

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.

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.

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

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

Here, ϕ 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 k in equation (1), which includes a real part and an imaginary part, are solved for, the following equations are obtained.

$$n = \frac{1 - R}{1 + R - 2\sqrt{R} \cos\phi} \quad (3)$$

$$k = \frac{-2\sqrt{R} \sin\phi}{1 + R - 2\sqrt{R} \cos\phi} \quad (4)$$

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

$$\ln r = \ln\sqrt{R} + i\phi \quad (5)$$

In equation (5), \sqrt{R} and ϕ are mutually dependent according to the Kramers-Kronig equation:

$$\phi(v_g) = \frac{2v_g}{\pi} \int_0^\infty \frac{\ln\sqrt{R}(v)}{v^2 - v_g^2} dv \quad (6)$$

Using this equation, the phase change at an arbitrary wavenumber v , 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

and k can be obtained. Consequently, if k is calculated the middle infrared region, e.g., $4600 - 400 \text{ cm}^{-1}$ 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 most commonly applied. By Maclaurin's method, change (v_g) is given by the equation (7), wherein the limit v_t , is set so that $v = v_g$ will not occur, and every data point is utilized. While, by the double transformation, $\phi(v_g)$ is obtained as an approximation equation (6) through the double Fourier transform, equation (8).

The Maclaurin method features higher calculation accuracy, but as it usually takes a relatively longer calculation, the double Fourier transform is used.

$$\phi(v_g) = \frac{2v_g}{\pi} \times 2h \times \sum_j \frac{\ln\sqrt{R}(v_j)}{v_j^2 - v_g^2} \quad (7)$$

where $h = v_{j+1} - v_j$ and if data interval

g is an odd number then $j = 2, 4, 6, \dots, g-1, g+1, \dots$, while if g is an even number then $j = 1, 3, 5, \dots, g-1, g+1, \dots$

$$\phi(v_g) = 4 \int_0^\infty \cos(2\pi vgt) dt \int_0^\infty \ln\sqrt{R}(v) \sin(2\pi vt) dv \quad (8)$$

Table 1 Analytical Conditions of Fig. 1 and Fig. 3

Resolution: 4 cm^{-1}
Accumulation: 100
Apodization: Happ-Genzel
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 Kramers-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.

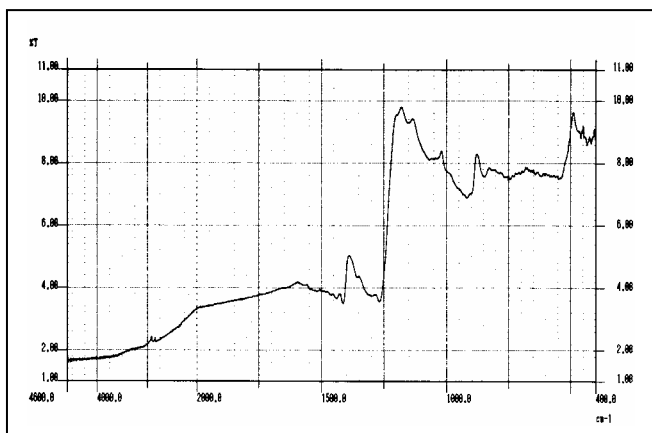


Fig. 1 Specular Reflectance Spectrum of Black Fluorinated Rubber

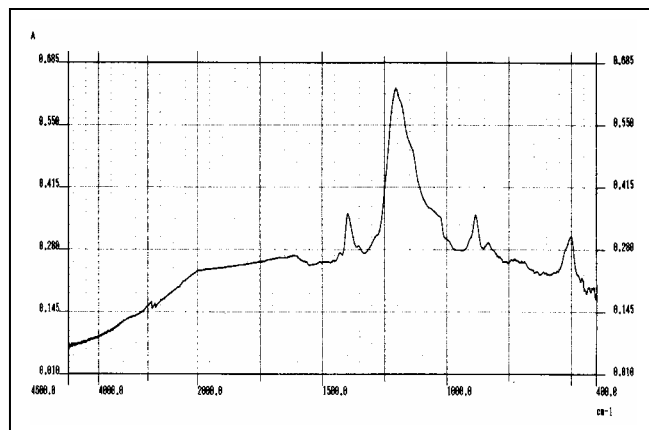


Fig. 2 Spectrum of Black Fluorinated Rubber after Kramers-Kronig Transformation

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.

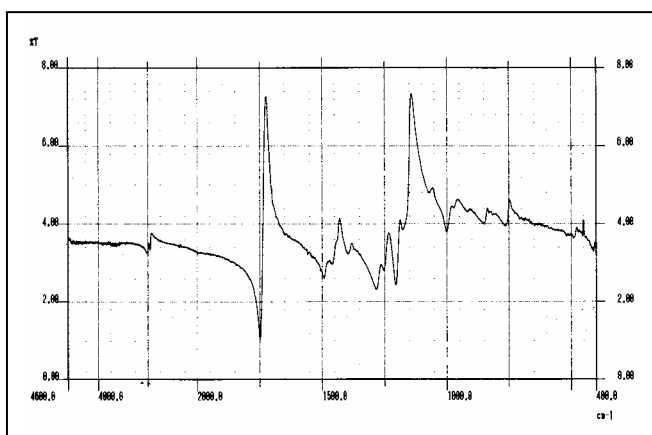


Fig. 3 Specular Reflectance Spectrum of Polymethylmethacrylate (PMMA) Slab

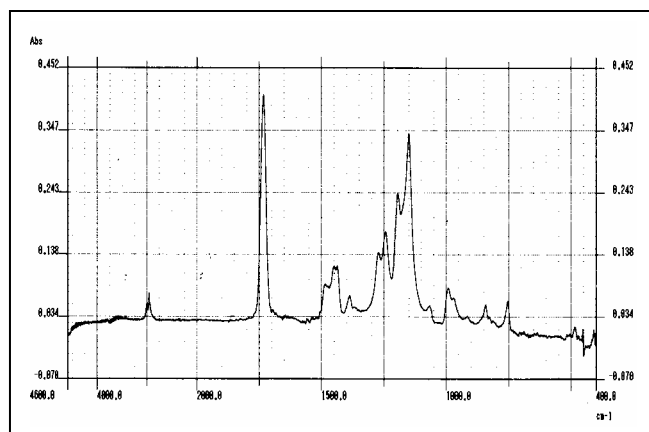


Fig. 4 Spectrum of PMMA Slab after Kramers-Kronig Transformation.