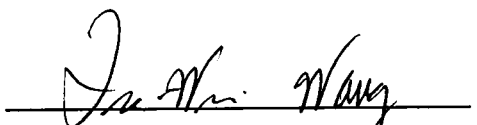
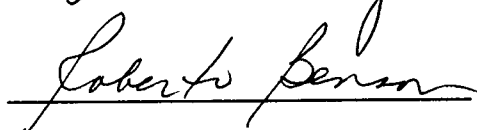
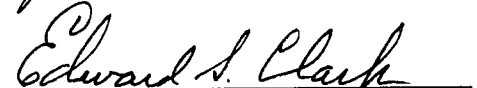


To the Graduate Council:

I am submitting herewith a dissertation written by Atul Khettry entitled "In-Line Monitoring of Molten Polymeric Processes." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.


Marion G. Hansen, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

IN-LINE MONITORING OF MOLTEN POLYMERIC PROCESSES

A Dissertation
Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

Atul Khettry
May, 1995

DEDICATION

This dissertation is dedicated to my parents

Mr. Hari Khettry & Mrs. Rani Khettry

and to my brother

Mr. Alok Khettry

who have inspired me at all times in my life.

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ABSTRACT

The principle of total quality management is the cornerstone of the success of any organization in today's competitive environment. There has been a tangible upheaval in process technology, and in-line process monitoring techniques are being promoted in all quarters, as a consequence. This current surge in interest in in-line process monitoring has had a resounding effect on the polymer industries. Near infrared spectroscopy, coupled with fiberoptics, is rapidly emerging as an in-line monitoring technique for molten polymers, during plastics manufacturing. In-line monitoring is not only desired for its numerous advantages, (such as high quality products, lower waste, lower developmental cycle time, and lower costs), but also because it eliminates the sample handling concerns associated with molten polymeric processes.

A big constraint in the application of this technique has been the unavailability of rugged probes that could withstand the severe conditions encountered in molten polymeric processes, i.e. high temperatures, high pressures, and harsh chemical environment. In this research, a series of rugged probes was designed and evaluated. The probes were tested using a polymeric system of blends of polystyrene and polyphenylene oxide. Finally, a thorough study of a system of poly(ethylene vinyl acetate) (EVA) random copolymers was performed. Rigorous multivariate analysis was used to develop robust calibration models for quantification of vinyl acetate (VA) concentration. The calibration models were also used to demonstrate real-time monitoring of VA concentrations. Also, the

performance of near infrared spectroscopy for quantification of trace level additives in EVA copolymers was studied.

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1. INTRODUCTION

Polymers are an important class of organic compounds with a variety of end products having numerous and widespread applications. This burgeoning field is the subject of constant research targeted towards new innovations and improvements in existing technology.

The properties of polymers can be affected during the course of polymerization (done in solution, suspension, emulsion, or melt) by the inclusion of one or two extra monomers, giving rise to copolymers and terpolymers, respectively. However, the incorporation and modification of most polymer properties is done through compounding, during which the polymer resin can be combined with additives (e.g., colorants, flame retardants, heat or light stabilizers, lubricants, etc.), fillers or reinforcements (such as glass fibers, particulate minerals, etc.), and other polymers (to form polymer blends or alloys). Compounding is done using mechanical mixing or melt state blending. The conversion of polymer compounds into end products involves shaping and is done through processes such as extrusion, injection molding, blow molding, compression molding, and so on. Extrusion is the most common process to convert polymers into resin pellets.

Polymer production and processing thus comprise a series of processes most of which are carried out in the melt state. Therefore, in-line monitoring of molten polymers is highly desirable in order to improve quality and reduce cost. In-line analysis means that the sensor is in direct contact with the main process stream. Thus, in-line analysis obviates the need for handling hot and highly viscous molten polymers and provides for process analysis without perturbing the system. Furthermore, it reduces time for off-line analyses, reduces the development cycle time of products, reduces waste, and results in more uniform quality products. All

these factors have an enormous impact on process economics and consequently the cost of the final product.

The concept of improved product quality and reduced costs has revolutionized on-line process control techniques in the polymer industry and has given sharp impetus to the use of near infrared (NIR) spectroscopy. In the past decade, near infrared spectroscopy (or the "sleeping giant" [1]) has carved a niche in the arsenal of rapid process analysis. Although NIR spectroscopy has sometimes been used as an off-line technique for polymers, the evolution of fiberoptics and the subsequent feasibility of in-line monitoring have made it a big boon for the polymer industry.

Spectroscopy in the mid-infrared (mid-IR) region has been extensively used to perform off-line analyses of polymers. This "fingerprint" region contains fundamental vibrations, and as such their absorptivities are very high. The region is characterized by sharp peaks representative of the fundamental groups present in the polymer. IR spectra of model compounds are available in literature and can be used to correlate the absorption peaks in polymers [2]. IR spectra have been used for structure characterization and polymer identification. The use of mid-infrared spectra for in-line monitoring of polymeric processes, however, poses certain limitations. The absorbances in this region are quite strong, and as such the pathlengths must be typically very small. Because this is not possible in the process stream, attempts have been made to perform polymer analysis on-line by using slip streams. Slip streams for process monitoring of viscous molten polymers are not adequate for closed-loop feedback control owing to the delay between the time the polymer sample leaves the process stream and before it is actually subjected to the optical beam. Remote monitoring using mid-infrared spectroscopy is further constrained by the fact that optical fibers of practical length are not available. This

problem is a consequence of the hydroxyl group absorption in silica fibers. Currently durable fibers longer than 3 ft are not available at reasonable cost.

In light of the problems associated with the use of mid-infrared spectroscopy, a viable alternative is to use the near infrared range of electromagnetic radiation. This region contains overtones and combination bands of the fundamental molecular vibrations. The low absorptivities of the bands prove to be advantageous by allowing much longer pathlengths. This flexibility is the key to the feasibility of this technique for in-line process monitoring. Further, remote sensing and multiplexing are made possible due to the availability of long optical fibers. There is a wealth of information in the near infrared region, but it is quite complex due to considerable band overlap. However, chemometric techniques help to extract useful quantitative information from the spectra. As defined by Workman [3], chemometrics is a term applied to the generic discipline involving computers and mathematics to derive meaningful chemical information from samples of varying complexity.

The application of NIR spectroscopy and fiberoptics to molten polymer analysis is challenged by the rigorous conditions typical of polymeric processes. Robust fiberoptic probes capable of withstanding high temperatures, high pressures, and a hostile chemical environment are the only solution to the above problems.

The basic underlying idea behind this research is to focus on the problems encompassing the feasibility of NIR spectroscopy as an in-line monitoring technique for molten polymers. Designs for fiberoptic probes that can withstand rigorous process conditions shall be developed. Finally, one of the goals of this research would be to utilize NIR spectroscopy, robust fiberoptic probes, and multivariate data analysis for *in situ* monitoring of different types of polymeric systems.

2. BACKGROUND

2.1 Theory

The molecules of a substance may undergo energy changes when acted upon by an external source of energy. The energy vibrations give rise to the electromagnetic spectrum, which comprises vibrations ranging from cosmic rays (wavelengths of the order of 10^{-5} nm) to radio waves (wavelengths of the order of 10^{16} nm). The infrared region is the part of the electromagnetic spectrum that extends from the visible region to 25000 nm. The IR region is subdivided into three regions: the near infrared region (NIR), the mid-infrared region (mid-IR), and the far infrared region. The NIR region ranges from 750 nm to 2500 nm, while the mid-infrared region ranges from 2500 nm to 15000 nm, and the far infrared region stretches from 15000 nm to 25000 nm. The absorption bands in the mid-infrared and far infrared regions contain the fundamental absorption bands. These bands arise from the excitation of a molecule from the ground state to the next higher energy level. The NIR region contains the overtones and combinations of the overtones and fundamental bands which arise due to energy transitions between the ground state and the second or third higher energy levels. The overtones are lower in intensity than the fundamental bands because fewer molecules undergo such transitions [4]. Although all fundamental bands can exhibit overtones, the overtones of O-H, N-H, and C-H groups are the most prominent. The combination bands are a result of the addition of stretching bands of C-H, N-H, and O-H groups with one or more bending or rocking vibrations [5].

The origin of the near infrared region is based on quantum mechanics and a phenomenon called anharmonicity. The vibration of covalent bonds in a molecule

can be approximated by an ideal harmonic oscillator that obeys Hooke's law. The vibration can be represented by the equation :

$$E_v = h\nu_{osc}(v + 1/2) \dots\dots\dots (2.1)$$

where

E_v = energy of vibration

h = Planck's constant

v = vibrational quantum number

ν_{osc} = frequency of vibration of the oscillator

For a strict harmonic oscillator, the energy change for a jump between two adjacent levels is equal to $h\nu_{osc}$. Quantum mechanical selection rules do not allow jumps between non-adjacent energy levels [4]. Thus, a strict harmonic oscillator would only have fundamental absorption bands in its spectrum. However, molecular vibrations have a certain degree of anharmonicity, which causes their energy levels to be unequally spaced. Transitions between non-adjacent energy levels and interaction between vibrations are possible.

For an anharmonic oscillator:

$$E_v = h\nu_{osc}(v + 1/2) - h\nu_{osc}x_e(v + 1/2)^2 + h\nu_{osc}y_e(v + 1/2)^3 + \dots\dots\dots (2.2)$$

where

x_e and y_e are anharmonicity constants, HOT implies higher order terms

Using the first two terms in the above equation, the energy difference between levels v and $v-1$ is $h\nu(1-2vx_e)$. The transitions between the ground state ($v=0$) and the first, second, or higher order excited state ($v=1, 2, 3, \dots$) give rise to first, second, or higher overtones, respectively. The overtones occur at a frequency slightly less than the appropriate multiple of the fundamental frequency. The observed frequency of the j th harmonic [6] is related to the frequency of the fundamental (ν_0) as:

$$\nu_j = j\nu_0(1-jx) \quad \dots\dots\dots (2.3)$$

where x = anharmonicity.

Figure 2.1 compares the energy diagram for an ideal diatomic harmonic oscillator to that of an actual diatomic anharmonic oscillator [3]. The value of anharmonicity usually lies between 1% and 5% of the wavelength. Thus the first overtone of a fundamental vibration occurring at 3500 nm will occur at 3500/2 plus a small shift to a higher wavelength depending on the value of the anharmonicity.

The natural frequency of vibration of two atoms joined together by a bond is given by

$$\nu = \sqrt{\frac{k}{\mu}} \cdot \frac{1}{2\pi} \quad \dots\dots\dots (2.4)$$

where :

k = force constant and μ is the reduced mass of the two vibrating masses

$\mu = m_1 m_2 / (m_1 + m_2)$, where m_1 and m_2 are the masses of the atoms

Thus it can be seen that ν is inversely proportional to the square root of the reduced mass. That is, the lower the value of reduced mass, the higher the frequency of vibration (i.e. lower wavelength). Hydrogen is the lightest atom, and is therefore important in NIR spectroscopy. The low mass of the hydrogen atom results in resonant molecular vibrations at high frequency, and the anharmonicity of these vibrations leads to overtones and combination bands in the NIR region. The fundamental vibrations of bound hydrogen atoms mostly lie in the 2700-3600 nm region. The overtones lie mainly in 400-2200 nm region, while the combination bands lie in the 1800-2500 nm region.

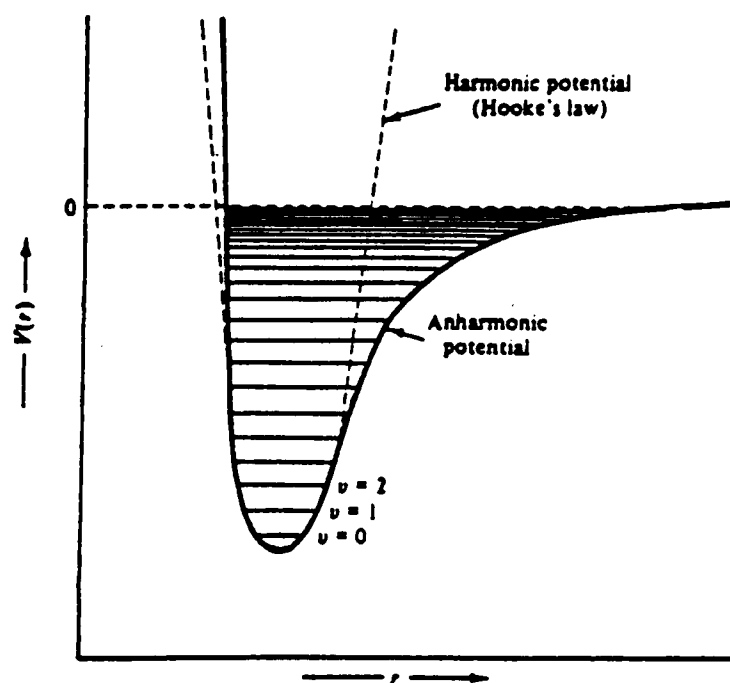


Figure 2.1 Comparison of harmonic oscillator with anharmonic oscillator [3].

2.2 Sampling Techniques

The samples (for NIR study) can be analyzed in two modes: (i) transmittance; and (ii) diffuse reflectance.

Transmittance:

This mode is used for solutions or melts that are optically translucent. The transmittance is calculated from the intensity of light passing with (I) and without the sample (I_0) in the path of the NIR beam.

$$T = (I/I_0) \times 100\% \quad \dots\dots\dots (2.5)$$

The transmittance, T , is related to the absorbance by the following equation:

$$A = \log_{10}(I_0/I) = \log_{10}(1/T) \quad \dots\dots\dots (2.6)$$

Percent transmittance is useful for physical measurements, such as characterization of the light absorption of optical filters, while absorbance is mostly used for chemical analysis. The absorbance at a specific wavelength is directly related to the concentration by the Beer-Lambert law [3]:

$$A = a l c \quad \dots\dots\dots (2.7)$$

where

a = absorptivity at a particular wavelength

l = pathlength of the sample

c = concentration of the absorber

If there are no interactions among the absorbing molecules, the absorbance at a particular wavelength is sufficient to correlate it to the concentration. In the transmittance mode, the sample solution is filled in a cuvette and the transmittance is recorded. Another way of collecting the spectrum is to mount fiberoptic probes across a cross union [7] as shown in Fig. 2.2.

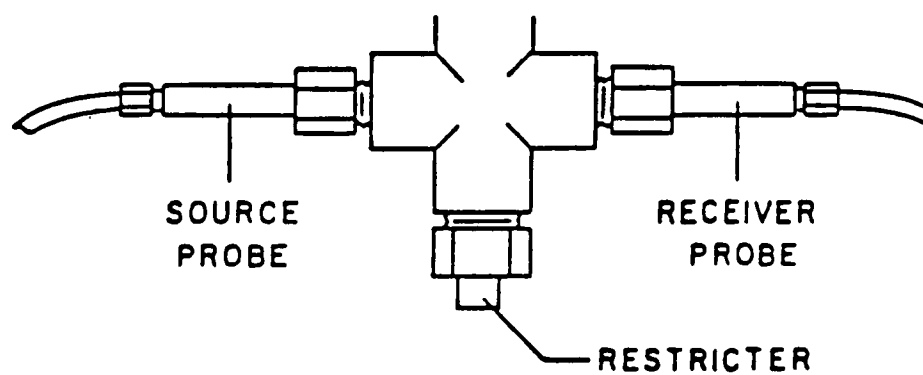


Figure 2.2 Configuration of probes for recording transmission spectra [7].

Diffuse Reflectance:

The diffuse reflectance method is used mainly for solid samples that either absorb or scatter the incident light. A variety of techniques are used to measure diffuse reflectance. The sample is packed well in a sample container and illuminated with light. A part of the incident light, which is reflected, is measured using detectors mounted on a 45° cone or an integrating sphere. Both specular and diffuse reflectance are superimposed. Incident light interacts with particles, which lie at all possible orientations. Reflectance, refraction, transmittance, and absorbance take place depending on the physical and chemical properties of the sample pack. Due to variations in scattering and the depths to which the incident light penetrates the sample, the pathlength does not remain constant. The sample should be packed well so that no light reaches the back of the container. The features of the sample that affect the effective pathlength are particle size, shape, crystalline form, bulk density, etc. [6]

A design described by Norris *et al* (Fig 2.3) [8] is extensively used in near infrared reflectance instruments. This design uses a large solid angle detector geometry. The detectors are placed quite close to the illuminated area in order to collect a large solid angle of the diffusely scattered radiation.

Just like the transmittance, the reflectance is also related to the absorbance,

$$A = \log_{10}(R_0/R) = a l c \quad \dots\dots\dots (2.8)$$

where

R_0 = reflectance from a background made of diffusely scattering material
(e.g. diffuse ceramic, stainless steel and diffuse gold-coated reflectors)

R = reflectance from the sample

l = pathlength

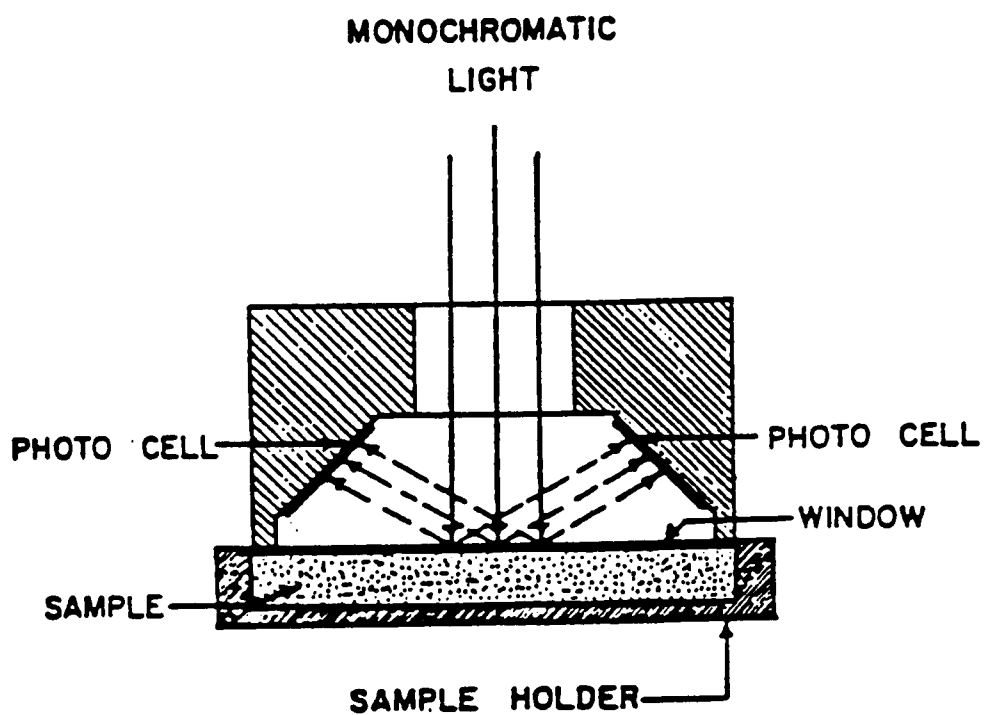


Figure 2.3 Norris's geometry for recording diffuse reflectance spectra [6].

2.3 Spectral Analysis

2.3.1 Band Assignments

For qualitative analysis, the utility of the near infrared region is very limited as compared to the mid-infrared region. The band assignments in the mid-infrared region are accurate because this region contains the fundamental absorptions. Band assignments in the near infrared region are always termed as tentative. Murray and Williams [6] had attributed this tentativeness to the following factors: (i) the anharmonicity of vibrations, (ii) sample-instrument interactions, (iii) variations due to differences in instruments, (iv) interactions among different constituents in a sample, (v) temperature variations, and (vi) molecular association and the formation of dimers, hydration, crystalline states and other forms of hydrogen bonding.

As explained in the previous chapter, the vibrations involving hydrogen atoms tend to have their first overtones in the near infrared region. The most prominent of these vibrations are those involving C-H, O-H, and N-H groups. Most of the work in the near infrared region is restricted to compounds containing these groups. Thus, the near infrared region proves to be quite conducive for the study of organic compounds, polymers, and so on.

(1) C-H vibrations [4]:

The C-H group has fundamental stretching bands in the range 3000 to 3600 nm. The first overtone stretching bands lie between 1600 and 1800 nm; the second overtone stretching bands are located in the region 1100 to 1200 nm; and the combination bands lie between 2000 and 2400 nm.

The C-H stretch is important in the study of (i) aliphatic hydrocarbons [5], (ii) aromatic hydrocarbons, (iii) olefins, and (iv) oxygenated compounds such as epoxides, aldehydes, and formates .

(2) N-H vibrations:

The N-H vibrations have their fundamental stretching bands in the 2800-3000 nm range. The first overtone of this vibration occurs at about 1500 nm, and the second overtone occurs at about 1000 nm. The N-H absorptions are particularly important in studying amines and amides [9].

Amines

Primary amines have first overtone bands at about 1500 nm. They have a very unique combination band at 2000 nm, which is due to N-H stretch and NH_2 bending. Secondary amines have first overtone bands only, while tertiary amines have no discernible bands in the near infrared region [5].

Amides

Primary and secondary amides have absorption bands very similar to those of amines. However, their spectra may have additional bands due to existence of cis and trans isomers. They also have combination bands of N-H with either C=O or C-N stretch or bending. The first overtones occur at about 1500 nm, and the combination bands at about 2000 nm.

(3) O-H vibrations:

The fundamental stretching band of the O-H group occurs at about 2800 nm. The first and second overtone bands occur at 1400 nm and 1000 nm respectively. In addition, the O-H group has a combination band at about 2000 nm. These absorption bands are useful in the study of water, alcohols, phenols, and other O-H

containing compounds. The NIR spectrum of water is very important and is used to determine the moisture content of many substances. Water has a unique combination band at about 1940 nm. Other important features in the spectrum of water are the first overtone of O-H stretch at 1440 nm, weak combination bands near 1200 nm, and O-H stretch second overtone at 960 nm.

Apart from the three vibrations described above, some other vibrations have weak features in the NIR region. Goddu [9] reported such bands for (i) thiols and P-H groups, (ii) carbonyls, and (iii) nitriles. Thiols have the first overtone of the S-H stretching band (3900 nm) around 1970-1980 nm. The first overtone of the P-H stretching vibration occurs at about 1890 nm. The first overtone of the C=O stretching vibration occurs at around 2800-3000 nm, and there is a weak second overtone at around 1900-2000 nm. Nitriles have weak bands in the 1800-2100 nm region that are probably overtones of combination bands involving $C\equiv N$ group.

Based on literature and his own laboratory data, Goddu [9] tabulated the main spectra-structure correlations in the near infrared region along with molar absorptivity data. This table (Table 2.1) is quite useful in making tentative band assignments in the NIR region.

2.3.2 Quantitative Techniques

2.3.2.1 Overview

As compared to mid-infrared, the quantitative analysis of NIR spectra is a formidable task. Mid-infrared spectra contain fundamental bands, and they are full of sharp and narrow peaks which can be easily modeled using univariate or multiple linear regression. On the other hand, NIR spectra are very complex and contain broad bands and considerable band overlap. The emergence of multivariate techniques of partial least squares (PLS) [10,11] and principal component regression

Table 2.1 Goddu's [9] table of spectra-structure correlations.

		Microns																					
		1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1
Terminal -CH_2	Vinyloxy(-OCH=CH_2)																						
	Other																						
Terminal -CH-CH_2																							
Terminal -CH-CH_2																							
Terminal -CH																							
cis- -CH=CH-																							
$\text{C(CH}_2\text{)}_2\text{O (acetone)}$																							
-CH_3																							
>CH_2																							
>C-H																							
-CH aromatic																							
-CH aldehydic																							
-CH (formate)																							
-NH_2 amine	Aromatic																						
	Aliphatic																						
>NH amine	Aromatic																						
	Aliphatic																						

Table 2.1 (continued)

Goddu's [9] table of spectra-structure correlations.

	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1
-NH ₂ amide					0.7	0.7				0.5	0.5								100		100	
>NH amide					0.5	0.5				0.4	0.4									50-100		
>NH imide	1					1																
-NH ₂ hydrazine	1					0.5	0.5															
-OH alcohol					2	2				(1)									50			
-OH hydroperoxide					1	1													30	30		
-OH phenol					2	2													80			
-OH carboxylic acid					3	3													200			
-OH glycol					1	1																
-OH water					0.7	0.7				1.2									30	7		
-OH oxime					1	1													100			
HCHO (possibly hydrate)																						
-SH																						
>PH										0.2												
>C=O																						
-C≡N										0.1												

^a Compiled from data from our laboratory and published data, which were mostly obtained in carbon tetrachloride solution.

(PCR) [10] has alleviated this problem, and these techniques have proved to be indispensable in the success of NIR as a feasible process monitoring technique. These techniques are based on data compression into a few factors that describe the main variations in the data. The difference between PLS and PCR lies in the way the data space is compressed. In PCR, it is assumed that the property being calibrated (Y) is directly related to the absorbance spectra (X), and thus only the X matrix is used for data compression. In PLS, no such *a priori* assumption is made, and as such both the X and Y matrices are used for data compression. The inclusion of the Y matrix in the calibration makes PLS more accurate than PCR, especially if there are some unknown spectral interferences or if the property being calibrated is a physical property and not directly related to the absorbance spectra [12].

The literature is replete with articles on chemometrics and its applications in process analysis [11,13-21]. The multivariate methods have been used for purposes such as dimensionality reduction, process monitoring, outlier detection, and dynamic modeling and control.

Other than PCR and PLS, two other regression techniques, called classical least squares (CLS) and inverse least squares (ILS) are also used for spectroscopic data. Both CLS and ILS are based on multiple linear regression analysis which uses the principle of least squares. This principle is based on the minimization of the average of the squared residuals. Residuals here implies the difference between the actual and predicted values of any variable that is being estimated.

Classical Least Squares (CLS):

This method [22], also called the K-matrix method, is based on the direct application of Beer-Lambert relation. For multicomponent analysis, the absorbance at each wavelength can be expressed as

$$A_i = \sum_{j=1}^l a_{ij} b c_j \quad \dots\dots\dots (2.9)$$

where

l = total no. of constituents in the mixture

A_i = absorbance of a sample at wavelength i

a_{ij} = absorptivity of constituent j at wavelength i

b = pathlength

c_j = concentration of the j th constituent

Replacing the product $a_{ij}b$ by k_{ij} and introducing a residual or spectral error (e_i) that is not fit by the model eq. (2.9) becomes

$$A_i = \sum_{j=1}^l k_{ij} c_j + e_i \quad \dots\dots\dots (2.10)$$

In matrix notation, the above equation can be expressed as

$$A = KC + E \quad \dots\dots\dots (2.11)$$

where

$A = n \times m$ matrix of the calibration spectra (m samples and n wavelengths)

$K = n \times l$ matrix of the k_{ij} terms

$C = l \times m$ matrix of constituent concentrations

$E = n \times m$ matrix of residuals

In fact, each column of K corresponds to the pure spectrum of that constituent at unit concentration and unit pathlength. A simple least-squares estimate of K is

$$\tilde{K} = AC'(CC')^{-1} \quad \dots\dots\dots (2.12)$$

In the above equation, the matrix CC' must be invertible, i.e. the rows of C should be linearly independent. The matrix $\tilde{K}$ can be used to predict the concentrations of all constituents in an unknown sample using the following equation

$$\tilde{C} = (\tilde{K}\tilde{K}')^{-1}\tilde{K}'A^u \quad \dots\dots\dots (2.13)$$

where

A^u = absorbance vector of the unknown sample ($n \times 1$)

The identifier $\sim$ represents estimated or predicted value of the corresponding quantity. The advantage of this method is that it provides the estimated spectra of the pure constituents. However, the method requires that all interfering constituents in the samples be included in the calibration. Moreover, the rows of the concentration matrix should be linearly independent so that the matrix CC' is non-singular and fully invertible.

Inverse Least Squares (ILS):

This method, also referred to as multiple linear regression (MLR) or the P-matrix method, is based on the inverse Beer-Lambert Law model. This model assumes concentration to be a dependent variable and to be proportional to absorbance. Here, the calibration model can be expressed as

$$C = PA + E \quad \dots\dots\dots (2.14)$$

where

$C = l \times m$ matrix of constituent concentrations

$P = l \times n$ matrix - proportionality matrix between C and A

$A = n \times m$ matrix of the calibration spectra (m samples and n wavelengths)

$E = l \times m$ matrix of residuals

The least squares estimate of P is

$$\tilde{P} = CA'(AA')^{-1} \quad \dots\dots\dots (2.15)$$

The estimates of the concentrations of the unknown samples is given as

$$\tilde{C} = \tilde{P}A^u \quad \dots\dots\dots (2.16)$$

where

A^u = absorbance vector of the unknown sample ($n \times 1$)

An advantage of this method is that it is a direct regression technique and requires only one matrix inversion. A major disadvantage of the method is that only a small number of wavelengths can be selected, to ensure that the rows of A are linearly independent. Moreover, collinearity problems can also lead to overfitting of data. This technique (MLR) is called linear regression (LR) or univariate regression when the absorbance at only one wavelength is considered.

