both of which have a relatively low refractive index. This is due to the increase in the refractive index of the samples as the carbon content increases to the point that the total reflectance method conditions of expression (1) are no longer satisfied. As a result of this phenomenon, the peak position shifts to the lower wavelength side of the original position. Further, when the refractive index of the sample is increased, the peak is generated in the reverse direction, thereby complicating qualitative analysis due to the abnormally generated spectrum. Considering these various factors, the Ge crystal may be more suitable for the analysis of samples having a high refractive index.

Conclusion

Here, a variety of samples were measured using three different crystals, and the differences in the resulting peak intensities and positions could be observed and compared. The information and data presented in this Application News are intended to assist in the selection of the optimal crystal in accordance with the sample being analyzed.

Reference:

- 1) Koichi Nishikida, Reikichi Iwamoto, et al., Kodansha Ltd. (1986), Material Analysis by Infrared Method: Fundamentals and Applications
- 2) Tsuguo Sawada et al., Dainippon Tosho Co., Ltd. (1988), New Chemical Library / Spectroscopic Analytical Chemistry