Utilizing Zero Crossover Points in the Near Infrared Reflectance Analysis of Industrial Polymers

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Synopsis

Near infrared reflectance methods were developed for the analysis of polymer pellets and films. Second derivative spectra were used to minimize the effects of scattering and to enhance spectral features. Zero crossover points, places in the derivative spectra where there is negligible response to concentration changes, were employed to minimize interferences at the measuring wavelengths. Two examples illustrate the utility of this technique for industrial quality assurance analyses. The examples include the measurement of three hydrocarbon polymers, directly in transparent pellets, and the determination of 0.1% MEK in an acrylic film. Precision and accuracy were found to be at least equal to that of other methods, and time savings were considerable.

INTRODUCTION

Near infrared reflectance (NIRR) techniques have found widespread application in the food and agricultural fields for the analysis of specific components such as moisture, protein, and carbohydrates in complex matrices. The technique and its application in these areas have been the subject of several reviews.[1-4] NIRR offers rapid, accurate analyses with little or no sample preparation. The relatively broad spectral features of the agricultural products are readily measured by either filter or scanning instruments.

Rapid analysis times by NIRR can offer cost savings in industrial quality assurance and process control areas. Many industrial materials, such as powders, coated plastics, and polymer pellets, can be analyzed directly by reflectance techniques. The development of methods for industrial compounds presents a challenge to the technique of NIRR. Each application is unique, the components may be spectrally similar to each other, and there may not be an adequate referee method for calibration. However, the spectral features are often sharper than in the agricultural products and pure compounds are usually available for comparative scanning.

THEORY

Near infrared absorption bands are caused by overtones and combinations of fundamental molecular vibrations. They are orders of magnitude weaker than mid-infrared bands, and many of the absorptions cannot be specifically assigned to given functional groups. The spectral region is complex, with considerable band overlap.

Although the NIR region is spectrally complex and ambiguous, it offers definite optical advantages over the mid-infrared region for reflectance measurements. The inherently weaker absorption combined with higher scattering coefficients provides scattered radiation whose reciprocal logarithm can be essentially linear with concentration. Sensitive optical components efficiently measure the reflected light, thus providing high signal-to-noise spectra. The problem of not having clearly defined, well-isolated spectral bands is addressed by making use of derivative spectroscopy and multiterm prediction equations. Measuring wavelengths are chosen statistically, and the equations generated for predictions include those wavelengths which appear to best measure the constituents of interest.

Statistical choice of analytical wavelengths is not very satisfying from a spectroscopist's point of view. Although many band assignments have been documented for the NIR region,[5] it is not always possible to explain the origin of a given absorption. However, one can usually prove that the measuring wavelength represents a distinct feature in the spectrum of the pure component being measured. Particularly with hydrocarbons, there is little interaction among the components of a mixture, and the spectra of isolated materials may be used as guides to their absorption features in the sample matrix.

Derivative spectroscopy provides three major aids to NIRR users: a minimizing effect on spectral differences due to particle size, improved separation of spectral features, particularly sharp ones, and the opportunity to minimize spectral interferences through the use of zero crossover points. Spectral changes due to particle size variations take the form of a scattering curve which underlies the true spectrum of a sample. The general form of a scattering equation is[6-8]

$$\tau = k\lambda^{-g} \tag{1}$$

where τ = turbidity or apparent absorbance, k = a constant, λ = wavelength, and g = wavelength exponent, 4.0 if the particle size is under 1/10 of the wavelength of the light, less for larger particle sizes.

As one takes the derivative of this equation, the denominator becomes large and the equation approximates a straight line. This effect is shown in Figure 1, the scattering curve of 0.03-in. Teflon sheeting. Since the figure is a plot of log $1/R$, where R is the reflectance reading, it shows the scattering curve to increase with increasing wavelength. Scattering effects decrease with an increase in wavelength, and therefore the reciprocal would increase. The figure shows the dramatic reduction in the scattering curve, relative to the true absorption peak at about 2100 nm.