Principal Component Regression (PCR):

This method explains the variance in the X data set (X is $m \times n$ absorbance data matrix for m samples and n wavelengths) through a lower number of variables (principal components or scores vectors - T matrix), by eliminating the redundancy in the spectral data at multiple wavelengths. The main task here is to determine the principal directions that describe the variability in the X data set. These principal directions, which are also called the principal loadings or the loadings vectors, are essentially the eigenvectors of the covariance matrix $X'X$. The eigenvalues represent the relative contribution of the corresponding eigenvector in explaining the overall variance of the data set. The scores vectors represent the projection of each object (spectral observation) onto the loading vectors. Qualitatively, the scores vectors represent the relationship among the various samples and the loadings vectors represent the relationship among the various variables. If X is a $m \times n$ matrix, then the first loadings vector $\hat{p}_1$ (which is the eigenvector of $X'X$ corresponding to the maximum eigenvalue of $X'X$) is related to the first scores vector $\hat{t}_1$ (the eigenvector of XX' corresponding to the maximum eigenvalue of XX') as

$$\hat{t}_1 = X\hat{p}_1 \quad \dots\dots\dots (2.17)$$

Here, $\hat{p}_1$ accounts for the greatest amount of variability in the data set and is called the first principal component. If only h of the n ($h < n$) eigenvectors are used, then X can be written as

$$X = TP' + E \quad \dots\dots\dots (2.18)$$

where

T is called the scores matrix (of size $m \times h$) and contains the scores for each sample.

P is called the loadings matrix (of size $n \times h$), and its columns correspond to the loadings vectors.

E is the matrix (of size $m \times n$) of residuals.

The basic underlying idea is to extract the optimal number of factors such that E contains only the random noise in the data. If only the process data is analyzed as described above, the method is called Principal Component Analysis (PCA). When there is some property data available, the regression of the property data to the process data is known as principal component regression.

The equations for PCR are:

$$Y = TQ' + F \quad \dots\dots\dots (2.19)$$

Since $T = XP$, Y becomes:

$$Y = XPQ' + F \quad \dots\dots\dots (2.20)$$

$$\text{or} \quad Y = XB + F \quad \dots\dots\dots (2.21)$$

where

Y is the property matrix (of size $m \times z$) where each of the z columns correspond to a different property.

Q is called the Y loadings matrix (of size $z \times h$), and its columns correspond to the loadings vectors.

F is the matrix (size $m \times z$) of unmodeled residuals of Y .

B is the regression coefficient matrix (of size $m \times z$), in which each column contains the regression vector for the corresponding Y column (Y variable). A distinct feature of PCR is that the scores and the loadings vectors of both X and Y matrices are mutually orthogonal. Therefore, the scores matrix (T) and loadings matrices (P & Q) have orthogonal columns.

Partial Least Squares (PLS):

This method is similar to PCR, except that the latent variables which describe the coordinated variation in both the X and Y data sets are determined. The first algorithm for PLS was described by Wold [11]. In his algorithm, called the nonlinear iterative partial least squares algorithm (NIPALS) for eigenvector estimation, the X and Y matrices are to be decomposed into the following equations:

$$X = TP' + E \quad \dots\dots\dots (2.22)$$

$$Y = UQ' + F \quad \dots\dots\dots (2.23)$$

where

T & U (size $m \times h$) are the scores matrices of X and Y, respectively.

P & Q are loadings matrices of X and Y, respectively.

The sizes of X, Y, T, P, Q, E, and F matrices are the same as in PCR. In the above method, only the scores vectors of the X matrix are mutually orthogonal. Thus, the T matrix has orthogonal columns.

The computation of the scores and loadings matrices is based on the NIPALS algorithm. The first set of loadings vectors are derived using cross regression between X and Y. The first scores vectors, $\hat{t}_1$ and $\hat{u}_1$, are generated by projecting the X and Y data on to their respective loadings vectors. The scores vectors are used to relate the X and Y matrices: $\hat{t}_1 = \hat{u}_1 b_1$. The contribution of the first component is subtracted from the X and Y matrices: (i) $X = X - \hat{t}_1 \hat{p}_1'$; and (ii) $Y = Y - \hat{u}_1 \hat{q}_1'$. The

process is continued on the new X and Y matrices until the optimal number of factors is determined.

Martens [10] developed an alternative PLS algorithm ($X = TP' + E$; $Y = TQ' + F$) that requires fewer parameters than Wold's algorithm. In the alternative algorithm the scores vectors are not orthogonal, and therefore the loadings vectors for the Y matrix cannot be determined independently. Both the algorithms provide identical prediction formulas. Recently algorithms such as SIMPLS [23] and SVDPLS [24], have shown that PLS based on non-iterative approaches of eigenvector estimation is numerically faster than the classical iterative algorithms.

2.3.2.2 Data Analysis Techniques (to be used in this research):

In developing the calibration models for our experimental data, the method of PLS using singular value decomposition (SVD) [25] is being used. This method is preferred because it works faster than the traditional PLS approach and is computationally more stable. The method comprises the use of SVD to extract the principal component that accounts for the largest variation of the covariance matrix $X'Y$. This extraction is equivalent to finding the first singular vector and singular value of $X'Y$. Then a new residual is formed after subtracting the contribution to $X'Y$ made by the first principal component. This residual is used to extract the second principal component. The process can be continued until the optimal number of factors has been extracted. The routine for this approach has been created in the MATLAB [26] environment where it, along with other routines from a chemometrics toolbox [27], provides a framework for chemometrics and covers the whole gamut of chemometric techniques. These routines provide the flexibility to employ a variety of chemometric techniques in our models, to tailor them to suit our needs, and to gain a thorough insight into the implications of multivariate analysis.

A variety of modeling techniques shall be used with the aim of developing robust calibration models: (i) that could identify the inherent factors of variation; and (ii) that work equally well on the calibration and prediction sets, and give low standard-errors-of-prediction (SEP). The statistical terms used in the validation of models are defined below [12].

1) PRESS (Predicted Residual Sum of Squares)

$$\text{PRESS} = \sum_{i=1}^N (y_i - \hat{y}_i)^2 \quad \dots\dots\dots (2.24)$$

where y_i is the actual value of concentration of sample i in the prediction set during cross validation, $\hat{y}_i$ is its predicted value, and N is the total number of samples in the prediction set.

2) SEC (Standard Error of Calibration)

$$\text{SEC} = \sqrt{\frac{\sum_{i=1}^{\text{NC}} (\hat{y}_{i,c} - y_{i,c})^2}{(\text{NC} - 1)}} \quad \dots\dots\dots (2.25)$$

where $y_{i,c}$ is the actual concentration of sample i in the calibration set, $\hat{y}_{i,c}$ is the predicted concentration of sample i , and NC is the number of samples in the calibration set .

3) SEP (Standard Error of Prediction)

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^{\text{NP}} (\hat{y}_{i,p} - y_{i,p})^2}{(\text{NP})}} \quad \dots\dots\dots (2.26)$$

where $y_{i,p}$ is the actual concentration of sample i in the test set used for validation, $\hat{y}_{i,p}$ is the predicted concentration of sample i , and NP is the number of samples in the test set.

2.4 Applications of NIR spectroscopy

2.4.1 Polymers

The history of polymer analysis using NIR spectroscopy dates back to the early '50s. Most of the work done during the period of 1950-80 involved qualitative analyses of polymeric materials and agricultural products, and their band assignments. NIR work in recent years has laid more emphasis on rigorous quantitative analyses.

In 1951 Glatt and Ellis [28] attempted to examine the orientation of different types of polymer samples. They used polarized radiation to study the pleochroism of aligned specimens of polyethene, nylon, polyvinyl alcohol, polyvinyl chloride, and polyvinylidene chloride. The absorption bands in the polymers were assigned to various vibration modes of $=CH_2$, N-H, and C=O groups. No follow-up work in this field has been done.

Miller and Willis (1956) [29] were the first researchers to exploit the utility of the NIR region for quantitative analysis of synthetic polymers. Their study included determination of molecular weight of polymers by end group analysis, determination of residual monomers in polymers, and analysis of copolymers. They pointed out that the molecular weight could be determined for polymers whose end groups have characteristic absorption bands. Molecular weights of polyethers (such as pol(ethylene oxide) and polyoxycyclobutane) were determined using the hydroxyl end group, which has a combination band at 2100 nm. Solutions of triethylene glycol in chlorinated triethylene glycol were used to develop a calibration curve relating

the hydroxyl content to the intensity of the combination band. This calibration curve was then used to determine the concentration of the end groups in the polymer and the molecular weights. The authors discovered that determination of residual monomers could be made in polymers where polymerizations proceed by the elimination of an unsaturated group $=CH_2$. This determination was possible because the overtone of the unsaturated methylene group is at a lower wavelength than the overtones of either the methyl or saturated methylene group. This criterion was used to determine levels of residual methyl methacrylate during the course of its polymerization to polymethyl methacrylate (PMMA), by using absorption bands near 1700 nm. The absorbance at 1650 nm was used to determine residual monomer concentrations up to 2.5 % w/w of monomer in PMMA. Concentration ratio of butadiene to styrene in butadiene/styrene copolymers was determined using absorbance ratios of aliphatic C-H absorbance in polybutadiene (about 2200 nm) to aromatic C-H absorbance in polystyrene (2400 nm). The authors recommended that the absorption bands used in copolymer analyses should be carefully selected because a monomer unit in the chain could be joined either to a similar monomer unit or a comonomer unit. Thus, only the absorption bands of molecular groupings that are not very sensitive to the environment should be chosen.

Miller and Willis *et al* (1959) [30] illustrated the use of difference spectroscopy in the near infrared region to detect presence of impurities. They pointed out that difference spectroscopy is particularly advantageous in analyzing components whose absorption bands are not very strong, have little variation, and are thus not readily distinguishable. Their study revealed that the difference spectrum of an impure sample and that of a pure sample had characteristics of the minor components and could be used for quantitative applications. The authors pointed out that difference spectroscopy is simpler in the NIR region as compared to

the mid-infrared region, because absorbances in the mid-infrared region are more sensitive to sample thickness and therefore very slight differences in the thickness of pure and impure samples lead to positive and negative peaks in the difference spectrum. This technique of difference spectroscopy was used for determination of residual monomer content in polymethyl methacrylate, as described earlier [29]. In the difference spectrum, the absorption band at 1700 nm due to the saturated C-H group disappeared, making the absorption band of the unsaturated =CH₂ group very clear. It was suggested that the technique would be useful in studying ester copolymers of methyl methacrylates, where the spectra of copolymer and homopolymer are very similar.

Foster *et al* (1961) [31] described the utility of the near infrared region in the determination of chemical groups in polymeric materials. Heat pressed films of polyethylene, polypropylene, polyisobutylene, nylon 66, polystyrene, polyvinyl acetate, polyvinyl chloride and a polyvinylidene-polyvinyl chloride copolymer were examined. Polyisobutylene was studied in carbon tetrachloride solution. Band assignments for the overtones and combination bands of the structural groups were made by using spectra of aliphatic and aromatic organic compounds. Other methods for band assignments were: (i) comparing spectra of polymers to that available in literature; (ii) making approximate calculations of the position of overtones and combination bands on the basis of the fundamental frequencies. These band assignments were useful in qualitative analysis of polymeric materials. For example, it was suggested that the hydroperoxide peak present in spectra of polypropylene, polystyrene and polyvinylidene chloride-polyvinyl chloride copolymer could be used to measure relative degradation. The hydroxyl (OH) peak was found to be particularly important because it indicated the moisture absorbed by the

polymer samples. It was mentioned that NIR spectroscopy could also be used to study reaction kinetics of some polymeric systems.

Le Fevre *et al* (1966) [32] demonstrated a very simple way to estimate molecular weights of polyethylene glycols dissolved in benzene. The spectra contained a strong absorption peak at 7140 cm^{-1} (about 1400 nm), which was assigned to intramolecular hydrogen bonding. Broad weak bands in the range $6400\text{--}6800\text{ cm}^{-1}$ were explained to be a result of polymeric associations of solute species. Weak shoulders at 7040 cm^{-1} were tentatively assigned to intermolecular hydrogen bonding and free hydroxyl groups, respectively. The absorbance at 7140 cm^{-1} was used to calculate the specific extinction coefficient (ϵ_{sp}) using Beer's law. The molecular weight of the polymers was determined by end group analysis. It was found that $\log \epsilon_{\text{sp}}$ varied linearly with $\log M$, with a satisfactory calibration obtained in the molecular weight range $190\text{--}7500$.

Willis *et al* (1968) [33] demonstrated the use of both IR and NIR spectrophotometry in determination of acrylonitrile-butadiene-styrene (ABS) terpolymer in polyvinylchloride (PVC) compounds. They pointed that ABS is incorporated as a modifier in PVC compounds to achieve certain desired properties, and therefore its analysis is essential in PVC quality control. Direct use of IR and NIR spectroscopy alleviates the problems associated with other analytical techniques, such as when ABS is separated from PVC using solvent extraction and analyzed by IR. Films of ABS and PVC (of fifteen mil thickness) were used to obtain IR spectra. A strong band at 4.4 microns found in IR spectrum of ABS was absent in the spectrum of PVC and was assigned to nitrile bonding of acrylonitrile. This band was used for the determination of ABS in PVC using 15 mil films of the modified polymer and containing ABS to a maximum of 15% . In the NIR region, the bands from $2100\text{ to }2200\text{ nm}$ present in the spectrum of ABS in PVC were

attributed to ABS and assigned to hydrogen bonding of saturated compounds, benzene rings, and a methylene group positioned next to a carbonyl group. These bands were absent in the NIR spectrum of PVC and thus were considered ideal for determination of ABS in PVC. The aromatic peak at 2100 nm was used for this determination. Both IR and NIR worked equally well, with NIR providing flexibility to work with relatively thicker samples (i.e. about 80 mil as compared to 15 mil in IR). The utility of the methods in quality control was emphasized by the fact that both methods take about half an hour, as compared to other analytical methods that are known to be more time consuming.

Giammarise (1969) [34] used NIR analysis to determine the styrene content in copolymers with aliphatic acrylates and methacrylates. For the purpose of calibration, spectra were recorded using solutions of polystyrene and methyl methacrylate homopolymer in chloroform. The absorbance at 2144 nm, which is due to benzene rings in polystyrene, was found to vary linearly with polystyrene concentration in the range 0 to 82.1 g/l. This calibration plot was used to determine styrene content in copolymers using absorbance values at 2144 nm. The values were validated with NMR-determined values and were found to be in good agreement with them. This analysis also proved that mixtures of homopolymers could be used to calibrate some copolymer systems where spectra are insensitive to monomer interactions.

Basch *et al* (1974) [35] reported the use of the near infrared spectrum of cellulose to determine crystallinity ratio. Samples were prepared as potassium bromide (KBr) disks by mixing with KBr, and transmission spectra were recorded. Absorbance peaks at 4760 cm^{-1} and 5190 cm^{-1} were found to be directly and inversely related to the crystallinity, respectively. These peaks were used to determine the crystallinity ratio. The NIR-determined crystallinity ratios agreed

well with X-ray determined crystallinity ratios, with a degree of correlation equal to 0.879. The absorbance band at 4760 cm^{-1} was assigned to a combination of O-H and C-H deformational bands occurring at $1282\text{-}1455\text{ cm}^{-1}$ and the O-H stretching band at $3275\text{-}3405\text{ cm}^{-1}$. The dependence of the 4760 cm^{-1} band on crystallinity was traced to the strong absorption band at 1372 cm^{-1} , which was solely attributed to crystallinity in cellulose [36]. The band at 5190 cm^{-1} , which was inversely related to crystallinity, was also found in the spectrum of bone dry cellulose which confirmed that it was not a water band that also exists in that range. It was also pointed out that the NIR crystallinity ratio may also depend on crystallite size.

Crandall *et al* (1975) [37] studied the ultraviolet (UV), visible, and NIR spectra of some polyamic acid resins with the aim of correlating effects of concentration and reaction temperature to spectral changes. An attempt was made to study the imidization process involved in the formation of polyamic acids from diamines (bis(4-aminophenylmethane) and dianhydrides (3,3,4,4'-benzophenonetetracarboxylic acid dianhydride). The imidization of the polyamic acids at elevated temperatures to form polyimides was also studied. A variety of polyamic acids were prepared with varying solute concentrations and reaction temperatures, and they were subjected to different curing conditions. The NIR region proved to be most useful in following the polymerization process. The first overtone of the C-H band at 1700 nm, an amide band at 2300 nm, and an amine combination band at 1950 nm were used to determine amide/C-H, amine/C-H and amide/amine ratios. These ratios were indicative of the degree of polymerization and the amount of imidization. It was found that the 2300 nm amide absorption band disappeared with curing and imidization, and could be used to follow the progress of these processes. In the visible region, absorption maxima bore a direct relationship

with reaction temperature and an indirect relationship with the solute concentration. The UV region was found to be of no use in this study.

Crandall and Jagtap (1977) [38] studied a variety of step reaction polymers including polyethylene, polystyrene, polyesters, polyamides and polyurethanes, with varying reaction and curing conditions. They pointed out that systems containing aromatic rings have absorption bands in the 2130-2160 nm region that are not present in aliphatic polymers. The first overtone of the C-H stretch band, which occurs at 1700 nm, was used as an internal standard to compare other band intensities. In addition to alkyl and aromatic C-H bands, overtone bands of carbonyl, amino and amide N-H, and alcoholic O-H were identified. Polyesters, polyamides and urea-formaldehyde polymers were all found to have C=O, O-H, and N-H overtones. Polyurethanes, polyamides, and urea-formaldehyde polymers all showed a strong amide N-H band in the 2000-2100 nm range. It was found that bands associated with terminal functional groups tend to decrease with heat curing, whereas the bands associated with linkages in the polymer backbone may increase or remain constant.

Till the early 1980s, NIR studies on polymers lacked rigorous quantitative analyses particularly due to the absence of sophisticated computers and robust chemometric techniques. With the advent of modern computers and chemometrics, spectroscopists have ventured far beyond univariate regression and other simple quantitative techniques. This improvement in quantitative analysis has widened the horizons of NIR spectroscopy and unraveled its actual potential. The significant increase in the number of NIR publications in the 1980s provides ample testimony of this fact.

Kirkbright and Menon (1982) [39] used near infrared photo-acoustic spectrometry and diffuse reflectance spectrometry for the determination of combined

vinyl acetate in polyvinyl chloride/polyvinyl acetate copolymers. In photo-acoustic spectroscopy, modulated radiant energy absorbed by the sample leads to an increase in the internal energy of the system. Subsequent de-excitation causes an increase in temperature which may be monitored as a periodic pressure change in the gas surrounding the sample by using a microphone transducer. This photo-acoustic technique has the advantage of analyzing a wide variety of sample types and optically opaque materials. Five copolymer samples containing 0-15% (w/w) of vinyl acetate and having three different particle mesh sizes were used for the study. The photo-acoustic spectra had five bands occurring at 1200 nm, 1400 nm, 1750 nm, 2100 nm, and 2400 nm. The 1200 nm, 1750 nm, and 2400 nm bands were assigned to second overtone, first overtone, and combination bands of C-H stretch, respectively, while the 1400 and 2100 nm bands were assigned to third and second overtones of the carbonyl bands, respectively. It was found that the ratio of absorbances at 2100 nm and 1750 nm could be linearly related to the concentration of vinyl acetate. Higher precision was obtained for smaller particle sizes. In the case of diffuse reflectance, the same five absorption bands were obtained. However, lower precision was obtained for smaller particle sizes. This lower precision was attributed to increased specular reflectance with decreasing particle size.

Davies *et al* (1985) [40] used near infrared spectroscopy to analyze packaging laminates of cast polypropylene (CPP), linear low density polyethylene (LLD), and nylon (NY). Films of the three polymers were used for calibrating relative thickness (mass per unit area) of each polymer to absorbance at a particular wavelength. This calibration was possible because each of the three polymers had a unique absorbance peak. The above calibration was used in determining the composition of laminate samples. Composite samples consisting of one layer of laminate and a layer each of the three polymers were scanned. The relative thickness of each layer in the

laminate was calculated by subtracting the amount of polymer in the films from the total amount of each polymer as predicted by the calibration equations. The predicted total relative thickness of the laminate samples was calculated by summing the individual predicted relative thicknesses of the polymers.

Weyer (1986) [41] described a new approach in the use of derivative spectra and applied it to near infrared reflectance spectra of some industrial polymers. Weyer pointed out that zero crossover points (i.e. places in the derivative spectra where there is negligible response to concentration changes) could be used to minimize interferences at the measuring wavelengths. In the first derivative curve, the zero crossover point represents the top of an absorption peak in the zero order absorbance spectrum, whereas in the second derivative curve it represents an inflection in the zero order absorbance spectrum. Weyer suggested that in a derivative spectrum, crossover points could be chosen where the substance of interest has a definite absorption, while interfering materials have zero crossovers or no absorption. This technique of utilizing zero crossover points was successfully applied in the analysis of methyl ether ketone (MEK) in a UV-curable resin and for the determination of three hydrocarbon polymers in a mixture.

Schirmer (1989) [7] was the first investigator to try remote optical monitoring of polymer processing over long fiberoptic cables. He demonstrated this technique for two specific applications. One application was to monitor a phenolic antioxidant (BHT- butylated hydroxy toluene) during extrusion of high density polyethylene (HDPE). This was done using a specific absorption band of the antioxidant near 280 nm, i.e. in the ultraviolet region. Spectra were recorded in the transmission mode, with probes mounted perpendicular to the molten polymer stream (Fig. 2.2) that emerged from a twin screw extruder (TSE). The pathlength used was 2 mm. It was shown that the absorption maximum at 280 nm could be linearly related to the

concentration of BHT. Concentrations of BHT as low as 50 ppm could be measured. It was also pointed out that the analyzer could be installed as far as 10 m away from the measurement site. The second application of this remote optical monitoring technique was to monitor the production of polyether polyols by measuring the hydroxyl number. Polyether polyols are produced by reaction of glycol with an epoxide, with the reaction being allowed to proceed until the desired chain length is achieved. The chain length is estimated by determining the concentration of hydroxyl groups. In the above study, the production of polyether polyols was monitored in real-time by using a reflectance probe mounted directly in the reactor. The near infrared absorption of the hydroxyl (OH) group was measured at 1450 and 2050 nm. The band at 2050 nm had a good resolution up to 50 m of cable length, after which signal attenuation took place. Both of the absorption bands were calibrated against the hydroxyl number. The absorption bands of water and other substances were displaced and did not interfere in the analysis. It was suggested that in case of any such interference, multivariate calibration could be used to quantitate all of the components.

Miller (1989) [42] used near infrared reflectance spectroscopy to study ethylene propylene diene monomer (EPDM) terpolymers. Diene units in the terpolymers were either 1,4 hexadiene (HD) or ethylidene norbornene (ENB). Polymer samples were analyzed both in bulk and in carbon tetrachloride (CCl₄) solution. The spectra were analyzed separately in second overtone (region I), first overtone (region II), and combination regions (region III). The spectra were analyzed both by PLS and MLR. Both intrachain and interchain interactions in polymer samples were studied. Data processing involved multiplicative scatter correction (bulk samples) and second derivatives. Differences in MLR and PLS calibrations suggested that there were unknown spectral variations arising from interactions

and crystallinity effects. These effects have been discussed in detail. It was found that the spectral resolution increased from region 1 to region 3. Bulk spectra helped to identify crystallinity effects due to ethylene units.

Nishio *et al* (1990) [43] used the near infrared attenuated total reflectance (NIR-ATR) technique to determine composition of monomer units in ethylene-propylene polymer (EP). The composition of the polymer is directly related to the durability of the polymer, and as such its determination is quite important. IR analysis of the polymers requires very thin films. Because -CH_3 and $\text{-CH}_2\text{-}$ bands are highly overlapped, the ATR method used with the fundamental vibration works only for a narrow range of compositions. This overlapping is absent in the overtone region, and thus the NIR-ATR method provides a sound non-destructive means to determine the composition of the polymer over a wide range of compositions. In the above study, the band at 5900 cm^{-1} (1694.9 nm) was attributed to be an overtone of the methyl C-H stretching vibration, present in propylene. The band at 5775 cm^{-1} (1731.6 nm) was attributed to overtone of $\text{-CH}_2\text{-}$ groups, present both in propylene and ethylene. It was found that the modified absorbance ratio (ratio of absorbance at 5900 cm^{-1} to sum of absorbances at 5900 and 5775 cm^{-1}) could be linearly related to the propylene content over the range 0-80%.

Miller *et al* (1990) [44] used near infrared transmission spectroscopy to determine the composition and microstructure of polybutadiene (PBD) polymers and styrene-butadiene (SBR) copolymers, in bulk and in CCl_4 solution. Using the classical least squares (CLS) method, the composition of the polymers was determined with reasonable accuracy. The spectral analysis was done separately in three regions: region I (1100-1350 nm), region II (1570-1850 nm) and region III (1950-2500 nm). It was concluded that region I provided best results for thick (10-20 mm thick) bulk samples; region II was ideal for thinner (upto 2-mm thick) bulk

samples and for solutions in which the solvent is near infrared transparent; and region III was best suited for dilute solutions. The CLS method also helped in qualitative interpretations. The CLS-estimated pure analyte spectra were found to be quite close to the spectra of the pure analytes in the polymers and were used for band assignments of specific functional groups. These estimated spectra were also used to detect interactions between different functional groups in the polymer chains and to detect differences in the structural states of specific groups in different states of the polymer. It was concluded that NIR spectroscopy could be successfully used to determine relative amounts of random and block segments in a copolymer and also to determine intermolecular properties, such as crystallinity and phase separation.

Spatafore and McDermott (1991) [45] used near infrared reflectance analysis for quantification of polyolefin additives. The additives studied included two antioxidants (Tetrakis {methylene {3,5-di-tert-butyl-4-hydroxyhydrocinnamate}} methane and Tris {2,4-di-tert-butylphenyl} phosphite) and one light stabilizer (Bis{2, 2, 6, 6-tetramethyl-4-piperidinyll} sebacate). Using plaques, thirty different compositions of a polyolefin containing varying ratios of the antioxidants and the light stabilizer were analyzed in the transreflectance mode. Data processing comprised first and second derivative transformation followed by use of MLR and PLSR. Actual concentrations of the additives were determined using Gas Chromatography (GC) and High Pressure Liquid Chromatography (HPLC). Sound calibrations were made for the additives in the concentration range of 0 to 1%.

McPeters (1991) [46] combined NIR spectroscopy along with fiberoptics cables and optical probes to study molten polymer streams emerging from an extruder. The compositions were determined: (i) of blends of styrene and acrylic polymers; (ii) of terpolymers comprising three methacrylate units. Spectral data in the range 1200-1650 nm was used. Owing to high absorptions and low signal to noise ratios, data

at higher wavelengths were discarded. Difference spectra, first derivatives and second derivatives were used to process the data and then PLSR and MLR were employed for data analysis. Standard deviations ranged from 0.34 wt. to 1.1 wt %. Other studies on the blends comprised: (i) variation in NIR spectra with temperature; (ii) variation in NIR spectra during the transition phase from one blend level to another. In the case of terpolymers, the calibration was relatively more complicated because of extensive band overlap. Here, PLS applied on second derivatives worked best with a standard deviation of 0.98% for component 1 and a standard deviation as low as 0.032 % for component 3.

Zhu *et al* (1992) [47] used near infrared reflectance and absorption spectrometry to determine the concentration of PBT (polybutylene terephthalate) in polycarbonate blends and to determine the intrinsic viscosity of polycarbonate samples. Six polycarbonate samples with different values of intrinsic viscosity ranging from 0.49 cm³/g to 0.53 cm³/g were used for NIR measurements. Reflectance spectra showed subtle variations that were calibrated by using MLR. It was found that at least four independent wavelengths (i.e. four degrees of freedom) were required for a reasonably low standard deviation. There was a positive agreement between the NIR-determined intrinsic viscosity values and actual values, with a coefficient of correlation equal to 0.979. In the case of PBT measurement in polycarbonate blends, 12 samples were used, with PBT content ranging from 35 to 69%. Films of the samples were used and absorbance spectra were collected in the range of 7500 cm⁻¹ (1333.3 nm) to 3500 cm⁻¹ (2857.1 nm) with a spectral resolution of 8 cm⁻¹. Ratios of first derivatives of absorbances were taken in order to correct for variations in thickness of the films. For multiple linear regression, five samples constituted the training set, and the remaining samples made up the test set. The number of independent variables was determined by factor analysis and was found

to be five. A new method for selection of optimal analytical wavelengths, called the cross search method, was employed. In this method, different combinations of five wavelengths were tested for different sets of five samples, and the combination which provided the best overall predictive ability was chosen. Out of the samples used in the study, five samples had the same PBT content but varying concentrations of other additives. It was found that the predictions of PBT content were not affected by the presence of additives, and the average relative standard deviation for PBT predictions was 0.041 %. The study proved that apart from measuring chemical constituents, the NIR method could also be used to measure physical properties such as intrinsic viscosity and could do so more rapidly and without a solvent or isothermal conditions. It should be pointed out that the quantitative analysis described above suffers from some limitations. The authors have assumed that the system is fully deterministic, and have used just five equations to determine the five regression coefficients. Since the system is not fully deterministic, the authors should have used more than five samples, and calculated the residuals (i.e. the difference between the actual and predicted values).

