

Specular Reflectance Infrared Analysis

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OVERVIEW

Specular reflectance Fourier transform infrared measurements allow thin coatings layers on reflective surfaces to be analyzed with little or no sample preparation¹⁻⁵. This technique is used mainly for samples such as lubricating or polymeric coatings on reflective substrates but can also be used successfully for many matte-surfaced samples such as paper or cloth products. The primary difficulties associated with specular reflectance measurements involve spectral distortions caused by the mixing of the absorption information and the refractive index variation in the measured radiation. A second difficulty more easily overcome is the low level of reflected energy than can occur when measuring highly absorbing samples. This low signal-to-noise ratio (SNR) situation can be overcome by increasing data collection times or by using more sensitive detectors such as those with mercury cadmium telluride (MCT) cooled photoconductive elements. The following paragraphs will detail the theory and practice of specular reflectance infrared measurements.

THEORY AND APPLICATIONS

When a beam of infrared radiation is focused onto the surface of a flat sample, several types of interaction can occur. Figure 1 shows the three types of reflectance that occur when the sample consists of a coating on a reflective substrate. The ray labeled as *true specular* (R_{s1}) simply reflects from the sample surface at an angle that is equal to the incident angle (mirror like reflection). This radiation has not been absorbed by the sample and therefore contains no direct information about the absorptivity of the sample. Because the radiation is reflected, according to Fresnel's equations, the intensity is a function of the refractive index of the sample. As will be discussed later, it is this refractive index component mixing with the absorption information that causes spectral distortions in the final

spectrum. The ray labeled *diffuse specular* (R_{s2}) has undergone mirror like reflections from surface irregularities of the sample but has not been absorbed. Unlike the *true specular* (R_{s1}) component, this ray may ultimately emerge at any angle relative to the incident radiation. The third component of the measured radiation ($R_T = \text{transflectance}$) has been transmitted through the coating layer, reflected from the coating/substrate interface and is finally transmitted back through the sample. This ray contains information about the absorptivity (α) of the sample. The mixing of the specular reflectance and transfectance components can cause spectral distortions. For many samples, the measured specular reflectance spectrum is a mixture of these components and the observed band shapes takes on a derivative shape. A mathematical operation known as the Kramers-Kronig⁶⁻⁸ transformation can often be used to correct spectra which are dominated by the contributions of the refractive index variation. A more detailed discussion of these effects and the application of the Kramers-Kronig transformation as applied to specular reflectance spectra will be discussed in a later section of this article.

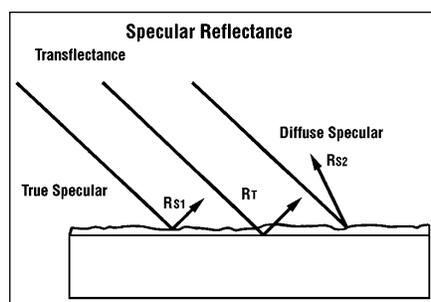


Figure 1: The three types of reflectance that can occur from coatings on reflective surfaces.

There are two different accessories (fixed 30- and 80-degree angles) commonly used for infrared specular reflectance measurements. The differences between these accessories are detailed in Figure 2. By increasing the incident angle, the effective pathlength through the sample can be increased. The 30 degree accessory is therefore most useful for thick coatings (layer > micron range) while the 80-

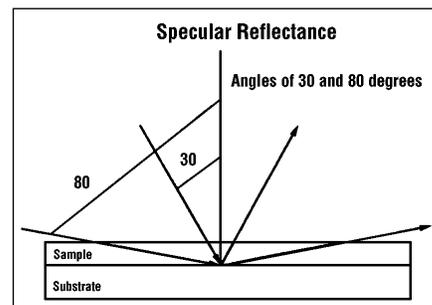


Figure 2: The effective depth of penetration variation as a function of the angle of the incident radiation.

degree accessory (often referred to as grazing angle) is more commonly used for samples with thin coatings (as low as monomolecular layers). In addition to the obvious increase in effective pathlength that occurs with an 80 degree accessory, there is an interaction enhancement that occurs as a result of the incident radiations electric field angular dependence. At high angles of incidence, the field strength near the surface is relatively high and will interact with those functional groups whose transition moments are normal to the surface. Polarizers can also be used to enhance the measurements for functional groups that are aligned in a regular manner relative to the sample surface. As an example, a carbonyl group oriented perpendicular to the surface will strongly absorb radiation which is polarized in a plane perpendicular to the surface.