An interesting feature of derivative spectroscopy is that the reading at a zero crossover point is independent of concentration. The zero crossover, or node, is the point in the first derivative curve which represents the top of an absorption peak in the zero-order spectrum. Because the slope at the top of a peak would be zero regardless of peak height, this point is always constant. Likewise, nodes in second derivative spectra represent inflection points in the zero order spectrum and are unaffected by concentration. Figure 2 illustrates this concept. This situation can be used as an advantage
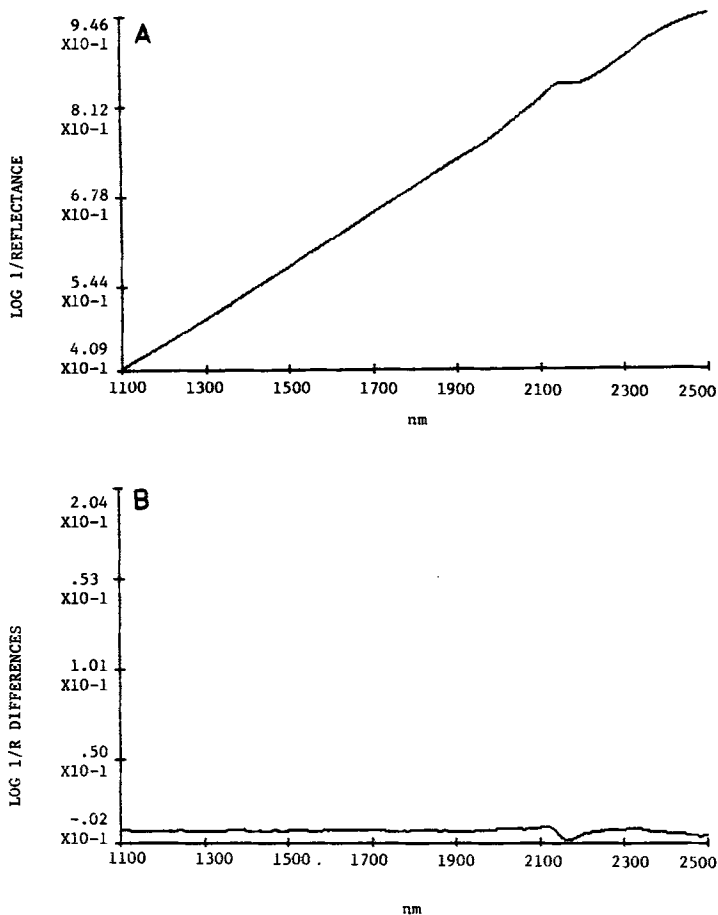
Fig. 1. A scattering curve (A) and corresponding first derivative (B). Note that, for approximately the same pen fluctuation for the absorbance peak at 2150 nm, the underlying scattering curve is much flatter in the derivative spectrum.

to eliminate the effects of interfering substances in the determination of an analyte. One would seek points in a derivative spectrum where the substance of interest shows definite absorption, while interfering materials have zero crossovers or no absorption.

EXPERIMENTAL

Clear polymer pellets in the shape of 3×3 mm cylinders were placed directly in the normal sample cup of a Pacific Scientific Co. (Silver Spring, MD) Model 6250 Spectrophotometer. A 0.03 in. thick Teflon backing sheet was used under the pellets because Teflon was found to have minimal NIR spectral features of its own. The pellets were also cryogenically ground and sieved, but these procedures did not improve the calibrations. Clear polymer films were scanned in the transmission and transflection modes illustrated in Figure 3. Interference fringes caused by internal reflections within the film were more severe in the transmission mode. The smaller diameter, ceramic-backed sample cup was used for these measurements.
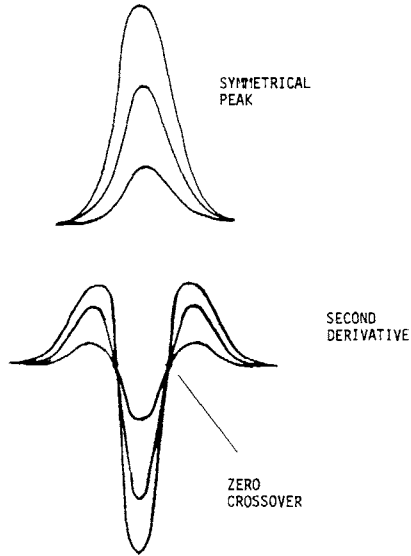
Fig. 2.   The concept of a zero crossover point (node). The nodes are independent of concentration changes since they represent the slope of the first derivative curve at the minimum and maximum points. The figure depicts the second derivative of a Gaussian curve.
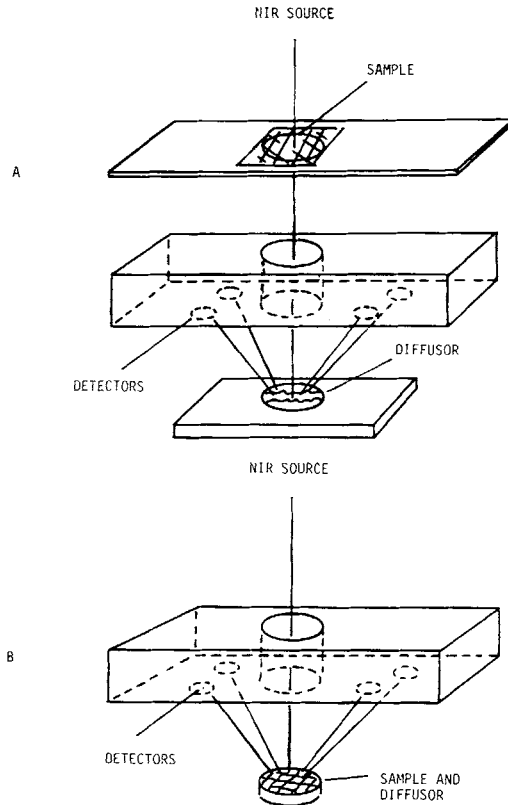
Fig. 3.   Transmission (A) and transflection (B) modes of sample presentation.

A Pacific Scientific Co. Model 3000, 3 tilted-filter instrument was also used for pellet analysis. A spinning sample cup was found to be important for good accuracy and precision. Filters with ranges of 1901–2080, 2000–2190, and 2070–2254 nm were employed.