Lee *et al* (1993) [48] used both NIR and mid-infrared spectroscopy to determine hydroxyl numbers in polyesters and compared the results for the two methods. Both methods have advantages over the chemical method because they are faster and do not involve exposure to irritating, highly toxic, and corrosive chemicals. The polymers used were copolymers of a hydroxy functional monomer and other acrylic polymers. To prepare the training set, polymers with hydroxyl numbers ranging from 125 to 175 were prepared. Reference values of hydroxyl numbers were determined by a laboratory method. NIR measurements were done in the transmission mode with 4 mm pathlength quartz cuvettes. Mid-infrared measurements were performed by spin coating thin films of polymer on IR crystals

and then recording transmission spectra in the region of 3700 cm^{-1} (2702 nm) to 800 cm^{-1} (12500 nm). Transmission data both in the NIR and mid-infrared regions were converted to absorbance data. NIR data were analyzed using standard regression analysis, while mid-infrared data were analyzed using PLSR technique. For NIR it was found that univariate regression using the OH stretching band at 2044 nm was sufficient to calibrate the hydroxyl number. In the case of mid-infrared there was more variation in the spectra because of inconsistencies in sample preparation. The deviations of predicted OH numbers were as high as 3 units. Four different approaches were employed to analyze the data: (i) calibration with no compensation; (ii) calibration without using linear features; (iii) calibration without the OH stretching region, $3700\text{-}3200\text{ cm}^{-1}$; and (iv) calibration by using second-derivative spectra. The prediction residuals were of the order of 2 hydroxyl numbers for the first three methods and still higher in the case of second derivatives. On the whole, the predictions of IR method and NIR method were quite comparable. One advantage of the IR method is that sample preparation is simple and thus it is much easier to deal with very viscous polymeric liquids which do not readily dissolve in typical solvents. However, the NIR transmission method has the advantage of having a fixed pathlength which leads to more robust calibration models. In the mid-infrared case, more than two samples of each polymer type were needed to achieve the same accuracy as with NIR. The authors concluded that both techniques worked equally well and could be used for OH number determination.

Miller (1993) [49] used NIR spectroscopy to determine the composition of high density and low density polyethylene coextruded films. The utility of this analysis lies in the fact that the blending of HDPE and LDPE provides materials with morphological properties that are intermediate between those of pure HDPE and LDPE, and they could therefore be used for specific applications. In this study,

HDPE and LDPE pellets were mechanically mixed prior to extrusion and then melt-extruded as films with seven different blend ratios (0, 2.5, 5, 10, 25, 50 and 100% HDPE). Film thickness varied from 25 mm to 40 mm. The films were examined as double layers in order to have sufficient thickness for NIR reflective-transmission spectra. The NIR reflective-transmission spectra were collected in the wavelength range of 2100 to 2500 nm in 2-nm increments. Data analysis was done using PCR, with cross validation providing the optimal number of factors. Three factors were sufficient to describe the variation, with first, second, and third factors describing 46.67, 49.25, and 2.56 % of the overall variation respectively. Analysis of the scores plots for the three factors revealed that the second factor adequately described the difference between the 100% HDPE and the rest of the samples (i.e., ranging from 0 to 50% HDPE). The third factor adequately described the variation among the samples containing 0 to 50% HDPE. Using three factors, the calibration model had an error of 2.31% HDPE for the calibration set and 2.48% HDPE for the validation set. It was pointed out that for samples containing 50 to 100% HDPE, the HDPE content is probably related to scattering and the degree of crystallinity. For samples containing 0 to 50 % HDPE, the HDPE content was related to the methyl group concentration and the degree of crystallinity. The variation between replicate samples was attributed to the direction and degree of orientation in the samples, and their contribution could not be determined. Also, the presence of weak interference fringes in the spectra of films added to random errors in the data. It was suggested that the accuracy of the NIR method could be significantly improved by experimental suppression of interference fringes, more accurate reference analyses, working with thicker samples, and using non-linear calibration modeling.

Miller *et al* (1993) [50] characterized polyethylene/nylon laminates using near infrared spectroscopy. Food packaging laminates containing polyethylene (PE),

polyamide-6 (PA-6), and ethylene vinyl alcohol (EVOH) layers were analyzed using the reflective-transmission mode in the wavelength region 1500-2500 nm. Two sets of samples were studied: (i) PE/PA-6/EVOH laminates that had known variations in the total thickness and polyethylene percentage (PE%); and (ii) coextruded films of PA-6 and EVOH (made up of a layer of EVOH sandwiched between two layers of PA-6 and referred to as NEN - Nylon-EVOH-Nylon - films), with known variations in the EVOH thickness percentage (EVOH%). The coextruded films had three layers, the top and bottom layers being that of PA-6 while the middle layer was EVOH. The laminate samples were used to test the ability of the NIR method to determine total laminate thickness and PE content (PE%). The NEN samples were used to test the ability of the NIR method to determine the EVOH content (EVOH%). For the laminates, test set prediction errors of PE% ranged from 0.74 to 1.43%, and prediction errors of total thickness ranged from 2 to 4 mm. The study of calibration models showed that the spectra were sensitive to the PE content, interferents (such as scattering from non-reproducible sample placement), and water absorption (by PA-6 and EVOH). In the case of NEN films, EVOH% was predicted within an error of 0.52%. This error is adequate for determination of EVOH% in thick NEN films. The NIR method proved sensitive to EVOH%, absorbed water content, crystallinity or orientation (of the PA-6 or EVOH), and the amount of polyurethane adhesive. The thickness of the laminate was found to be critical in calibration models. Laminates thicker than 250 mm could cause non-linearity for the $\text{-CH}_2\text{-}$ polyethylene bands at 2310 and 2350 nm, while film samples that are very thin (about 25 to 50 mm) could produce interference fringes that may lead to poor predictions.

A recent article published by Mark & Castro (1994) [51] described the utility of NIR spectroscopy for recycling applications. Plastics constitute a major part of the solid waste stream and therefore their recycling is very important. However,

different types of plastics have to be separated before recycling in order to avoid contaminant plastics ruining the recycling process. The authors pointed out that NIR spectroscopy could be very useful for recycling applications: (i) it is a rapid and non-destructive method for qualitative identification; and (ii) for polymer identification, detailed qualitative band assignments are not necessary and distinct absorptions in the combination region can provide easy identification of the polymer samples. In the above study, thirty different polymer samples were analyzed by collecting transmission spectra from films with thickness ranging between 10 and 150 mils. In order to obtain well-defined transmission spectra, polymers that did not have clear and transparent films were not considered for the study. The most notable among the polymers not considered were polyethylene and polyphenylene oxide. For all the polymers, analytical wavelengths (in the first overtone, second overtone, and combination regions) that could be useful for polymer identification were determined. It was shown that identification of polymers belonging to the same class is also possible, by using some unique weak features in their spectra. This was illustrated for: (i) three different styrene based polymers (polystyrene, styrene-butadiene copolymer and styrene-acrylonitrile copolymer); (ii) three halogen substituted polymers (polyvinylidene chloride, polyvinyl chloride and polyvinylidene fluoride); (iii) three hydrocarbon-based polymers (polypropylene, polybutylene and polymethylpentene); (iv) several polyesters; and (v) aromatic polymers (poly(phenylene sulfide), polyarylate, polyarylsulfone, and styrene maleic anhydride copolymer). The styrene-based polymers exhibited weak features at 1720, 1750, 1904, 1944, 2118, and 2234 nm that could be used to differentiate the three polymers. The spectra of the three halogen substituted polymers showed distinct differences in the combination region, thus proving the sensitivity of the NIR method to chemical structure. Although C-X (X = halogen atom) stretches do not

show up in the near infrared region, the combination bands of C-C and C-H are susceptible to halogen substitution. The spectra of polyesters and aromatic polymers showed that each of the polymers had unique distinguishable features in the combination region. Apart from looking at polymers within a certain class, the authors also compared polymers belonging to different classes (e.g. Nylon, polycarbonate, polyethylene terephthalate, etc.). It was found that the above polymers had distinct differences in their spectra, and NIR spectroscopy alone was sufficient for identification purposes. Based on their findings, the authors concluded that NIR spectroscopy is an effective technique for rapid qualitative identification, and it can be used for any high-speed sorting process.

2.4.2 Miscellaneous

Apart from the applications of NIR spectroscopy in polymer analysis, NIR spectroscopy has widespread applications in other chemical processes. A few of these applications shall be presented here.

Holman and Edmondson (1956) [52] reported the near infrared spectra of certain fatty acids and lipids, and explained the utility of this technique in structure identification. They used the spectra to distinguish and make band assignments for methyl groups, methylene groups, double bonds, triple bonds, carboxyl groups, hydroxyl groups, amine groups, esters, and carbonyl groups. Identification of cis unsaturation was found to be easier with NIR spectra than with IR spectra.

Goddu (1957) [53] also used NIR spectroscopy to study unsaturation in organic compounds. He studied a variety of materials and pointed out that NIR spectra can determine both terminal unsaturation (bands around 1.62 microns and 2.10 microns) and cis unsaturation (band at 2.14 microns). The terminal methylene

groups were identified with a sensitivity of about 100 ppm and precision within ± 1 to 2%. However, NIR spectra were found to be insensitive to trans unsaturation.

A vivid description of the qualitative and quantitative applications of NIR spectroscopy was published by Goddu in 1960 [9]. Based on his own laboratory work and other published data, Goddu compiled and tabulated positions and intensities of a number of bands in the near infrared region. This table of spectra-structure correlations is useful in making band assignments.

Jones (1982) [54] used NIR spectroscopy for in-stream composition measurements of trace water in ethylene dichloride. He pointed out that selective measurements could be done in the NIR region by using only those wavelengths that are relevant to the measurements. By using its absorbance at 1900 nm, trace water in ethylene dichloride was adequately measured in the range 0 to 100 ppm. It was suggested that measurements could also be done in the range of 0 to 20 ppm by using thermoelectrically cooled detectors and measuring absorbance at 2.72 microns.

Cooper (1983) [55] reviewed the advantages of NIR analysis for process control. He pointed out the disadvantages of using off-line analyses and described the various ways in which untimely analysis leads to extra manufacturing costs.

Fitch and Gargus (1985) [56] were among the first investigators to report on the use of fiberoptic chemical sensing for remote ultraviolet-visible (UV-VIS) and NIR spectroscopy. They classified the areas of application into four major categories: (i) analytical laboratory with applications such as biological samples, pharmaceuticals, dye transfer studies, chromatography etc.; (ii) process research laboratory with applications such as homogeneous catalysis studies, study of reaction kinetics and mechanisms, monitoring of reaction intermediates and byproducts, supercritical fluid extraction etc.; (iii) on-line process monitoring with applications such as endpoint detection for batch processes, control of polymer

additive levels before processing, etc.; (iv) plant-wide chemical monitoring by making measurements during unloading, distribution, packaging operations, and detecting spills and emissions. The authors have described a family of fiberoptic probes for applications such as transmission, emission, fluorescence, and reflectance. It was also mentioned that a high performance fiberoptic multiplexer could couple up to ten monitoring points to one analyzer.

Honigs *et al* (1985) [57] used NIR spectroscopy and chemometrics to determine several physical properties of hydrocarbons. In a series of hydrocarbon mixtures, properties such as heat of formation, molecular weight, and the number of methyl groups per molecule were determined directly from their near infrared spectra. The rationale for this approach was that since the near infrared spectra are directly related to the chemical constituents, all physical properties that have a first order relationship dependence on concentration could be directly related to the spectra.

Murray (1986) [58] reported the near infrared spectra of a homologous series of organic compounds. These compounds included hydrocarbons (aliphatic and aromatic), fatty acids, alcohols, phenols, polyols, and nitrogen compounds (such as ammonia, urea, nylon etc.). Band assignments for various functional groups were made, and in some cases also related to the fundamental absorptions. The spectra and the band assignments are useful in making and verifying band assignments in the near infrared region.

Gargus (1986) [59] followed up on his earlier paper and further evaluated the role of fiberoptics in remote chemical sensing using UV-VIS-NIR spectroscopy. The paper mentioned that fibers of practical length are available only in the range 200-2200 nm. The IR region is excluded because of absorptions by the hydroxyl group in silica at higher wavelengths. Transmission losses within the fiber are sensitive to

slight disturbances, especially if the bends in the cable change. The effects (if any) of fiberoptics window fouling or scratching could be eliminated by using a variable pathlength probe and measuring absorbance values at two pathlengths, and then relating their difference to sample concentration. The following applications of remote chemical sensing using fiberoptics were described : (i) monitoring conversion of a primary or secondary amine to a tertiary amine or amide, by measuring decrease in intensity of N-H stretch overtone at approximately 1540 nm; (ii) monitoring the dissolution of an aspirin tablet in 0.1 N HCl, using UV spectroscopy; (iii) real-time, *in situ* NIR determination of water in many substances; (iv) monitoring the chlorination reaction of benzene by measuring the decrease in the intensity of C-H band between 1650 and 1700 nm.

Weyer *et al* (1987) [60] demonstrated that the union of fiberoptics, NIR spectroscopy and chemometrics could make on-line composition analyses feasible. Their remote monitoring system consisted of a NIR analyzer, fiberoptic cables, probes and computer for data acquisition and analysis. Some key factors in the operation of the analyzer and probes were described: (i) multiple scan averaging to reduce noise, and changes arising from inhomogeneities in the sample; (ii) periodical recording of reference scan in order to account for lamp and instrument changes; and (iii) temperature regulation in the ambient conditions. The monitoring system was tested in plant trials to monitor the composition of mixed alcohol purification streams, mixed solvent distillate, and a fatty acid derivative. Chemometric data treatment, which comprised use of derivative spectra and multiple linear regression, provided models with low errors of prediction for on-line composition analyses.

Callis *et al* (1989) [61] investigated the utility of NIR spectroscopy in quality control of fuels and fuel stocks. SW-NIR (short wave near infrared) spectra of a series of gasoline samples of different grades were collected in the 660-1215 nm

range. The purpose was to relate the octane number, which is a primary indicator of fuel performance, to features in the absorption spectra. The SW-NIR region was chosen because weak intensities in this region provided the flexibility of using large pathlengths. The rationale behind the study was that the octane number is related to the chemical structure. The octane numbers of the 43 unleaded gasoline samples used in the study were found to be negatively correlated to the methylene content and positively correlated to both methyl and aromatic content. This correlation was found to be consistent with gasoline blending methods, which decrease straight chain hydrocarbon content and increase branched and aromatic hydrocarbon content in order to increase octane number. Although there was considerable band overlap in the spectral region, multivariate analysis could successfully extract the useful information with three wavelength regression equations that had reasonably low standard errors (about 0.3-0.4 octane numbers).

A paper published by two Australian chemists (1991) [62] also described the determination of octane numbers of gasolines. Sixty-five reformat samples of Australian refined motor gasoline were used in the study, and spectral data was collected in the wavelength range 7000 cm^{-1} (1428.5 nm) to 1557 cm^{-1} (6422.6 nm), i.e. both IR and NIR regions. The NIR data in the 2000-2500 nm range (due to the hydrocarbon absorbance bands) gave the best correlation values for the octane number. As reported by Callis *et al* [61], the aliphatic and aromatic CH bands were found to be positively correlated to the octane number, while the methylene bands were negatively correlated to the octane number. Principal component analysis (PCA) was used to classify samples according to the origins of the parent crude oils of the reformat. Scores plots of principal component 1 versus principal component 2 revealed that the samples were present in three clusters. The samples were subdivided into three subgroups, corresponding to the three clusters. When

separately used as a calibration set, each subgroup provided a lower standard error of calibration as compared to the whole group. Thus, the effect of geographical origins of the parent crude oils on the calibrations was shown.

Brown *et al* (1992) [63] determined the concentrations of NaCl in aqueous solutions by measuring NIR spectra in the 1100-1900 nm range. The dissolution of NaCl caused shifts (to lower wavelengths) and a decrease in the intensity of water bands. The shift of water bands to lower wavelengths is due to the hydration of Na^+ and Cl^- ions, which causes (i) a relative increase in the number of water molecules that have no -OH group hydrogen bonded (i.e. OH bond is strongest and is at shortest wavelength); and (ii) a relative decrease in the number of water molecules that have two -OH groups hydrogen bonded (i.e. OH bond is weakest and is at longest wavelength). The spectra were sensitive to changes in temperature because temperature changes caused changes in the H-bonding of -OH groups in water. For samples at constant temperature, simple linear regression could model NaCl concentrations, but for varying temperatures, PCR used on the entire water band provided better calibrations.

Haaland *et al* (1992) [64] applied NIR spectroscopy in the determination of glucose in whole blood. Glucose-doped whole blood samples were used for the study and the NIR spectra were obtained in the 1515.2-2352.9 nm region. The spectral features of glucose were overshadowed by the presence of a strong water band around 1960 nm. Multivariate calibration was constrained by the presence of only four different concentrations. Models developed on the basis of three concentrations produced large prediction errors for the remaining sample. This was attributed to large differences in blood chemistry and the presence of different levels of cholesterol, triglyceride, and total protein levels. The baseline differences were found

to be correlated to the varying hematocrit levels (fraction of red blood cells by volume) in the blood.

Mackison *et al* (1992) [65] demonstrated a system for remote in-line near infrared analysis. The efficiency of long fiberoptic cables was explored. Spectra of mixtures of ethanol, 1-propanol, and 2-propanol in methanol were collected using (i) a conventional spectrometer with no fiberoptic cables; (ii) a process spectrometer and 2 km of fiber; and (iii) a process spectrometer and 2 m of fiber. Signal to noise ratio of the spectrum with 2 m fiber was worse than that obtained with the laboratory instrument. However, the signal to noise ratio for 2 km fiber was comparable to the laboratory instrument. This difference was because in shorter cables high modes of propagation are not lost and are sensitive to bends in the fiber. Thus, the transmission characteristics are affected by slight movements of the fiber. Calibrations of the compositions of the alcohol mixtures showed high prediction errors for ethanol. This outcome was attributed to the similarities in the spectra of ethanol and the solvent, methanol.

Miller *et al* (1992) [66] investigated the feasibility of using near infrared diffuse reflectance and transmittance spectroscopy in determining protein, fat, and water contents in plastic-wrapped (polyamide/polyethylene laminates), homogenized meat. The motivation behind the study was to examine the possibility of studying packaged food samples noninvasively, which is particularly desirable for food products which degrade when exposed to the atmosphere. One hundred samples were used in the study, and each sample was analyzed with and without the laminate covering. The diffuse reflectance spectra were collected in the 1100 to 2500 nm region, whereas the diffuse transmittance spectra were collected in the 850 to 1050 nm region. For protein content, the diffuse reflectance method provided very high prediction errors as compared to the transmittance method. This discrepancy

was attributed to the presence of strong water bands in the region of protein N-H and C=O bands. Multiplicative scatter correction (MSC) resulted in lowering the prediction errors for both of the methods. For fat content, the diffuse reflectance method provided better results than the reflectance method. This effect was due to the presence of the fat-sensitive C-H bands (1700-1800 nm and 2250-2400 nm) in the diffuse reflectance spectra, whereas no unique fat band was present in the transmittance spectra. MSC greatly increased the prediction ability of the transmittance spectra and lowered the prediction ability of the reflectance spectra. This was possibly due to (i) very large baseline offsets in the transmittance spectra; (ii) large contributions of laminate variations in the reflectance spectra, which were not completely removed by MSC; and (iii) MSC may have removed scattering information that could have been useful for prediction of fat content. For water content, the transmittance method provided better results owing to the presence of highly absorbing (non-linear) water bands in the reflectance spectra. MSC resulted in the same effects as for fat content. The interaction effects between the meat and the laminate were found to be insignificant. The laminates caused a refractive index scattering effect, which led to differences in the baseline and absolute peak intensities. There was no indication of any chemical interaction between the meat and the laminate.

Swarin and Drumm (1992) [67] determined a number of physical and chemical properties of gasoline by using NIR spectroscopy. Three hundred fifty nine samples of unleaded gasoline from 23 US. cities were used in the study, and transmission spectra were recorded in two spectral regions (900-1800 nm and 1200-2400 nm). In addition to determination of octane number and hydrocarbon classes, the properties that were predicted included MTBE (methyl tert-butyl ether) content, oxygen content, benzene content, sulfur content, distillation point, Reid vapor

pressure, temperature at which vapor-to-liquid ratio is 20 by volume(TVL=20), specific gravity, and unwashed and washed gum contents. The NIR method could not successfully model sulfur content and gum contents. The calibration models required fewer factors when the calibration set comprised samples from the same geographical region. This analysis explained the fact that the extra factors required in full-data-set models account for the variance due to differences in oil samples from different geographical regions.

Brown and Lin (1993) [68] developed a near infrared fiber temperature sensor based on the variations in intensity and position of water bands with changes in temperature [69]. The water band at 6900 cm^{-1} (about 1449 nm), which is the first overtone of the O-H stretching vibration, was used in the study. For a temperature change of 60°C , the position of this band was found to shift by 165 cm^{-1} (from 6851 cm^{-1} to 7013 cm^{-1}), while the intensity increased by about 10%. The changes in absorbance appeared to be linear with the change in temperature, and were modeled using linear regression (LR), MLR, and PCR. PCR provided the lowest standard errors of prediction, which were 0.16 to 0.32°C over a temperature range of 5 to 85°C .

NIR spectroscopy is also used in the study of agricultural products [6,70], and in the analysis of tobacco [71,72], wool [73,74], textiles [75,76], pharmaceuticals [77,78], and dairy products [79,80]. Numerous review articles have been published in the field of near infrared spectroscopy [4,5,81-84]. The articles by Weyer, Stark *et al*, Whetsel, and Kaye are very comprehensive. The potential of this technique for numerous quality control applications has been reviewed by Davies [1], and Baughman *et al* [85].

3. OVERVIEW OF RESEARCH

The emergence of NIR as a process monitoring technique has prompted widespread application studies in the polymer industry. However, in transferring analytical techniques from the laboratory to the process line, many problems need to be addressed. These problems can be either equipment related or process related. Different polymer processes involve different types of variables and parameters, which have to be identified and taken into consideration before a particular process can be analyzed in real-time.

The research in the use of near infrared spectroscopy on polymers has focused primarily on polymers as solids (by using diffuse reflectance spectroscopy), and sometimes on polymers in solution (by using transmittance spectroscopy). Relatively little work has been done on polymers in the molten state. The biggest constraint in the monitoring of polymer melts has been the unavailability of rugged probes that could survive the rigorous process conditions. A complete definitive study of molten flowing polymers was therefore needed, that could thoroughly evaluate the viability of NIR spectroscopy as a potent polymer process monitoring technique. This research was directed at developing a system for continuous in-line monitoring of molten polymers, and for characterization of different types of polymeric systems. The research can be classified into the following broad categories:

- (i) Development of fiberoptic probes that could withstand severe conditions typical of polymeric processes, i.e. high temperature, high pressure, and adverse chemical environment.
- (ii) Monitoring of composition of molten polymer blends.
- (iii) Monitoring of composition of random copolymers with varying comonomer ratios and additive content.

The first phase of this research focused on the setting up of a system for in-line monitoring and the development of feasible probe designs. A variable pathlength flow cell that could be attached to the exit port of a single screw extruder was designed. The basic idea in the development of probe designs was to shield the collimating lens and the optical fiber by means of a cladding and a protective window, respectively. Sapphire was considered as an ideal choice for the window. Apart from the constraints imposed by process conditions, it was desired that the transmission characteristics of the rugged probes should be comparable to other existing commercial probes. The details of the probe designs shall be discussed in the fifth chapter.

A system of blends of polystyrene (PS) and polyphenylene oxide (PPO) was chosen as the initial test system. This system was selected because (i) the polymers are soluble in one another (miscible blends), and (ii) the polymers do not react with each other. In addition, owing to its high viscosity and high processing temperature, PPO provided a means to test the durability of the probes. The details of the study shall be included in the sixth chapter.

After successfully demonstrating the experimental setup using the above test system, a random copolymer system was chosen to be the subject of a full fledged study. The study encompassed ethylene vinyl acetate (EVA) random copolymers, with vinyl acetate (VA, the comonomer) varying in the 0 wt.% to 40 wt.% range. In addition, one of the copolymers contained an additive (namely, erucamide) in the range 0 to 2300 ppm. In all, twenty-one samples of the copolymers were used in the study. The optimum pathlength for the determination of vinyl acetate content and the additive content were determined from experiments. Multivariate techniques were used to build calibration models and to determine concentrations of vinyl acetate and erucamide. The effects of different spectral regions and pathlengths on

the calibration models were explored. Further, the study also examined the variations in spectra with time, and the robustness of the calibration models in handling these variations. The robustness of the calibration models was also be tested by using data collected on EVA copolymers from another independent source. This source provided eight samples of EVA copolymers, with VA varying in the same (0-40 wt.%) range. Furthermore, the robustness of the calibration models was also tested by using the models for real-time predictions. Different approaches, analogous to statistical process control charts, were used to study the results of real-time predictions. These approaches facilitated outlier detection in real-time, before using the model for predictions. The details of the studies on EVA copolymers shall be discussed in the sixth chapter.

The application of chemometrics techniques was a critical part of the overall research. In this respect, self-developed algorithms and codes for PCR and PLS, as described in chapter 2.3.2, were used. The spectral data files from the NIR experiments were transported to a Sun Sparcstation, where after the headers were stripped off, the files could be easily loaded in MATLAB. The results of the self-developed chemometrics routines were comparable to those obtained with commercial software packages (the so-called 'black-boxes'). Moreover, our codes provided the added advantages of higher computation speed and ease of data manipulation (Appendix B).

The two different polymer systems (blends and copolymers) that were chosen for the proposed research are (i) challenging to work with, (ii) ideal for fundamental studies, and (iii) have numerous applications in the plastics industry. The results of the studies have proved to be very valuable in demonstrating the utility of NIR spectroscopy for in-line monitoring of polymeric processes.

4. EXPERIMENTAL SETUP

Figure 4.1 shows the system for in-line molten polymer analysis. A 3/4 inch Brabender single screw extruder, with a L/D ratio of 25:1, is used to melt particulate solid polymers. A continuous purge of nitrogen gas in the feed hopper prevents any possible moisture absorption from the ambient atmosphere. Molten polymer from the extruder is pumped through a multifunctional variable pathlength flow cell installed at the exit port of the gear pump. The gear pump is used to ensure a uniform mass flow rate of the molten polymer to the flow cell. This arrangement prevents any perturbations or flow instabilities in the screw region to be propagated to the flow cell. A temperature and pressure control unit regulates the temperature and pressure conditions inside the flow cell.

Figure 4.2 shows a detailed schematic of the flow cell. This flow cell provides a flow channel of rectangular cross-section that is 20 mm long and 9.5 mm wide. The extruder die head has a circular opening of 3/8" diameter. A transition piece is present between the die head and the flow cell. This transition piece, machined by the EDM method, ensures that, from a rheological perspective, the complete flow area is free of dead spaces [86], where polymer might accumulate and degrade. Double-insertion transmission type fiberoptic probes are used to transmit light through the flowing polymer stream. These probes are mounted into specially designed housings whose internal dimensions match standard industry pressure transducer dimensions. The separation between the probes (i.e., the pathlength) is varied using spacers of different thickness. Ring-shaped spacers are mounted on the neck of the housings. Thus, the thickest spacer makes the housings flush with the walls of the flow channel, and by reducing the thickness of this spacer, the pathlength can be varied between 1 to 9.5 mm. Two more ports downstream of the

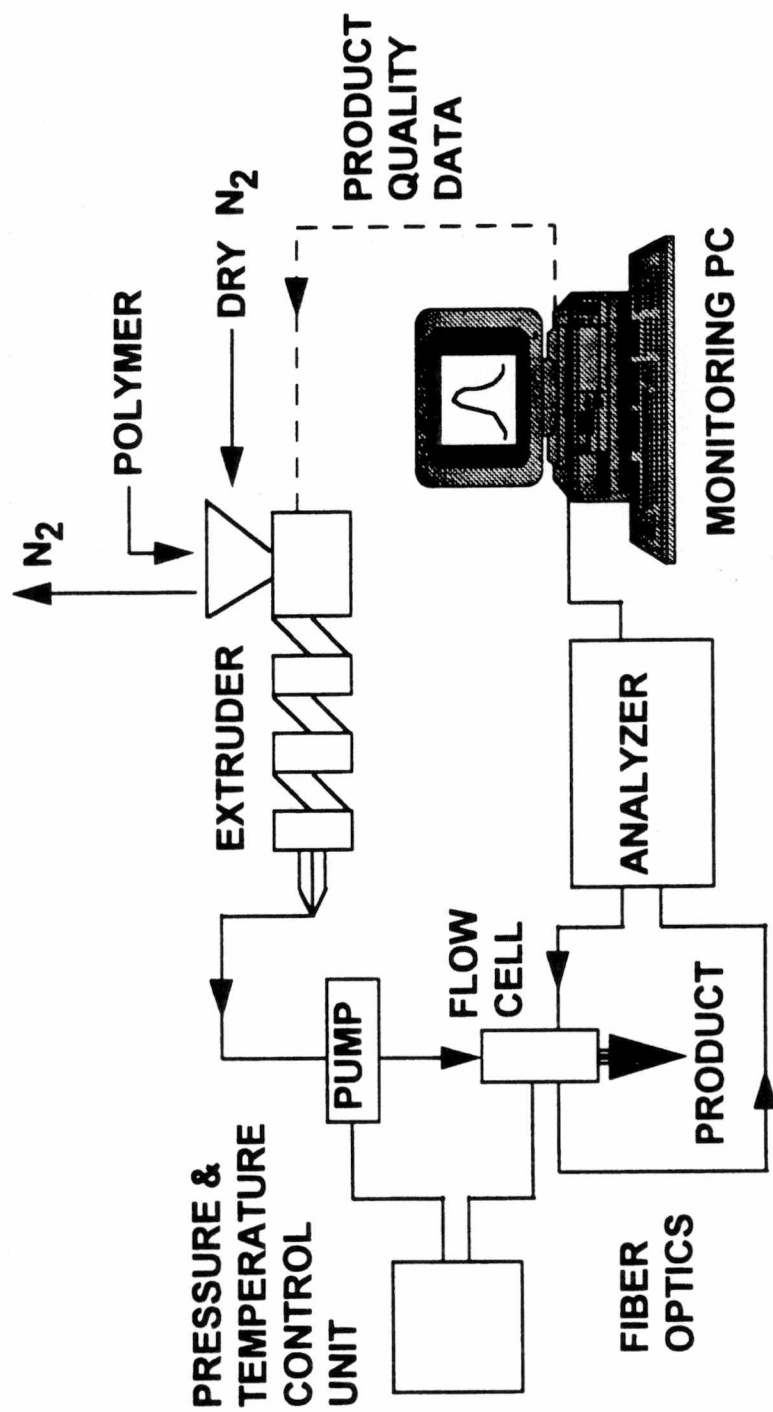


Figure 4.1 System for in-line molten polymer analysis.

