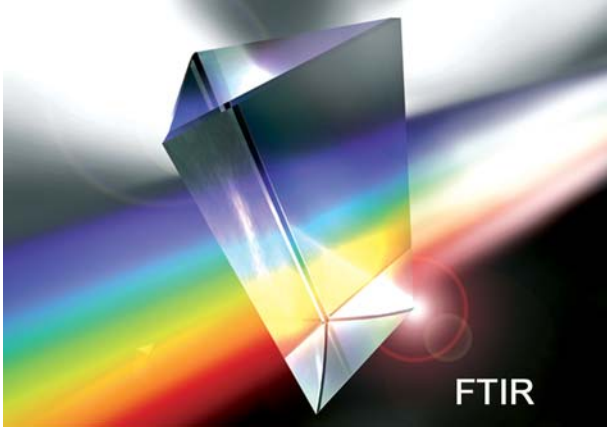

Application Note

Kramers-Kronig Transform and Applications

Spectral measurement can be made easily using specular spectrometry without destroying the sample. However, when it is applied to the measurement of a sample which is highly specular like a glassy or crystalline substance and which exhibits absorption in the infrared region, abnormal dispersion occurs, making the peaks of the spectrum distorted to look like those of a first derivative curve. From such a spectrum, analysis and identification of functional groups is difficult. Therefore this distorted spectrum needs to be transformed into an ordinary spectrum for interpretation. The Kramers-Kronig transform is used for that purpose. Given here is an explanation of the Kramers-Kronig transform and its applications.

Kramers-Kronig Transform

Assuming the infrared radiation is incident normal (90") to the surface of the sample, when the complex index of refraction (n*) of the substance is n* = n + ik (n,k : refractive index and absorption coefficient of the substance), the reflectivity amplitude r for vertically incident light and the reflectivity energy R that is directly obtained from the specular reflectance spectrum are expressed as follows.

$$r=\sqrt{R}e^{i\phi}=\sqrt{R}\,(\cos\phi+i\sin\phi)=\frac{n-ik-1}{n-ik+1} \tag{1}$$

$$R=|r|^{2}=r\cdot r^{*}=\frac{(n-1)^{2}+k^{2}}{(n+1)^{2}+k^{2}} \tag{2}$$

Here, Ø represents the phase change from the absorbance that occurs with reflection from the surface of a substance. The term r* is the complex conjugate of r. When n and kin equation (1), which includes a real part and an imaginary part, are solved for, the following equations are obtained.

$$n=\frac{1-R}{I+R-2\sqrt{R}\,\cos\phi} \tag{3}$$

$$K=\frac{-2\sqrt{R}\,\sin\phi}{1+R-2\sqrt{R}\,\cos\phi} \tag{4}$$

The logarithmic expression of equation (1) is as follows:

$$\ln r=\ln\sqrt{R}+i\,\phi \tag{5}$$

In equation (5), √R and Ø are mutually dependent according to the Kramers-Kronig equation:

$$\phi(v_{g})=\frac{2\,v_{g}}{\pi}\int_{o}^{\infty}\frac{\ln\sqrt{R}(v)}{v^{2}-v_{g}^{2}}\,dv \tag{6}$$

Using this equation, the phase change at an arbitrary wavenumber v_g can be calculated if the reflection energy can be measured over the entire wavenumber range, and then from equations (3) and (4), the optical constants n From such a spectrum, analysis and identification of functional groups is difficult. Therefore this distorted spectrum needs to be transformed into an ordinary spectrum for interpretation. The Kramers-Kronig transform is used for that purpose. Given here is an explanation of the Kramers-Kronig transform and its applications. and k can be obtained. Consequently, if k is calculated for the middle infrared region, e.g., 4600 - 400 cm^{-1}, at a given wavenumber interval, an absorption coefficient spectrum equivalent to a transmission spectrum can be obtained from the specular reflectance spectrum. The integral (6) has $v = v_g$ as a limit. Several integration methods have been proposed, among which Maclaurin's method and the double Fourier transformation are the most commonly applied. By Maclaurin's method, phase change (v_g) is given by the equation (7) wherein the lower limit v_j is set so that $v = v_g$ will not occur, and every other data point is utilized. While, by the double Fourier transformation, Ø(v_g) is obtained as an approximation of equation (6) through the double Fourier transform, as in equation (8). The Maclaurin method features higher calculation accuracy, but as it usually takes a relatively longer time for calculation, the double Fourier transform is used.

$$\phi(v_{g})=\frac{2\,v_{g}}{\pi}\times 2h\times\sum_{j}\frac{\ln\sqrt{R}(v_{j})}{v_{j}^{2}-v_{g}^{2}} \tag{7}$$

where $h = v_{j+1} - v_j$ and if data interval g is an odd number then j = 2,4,6, .., g-1, g+1, . .., while if g is an even number then j = 1,3,5, ..., g-1, g+1, ...

$$\phi(\nu_g) = 4\int_0^\infty \cos(2\pi\nu g t)\,dt \int_0^\infty \ell n\sqrt{R(\nu)}\,\sin(2\pi\nu t)\,d\nu \qquad (8)$$