Referee analytical methods for polymer calibrations ranged from simply weighing individual ingredients before mixing to more complicated techniques such as employing radioactively tagged monomers. For the residual solvent example, calibration samples were prepared by cutting circles from a solvent-wet film as the film dried. The circles were scanned as described above, and then sealed into small, septum-capped bottles for GC analysis. For the pellet example, referee methods consisted of exhaustive extraction of known mixtures for one component of the pellet, and mid-infrared transmission for the determination of the second component. The three components in the calibration set were varied randomly.

Data points were taken every 2 nm through the 1100–2500 nm spectral range. Samples were generally repacked four times each and averaged. Fifty scans were averaged for each spectrum. The sample cup was rotated during the spectral scanning. Calibrations were performed with the stepwise multiple linear regression programs supplied by the instrument manufacturer. These programs choose measuring wavelengths by seeking the highest correlation coefficient in a linear relationship between concentration of analyte and $\log 1/R$, or a point on a derivative of the $\log 1/R$ spectrum. Prediction equations are then improved by addition of a limited number of terms, again chosen by the maximization of the correlation coefficient. This process is repeated as many times as necessary with different zero order, first, and second derivative variations of the recorded spectra. The derivative spectra may be generated a large number of ways by varying the segment (number of wavelengths averaged) and gap (number of wavelengths between segments) sizes. Additional information, such as intercorrelation tables and standard errors of calibration, are provided to aid in the development of calibrations.

RESULTS AND DISCUSSION

Polymer Systems

Two examples of polymeric applications are described: One is the analysis of methyl ethyl ketone (MEK) in a UV-curable resin, and the other is the determination of three hydrocarbon polymers in a mixture. The first problem required monitoring very low (0.1%) levels of residual MEK in a photoresistive mixture of acrylic polymers and monomers. The currently used GC method requires 35 min to complete and is not amenable to real-time control. Because the resin is being transported at a rate of 50 ft/min while it is drying, 1700 ft of film could be out of specification before an analysis is completed.

The second application needed very precise measurement of three spectrally similar resins, present in a ratio of 89:10:1 in clear pellets. The present analysis procedure for one of the ingredients is a 16-h solvent extraction, which is not only an extremely slow control technique, but can also provide

erroneously low results under some conditions. The second resin is normally measured by mid-IR spectroscopy; this method occasionally encounters problems with crystallinity and requires that a film be pressed and its thickness measured accurately.

Calibration Development

Figure 4 illustrates the near IR spectra of MEK and of the acrylic matrix. Although there are minor differences in the intensities and shapes of many of the absorption bands, it is apparent that the analyte and its matrix have common spectral features: Both have methyl, methylene, and carbonyl groups. At the 0.1% level, measurement of MEK in this matrix appeared to be impossible.
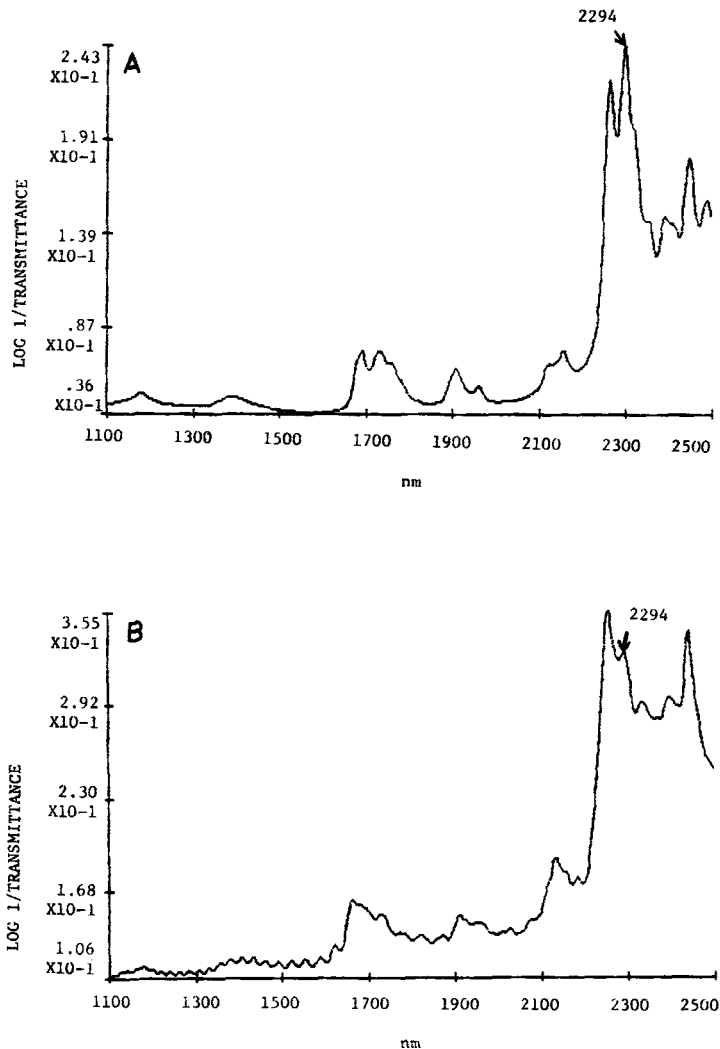

Fig. 4.   Near infrared spectra of methyl ethyl ketone (A) and a sample matrix of acrylic polymers (B).