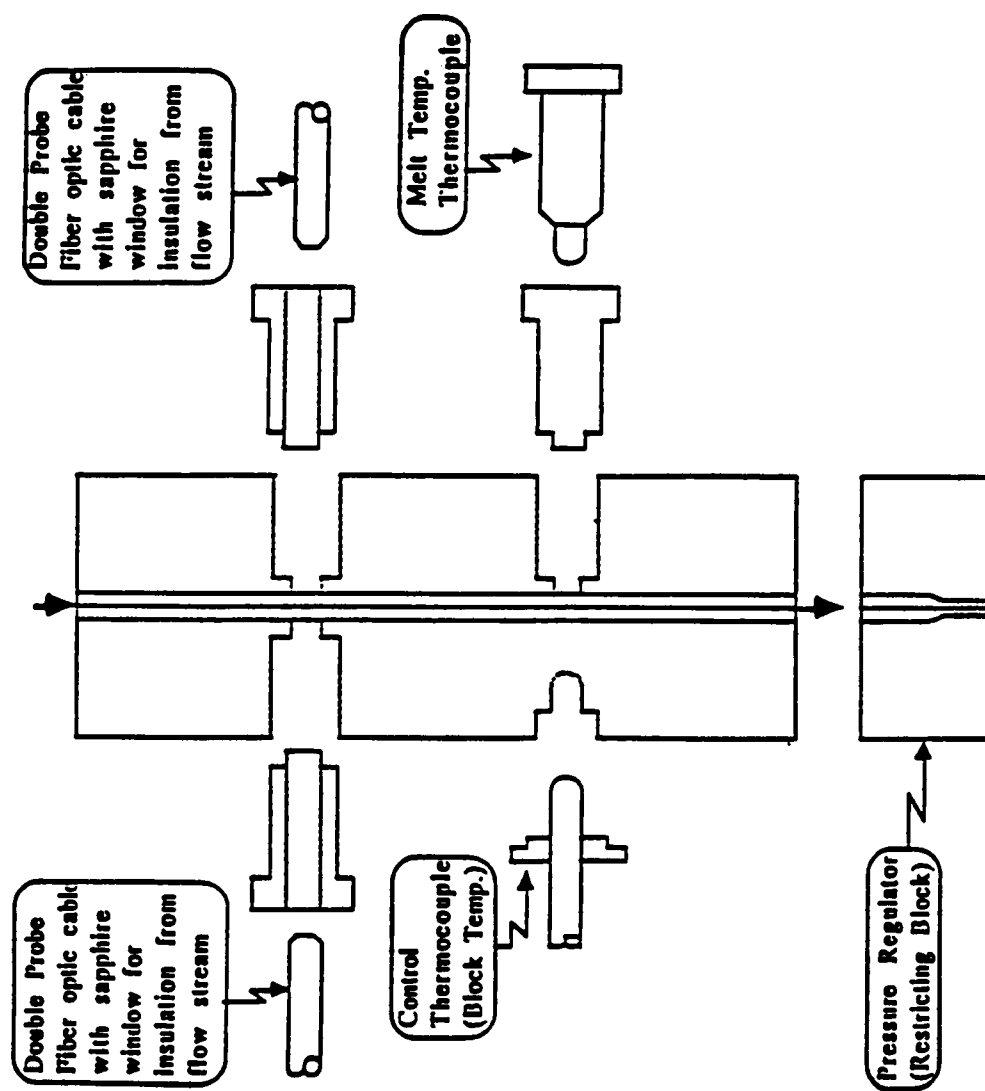


Figure 4.2 Detailed schematic of multifunctional variable pathlength flow cell

fiberoptic probes are used for temperature and pressure measurement. Finally, a pressure restrictor attached to the flow cell can be used to vary the pressure of the flowing polymer stream.

The fiberoptic probes installed in the flow cell are connected via fiberoptic cables to a Guided Wave 260 spectrophotometer [87]. This spectrophotometer comprises a tungsten halogen lamp, a lead sulfide detector, and a holographic diffraction grating. The grating is installed between the transmitted beam and the detector, thus making this instrument a post-dispersive instrument. The post-dispersive instruments allow more light to be channeled into the fiber before the light strikes the sample [3].

The grating surface is concave and thus it is self-focusing. It refocuses the divergent beam of light from the collection port of the analyzer onto the detector. The grating is grooved with 300 lines per mm of the surface. The linear dispersion of the grating is 16 nm/mm. The bandwidth of the instrument is determined by the product of the slit width (0.50 mm) and the linear dispersion of the grating. This bandwidth (8 nm) defines the resolution of the instrument and corresponds to the number of wavelengths reaching the detector simultaneously. Therefore, the lower the bandwidth, the higher the resolution of the instrument [3]. But, a very low resolution (of the order of 1 nm) has the disadvantage of limiting the light to the detector, which adversely affects the signal to noise ratio. The bandwidth of 8 nm is acceptable in the NIR region.

A 1543 nm narrow band filter is used to calibrate the spectrophotometer. The spectrophotometer is interfaced to a PC 286 computer which acquires and stores the spectral information. The software package provided by Guided Wave (Scanner & Examiner) is used for data acquisition and manipulation.

5. DEVELOPMENT AND EVALUATION OF RUGGED FIBEROPTIC PROBES

The fiberoptic probes hold the key to this type of contact and non-destructive process analysis. This necessitates fabrication of probes that can survive the onslaught of the hot and highly viscous molten polymer stream. Furthermore, they must withstand thermal cycling due to process startup and shutdown, without mechanical failure. A great deal of research in this direction led to the development of two types of probe designs.

The first probe design involves the development of a protective housing for standard transmission (Guided Wave, Inc.) probes (Fig. 5.1), wherein the probe could be shielded from the process stream by means of a cladding and a protective window. This housing comprises a sapphire window coupled to a tube made of a nickel-iron alloy, by a patented process called Mallory bonding [88]. In this bonding process, the sapphire and the alloy are each sputtered successively with a layer of chrome and gold, and then joined together using an eutectic soldering washer. Fig. 5.2 shows the schematic of a Mallory bond. The nickel-iron alloy tube is finally brazed to a stainless steel housing. The vast difference between the thermal coefficients of expansion of stainless steel and sapphire necessitates the introduction of the alloy as an intermediate. This probe housing seems sound conceptually but was not fabricated.

The second probe design, which is a subject of constant evolution and evaluation, is the result of a collaborative work with Sensotron, Inc., a pressure transducer manufacturing company [89]. The company uses state-of-the-art silicon-on-sapphire technology in which piezoresistive silicon strain gages are epitaxially grown onto a sapphire diaphragm. The sapphire diaphragm is guaranteed to

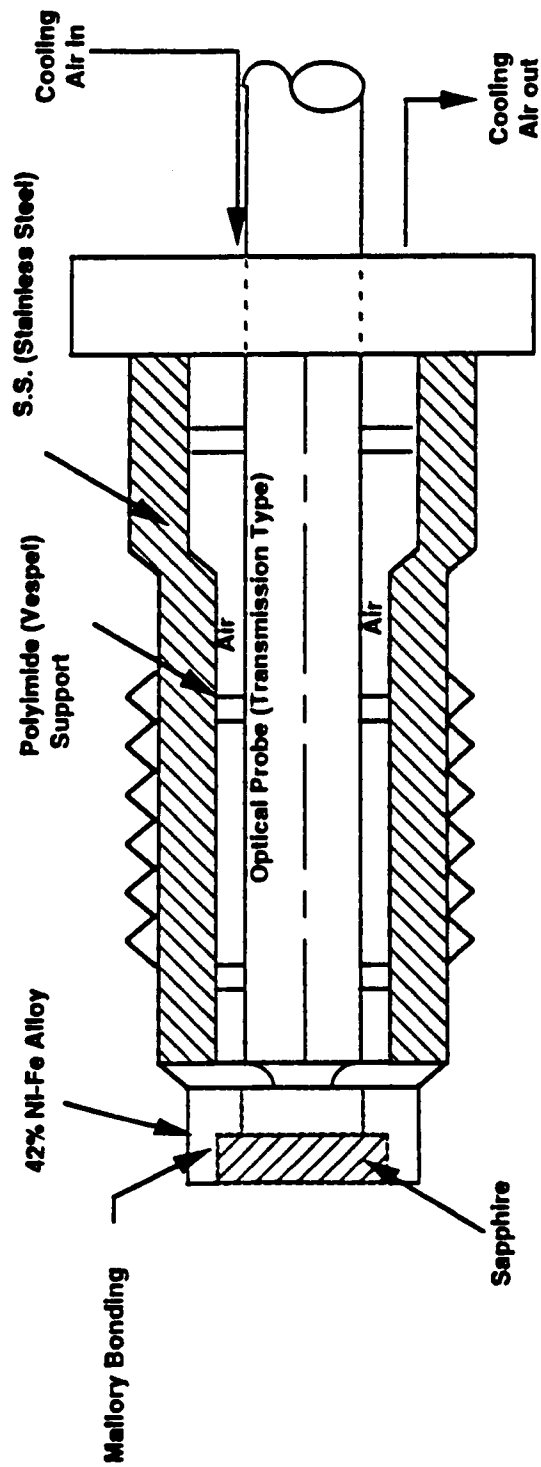


Figure 5.1 Protective housing for standard Guided Wave transmission probes.

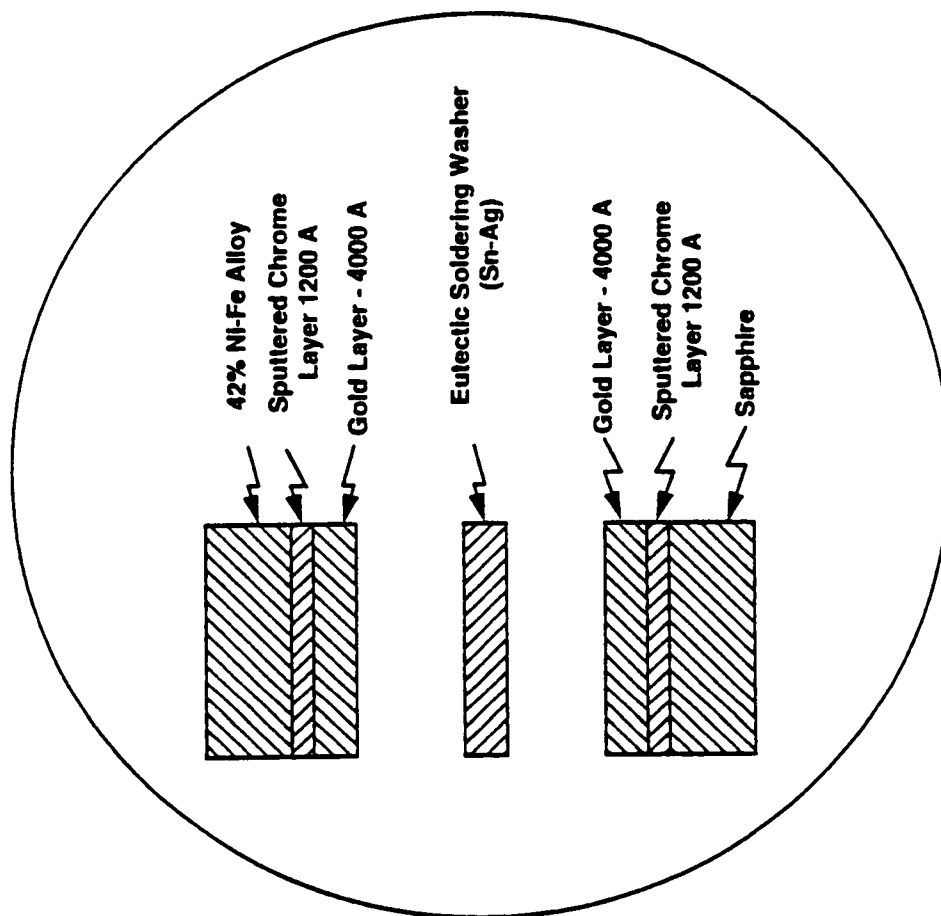


Figure 5.2 Schematic of Mallory Bonding [88].

withstand temperatures as high as 400 °C and pressures as high as 30,000 psi. The first series of tests was conducted by using the pressure transducer, without its pressure and temperature sensing elements, as a protective housing for our self-designed fiberoptic probe assembly. Figures 5.3, 5.4, and 5.5 show the Sensotron probe housing, the fiberoptic assembly, and the composite probe. The fiberoptic probe assembly consists of a plano convex lens mounted at its tip, and a single 500 μm diameter fiber running inside such that its front end is positioned at the focus of the plano convex lens and a SMA connector is mounted at its rear end. The truncated ends of the fibers had to be polished to provide the smooth surfaces to maximize the transmission efficiency of the fibers. These composite probes were tested on blends of PS and PPO upto a maximum temperature of 300 °C. The success of this concept prompted the company to incorporate fiberoptics into their housing and build the complete fiberoptic probe (Fig. 5.6).

The evaluation tests focus on the following issues: (1) maximum transmission efficiency of the probe after losses due to spectral attenuation in the probe fiber and during collimation; (2) the variation in the intensity of collimated beam with distance; (3) the variation in the intensity of collimated beam with azimuthal orientation; (4) the external dimensions, so as to match standard industrial pressure transducer dimensions; (5) durability of the probes in withstanding high temperature and highly viscous molten polymer streams; (6) fouling on the surface of the probes both due to flowing polymer and deposition of the degraded polymer; (7) ability to withstand thermal cycling due to process startup and shutdown; (8) secondary containment of the probes, i.e. the maximum pressure that the probe body can withstand, before failure, if the lens is accidentally knocked off. Comments on the aforementioned evaluation criteria shall be described in the following paragraph.

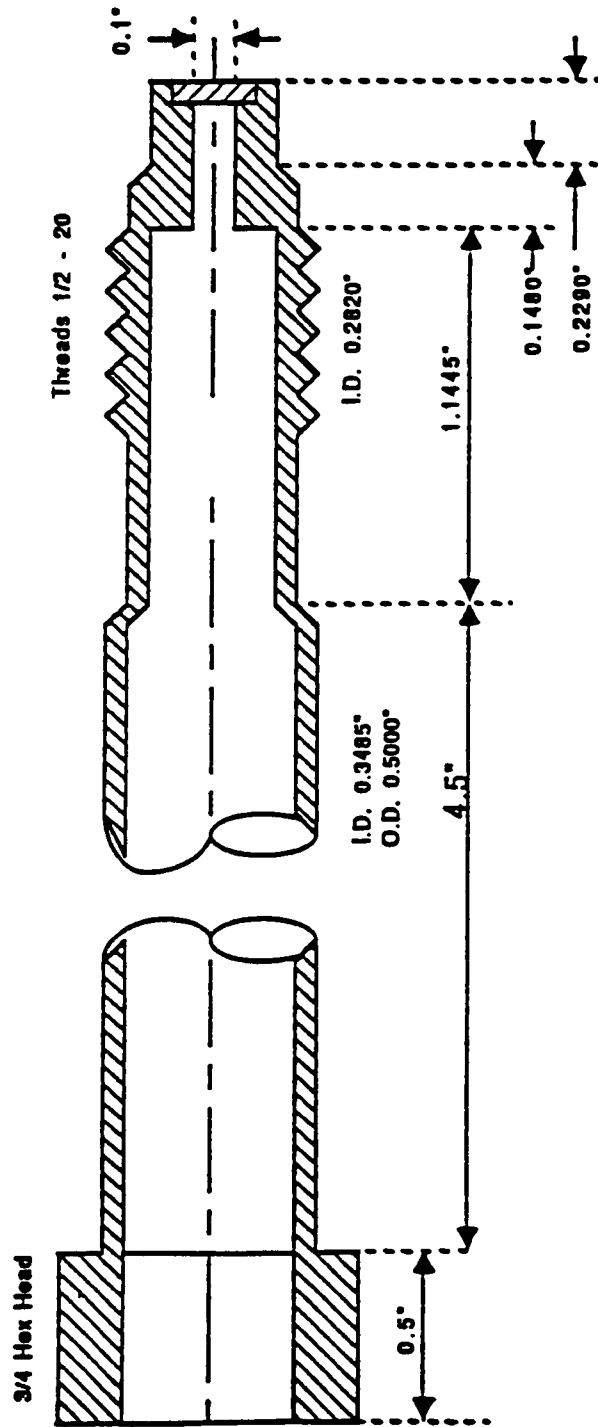


Figure 5.3 Schematic of Sensotron probe housing.

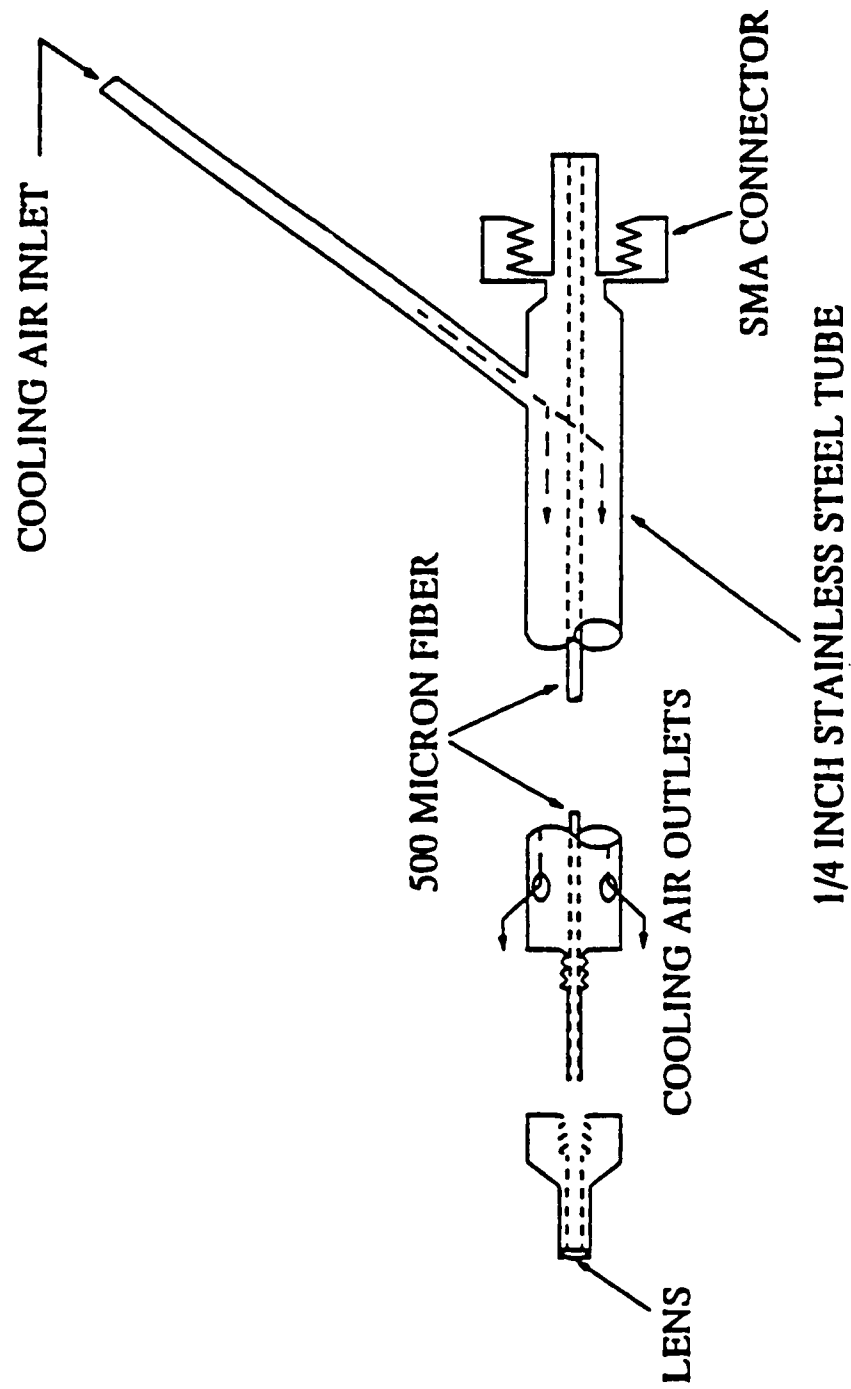


Figure 5.4 Self-designed fiber optics for Sensotron probe housing.

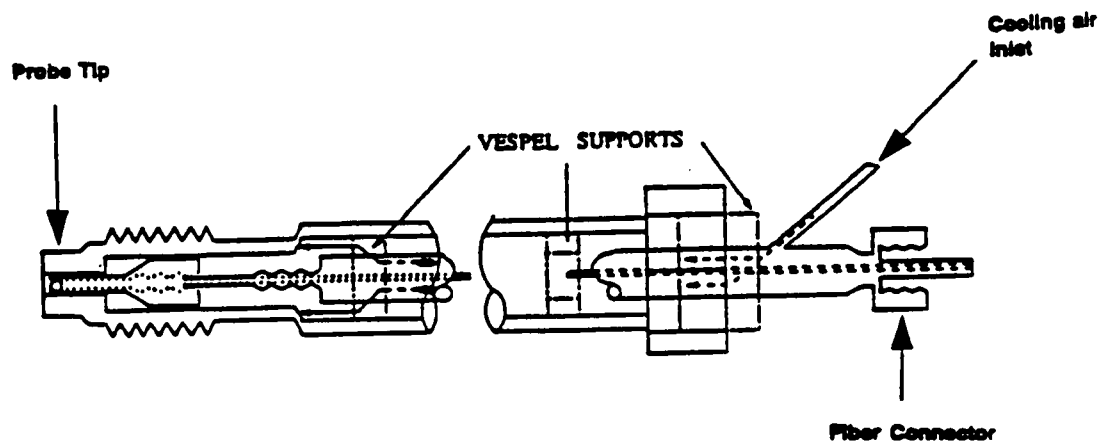


Figure 5.5 Composite probe using Sensotron probe housing and self-designed fiberoptics.

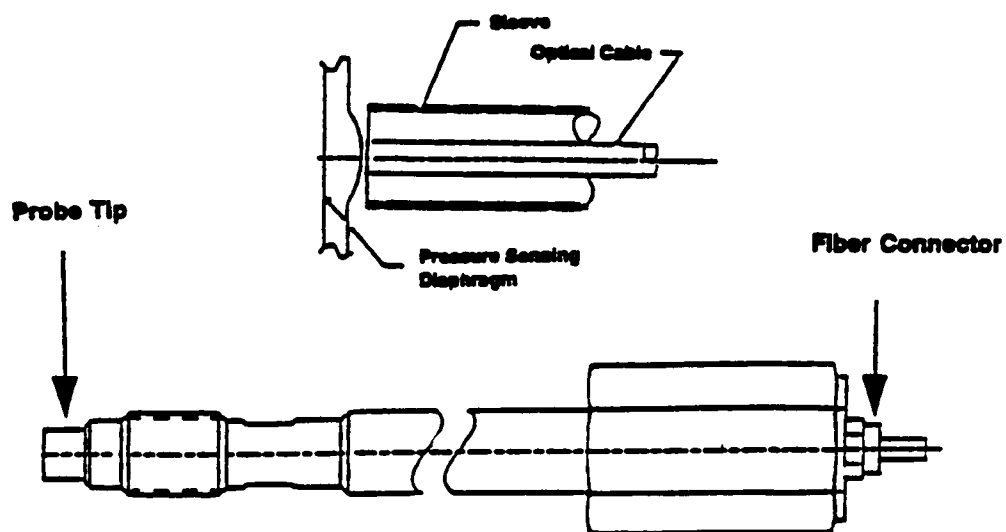


Figure 5.6 Commercial prototype of Sensotron NIR transmission probe. Inset shows details of the tip of the probe.

The transmission efficiency of the probes is calculated by measuring the ratio of the intensity of light passing through the probes and the fibers to the intensity of light passing through the fibers alone. The transmission efficiency of the probes has been found to vary between 20 % and 40%, which is comparable to standard commercial probes. Figure 5.7 shows a comparison of the transmission efficiency of two different sets of probes. The intensity of the collimated beam is almost uniform up to a maximum separation of 1 cm, which is perfectly suited for polymer samples. The variation of transmission with azimuthal orientation, was slightly present in earlier probe designs but has been eliminated in later versions. The external geometry of the commercial prototype of the probes has been made identical to that of standard commercial pressure transducers. The basic idea is that the probes should be such that they could be easily installed in the process stream by removing one or more pressure transducers. This flexibility would therefore obviate designing and machining of any special fixtures in order to install the probes. Figure 5.8 shows a comparison of the dimensions of Sensotron probes and standard industry dimensions. It can be seen that the Sensotron dimensions do match the industry dimensions, albeit with some tolerances that warrant slight modifications.

Evaluation criteria 5-7 are based on experiments with molten polymers. The durability of the probes, in terms of temperature, pressure and chemical environment, has been tested by working with a variety of polymers, among which the blends of polystyrene and polyphenylene oxide are the most notable. The probes have been tested up to a maximum temperature of 350 °C and a maximum pressure of 3000 psi (which is the maximum limit of the pressure transducers installed in the extruder). The probes have been tested for fouling concerns. It has been previously reported [90] that fouling is not a major concern with molten flowing polymers and hydrodynamically designed probes, because of the enormous shear stresses that are

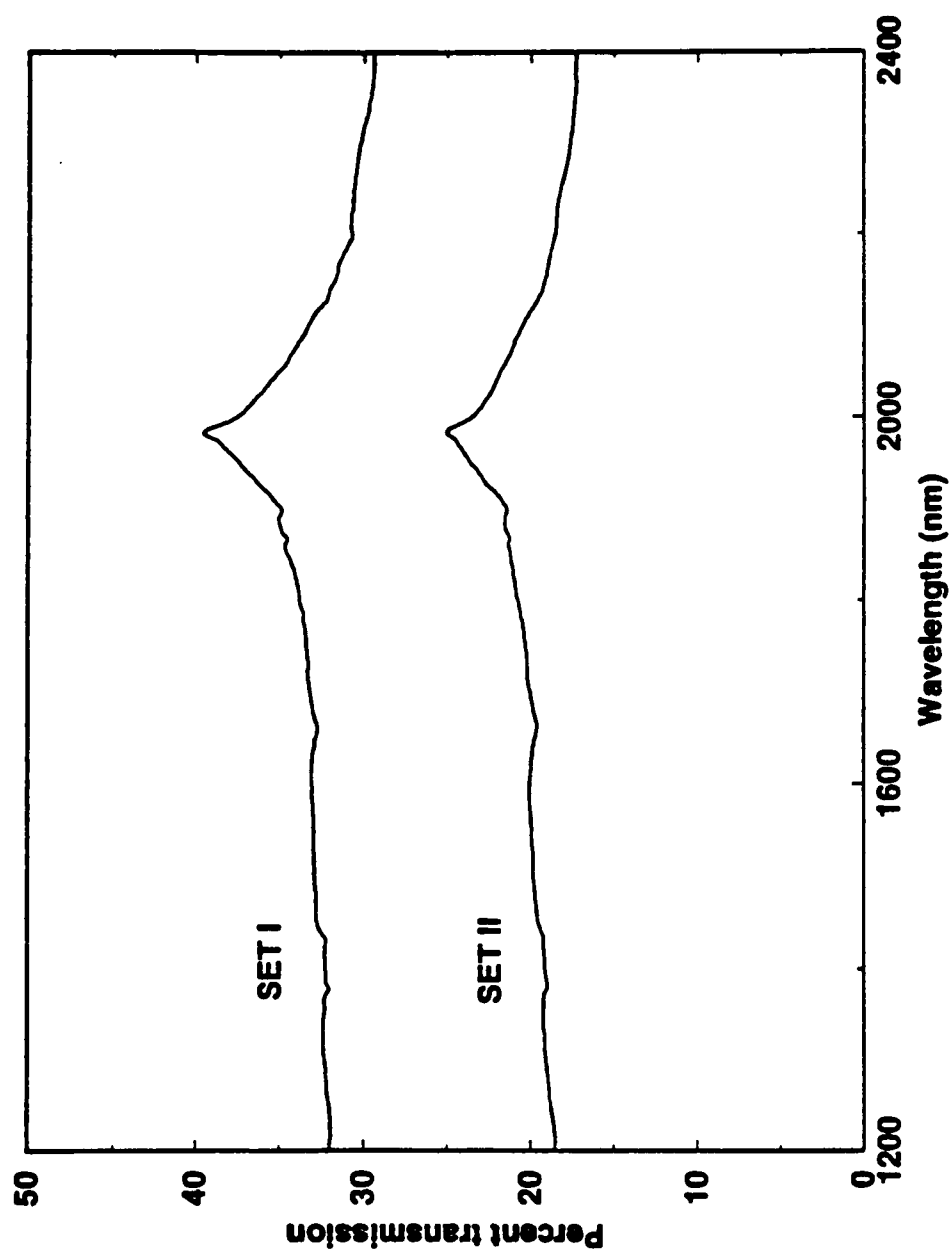
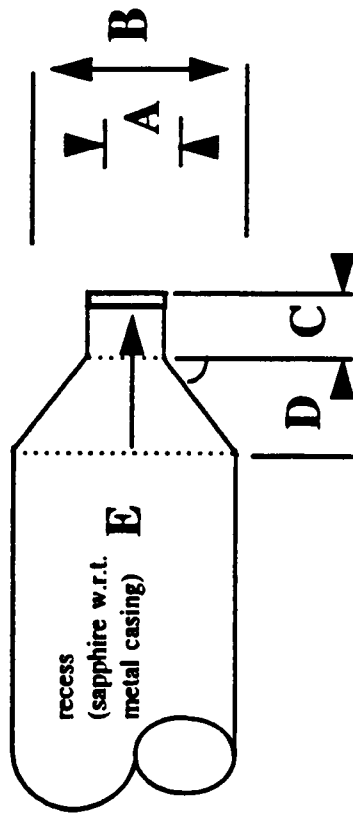


Figure 5.7 Comparison of the transmission efficiency of two sets of Sensotron probes.