For simple transmittance measurements as those encountered when analyzing samples such as polymer films or liquids in sealed cells, a background is measured with no sample in the optical path. The sample is then placed in the infrared beam and a transmittance spectrum calculated by dividing the single beam spectrum of the sample by that of open beam background. This can be represented as:

$$\% \text{ Transmittance} = \left(\frac{\text{Single Beam Sample}}{\text{Single Beam Open Beam}} \right) * 100$$

If quantitative results are desired it is common to express the spectrum in absorbance units where absorbance is defined as:

$$\text{Absorbance} = \text{Log} (1/T)$$

where T is the fractional transmittance.

For almost any accessory it is important to measure the background through the accessory rather than use an open beam spectrum. For specular reflectance measurements, the background is typically obtained by measuring the spectrum of a silver or gold coated front surface mirror. The sample spectrum is then obtained and the reflectance spectrum calculated in a manner that is analogous to transmittance.

$$\% \text{ Reflectance} = \left(\frac{\text{Reflectance Sample}}{\text{Reflectance mirror}} \right) * 100$$

If one is interested in quantitative information, the spectrum can be expressed as:

$$\text{Log (I/R)}$$

where R is the fractional reflectance. The Log (I/R) expression is mathematically equivalent to absorbance.

Effect of Incident Angle and Depth of Penetration

The angular dependence on the effective depth of penetration is demonstrated in the results shown in Figure 3. In this case, a thin coating of an epoxy polymer is measured using both the 30 degree and the 80 degree (grazing angle) accessories. The Log (I/R) spectra are plotted on the same ordinate scale with a linear offset to show the longer effective pathlength obtained with the 80 degree unit. The broad absorption around 2300 and 1900 wavenumbers for the 80 and 30 degree accessories respectively are fringes caused by internal reflections within the polymeric layer.

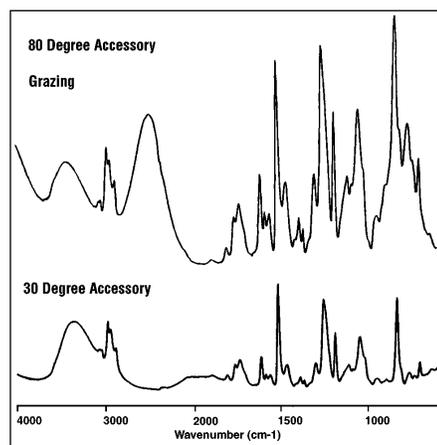


Figure 3: The depth of penetration effect on epoxy coated metal surface for (top) grazing 80 degree and (bottom) 30 degree accessories.

Epitaxial Silicon Layers

The difference in pathlength experienced by radiation reflecting from a surface and also at a deeper boundary layer interface can be used to determine the thickness of

the intermediate layer. It is important in semiconductor fabrication that very consistent layers of silicon be deposited during the integrated circuit manufacturing process. These layers are typically 0.5-100 microns in thickness. If infrared radiation is reflected from the surface of a silicon wafer with an epitaxial silicon layer, a fraction of the radiation will reflect from the surface while the rest will be transmitted through the coating layer. Another reflection will occur at the interface between the layer and the substrate. The rays from these two reflection have traveled different distances and the combined information that is measured can be used to calculate the layer thickness. (See Nicolet Technical Bulletin #1019 for more details.)

Polymeric Coatings on Metals

Examples of the spectra obtained from a number of different can coatings measured using a 30 degree accessory are shown in Figure 4. The top spectrum suggests that this particular coating is an aliphatic polyester while the middle and bottom spectra are probable epoxy type coatings. These last two spectra are exterior coatings and the question to be answered for these quality control related samples concerned whether or not they were the same material. It is obvious from these spectra, obtained by simply cutting 2 x 2 inch sections from each sample, that they are not identical.

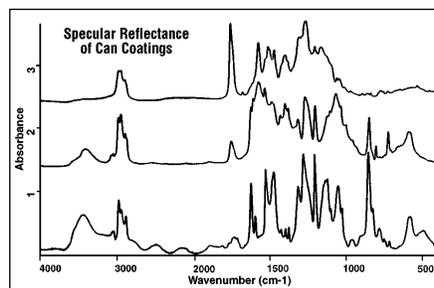


Figure 4: Specular reflectance spectra of can coatings.