Nevertheless, a good calibration was developed with chemometric techniques by varying the geometry of the spectra until the best calibration was achieved. The multiple linear regression programs provide statistical data to help the operator chose the best measurement conditions. This approach provides a large number of spectral features and improves the chances of producing a good calibration for any analyte. Figure 5 shows the spectral shape created when a large gap size (40 nm), and second derivative spectra were used for this analysis. A zero crossover point is present at 2294 nm in the spectrum of the matrix, whereas MEK has a sharp peak at the same location. This is an ideal outcome; measurements made under these conditions are very sensitive to low levels of MEK. A second wavelength at 1736 nm apparently helps to correct for sample thickness. The 2294-nm band is probably a $C=0$ stretch/C—H stretch combination, while
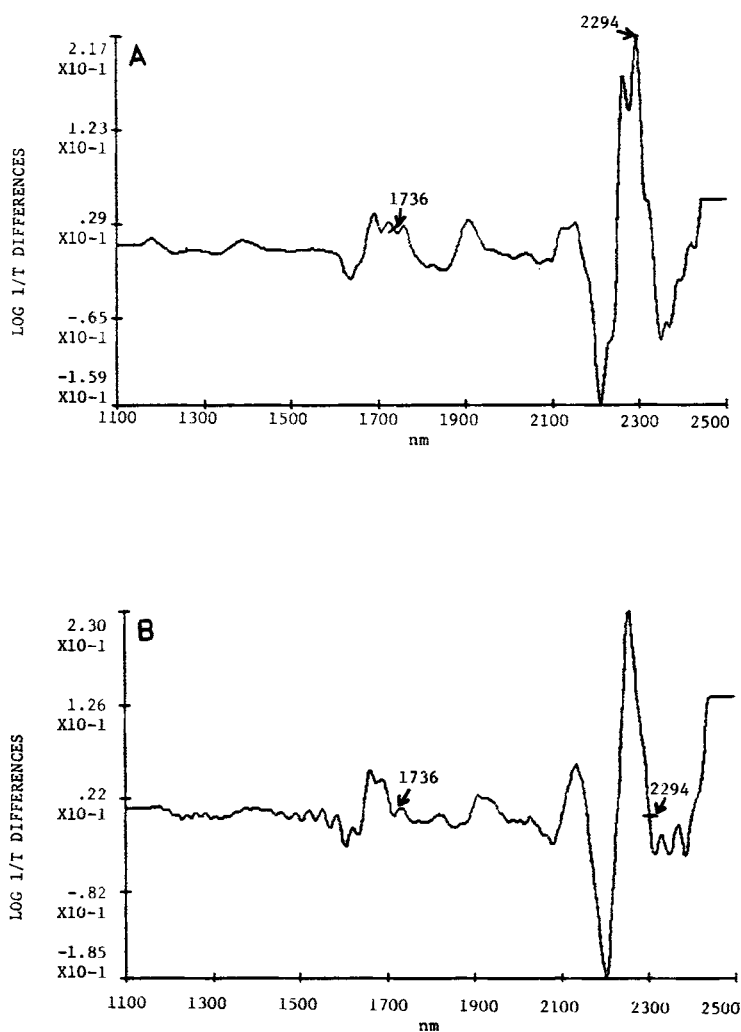

Fig. 5.   40-nm second-derivative spectra of methyl ethyl ketone (A) and the sample matrix of acrylic polymers (B).

the 1736-nm peak is probably a C—H stretch first overtone. It should be noted that all second-derivative spectra are inverted for display purposes by the instrument's software. Normally, a second-derivative "peak" would be in the opposite direction.

The prediction equation for MEK was

$$\% = -13.315 + 233.142\,\frac{d^2\,\log\,1/R_{2294}}{d^2\lambda} + 83.662\,\frac{d^2\,\log\,1/R_{1736}}{d^2\lambda} \qquad (2)$$

Figure 6 illustrates the NIR spectra of the three hydrocarbon polymers included in a 89:10:1 mixture. The spectra of the branched and cyclic resins, in particular, are very similar. Even though the level of cyclic polymer is in the 10% range, spectra of mixtures do not show any features characteristic of that component. Figures 7 and 8, however, indicate that spectral features can be identified for monitoring the cyclic and linear resins. Second derivative spectra were again used for this analysis, except this time the gap size was much smaller than it was in the MEK analysis.

The prediction equation for the cyclic polymer was

$$\% = 5.156 + 920.120\,\frac{d^2\,\log\,1/R_{1414}}{d^2\lambda} - 1725.794\,\frac{d^2\,\log\,1/R_{2020}}{d^2\lambda}$$

$$-1554.198\,\frac{d^2\,\log\,1/R_{2064}}{d^2\lambda} \qquad (3)$$

The prediction equation for the linear resin was

$$\% = 8.062 - 7.542\,\frac{d^2\,\log\,1/R_{2014}}{d^2\lambda}\bigg/\frac{d^2\,\log\,1/R_{2030}}{d^2\lambda}$$

$$+ 0.889\,\frac{d^2\,\log\,1/R_{1920}}{d^2\lambda}\bigg/\frac{d^2\,\log\,1/R_{2176}}{d^2\lambda} \qquad (4)$$

The peaks noted in Figures 7 and 8 are small spectral features and, except for the 1414-nm C—H combination band, cannot be readily assigned to any molecular structural units. It is evident, however, that the primary measuring wavelength of 1414 nm in the cyclic resin spectrum is a specific peak for that resin, and that there is minimal interference from the other constituents at that wavelength. It is less clear why the second two wavelengths were chosen, but, presumably, they help account for interferences.