Dimension	Standard Dimensions	Sensotron I	Sensotron II
A	0.305-0.307"	0.2912"	0.2918"
B	0.412-0.414"	0.3995"	0.3986"
C	0.214"	0.224-0.226"	0.2235-0.2265"
D	44.5-45.5°	45°	45°
E	-	-(0.0035 - 0.004)"	+(0.002-0.0035)"

Figure 5.8 Comparison of the dimensions of two Sensotron probes with standard dimensions.

present in the flow stream and the resultant scouring effects on the probe window. Furthermore, it was ensured that the sapphire window is not recessed with respect to the outer metal casing, which in turn may lead to deposition of polymer on the probe tip. During the course of the experiments, the probes have been retracted on many occasions, and the tips have been examined for any fouling effects. In all cases, it was confirmed that there was no buildup of material on the probe tip. Another major criterion in probes evaluation was to test the ability of probes in withstanding thermal cycling, without any mechanical failure. The probes have been tested both in continuous and intermittent operation. For example, in the case of PS-PPO blends the experiments were run continuously over a 24 hour time period, with temperatures varying in the range 250-350 °C. The second set of experiments were run following a gap of two days. The probes were able to withstand the thermal cycling due to process startup and shutdown.

Lastly, the probes have been tested for secondary containment. Secondary containment is a major concern in dealing with toxic process streams, where extreme care has to be exercised to avoid any leakage of the process fluid. In this respect, it was imperative to determine the maximum pressure that the steel body of the probes could withstand (once the sapphire window is accidentally knocked off in the process stream), before it ruptures and squirts the toxic fluid onto the process floor. It was found that the probe body could withstand a maximum pressure of 8000 psi before it ruptured. Such a pressure limit was deemed satisfactory.

6. NIR MONITORING OF POLYSTYRENE-POLYPHENYLENE OXIDE BLENDS

Introduction:

PS can be blended with PPO over a wide range of ratios, and variations of these blends are available commercially [91]. Owing to its low T_g (104 °C), PS provides excellent melt flow characteristics but reduces the heat distortion temperature of the blend. PPO with its high T_g (208 °C) increases the heat distortion temperature of the polymer blend but also increases the melt viscosity of the blend. PPO has better flame retardant characteristics than polystyrene. Thus the properties of the two polymers result in the blends having a wide range of physical properties, high heat resistance, and flame retardancy. The products have a number of properties and are used in a variety of applications such as appliances, business machines, and industrial equipment.

Experimental:

In our series of experiments the PPO composition was varied from 0 wt. % (i.e. pure PS) to 85 wt. % in increments of 5 wt. %. This range covers nearly all ratios of PS/PPO used for commercial blends and provided us enough samples to build a sound calibration model. Precisely because of the above reasons, blend compositions greater than 85 wt. % were not run through the system. However, the spectrum of pure PPO was obtained using compression molded films.

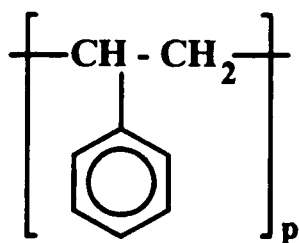
PS was available in pellet form and was ground to a fine powder using a grinder. This was done to ensure proper mixing with PPO powder. The two powders were mixed in a tumble type mixer. The spectra were collected in the wavelength range 1200-2400 nm with a step size of 1 nm and a spectral average of 2 (i.e. 2 scans

per spectrum). The entire range of compositions was run at four temperature setpoints. Samples containing 0% - 20% PPO were extruded at 250 °C, samples with 25% - 45% PPO at 275 °C, samples with 50% - 70% PPO at 300 °C and samples with 75% - 85% PPO at 325 °C. Actual temperature of the molten polymer stream was recorded using the thermocouple in the flow cell. The downstream pressure in the flow cell was about 1000 psi. Each polymer was run for 1 hour approximately. This allowed flushing of the preceding sample and stabilization of the spectra with good reproducibility. Spectra of each sample were saved after each sample scan had stabilized. A constant pathlength of 2 mm was used throughout the experiments. This ensured that the maximum absorbance was less than 1.0 absorbance unit. Since the polymers were completely miscible in one another, there were no scattering effects.

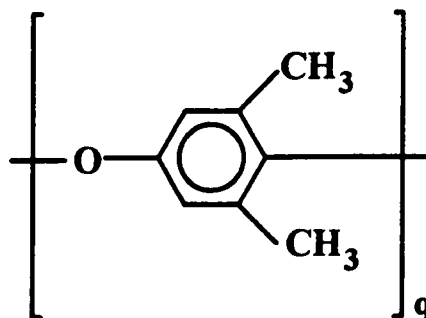
Results & Discussion:

The usefulness of the NIR region for qualitative analyses is limited owing to the complexity of information available. The harmonics of the fundamental bands and their combinations give rise to broad bands with considerable overlap. Hence band assignments in the NIR region are always tentative. Nevertheless, they complement the quantitative analyses and improve our understanding of the polymeric process.

Fig. 6.1 shows the chemical structures of polystyrene and polyphenylene oxide. Fig. 6.2 shows the overlaid spectra of PS and PPO films. There are two main regions of interest in the spectra. The first region comprising wavelengths 1500-1900 nm contains mainly the first overtones of the C-H stretch vibrations, while the second region comprising wavelengths 1900-2400 nm contains combination bands arising from C-H stretch and other principal modes of vibration [9]. In the spectrum



Polystyrene



Polyphenylene oxide

Figure 6.1 Chemical Structures of polystyrene (PS) and polyphenylene oxide (PPO), where p and q represent the number of repeat units in PS and PPO, respectively.

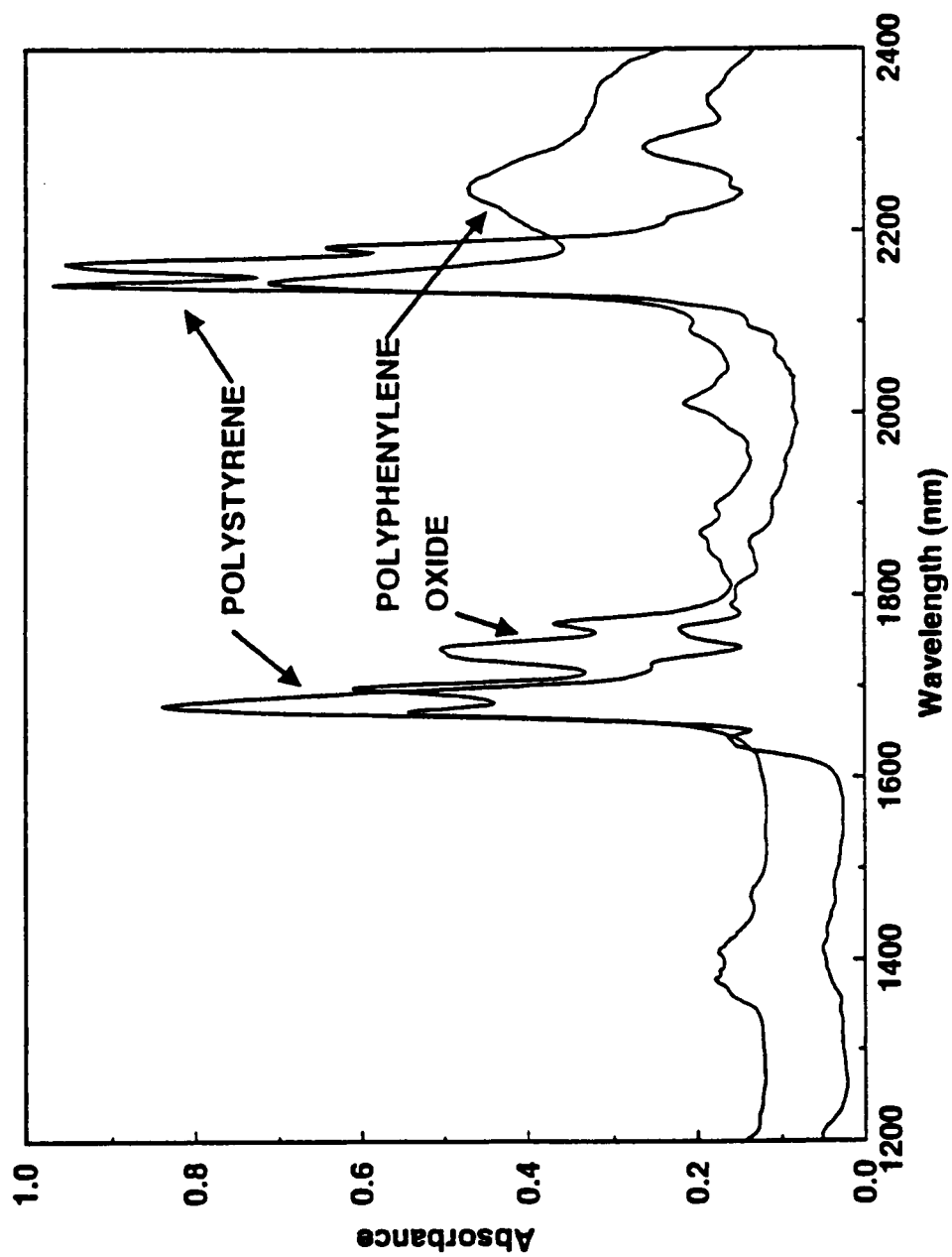


Figure 6.2 Spectra of PS and PPO films, overlaid on one another.

of PS the peaks at 1680 nm and 2167 nm can be tentatively assigned to the first overtone and combination bands of aromatic C-H group respectively [29,31]. The smaller peaks at 1763 and 2289 nm can be tentatively assigned to the first overtone and combination bands of the methylene group in PS respectively [29,31]. In the spectrum of PPO the peaks at 1674 nm and 2148 nm can be tentatively assigned to the first overtone and combination bands of aromatic C-H group respectively, while the peaks at 1739 nm and 2233 nm can be assigned to the first overtone and combination bands of the methyl group respectively [31]. Thus it can be seen that there are distinct differences in the spectra of these two pure polymers, which suggests that the spectra of blends would reflect these differences.

Figs. 6.3 and 6.4 show the overlaid spectra of blends in the overtone and combination regions, respectively. In both the regions there is a systematic evolution of PPO peaks with increasing PPO concentration. In the overtone region as PPO concentration increases, the aromatic C-H peak of PS at 1680 nm gradually diminishes in intensity and is gradually replaced by the aromatic C-H peak of PPO at 1674 nm. The methylene peak of PS at 1763 nm is replaced by the PPO methyl peak at 1739 nm. Similar changes can be observed in the combination region. With increase in PPO concentration, the aromatic C-H combination band of PS at 2167 nm gradually diminishes and is replaced by the aromatic C-H combination band of PPO at 2148 nm. Similarly the methylene combination band of PS at 2289 nm is gradually replaced by the methyl combination band of PPO at 2233 nm. This kind of systematic variation, which is visually quite clear, can be effectively modeled using multivariate analysis.

Ten spectra for each blend composition (i.e., a total of 180 samples for the eighteen blend compositions) were used as the initial data set. All these spectra were corrected for baseline offsets, using the absorbance at 1550 nm, and visually

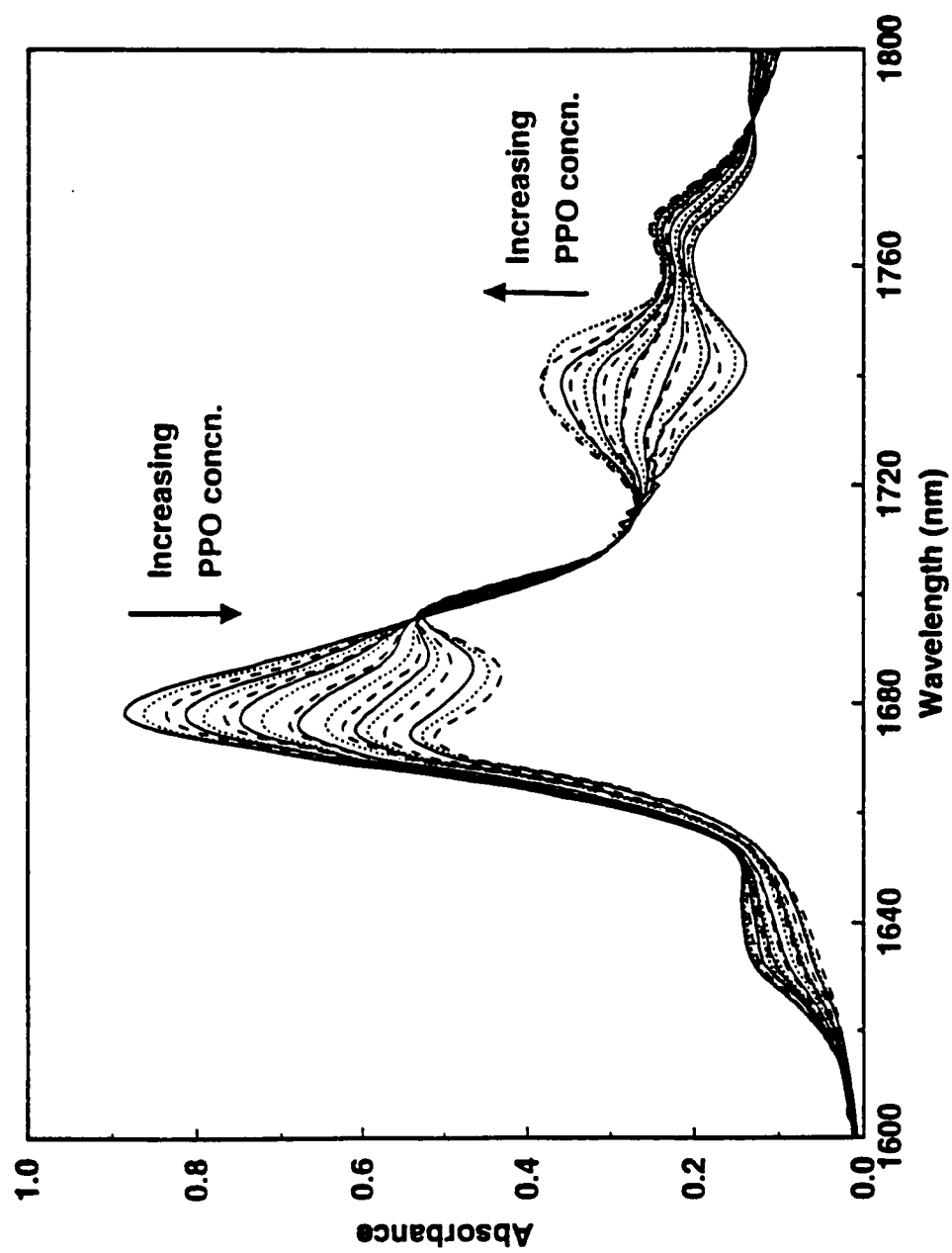


Figure 6.3 Spectra of blends, in the wavelength range 1600-1800 nm.

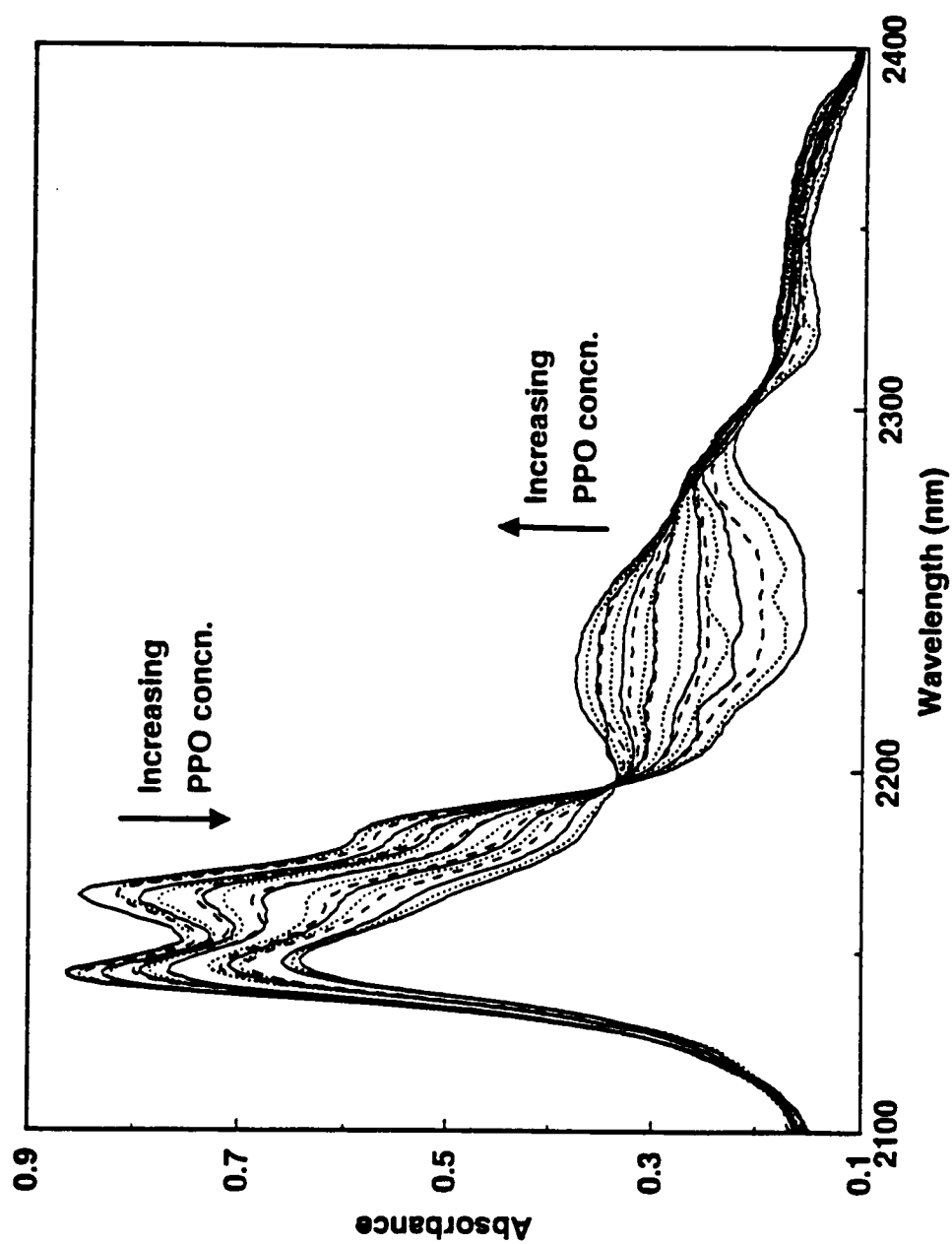


Figure 6.4 Spectra of blends, in the wavelength range 2100-2400 nm.

examined. Fifty-six samples were rejected because they could be identified as outliers. This is mainly due to the fact that there is a certain degree of variability attached to dry powder mixing and as such the composition is not uniform. Thus, 114 samples were finally chosen for multivariate data analysis. Eighteen samples with one representative of each concentration were chosen to constitute the calibration set, while the remaining 96 samples constituted the test or validation set.

First, the overtone region was used for multivariate analysis. The absorbance data constitute the X matrix while the concentration data constitute the Y matrix. For the absorbance matrix, wavelengths in the range 1600-1800 nm (i.e., 201 wavelengths) were chosen, with temperature included as an extra predicting variable. Temperature changes cause a change in absorbance spectra because of the resultant density variations and changes in the refractive index. Temperature effects can be either discarded (leaving the model to identify them as interferences) or used in calibrations by including temperature as an additional predicting variable [10].

The data set was standardized using mean centering and normalization with respect to column standard deviation, which gave equal variance to each variable. The standardized data set was finally used for PLS calibration. The variance accounted for by the model with increasing number of factors is shown in Table 6.1. It can be seen that only 88.38% of the X variance is modeled after one factor. Because this is a binary system, we are reasonably certain that the data set has only one factor of variation, and as such one factor should account for most of the variance in the X data. In order to determine the contribution of individual original laboratory variables in the model, the percent explained variance of each laboratory variable with modeling by just one principal component was calculated. This has

Table 6.1 Variances explained by the model with increasing factors

Factors	Before Weighing		After Weighing	
	X Block	Y Block	X Block	Y Block
1	88.3786	99.8455	98.2434	99.8775
2	92.9024	99.9050	99.1373	99.8962
3	94.3936	99.9460	99.2932	99.9477
4	95.8137	99.9597	99.5033	99.9597
5	97.4602	99.9675	99.6028	99.9786

been plotted in Fig. 6.5. It was determined that for 32 variables out of the 202 variables, less than 90% of the variance was accounted for after one factor, and that these variables had a higher residual standard deviation than the total residual standard deviation. Because these variables could not be adequately accounted for after one factor, we decided to down weigh them (i.e. reduce their contribution in the model) and see the effect on the calibration model. Here a weight of 0.1 was given to these 32 variables in the standardized data set, against a weight of 1.0 for all other variables, and the calibration model was developed again. Table 6.1 shows the overall variances accounted for by the model after weighting. This time it can be seen that the model explains 98.24% of the X variance after one factor, with a fractional improvement in the Y explained variance too. This reinforces our initial observation that the data has inherently one factor of variation. However, some more tests were performed to validate the model and to determine the optimal number of factors. The model was cross validated [10] using two approaches. In the first approach (leave-a-sample - LAS) the data set was calibrated 18 times, with one sample being removed each time and then the model being used to predict its concentration. The PRESS value for each sample at each factor was calculated using its predicted value when it was not included in the calibration, and the cumulative PRESS value at each factor was obtained by summing up the individual PRESS values at that factor. The PRESS plot in Fig. 6.6 shows that the PRESS is a minimum at one factor. In the second approach the data set was split into two groups (leave-a-group - LAG) using even-numbered and odd-numbered objects, and the calibration was done twice using one group for calibration and the other for prediction. This approach also gave one factor, as can be seen by the PRESS plot (Fig. 6.6).

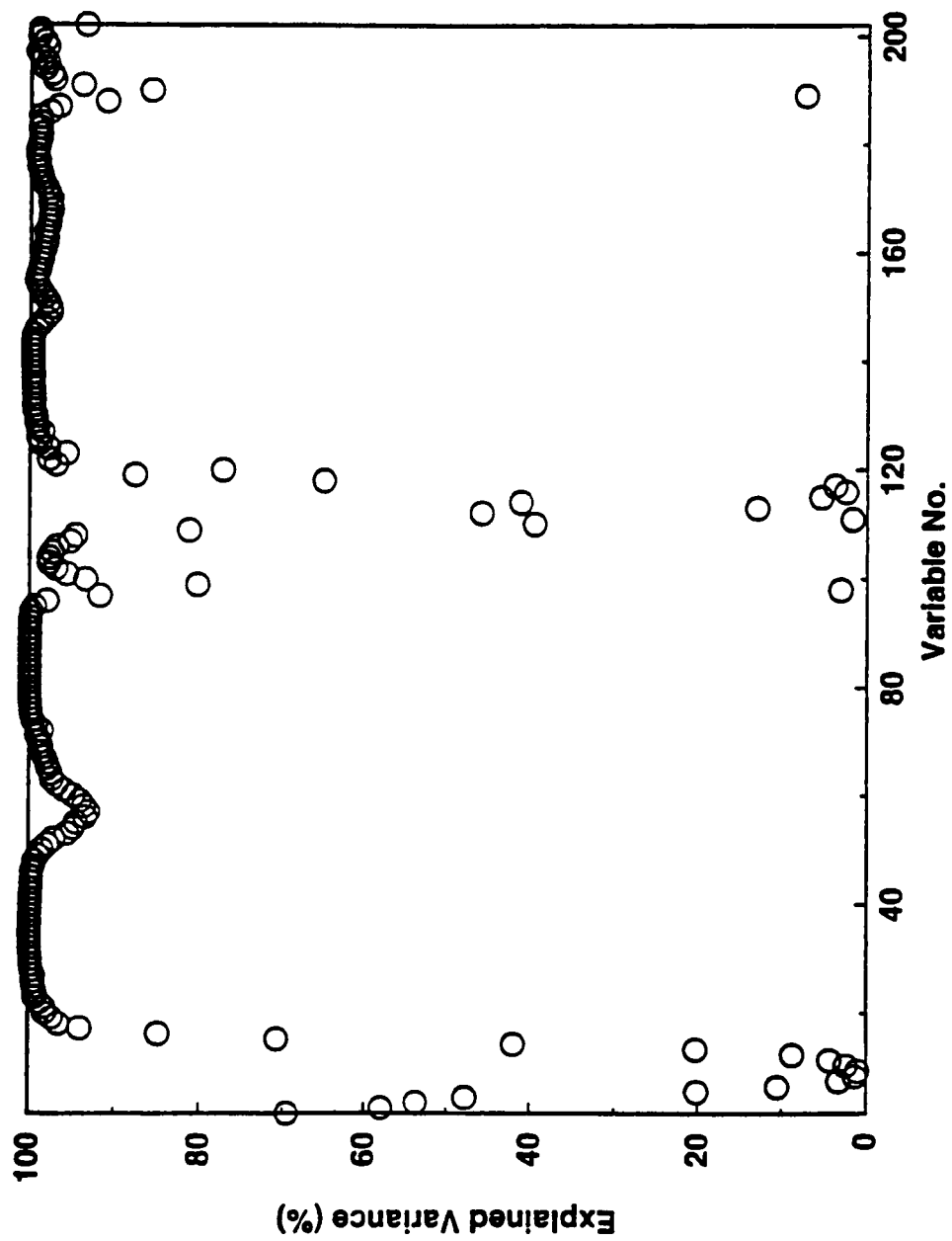


Figure 6.5 Variances explained by individual variables after 1 factor (before weighting).

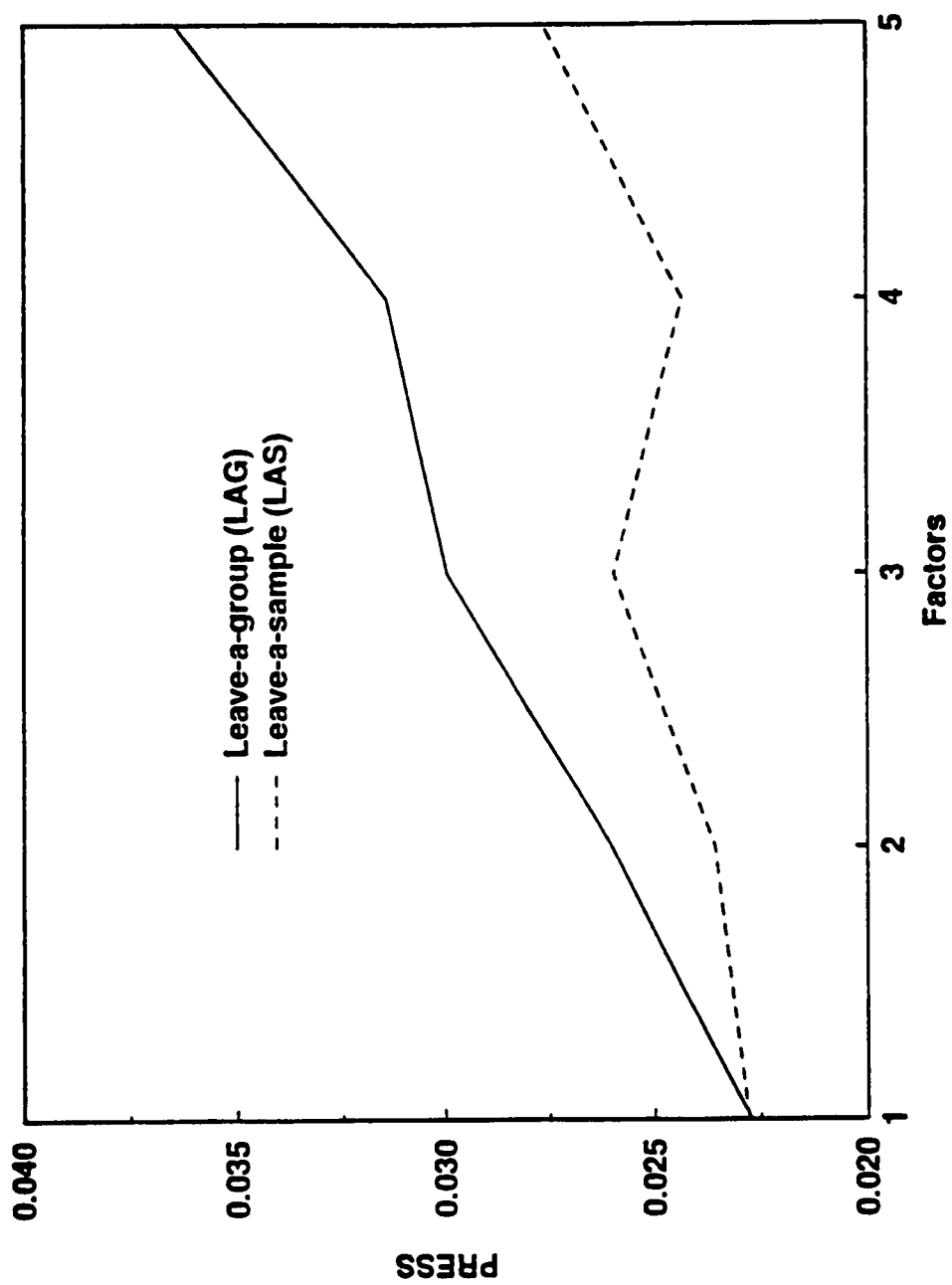


Figure 6.6 PRESS plots for cross validation.