Lubricants on Steel Plates and Magnetic Disks

The proper application of a coating material is critical for many important industrial products. There are many types of lubricating films used on metal surfaces. If the coating layer is too thin, the lubricating characteristics will be impaired, while excessively thick coatings result in additional production costs and may even cause component failure.

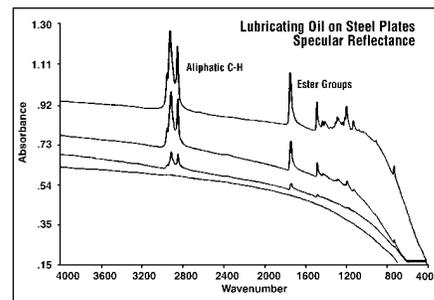


Figure 5: Ester containing organic lubricating coating on steel plates at various coverage levels.

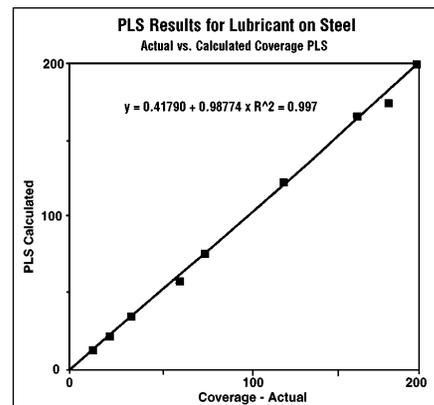


Figure 6: Partial least squares calibration results for the ester lubricant on steel plate samples.

A system consisting of an alkyl ester coating on steel plates was examined. The spectra were run on a Nicolet 710 spectrometer equipped with a 30 degree specular reflectance accessory. The coating coverage ranged from 12 to 199 mg/ft². The spectra obtained from a number of the samples with different coating levels are shown in Figure 5. The data was analyzed using the Nicolet PLS (Partial Least Squares) quantitative analysis software package. The results of the calibration are shown in Figure 6. As noted in the Figure, a linear correlation coefficient of 0.997 is obtained when comparing the actual and calculated coverage values. (See Nicolet Application Note #AN0-8930 for more details.)

An approach similar to that described above is widely used to measure the lubricant coating thickness on magnetic disks. In this case, the coating layer is quite thin and an 80 degree accessory is employed.

Specular Reflectance of Paper Samples

The specular reflectance spectrum of a paper sample with and without an adhesive coating and the resulting difference spectrum obtained by subtracting the spectrum of the blank paper from that with the adhesive are shown in Figure 7. This difference spectrum allows the spectral

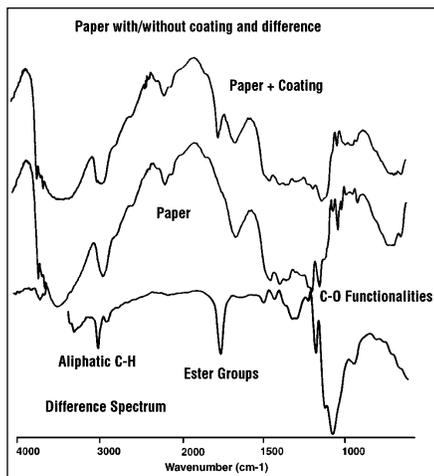


Figure 7: Specular reflectance spectra of paper: (top) coated, (middle) uncoated and (bottom) difference spectrum obtained by subtracting the spectrum of the uncoated sample from that with the coating.

features due to the adhesive to be observed by removing the common absorptions of the paper matrix. There is, however, a cause for concern in these spectra. The transmittance spectra of cellulose type materials show a very strong band -C-O absorption centered around 1050 cm^{-1} . This absorption would be expected to be more intense (in a relative sense) than is observed in the paper spectra of Figure 10. This is another example of the spectral distortions caused by the mixing of the absorption information and the reflectance due to the variation in the refractive index. In spite of these concerns, valuable information can often be obtained from the specular reflectance spectra of these types of samples.

Mono-Layers on Reflective Substrates

Grazing angle measurements can be used to measure coverages as low as mono-molecular layers on reflective surfaces. The results obtained from a mono-layer of an organic phosphorous containing compound on an aluminum surface are shown in Figure 8. In this case, 512 scans were co-added to yield the final spectrum. The spectrum of a blank piece of the aluminum plate was obtained and subtracted from that of the coated specimen to yield the final spectrum. The sensitivity of this approach becomes apparent when the absorbance scale (0.0002 absorbance units per division) is examined. These results represent only 1-2 molecular layers of coating on the metal surface.