Figure 9 illustrates how small a spectral difference is employed in this example. The figure shows second derivative spectra representing the highest and lowest levels of the cyclic polymer. The spectra must be expanded 20 times before any difference is discernable at 1414 nm, the measuring wavelength. The expansion also attests to the excellent signal-to-noise characteristics of this type of instrument, and the data in Table I show that the analysis is accurate even at this low signal level.

Figure 9 also illustrates the reason why no measuring wavelengths in the 2200-2500 nm region were chosen by the regressions. The second de-
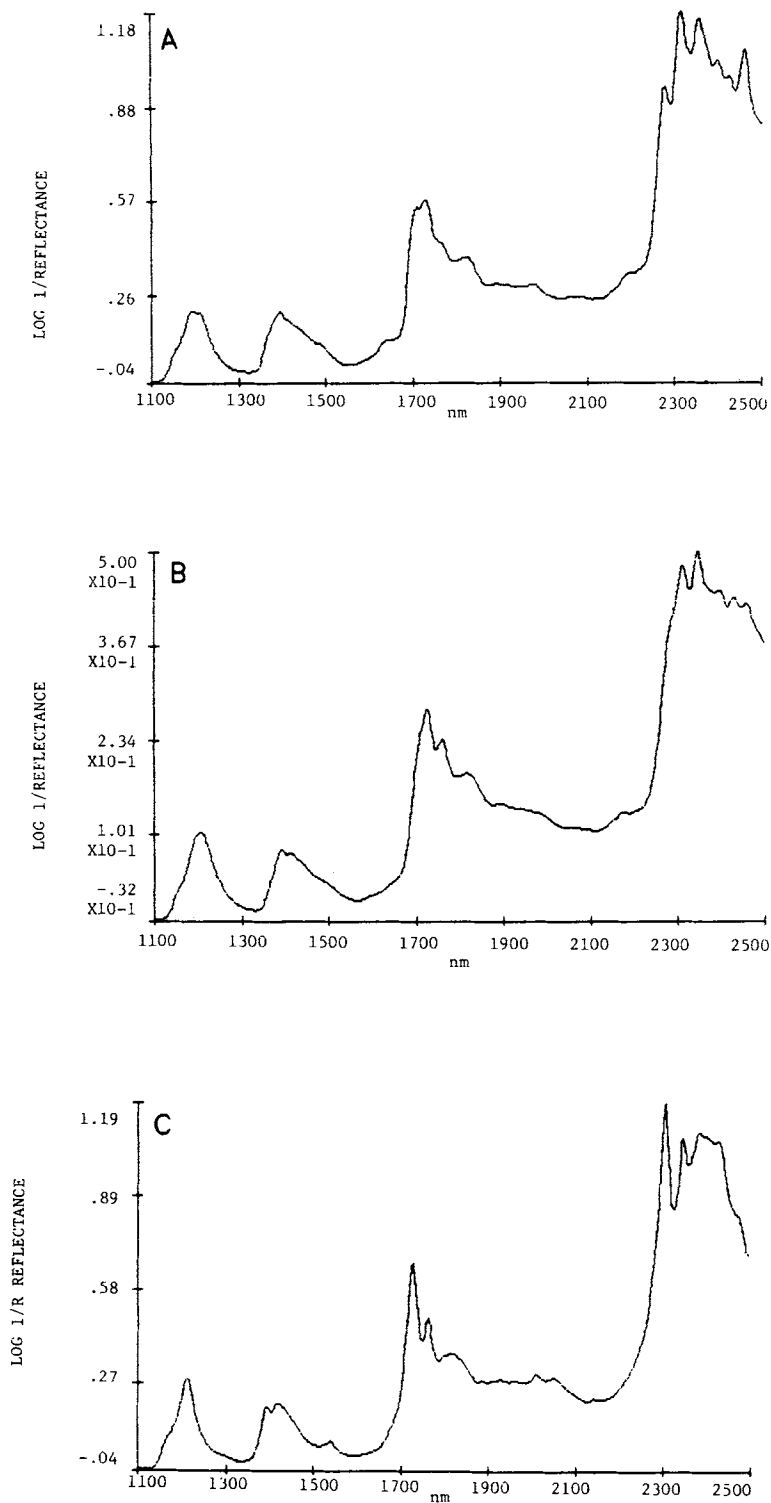
Fig. 6. Near infrared reflectance spectra of a branched polymer (A), a cyclic hydrocarbon polymer (B), and a linear hydrocarbon polymer (C).
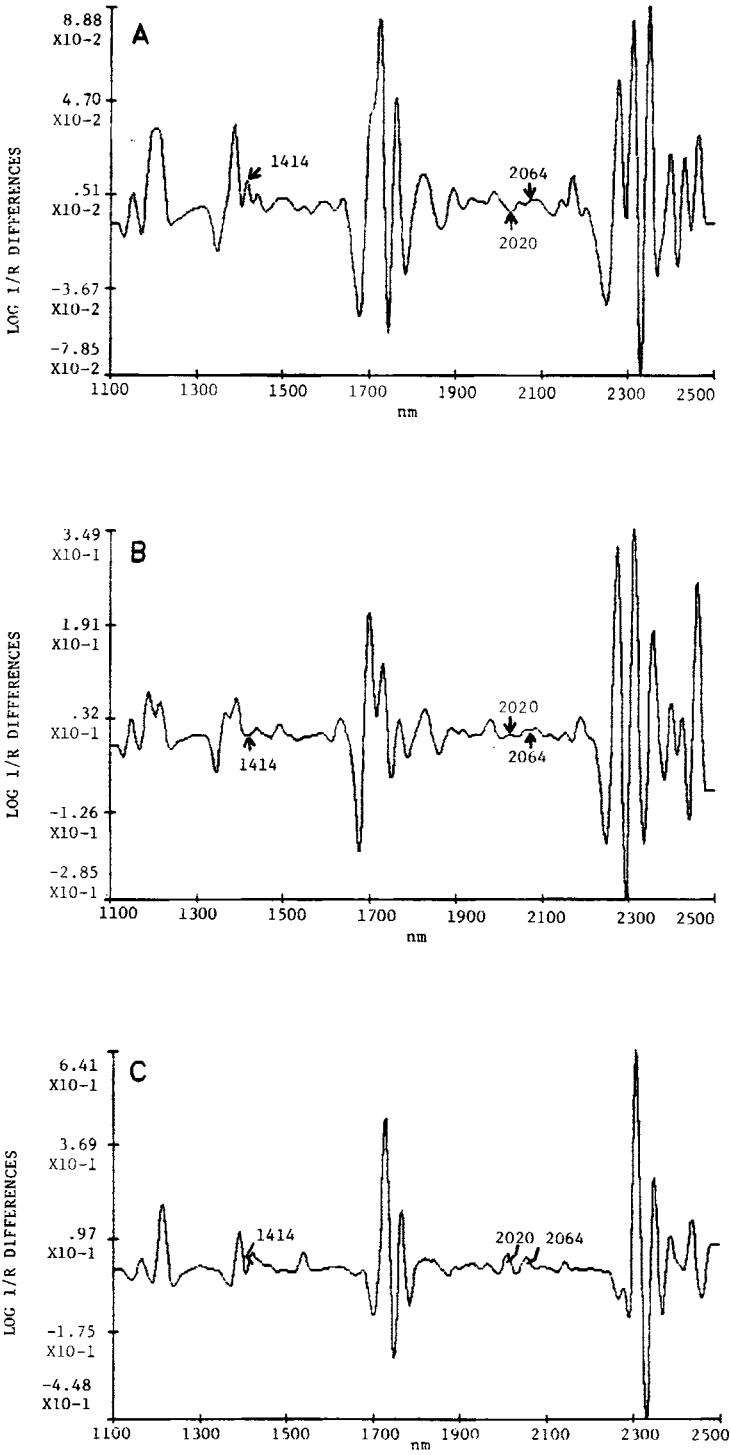
Fig. 7.   Second derivative spectra of a cyclic polymer (A), a branched polymer (B), and a linear polymer (C). Analytical wavelength choices for measurement of the cyclic polymer are indicated.