Now that we were convinced that the data set had indeed one factor of variation, the ultimate test of robustness was to use our model on a test set. This was done using our previously described test set consisting of 96 samples. The SEP of the test set was calculated for 1-5 factors and plotted in Fig. 6.7. The SEP is a minimum at one factor and is equal to 0.95 wt. % PPO, and the SEC is 0.93 wt. % PPO. This supports the choice of factors and the accuracy of the prediction model.

Finally, the predictions of the model for the calibration samples and the test samples have been shown as scatter plots in Figs. 6.8 and 6.9. From the SEP values and the scatter plot, it can be concluded that the calibration model is robust and has sound predictions.

To gain some qualitative insight into this calibration model, the loadings and scores [10] vectors for this factor were plotted. The loadings give the relation among the variables in the model, while the scores give the relation among the objects. The loadings plot for the first factor, as shown in Fig. 6.10, has broad bands instead of sharp peaks. This can be explained by the fact that the data were standardized prior to calibration and all variables were brought to equal variance. This plot helps us to identify the variables which are positively and negatively correlated to the concentration of PPO. However, a better understanding of the loadings spectrum can be derived by descaling with respect to the standard deviation. The descaled loadings vector is plotted in Fig. 6.11. The positive peaks around 1700, 1740, and 1770 nm are PPO peaks (Fig. 6.3) and thus have positive loadings. The negative peak at 1680 nm is the PS aromatic C-H first overtone, which decreases with increasing PPO concentration. Although PPO also has its aromatic C-H first overtone in this region, the intensity of PS peak is higher, and thus there is an overall decrease in peak height as seen in Fig. 6.3. The scores plot shown in

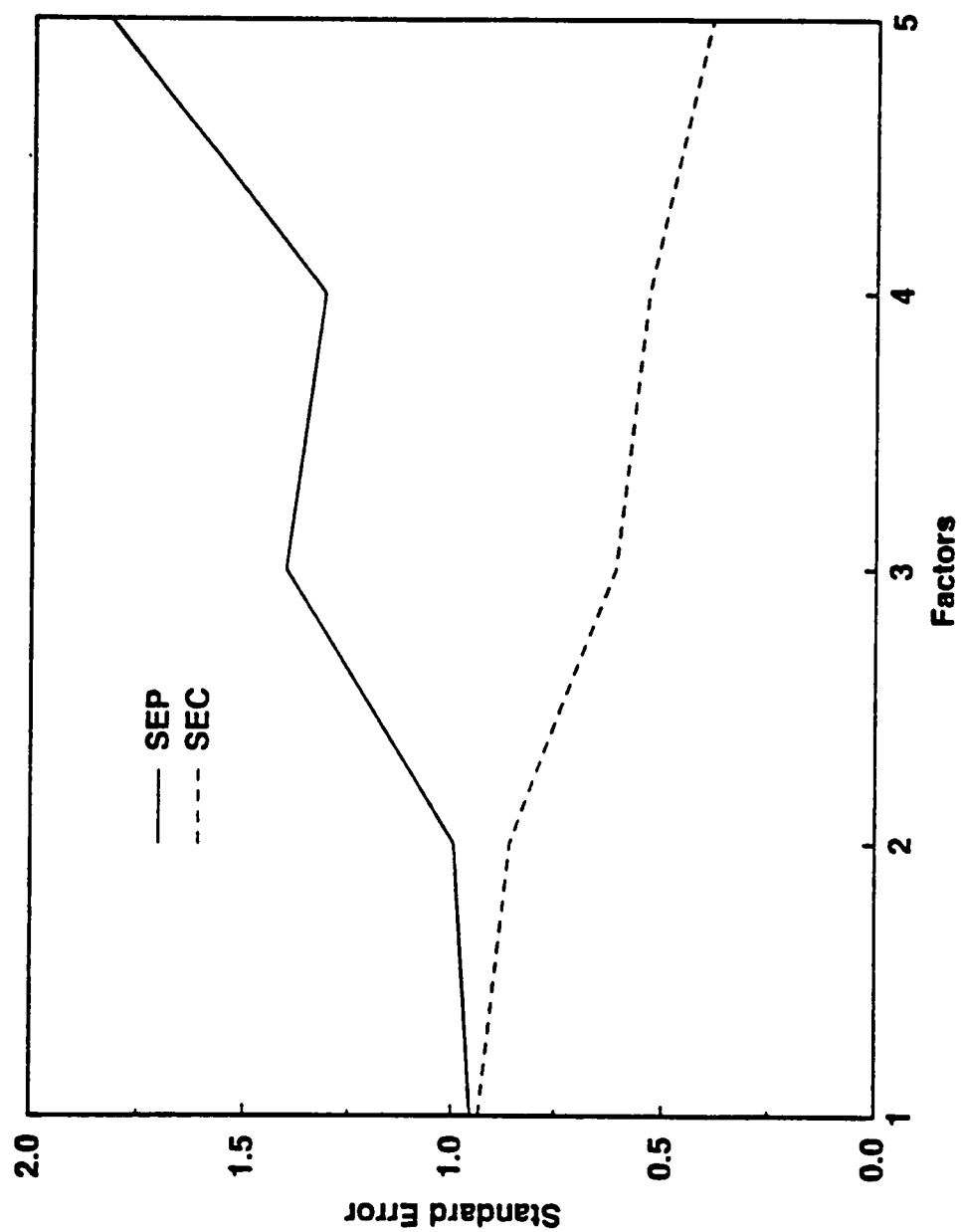


Figure 6.7 Plot of SEP and SEC, versus number of factors.

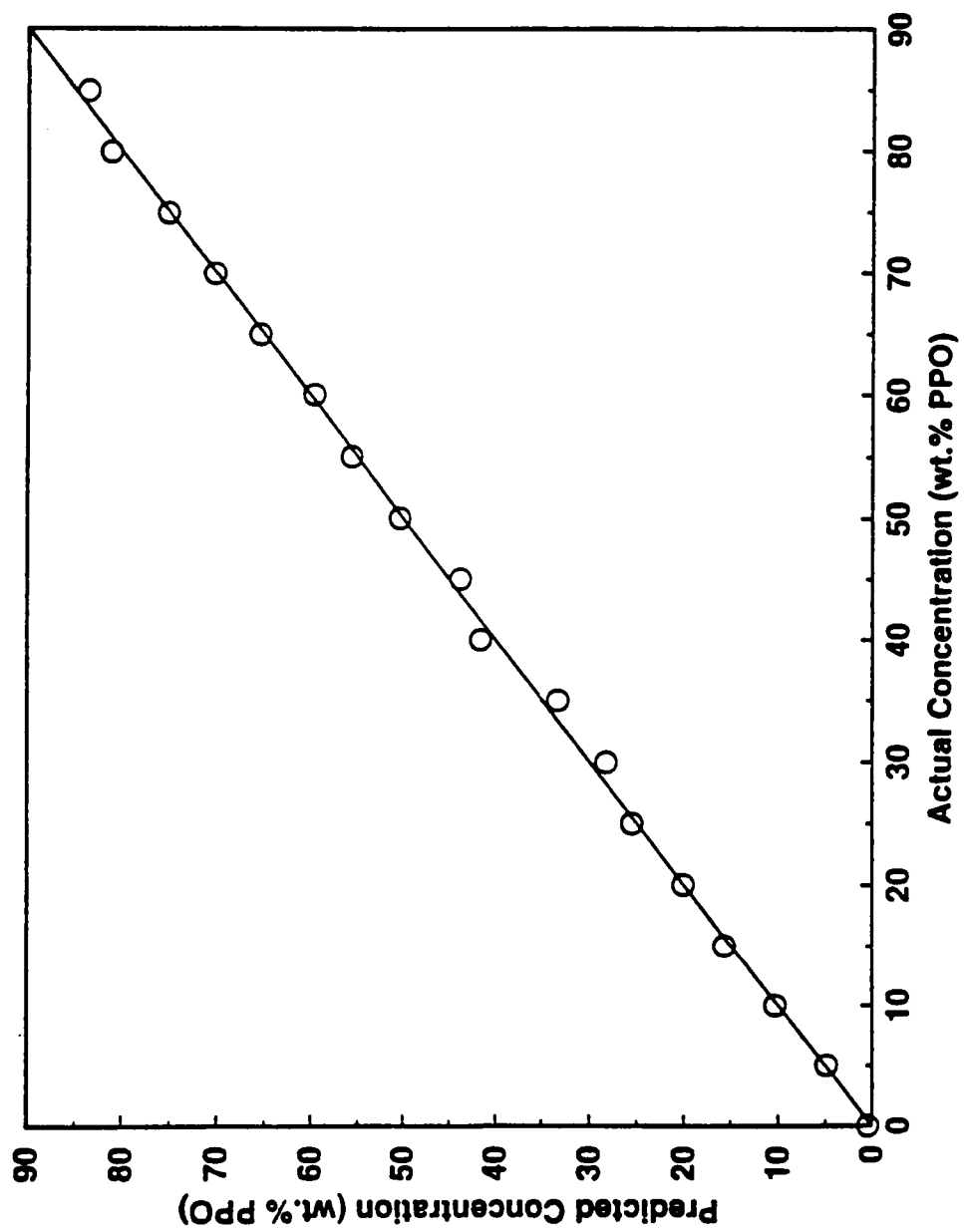


Figure 6.8 Predictions of model for samples in calibration set.

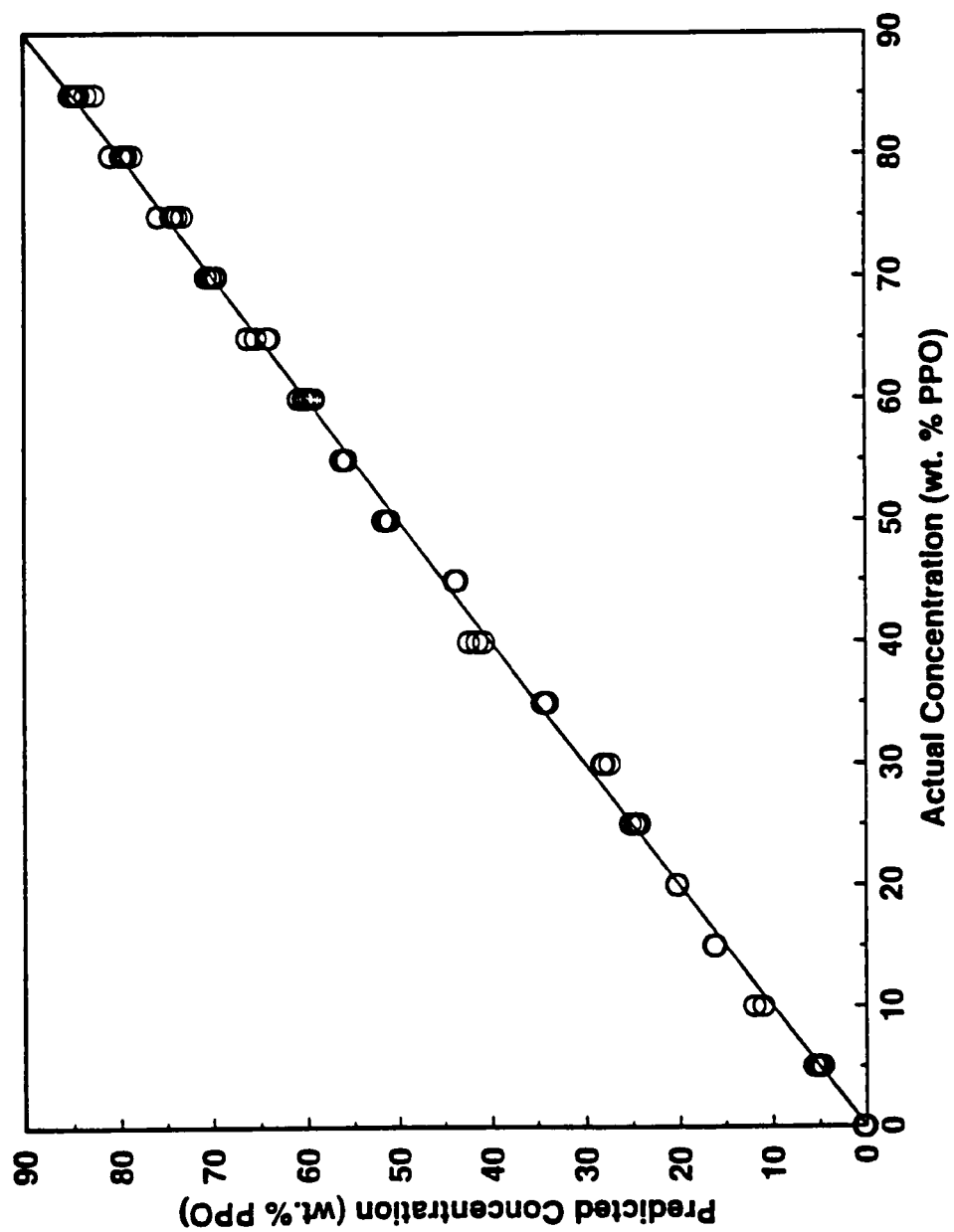


Figure 6.9 Predictions of model for samples in validation set.

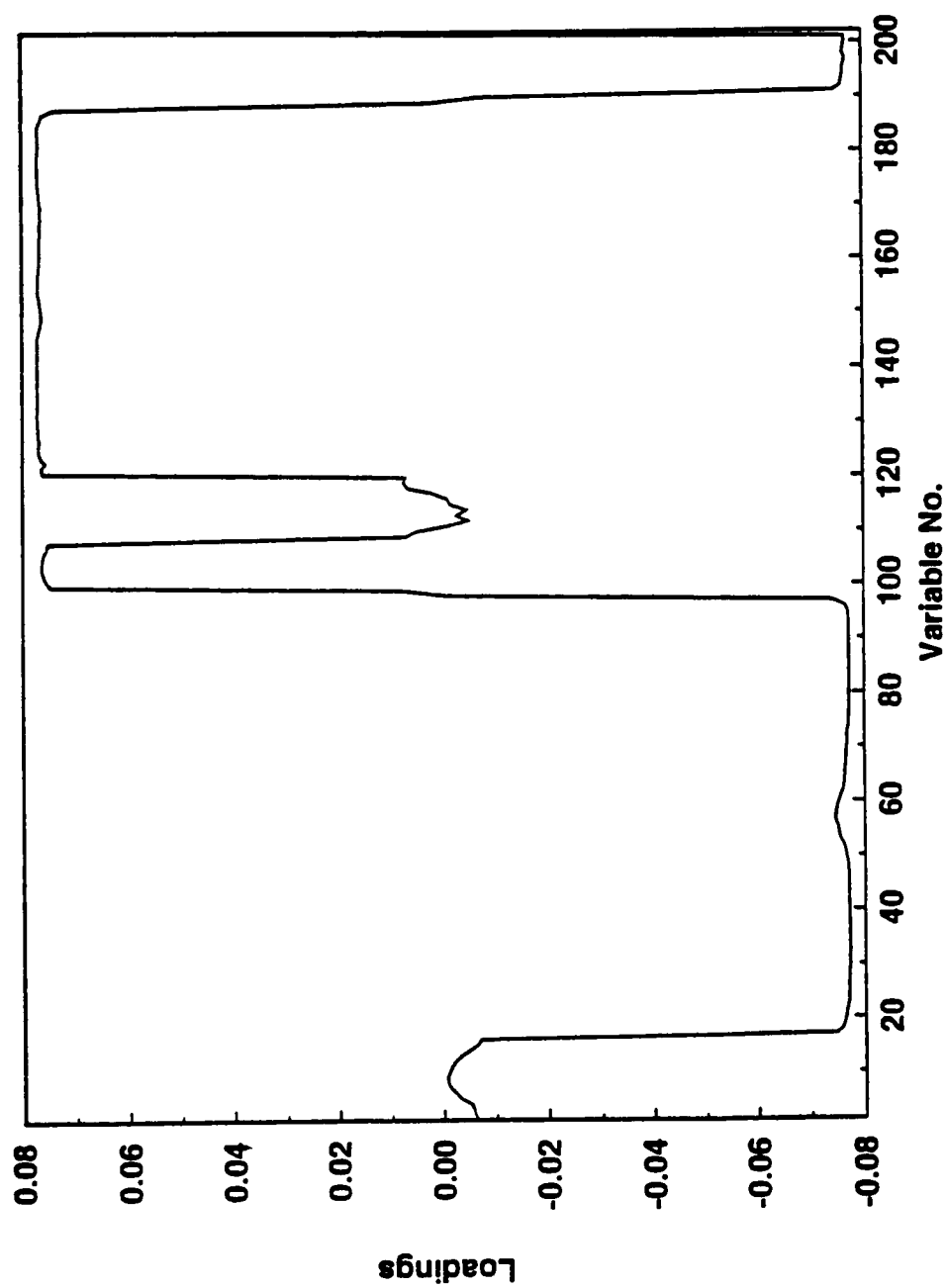


Figure 6.10 First factor loadings spectrum for scaled data set.

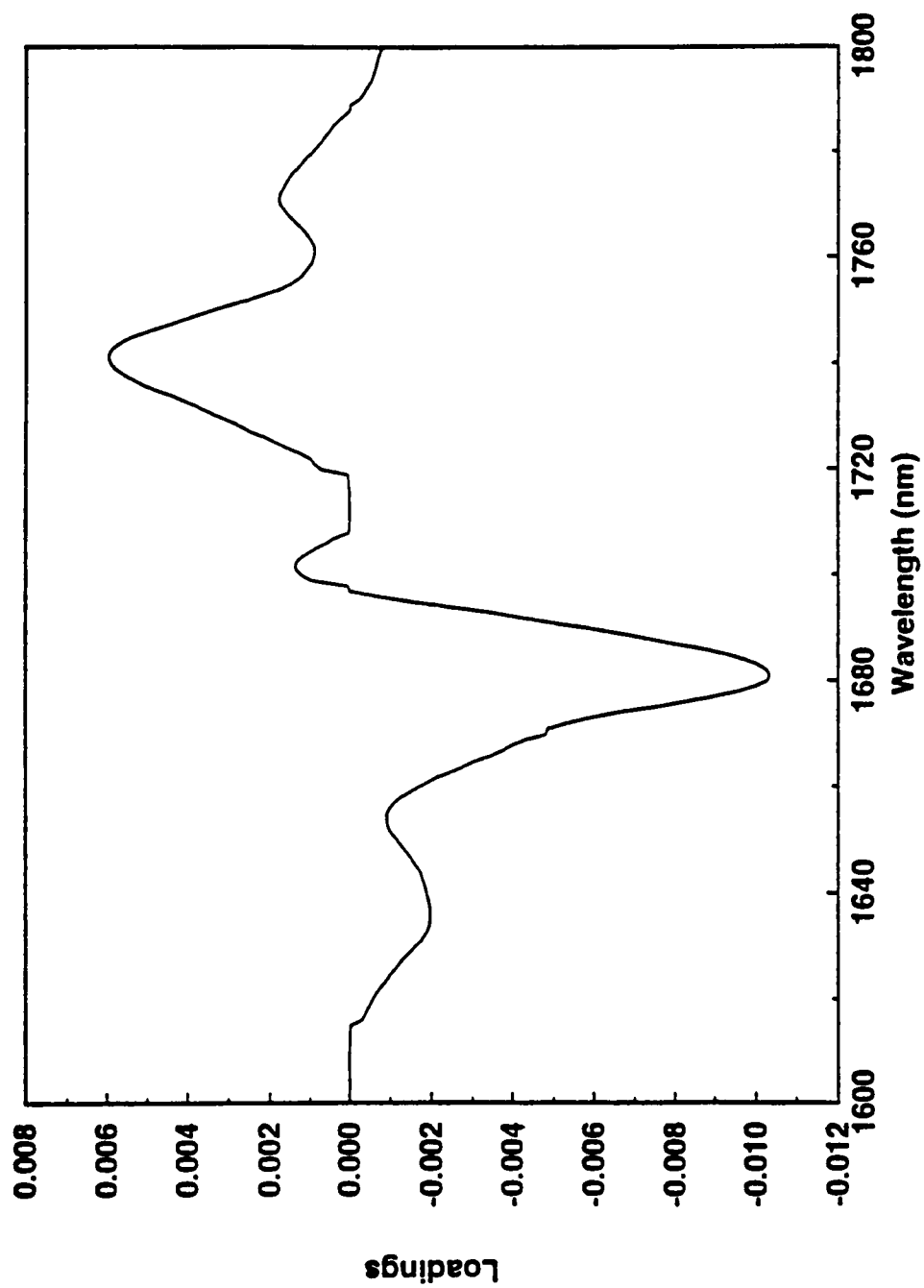


Figure 6.11 First factor loadings spectrum, after rescaling back to raw data.

Fig. 6.12 has two salient features. It shows increasing object scores with increasing PPO concentration, and it shows that all the 18 samples can be clustered in one group. This implies that the first factor adequately describes the relationship among the various samples, and that the first factor is positively correlated to the variation in PPO content.

In the combination region, similar tools as described above were used. However, here a lesser number of wavelengths (2050-2130 nm) was used. After one factor, 96.94% of the X data variance was explained, which was improved to 98.87% after down weighing four variables. Cross validation and external validation using the test set yielded 1 factor. Table 6.2 summarizes and compares the results of the two regions. It can be seen that the predictive abilities of both regions are quite comparable.

Our discussion about multivariate analysis shall be incomplete without mentioning the use of derivative spectra. Derivative spectra offer the advantage of removing baseline offsets and sharper features due to peak deconvolution, but they suffer from some drawbacks. They are very noisy even after repeated smoothing. Further, it is difficult to extract qualitative information from the loadings and scores plots. Second derivative spectra were used on these data sets, but the SEPs were higher.

Conclusions:

NIR spectroscopy, fiberoptic cables, robust optical probes, and multivariate analysis make in-line monitoring of molten polymers feasible. It has been shown that the composition of two mutually soluble and non-reacting polymers can be easily monitored in-line. In spite of variation in composition owing to mixing of polymers, the calibration models have low standard-errors-of-prediction. It leads us

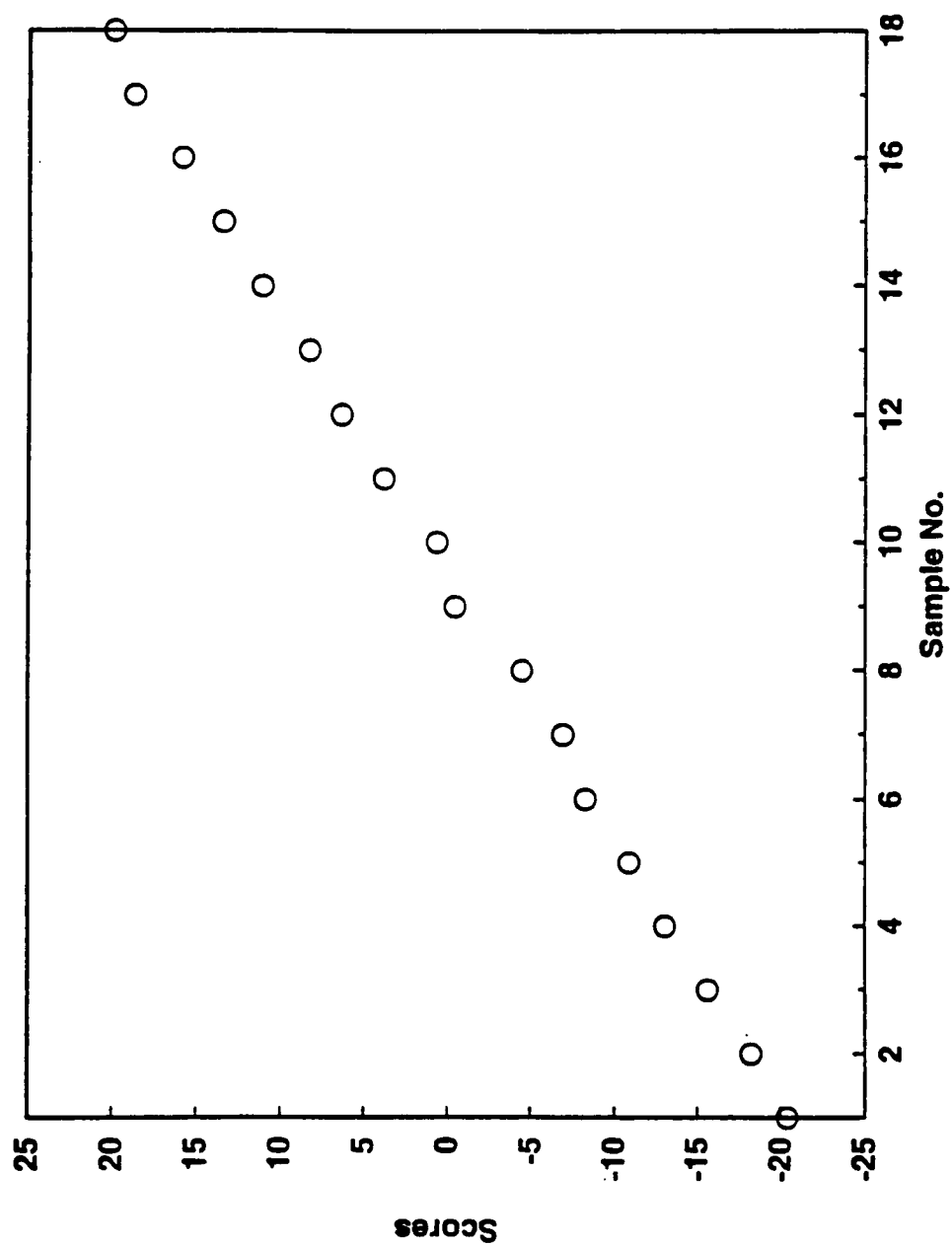


Figure 6.12 Scores plot for first factor.

Table 6.2 Comparison of predictions in the overtone and combination regions

Factors	Overtone Region		Combination Region	
	SEC	SEP	SEC	SEP
1	0.9341	0.9537	0.9013	1.0253
2	0.8601	0.9962	0.8751	1.0262
3	0.6104	1.4015	0.7993	1.0260
4	0.5361	1.3112	0.6675	1.1731
5	0.3904	1.8235	0.4592	1.6009

to conclude that the predictions would improve by using samples of uniform composition or by determining the actual concentration of the extrudate through a laboratory method.

Probes have performed satisfactorily during these evaluations. They have been tested to a maximum of 350 °C using a PS-PPO blend containing 85% PPO. At this temperature the PS in the blend degraded, leading to a lot of scattering and a noisy spectrum, but still without any negative effect on the probes. Further tests would involve going to higher temperature and pressure.

7. NIR STUDY OF EVA RANDOM COPOLYMERS

Introduction:

Poly(ethylene vinyl acetate (EVA) copolymers are random copolymers that are obtained by the copolymerization of ethylene with vinyl acetate under high pressure. The incorporation of vinyl acetate (VA) reduces the crystallinity of the polymers, which in turn improves their flexibility, clarity, and impact strength, and reduces the hardness. Variations in the concentration of vinyl acetate lead to variations in the properties of EVA copolymers, which are used for a variety of applications [92]. Polymers with low concentrations of VA (less than 20 wt.%) are primarily used to make extruded film for flexible packaging. The rubber-like properties of the polymers are used in applications such as bumper pads, flexible toys, etc. Concentrations of VA greater than 20 wt.% are mainly used as hot melt adhesives by further mixing the copolymers with waxes and tackifiers. Thus, the properties of the polymers are largely dependent on the concentration of vinyl acetate in the polymer. For quality control purposes, it is therefore imperative that the VA concentration be monitored.