Table 1 Analytical Conditions of Fig. 1 and Fig. 3
Resolution : 4 cm^{-1}
Accumulation : 100
Apodization : HappGenzel
Mirror Speed : 2.0 mm/sec
Detector : Pyroelectric Detector

Application to Black Rubber

In the infrared spectrometry of black rubber containing carbon black, the **ATR** method with a Ge prism is applied in general. But, in the low wavenumber range below 650 cm^{-1}, Ge itself absorbs infrared rays, which interferes with the sample absorption spectrum. In the case of a lustrous or shiny black rubber, the infrared spectrum can be measured up to 650 cm^{-1} easily by acquiring the specular reflectance spectrum and converting it with the Krarners-Kronig transform. Fig. 1 shows the specular reflectance spectrum of a black fluorinated rubber. Under these conditions, the spectrum is distorted, which makes it difficult to obtain any qualitative information. From the spectrum after the Kramers-Kronig transform, as shown in Fig. 2, it can be confirmed that the sample is a fluorinated rubber.

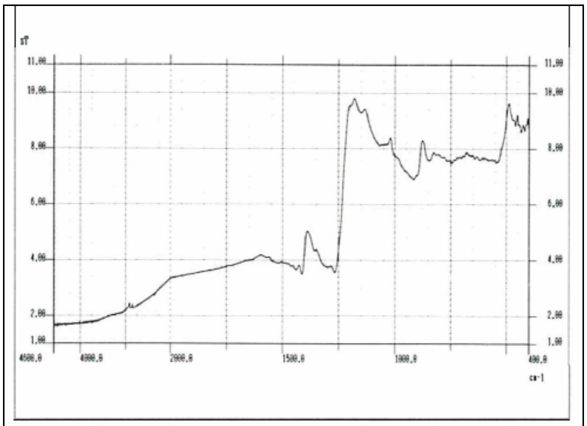

Fig. 1 Specular Reflectance Spectrum of Black Fluorinated Rubber

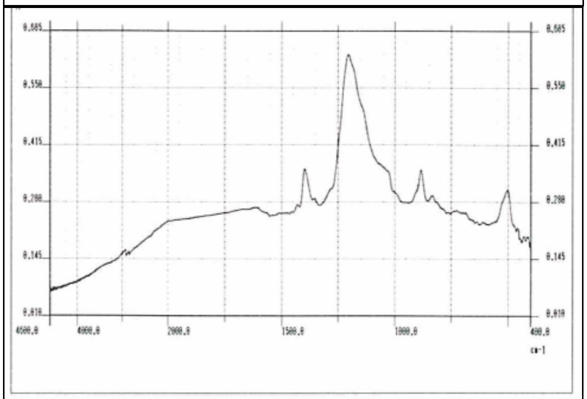

Fig. 2 Spectrum of Black Fluorinated Rubber after Kramers-Krönig Transformation

Application to Plastic Slab

Fig. 3 shows a specular reflectance spectrum of a polymethylmethacrylate **(PMMA)** slab of a thickness of 1 cm. In the case of such a thick sample, the usual **ATR** method would require some preparation of the sample, but the specular reflectance measurement enables spectrum acquisition to be easily conducted without the need for any preparation.

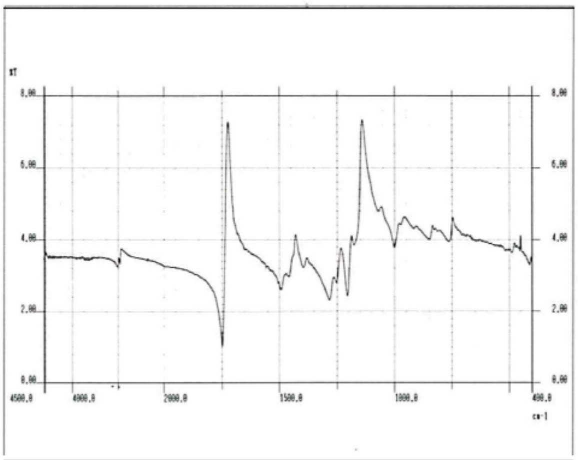

Fig. 3 Specular Reflectance Spectrum of Polymethylm Ethacrylate (PMMA) Slab

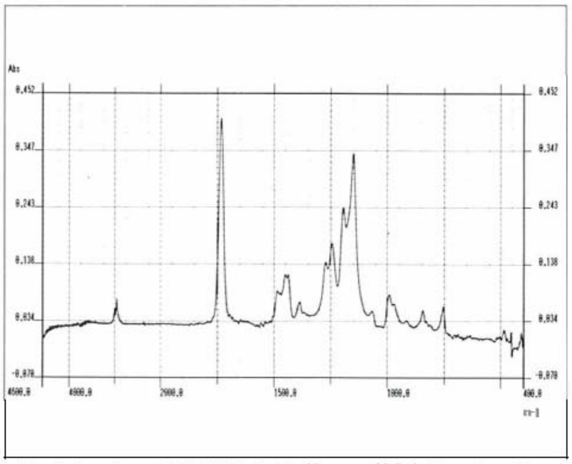

Fig. 4 Spectrum of PMMA Slab after Kramers-Krönig Transformation.

Reference: Shimadzu C103-E031 No. 228