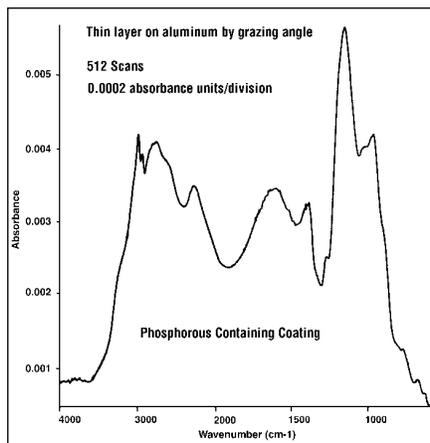


Figure 8: Mono-layer of organic phosphate on aluminum measured with 80 degree grazing angle accessory.

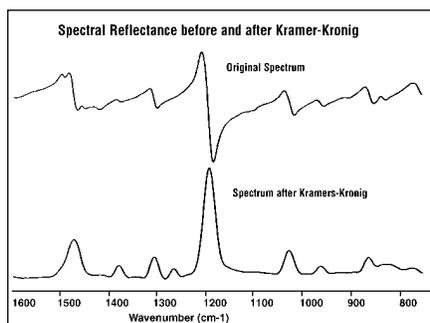


Figure 9: Spectral reflectance from eye glass lens (top) and result of Kramers-Kronig transformation (bottom).

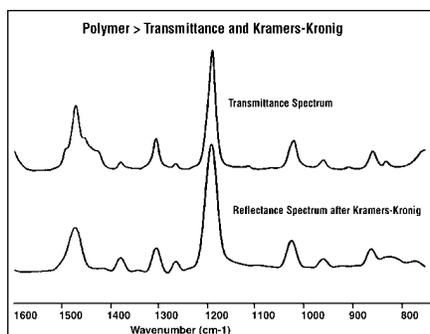


Figure 10: Kramers-Kronig transformation of reflectance spectrum from eye glass lens (bottom) and transmittance spectrum from a thin film of the same sample (top).

The Kramers-Kronig Transformation and Specular Reflection

A plastic prescription eyeglass lens was analyzed using a 30 degree reflectance accessory and is shown in Figure 9 along with the spectrum after applying the Kramers-Kronig (K-K) transformation. The large spectral distortions in the specular reflectance spectrum are caused by the presence of a large refractive index component for this type of sample. These distortions are effectively removed by the transform. A comparison of the spectrum after applying the Kramers-Kronig trans-

formation and the transmittance spectrum of a thin film of the same sample are shown in Figure 10. These results demonstrate that through the use of the K-K transformation a spectrum showing the expected absorptivity information can be calculated from one which consists of primarily refractive index variation information.

SUMMARY

Specular reflectance infrared spectroscopy is a very useful technique for analyzing thin layer samples which are coated on a reflective surface. The biggest difficulty with the technique is that care must be taken to account for artifacts caused by the variations in the refractive index of the sample. It can be used for the analysis of a variety of sample types including coatings on metal or other reflective surfaces or even diffusely reflecting samples such as papers.

REFERENCES

1. *Advances in Applied Fourier Transform Infrared Spectroscopy*, John Wiley and Sons, ISBN 0 471 920347, 1989.
2. J.H. Wang, *J. Appl. Spectrosc.*, Vol. 44, pg. 447-450, 1990.
3. N.J. Harrick and M. Milosevic, *J. Appl. Spectrosc.*, Vol. 42, pg. 519-522, 1990.
4. Y. Ishino and H. Ishida, *J. Appl. Spectrosc.*, Vol. 42, pg. 1296-1302, 1988.
5. D.L. Wooten and D. W. Hughes, *Lubrication Engineering* pg. 736-744, Sept. 1987.
6. J.P. Hawranek, P. Neelakaantan, R. P. Young, and R. N. Jones, *Spectrochim. Acta*, 32A, pg. 85, 1976.
7. T.G. Goplen, D.G. Cameron, and R.N. Jones, *J. Appl. Spectrosc.* 34, pg. 652, 1980.
8. R.T. Graf, J.L. Koenig, and H. Ishida, *J. Appl. Spectrosc.* 39, pg. 405, 1985.