7.1 Experiments - EVA copolymers with varying VA concentration, and using 2.5 mm pathlength:

Experimental:

The copolymer samples were obtained from two sources and shall be referred to henceforth as Class I and Class II. Class I comprises sixteen samples of EVA copolymers and Class II comprises eight samples of EVA copolymers. The existence of two separate sets of polymer samples provided the advantage of preparing the calibration models on one set of polymer samples and using the second set as an

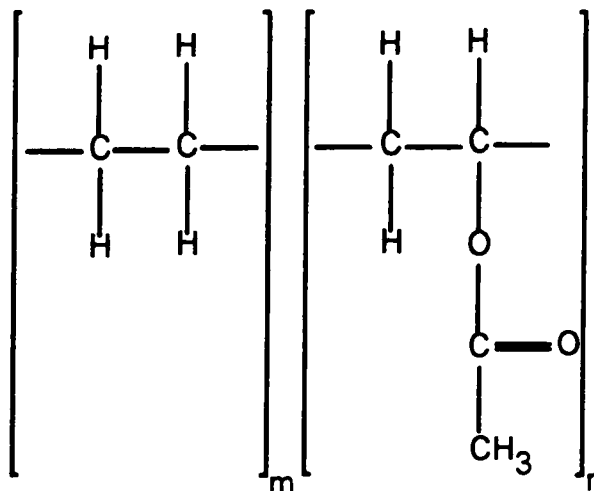
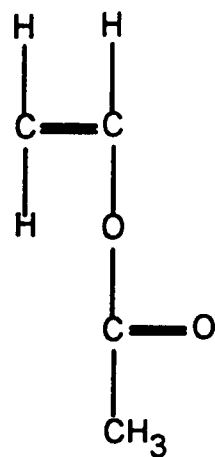
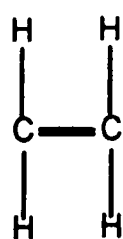
independent test set to validate the precision of the calibration models. The sixteen samples of Class I actually comprised nine target concentrations (0, 9, 12, 15, 18, 25, 28, 32, and 36 wt.% VA). The eight samples of Class II actually comprised four target concentrations (19, 21, 27, and 35 wt.% VA). The actual concentrations of vinyl acetate in the twenty four samples has been tabulated in Table 7.1. The chemical structure of the copolymer is illustrated in Fig. 7.1. The melting point of the EVA copolymers lies in the 103°C-108°C temperature range. Processing temperatures range from 150 °C to 210 °C.

The first set of experiments was performed using a fixed pathlength of 2.5 mm. This pathlength ensured that the maximum absorbance, over the full range of the spectrum (i.e., 1200-2400 nm), would be less than 1.0 AU. The main reason for working with absorbances in the range 0-1 AU is to preserve the linearity of Beer's law. Absorbances greater than 1.0 AU mean that the overall transmittance is less than 10%. All polymer samples were extruded at a fixed setpoint of 200 °C. The screw speed (20 rpm) and flow rate (1.2 lb./hr) were kept fixed for all except three of the samples (samples 10, 12, and 13 of Class I). These three samples had a very high melt index and had to be extruded at a higher flow rate (2.4 lb./hr) in order to prevent the polymer flow stream from draining out of the flow cell and forming bubbles in the optical measurement beam. The maximum pressure attained downstream of the gear pump was about 1400 psi. A continuous purge of dry nitrogen gas in the hopper prevented any moisture absorption from the ambient atmosphere. The spectral data for the two sets of polymers were collected on two separate days.

Table 7.1

Details of the EVA samples, with varying VA concentrations.

Class I		Class. II	
Sample Number	Wt.% VA	Sample Number	Wt.% VA
1	0	1	18.72
2	9.08	2	18.82
3	9.11	3	21.01
4	12.12	4	20.90
5	12.04	5	26.70
6	15.18	6	26.87
7	17.91	7	34.80
8	18.06	8	34.95
9	24.89		
10	25.22		
11	28.49		
12	27.84		
13	28.59		
14	28.37		
15	32.05		
16	35.57		



Ethylene

Vinyl Acetate

EVA - Random Copolymer

Figure 7.1 Chemical structures of ethylene, vinyl acetate, and EVA copolymer

Results and Discussion:

Figure 7.2 shows the overlaid spectra of polyethylene (PE) and EVA containing 28 wt.% VA. The spectrum of pure polyvinyl acetate (PVA) has also been overlaid on the spectra in order to determine spectral features that could be attributed to vinyl acetate. The structure of the copolymer (Fig. 7.1) shows that although both the comonomers have C-H vibrations, the vibrational overtones and combinations of the C=O stretch, if identifiable and distinct, could be used to quantify the amount of VA present.

A closer look at Fig. 7.2 shows that there are some changes in two spectral regions: (i) spectral region A, which comprises wavelengths 1600-1950 nm, contains the first overtones of the C-H vibrations [4,5,9]; and (ii) spectral region B, which comprises wavelengths 2000-2200 nm, contains combination bands [4,5,9]. These two regions have been enhanced in Figs. 7.3 and 7.4, respectively. Spectral region A shows that the incorporation of VA leads to a decrease in the intensity of the polyethylene doublet around 1700 nm. This doublet in polyethylene is probably due to the methylene stretch [9]. With the incorporation of VA in the chain, there is a decrease in the overall methylene content that leads to a decrease in the intensity of the methylene doublet. The presence of VA also leads to subtle changes in the slope of methylene doublet. Furthermore, there is a small peak at about 1680 nm that evolves with the increase in VA concentration. This peak is also present in the spectrum of pure PVA and is absent in the spectrum of pure PE. Thus, this peak can definitely be assigned to VA and is probably an overtone of the methyl group in VA [6,9]. The slight variation in the slope of the methylene overtone around 1700 nm is possibly due to the superposition of the VA absorbance in this region.

In the spectrum of pure PVA, there are some distinct peaks around 1900 nm and 2100 nm. The second overtone of the carbonyl band is known to exist in the

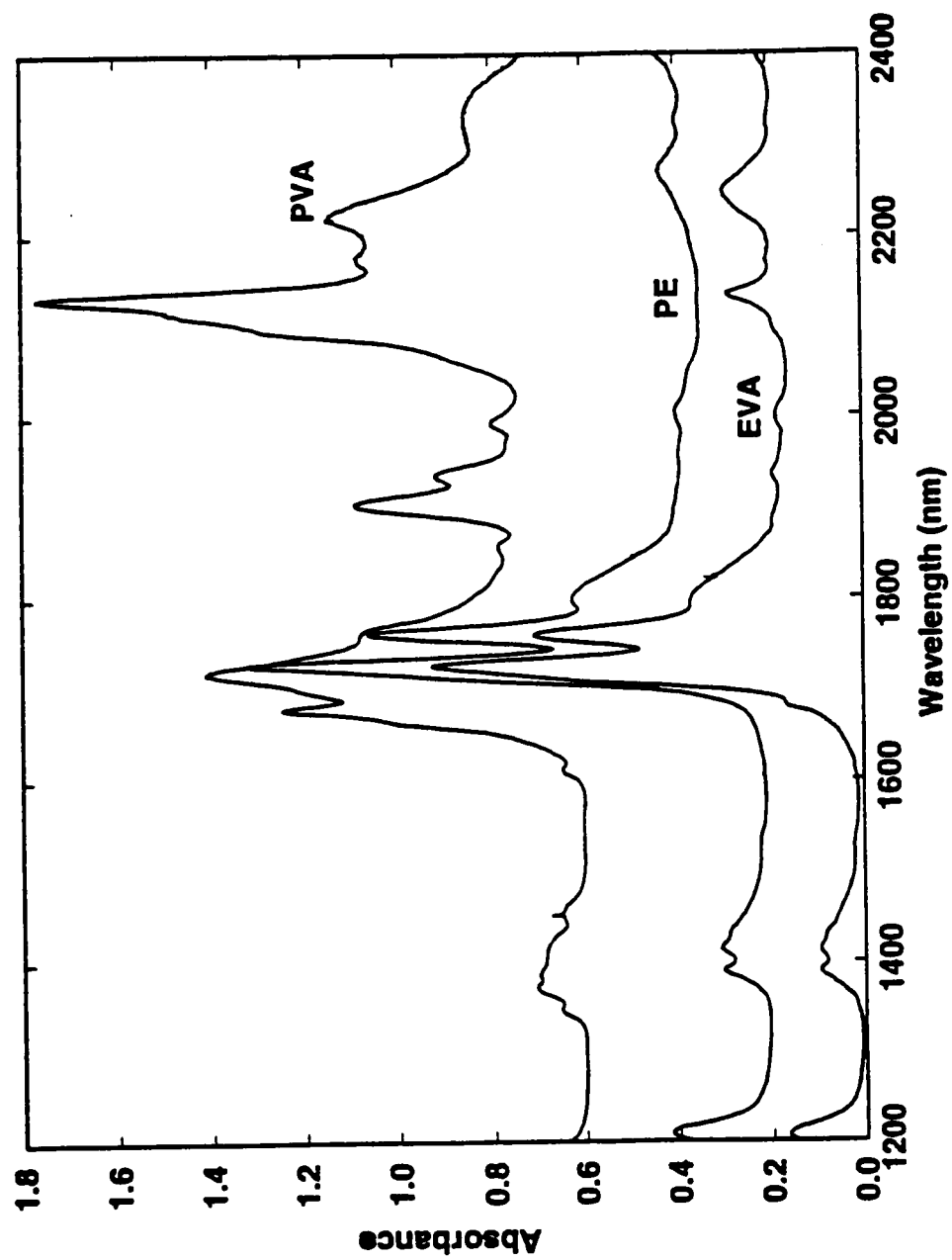


Figure 7.2 Overlaid spectra of PE, PVA, and EVA (containing 28 wt.% VA).

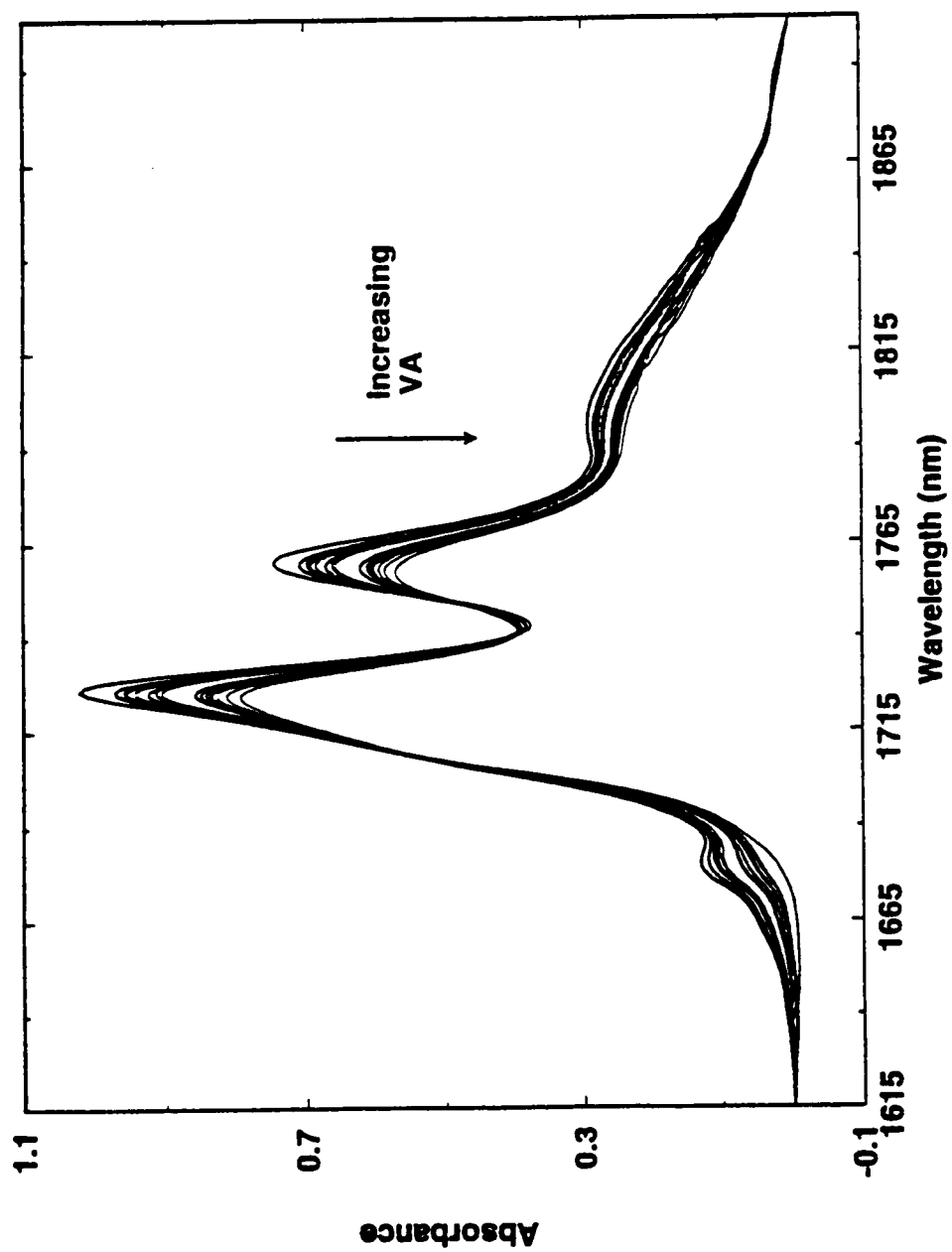


Figure 7.3 Overlaid spectra of EVA samples, in region A.

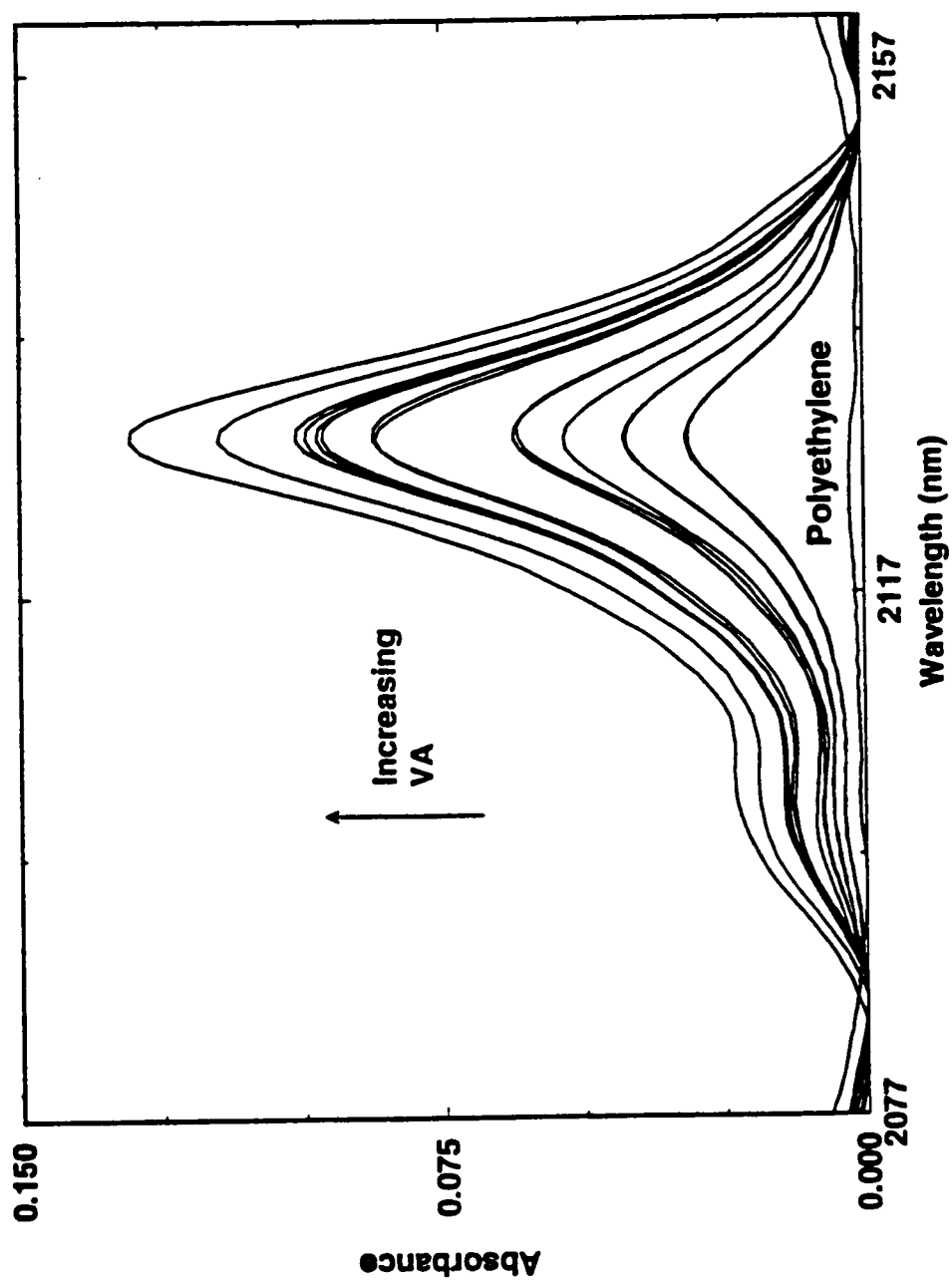


Figure 7.4 Overlaid spectra of EVA samples, in region B.

1900-2000 nm range [6,9], while a combination band of C-H stretch and C=O stretch is known to exist around 2140 nm [3]. In the spectra of EVA samples, there is a peak present at about 2135 nm, which evolves with increase in VA content. Although the intensity of this peak (2135 nm) is much lower than the C-H overtone peaks, it shows the variation in VA content much more clearly, and is free of interference from polyethylene. Our conjecture is that this peak (2135 nm) is probably a combination band of C-H stretch and C=O stretch.

As mentioned earlier, all calibration modeling was performed on one set of polymer samples. Since the number of samples in Class I is higher than in Class II and that samples in Class II lie within the concentration range encompassed by Class I, the samples of Class II were chosen to constitute the independent test set. A three pronged approach was used to test the robustness of the calibration models: (i) validation of all the calibration models against test sets from Class I; (ii) validation of the lowest-SEP calibration model against an external test set (Class II samples); (iii) validation of the lowest-SEP calibration model by real-time monitoring of VA concentrations in samples from Class II. Moreover, it must be mentioned that the collection of experimental data on Class I samples, Class II samples, and real-time monitoring experiments were conducted on three separate days. Thus the robustness of the calibration models in handling variations with time was also tested simultaneously.

Ten spectra corresponding to each of the sixteen samples (in Class I) were chosen for data analysis. These spectra were chosen after visual examination to remove any possible outliers. These 160 spectra were divided into two groups comprising 80 spectra each (five spectra for each of the sixteen samples), one for calibration and the other for validation. Both of the spectral regions were treated separately for data analysis. Spectral pretreatment consisted of removing baseline

offsets by one of two methods: (i) simple 2-pt. baseline correction; and (ii) computation of the first derivative of the spectra. The sloping-baseline corrected data are more useful in qualitative analysis, but sometimes they may not be as accurate as the derivative spectra, which not only provide a very flat baseline but also expose many subtle variations in the spectra. On the other hand, derivative spectra are very noisy and have to be repeatedly smoothed before performing any kind of multivariate analysis. In forming the data sets, the 1615-1903 nm wavelength range was used for the first spectral region, while the 2040-2160 nm range was used for the second spectral region. From the calibration data (eighty spectra), four data sets, two sets each (derivative and baseline corrected data) corresponding to the two spectral regions, were constructed. The four data sets were then used as calibration sets, and the multivariate techniques of partial least squares (PLS) and principal component regression (PCR) were used. Thus, a total of eight calibration models (Fig. 7.5) were developed for the four data sets. This kind of extensive calibration modeling was aimed at identifying the best spectral region and also at comparing the performance of common data pretreatment techniques and factor based regression methods. The optimal number of factors was determined using the leave-one-out cross-validation method [10] and was found to be one factor, in each case. This result explains that there is one prominent source of variation in the data, i.e. the VA content.

From the validation data (eighty spectra), just like the calibration data, four data sets were constructed for validation purposes. The predictive ability of each of the eight calibration models, developed above, was tested by using the corresponding validation set for predictions. By using one factor, the standard errors of prediction of the data sets using the corresponding calibration model were computed, and they are tabulated in Table 7.2. The performance of the combination region was better

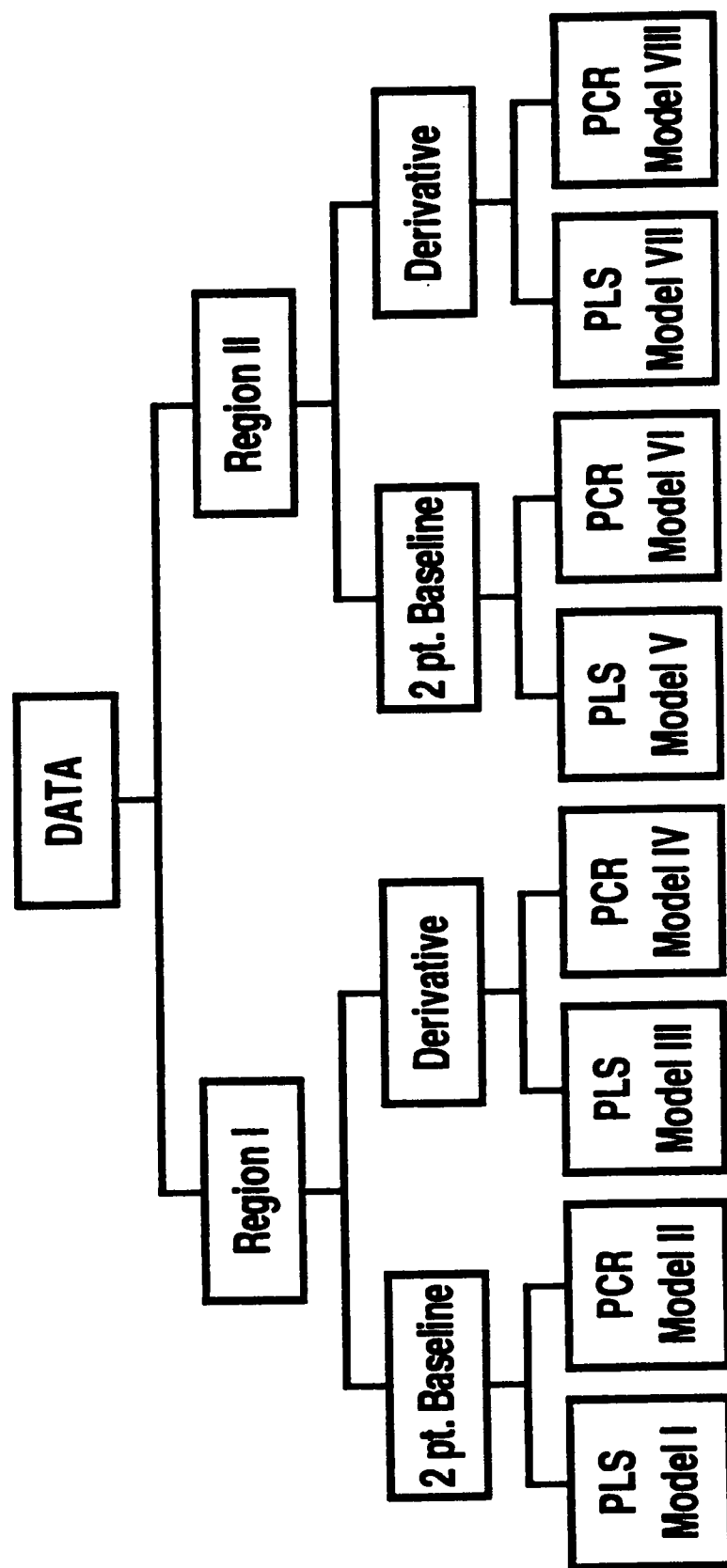


Figure 7.5 Schematic of calibration modeling techniques for Class I EVA samples.

Table 7.2 **Predictions of the eight calibration models for the Class I**
validation sets

Model No.	Preprocessing Method	Modeling Method	SEP (wt% VA)
1	Overtone Region - Baseline Corrected	PLS	0.9384
2	Overtone Region - Baseline Corrected	PCR	0.9400
3	Overtone Region - First Derivative	PLS	0.8254
4	Combination Region - First Derivative	PCR	0.8291
5	Combination Region - Baseline Corrected	PLS	0.7858
6	Combination Region - Baseline Corrected	PCR	0.7870
7	Combination Region - First Derivative	PLS	0.3837
8	Combination Region - First Derivative	PCR	0.3841

than that of the overtone region. In both the regions, the derivative spectra provided better results than the baseline corrected data. This is because 2-pt. baseline-correction does not remove baseline offsets completely. Moreover, the information content of the near infrared spectra is quite complex due to the presence of overlapping absorbances. The derivative spectra help to alleviate this complexity by deconvoluting many subtle variations and overlapping peaks in this region. Also, the results illustrate that the performance of PLS is always fractionally better than PCR. The main reason for this performance is that PLS takes into account the variation in both the absorbance and the property data, while PCR assumes that the property data are proportional to the absorbance data. The advantage of PLS based regression becomes more obvious in situations where the property data has an indirect relationship with the absorbance data. In the present case, even when the absorbance data are directly proportional to the concentration data, it can be seen that PLS outperforms PCR. Thus, it can be concluded that PLS should be the method of choice in all EVA calibrations.

Before proceeding on to the results of external validations, the existence of one optimal factor in EVA calibrations shall be described both qualitatively and quantitatively, using different approaches. The determination of the optimal number of factors in multivariate analysis is a very subjective task, and it requires that the number of factors chosen should be such that there is no underfitting or overfitting, thereby distinguishing between information removal and noise removal, respectively [10]. One way of identifying the ideal number of factors in a calibration model is to compare the residuals and the regenerated spectra, after each factor, to the original spectra. The plot of residuals is also useful in detecting outliers, both in individual samples and variables. Thus a sample or a variable having abnormal values of residuals could be easily identified as an outlier. Figure 7.6 shows the

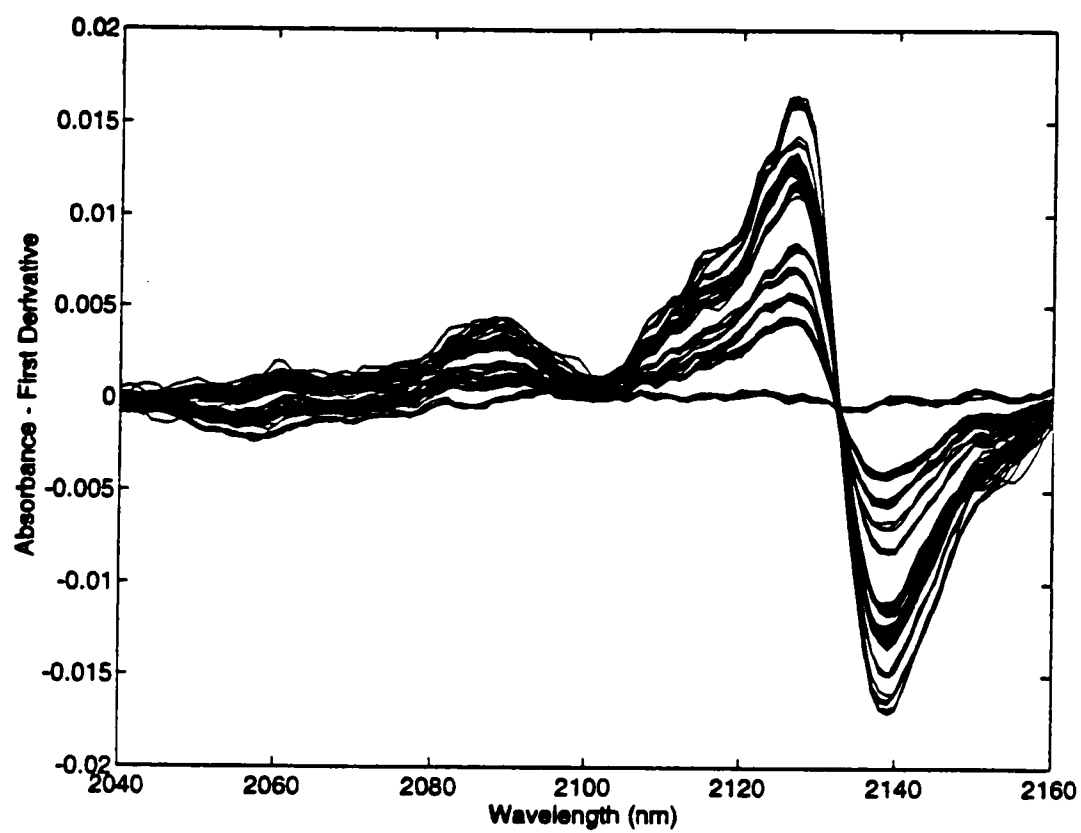


Figure 7.6 Overlaid plot of the first derivatives of all the spectra in Class I calibration set.

overlaid derivative plot of all eighty calibration spectra. Figures 7.7 and 7.8 show the regenerated spectra and the spectral residuals, using one factor. Both plots show that the first factor adequately accounts for most of the useful information in the spectra, while random noise constitutes the spectral residuals.

Another approach that was adopted in determining the optimal number of factors was to examine the effect of increasing number of factors on the singular values of the covariance matrix (i.e. $X^T Y$ in PLS). In the present study, a residual-norm-ratio (RNR - defined as the ratio of the norm of the residual covariance matrix used to determine a particular factor to the norm of the matrix used to extract the first factor, i.e. the original covariance matrix) was determined for each factor that was included in the calibration. The residual-norm-ratio was chosen because it gives a measure of the degree of information still contained in the residual covariance matrix relative to the information contained in the original covariance matrix. Thus, the residual-norm-ratio provides an estimation of the major principal components of the original covariance matrix. Furthermore the residual norm ratio is easier to plot, because it varies from 0 to 1. Figure 7.9 shows the variation of the residual-norm-ratio with increasing factors for model 7. The plot illustrates that the residual-norm-ratio of the residual covariance matrix after one factor is close to zero, implying that the original covariance matrix has one principal component. This observation further justifies that the data set has one major factor of variation. This concept would have more utility for complex systems that have more than one factor.