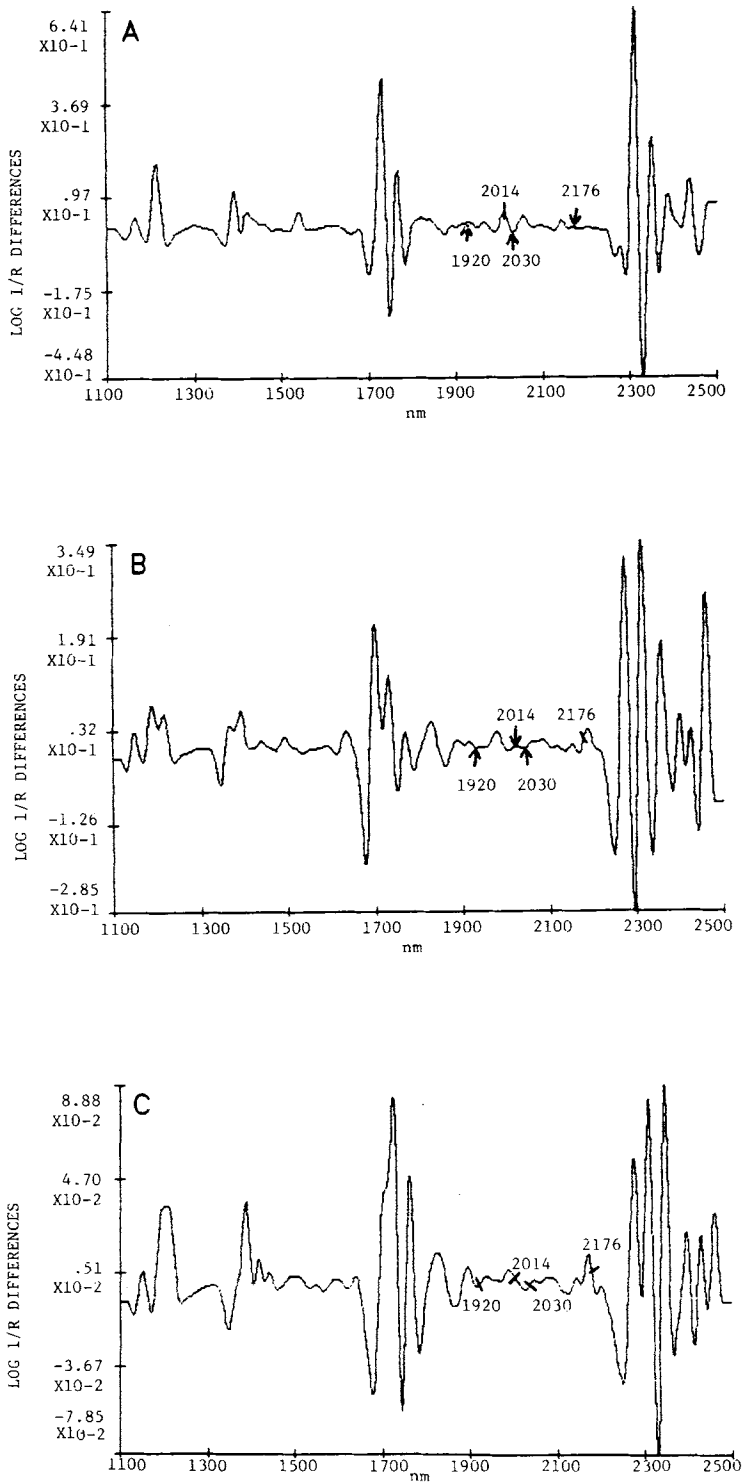
Fig. 8. Second derivative spectra of the linear polymer (A), the branched polymer (B), and the cyclic polymer (C). Analytical wavelength choices for the linear polymer are shown.
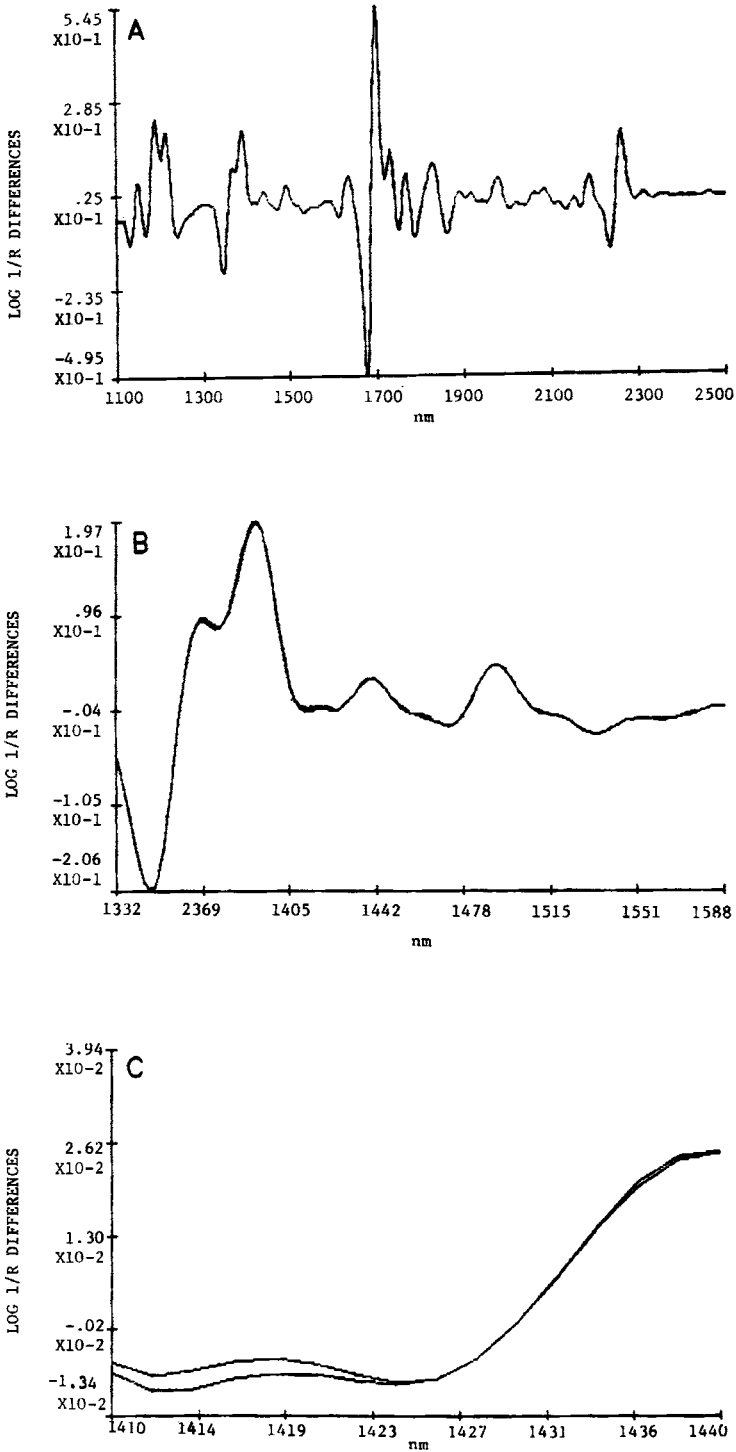
Fig. 9. Illustration of the spectral difference being used for analysis. (A) shows the second derivative spectra of the highest and lowest cyclic polymer levels, (B) and (C) show spectral expansion of about 2.6× and 20×, in the region around the primary measuring wavelength.

TABLE I
Calibration for Hydrocarbon Polymers in Pellets

Sample set	Number of samples	Math treatment	Correlation coefficient	Standard error	Range of polymer (%)
Calibration, cyclic polymer (Model 6250[a])	38	Second derivative, segment 10 nm, gap 4 nm, three terms	0.98	0.30	9–14.5
Prediction, cyclic polymer (Model 6250)	7 (×4)		—	0.24	9–14.5
Calibration, linear polymer (Model 6250)	36	Second derivative, segment 10 nm, gap 4 nm, two divisor terms	0.98	0.06	0–1.50
Prediction, linear polymer (Model 6250)	7 (×4)			0.09	0–1.50
Calibration, cyclic polymer (Model 3000[a])	34	Second derivative, segment 10 nm, gap 4 nm, three terms	0.97	0.38	9–14.5
Prediction, cyclic polymer (Model 3000)	7		—	0.4	9–14.5

[a] Model refers to Pacific Scientific Co. spectrophotometer.

rivative peaks in this region are much smaller than would be predicted based on the second derivative spectra of the pure components (Figs. 7 and 8). This is because the log $1/R$ spectra of the sample pellets have values above 1.5 units (very low reflected energy) and the linear range of the instrument has been exceeded. Readings at these wavelengths are therefore meaningless.

In the second-derivative spectrum of the linear resin, the first two wavelengths chosen (2014 and 2030 nm) were both small, but obvious spectral features. Dividing the contribution of one wavelength by that of the second provided a more sensitive measure of resin content. The second two wavelengths (1920 and 2176 nm) again represent minor corrections for interferences.

It is not always obvious why a given wavelength provides better statistical data than another wavelength, or why small spectral features are chosen over large bands. However, linearity may play a major role. The regressions seek linearity of response over the entire concentration range encountered in the calibration set.

Data Analysis

Table II provides the calibration and prediction data obtained in the MEK analysis. Although the sample sets were small, very good predictions were achieved. The table also shows that predictions outside of the range of the calibration were performed satisfactorily. This indicates that the prediction equation is robust.

Table I lists the calibration results of the resin analyses. Predictions were performed by the cross validation method. Seven samples were withheld from the calibration set, a calibration generated from the remaining samples, and the seven were then entered as a prediction set. This was done four times, and the resulting data were pooled. Additional prediction sets from a second source were also analyzed with similar results. The shape of the pellets in this second source was different from the calibration set, but this did not affect the accuracy of the predictions.

Table I also lists data obtained from a calibration on the Model 3000. In spite of the limited wavelength range available at the time of the experiments, the standard error of calibration and correlation coefficient were only slightly poorer than those from the Model 6250. In addition, the prediction set of pellets gave similar results with both instruments.

Table III includes "accuracy" in its comparison between the referee and the NIRR methods. Accuracy is difficult to measure because it is dependent

TABLE II
NIRR Calibration for MEK in an Acrylic Matrix[a]

Sample set	Number of samples	Correlation coefficient	Standard error	Range of MEK (%)
Calibration	14	0.97	0.12	0.02–1.7
Prediction	14	0.96	0.15	0.1–2.8

[a] Math treatment: second derivative; segment 10 nm; gap 40 nm; wavelengths 2294 and 1736 nm.

TABLE III
Comparison of Methods

Method	Component	Precision (%, absolute)	Accuracy (%, absolute)	Number of replicates
NIRR	Cyclic polymer	0.28	0.24	12
Extraction	Cyclic polymer	0.11	0.58	5
NIRR	Linear polymer	0.05	0.09	5
Mid-IR	Linear polymer	0.08	0.21	4

on the method itself. In this case, the "true" value was taken as that which was weighed into the mixtures before extrusion of pellets. Again, these predictions were done by removal of seven samples at a time from the calibration sets. The same technique was used for the referee method, with the results, shown in Table III, indicating that the NIRR method was slightly more accurate.

The precision of replicate determinations represents one sample cup loading in the case of the NIRR measurement, and one extraction or mid-IR analysis. The precision of individual readings was not as high for the NIRR analysis of the cyclic polymer, partly because a smaller sampling is taken and there may be some nonuniformity in the pellets. However, replicate determinations take only 20 s each in the NIRR analysis and are therefore much more practical to perform.

CONCLUSIONS

Near infrared reflectance techniques can provide rapid, accurate quality assurance methodology for industrial products. The use of derivative techniques, including maximizing the potential of zero crossover points, can be very helpful. The combination of high signal-to-noise spectra with statistical and mathematical data treatments is very powerful. It has been demonstrated that precision and accuracy of NIRR determinations performed in seconds upon untreated materials are at least as good as that of much slower current methods.

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