The scores plots were used to interpret the contributions of the first two factors and also to identify clusters of samples that have similar concentrations of VA. Figure 7.10 shows that the scores of the samples (using model 7) increase with increasing sample number (i.e. increasing VA concentration), implying a positive correlation between the first factor and the VA concentration. Also, the relationships

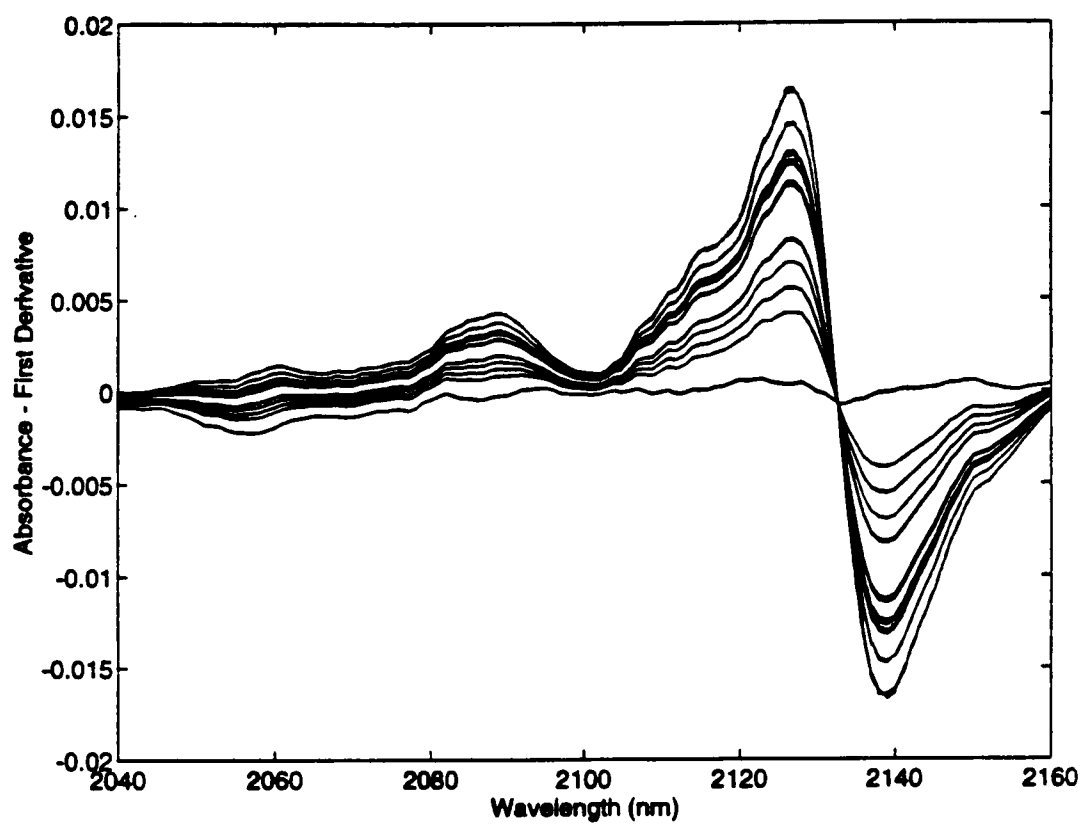


Figure 7.7 Overlaid plot of the spectra (of Fig. 7.6) regenerated using one factor.

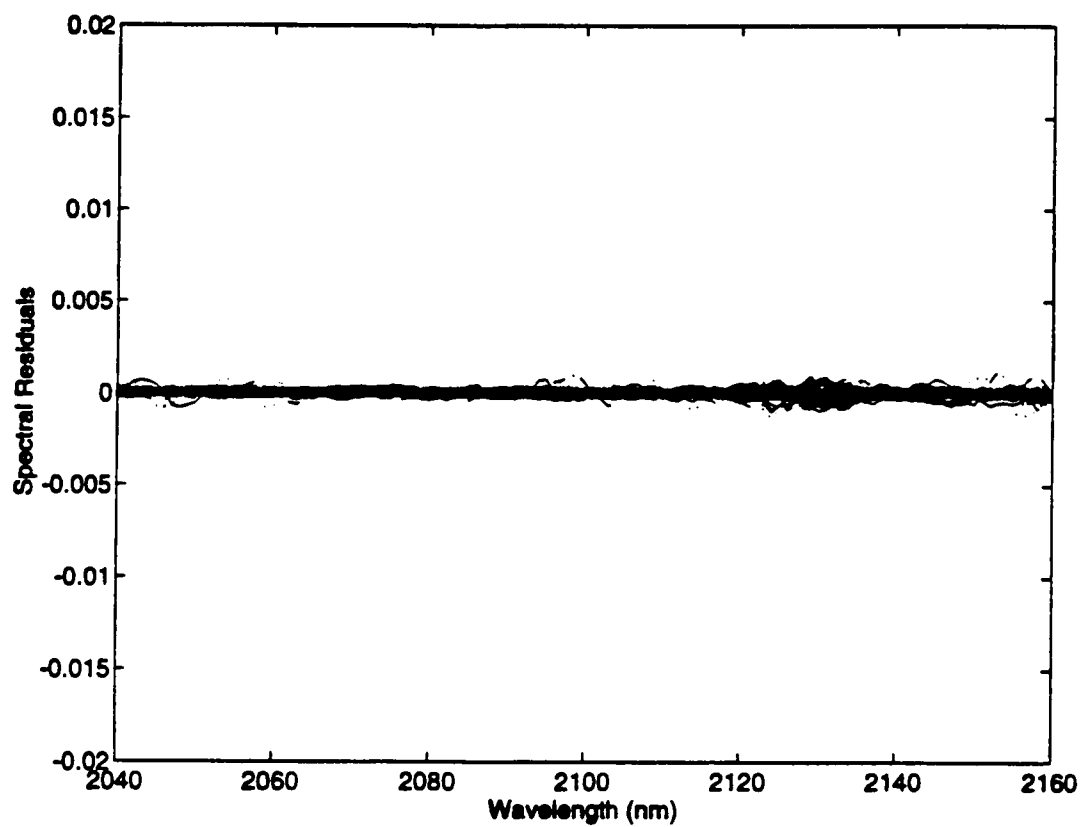


Figure 7.8 Overlaid plot of the residuals of the spectra (of Fig. 7.6) after one factor.

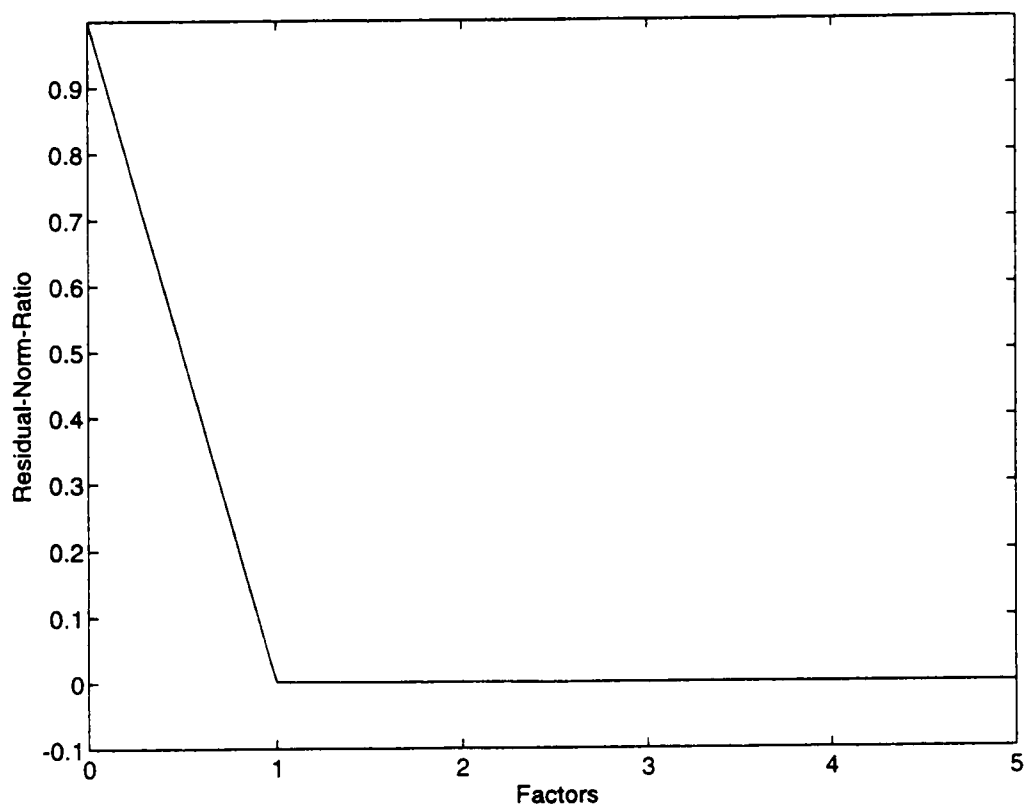


Figure 7.9 Plot of the residual-norm-ratio of the PLS covariance matrix (for model 7), with increasing factors.

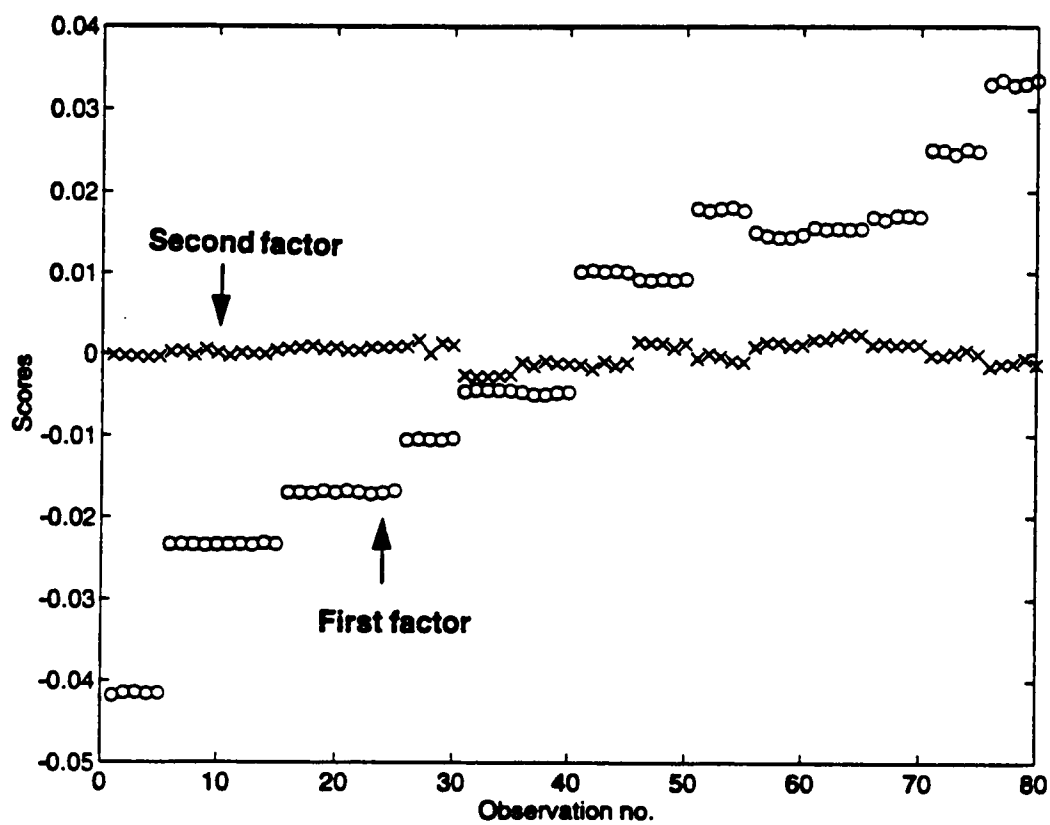


Figure 7.10 Scores for the first two factors, in model 7.

among the samples is effectively modeled by the first factor, where nine separate clusters can be attributed to the nine target concentrations in the sample set. The scores of the samples for the second factor are negligible, thereby justifying once again that the first factor accounts for the main information content in the spectra.

The multivariate analysis of the EVA spectra leads us to conclude that one-factor calibration models on derivative data in the 2040-2160 nm wavelength range are the most ideal for correlating the VA content in the copolymers. The robustness of this calibration model (model 7) was tested by validation against the spectral data obtained from Class II samples. Ten spectra corresponding to each of the eight samples were chosen for data analysis. The first derivative data, in the 2040-2160 wavelength range were used to construct the data set. It was found that one factor models provided the best results with standard error of prediction (SEP) as low as 0.49 wt.% . This test proved two points: (i) the calibration models are robust; and (ii) the optimal number of factors is indeed one. The predictions for VA concentration for both the validation sets (i.e., Class I and Class II) are shown in Fig. 7.11.

Finally, the ultimate test of the robustness of the calibration model was to use the model for real-time on-line predictions. For real-time predictions, the "Monitor" module of the Guided Wave spectral system software was used. This module acquires spectral data in real-time, preprocesses them as instructed, and then uses an existing model for predictions of the calibrated properties (such as concentration, etc.). Figure 7.12 shows a block diagram that describes the procedure used for real-time predictions. Three samples of Class II were used for real-time predictions and the calibration model for derivative data in the combination region was used. Each prediction took about eight seconds. Thus, even with a slow scanning instrument, where each spectrum takes almost 1min. 10s, the prediction time is drastically lower than the scan time for the full spectrum. The real-time in-

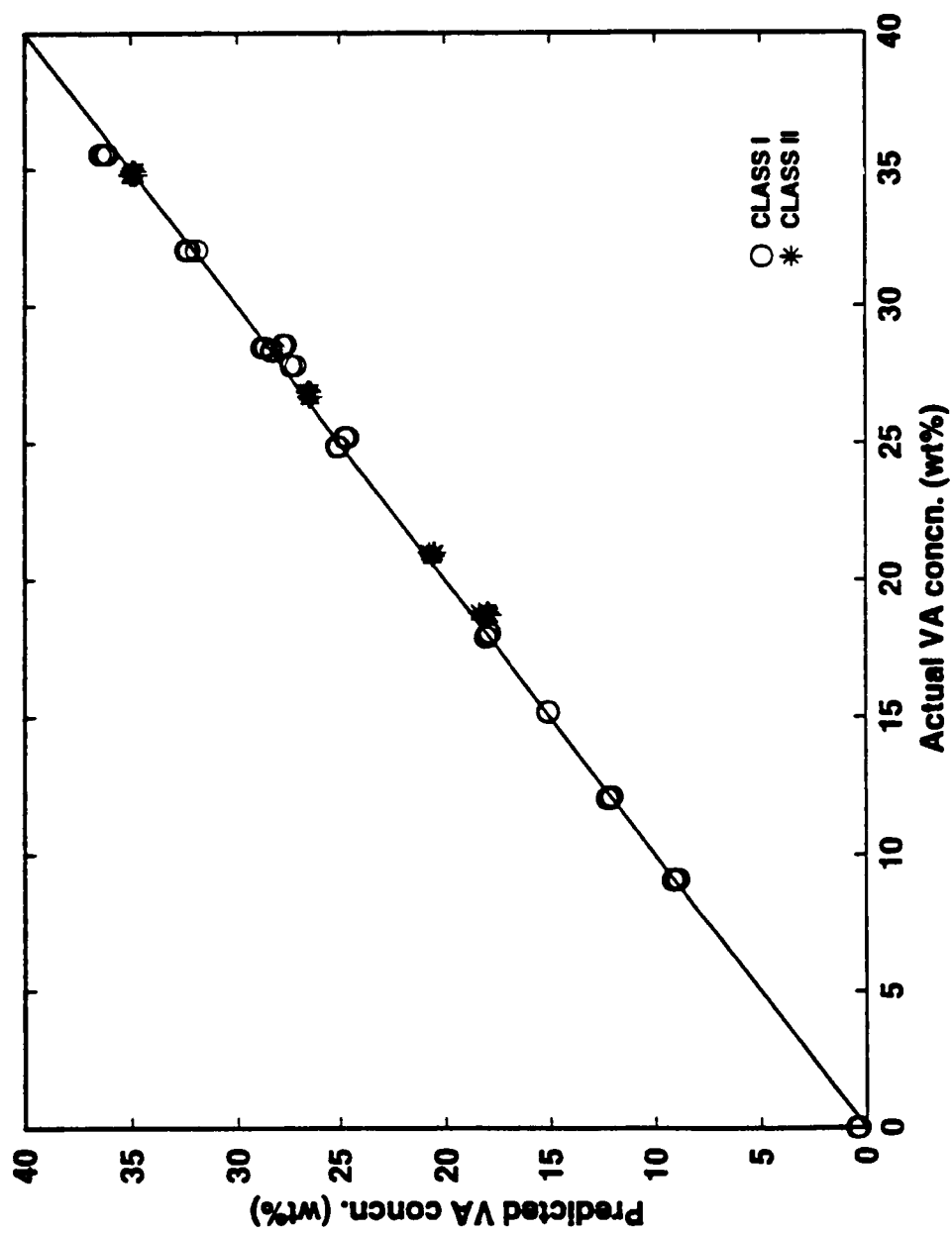


Figure 7.11 Predictions of the calibration model (# 7) for Class I and Class II validation sets.

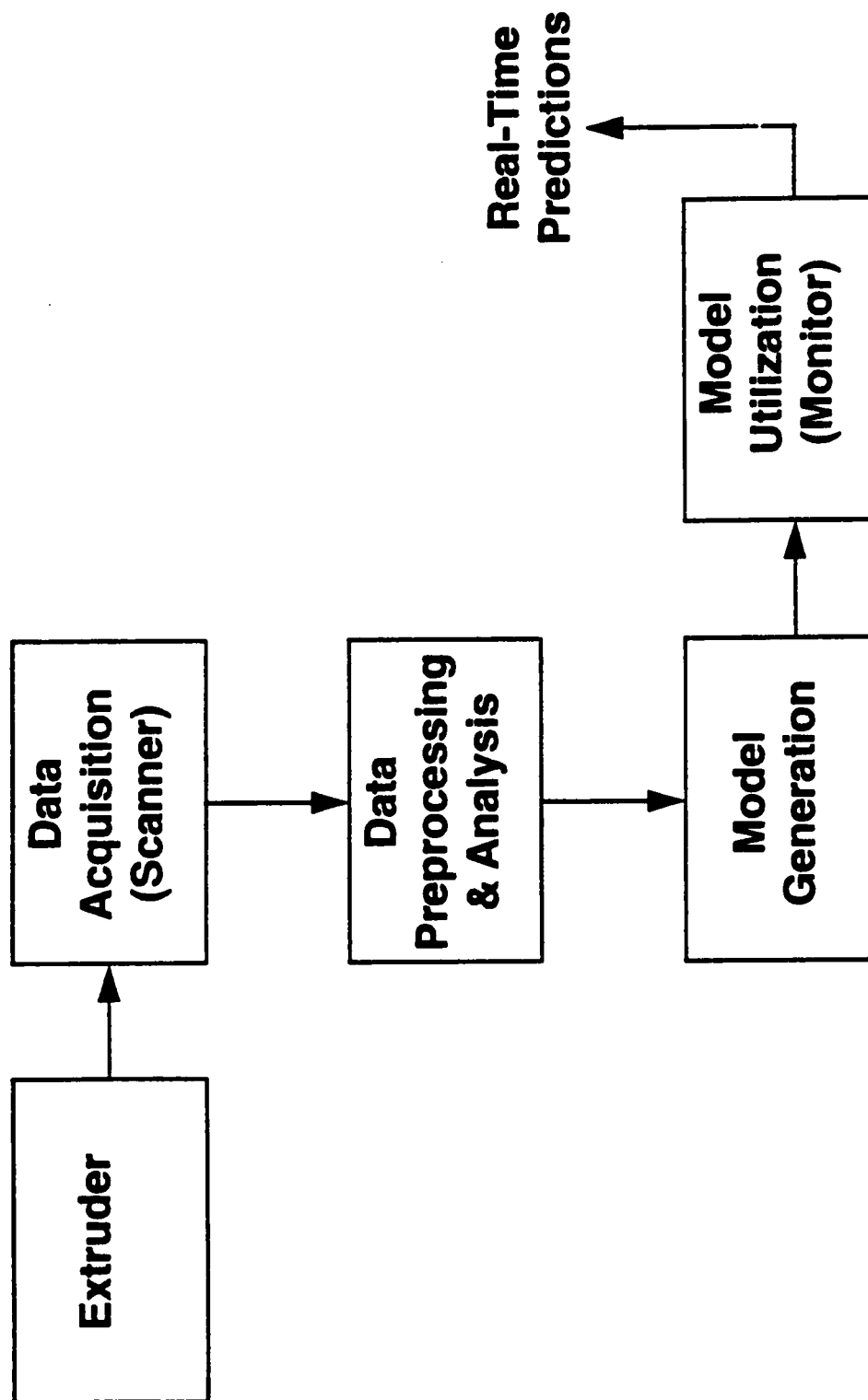


Figure 7.12 Block diagram for the procedure used for real-time predictions.

line predictions have been illustrated in Fig. 7.13. It can be seen that almost all the data points lie within the control limits. The control limits were determined by the SEP value of the model for Class II samples (i.e. 0.49 wt.%). It has also been illustrated that even by randomly feeding the samples (34.80% VA followed by 20.90% VA, followed by 26.70% VA), the calibration model can adequately account for the variations in VA concentrations. The transition region from one sample concentration to another is smooth, instead of a sudden step change, primarily because the samples were continuously fed into the extruder and the transition region thus corresponds to the residence time of the extruder.

Conclusions:

In-line monitoring of the VA content in molten EVA copolymers is extremely useful for quality control. This study has demonstrated that NIR spectroscopy, coupled with fiberoptics and chemometric data analysis, is ideal for real-time analysis of VA content in molten EVA copolymers. The robustness of the calibration models was tested by using data from two independent sources, and also during real-time in-line predictions. In each case, the results were very promising for implementation in a polymer manufacturing plant.

In this study, it has been shown that the most precise calibration models for quantification of the VA concentration in EVA copolymers were obtained by using the derivative spectra in the combination region (2000-2200 nm). However, it can be seen that the maximum absorbance for the C-H stretch/C=O stretch combination peak is less than 0.15 AU. A major concern at such wavelengths is that there is considerable attenuation in the fibers, as the length of the fibers is increased. In that case, the 2135 nm absorbance peak shall be completely masked by the high baseline. There are two possible ways to circumvent the problem: (i) to use the

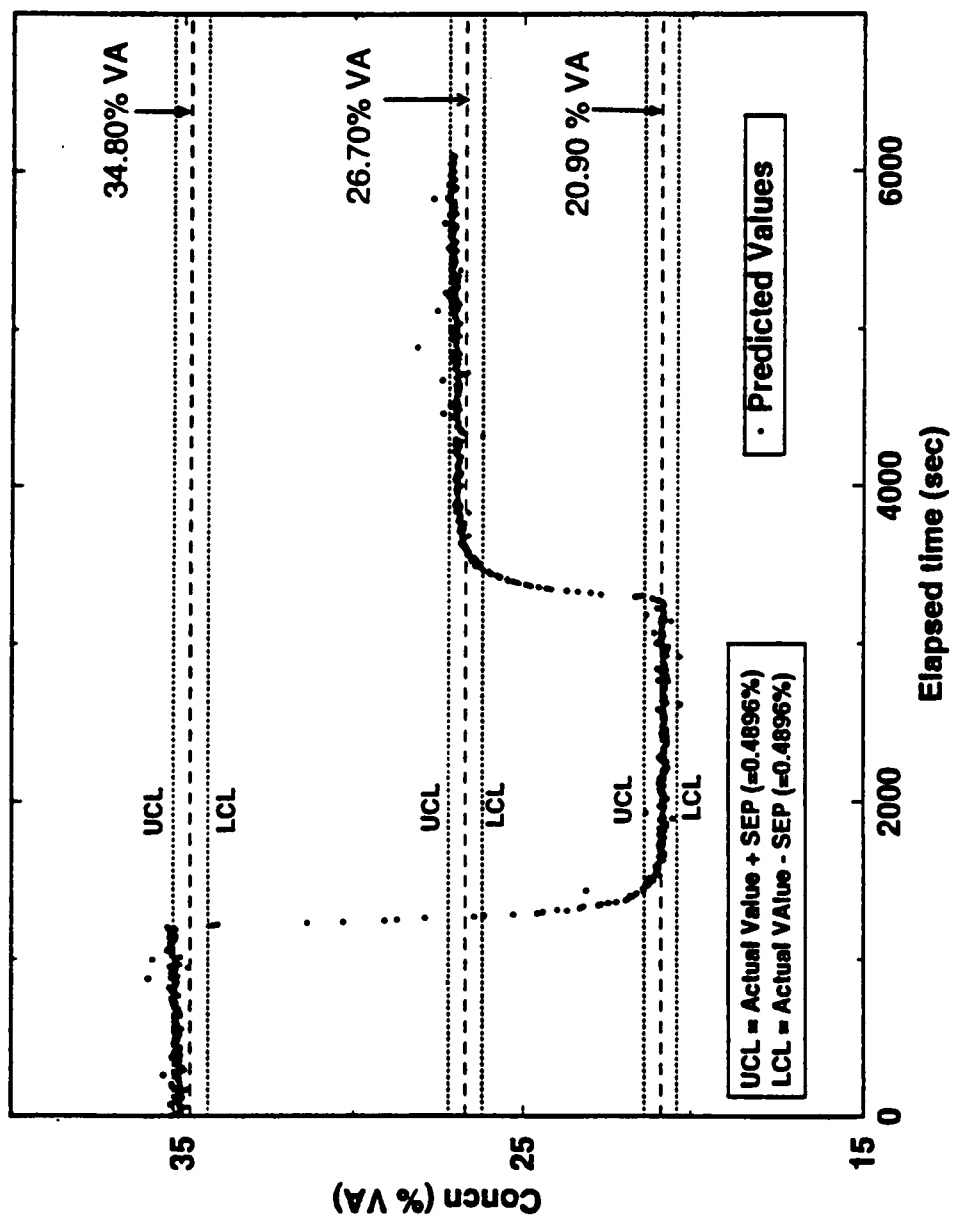


Figure 7.13 Real-time in-line predictions for three samples of Class II.

absorbance data in the C-H overtone region, but at the expense of a higher prediction error; or (ii) to amplify the absorbance of the 2135 nm peak by utilizing the maximum pathlength of the flow cell. The following section shall describe the advantages and pitfalls of the latter alternative.

7.2 Experiments - EVA copolymers with varying VA concentration, and using 9.5 mm pathlength:

Experimental:

As mentioned previously, the low absorbance of the 2135 nm carbonyl combination band in vinyl acetate was a cause for concern in using this peak for monitoring a manufacturing process, where fiber lengths could be very high. In order to amplify the absorbance of this peak, the full pathlength of the flow cell (9.5 mm) was used. At this pathlength, the absorbance of the sample containing maximum amount of vinyl acetate (i.e. 35.57 % VA) was less than 1.2 AU. Since all the other samples had absorbances less than 1.0 AU, this pathlength was utilized for the study of EVA samples in the 2000-2200 nm wavelength range. In order to ensure consistency, all the other experimental conditions were the same as those used in the first set of experiments. Thus, the temperature setpoint in the flow cell was fixed at 200 °C, the screw speed was kept constant at 20 rpm and the mass flow rate maintained at 1.2 lb./hr.

However, there was one problem with this higher pathlength. All the EVA samples do not have the same melt index. Their melt index varies in the range 0.3-400 g/10 min. The variable melt index results in variation in the viscosity of the flowing polymer. In the first set of experiments, the main variation in the spectral information was due to the variation in VA content. Other variations, such as slight variations in temperature or variations in downward pressure (due to changes in

viscosity of the molten polymer) did not have any major effect on the absorption spectra. In the case of the higher pathlength, the polymers with melt index greater than 10 g/10 min. posed a tricky problem. Owing to their low viscosity, they were not able to fully fill up the complete flow path and also they were not able to flush out the preceding viscous polymers. The only way of obtaining the spectra of these polymers was to dismantle and clean the flow cell before running each of these samples. Such a process is, however not feasible while acquiring data for a calibration model, where it is extremely critical that all the data be acquired without minimal perturbation to the experimental setup. Thus, the only other option was to exclude the high MI samples from these experiments. A closer examination of the samples revealed that five of the sixteen Class I samples (25.22%, 27.84%, 28.37%, 28.59%, and 32.05%) had to be excluded. Four of these five samples had low MI counterparts in the sample set. Thus, only one out of the nine target VA concentrations was totally eliminated from the Class I sample set. For the Class II samples, two (19% and 35% concentrations) of the four target concentrations had to be eliminated. The reduction of the number of samples in the Class II set was not a major concern because this sample set was only used for validation purposes.

Results and Discussion:

Figure 7.14 shows an overlaid plot of the eight Class I samples, in the 1200-2400 nm wavelength range. The pronounced effect of the increased pathlength is very distinctly noticeable in the spectra. The first overtone C-H peaks in the 1600-1850 nm range have very high absorbances, with virtually no light reaching the detector. The 2135 nm C=O combination band is clearly amplified at this pathlength. Once again, it can be noticed that this peak is virtually free of interference from polyethylene, which does not have any absorption in the region. In

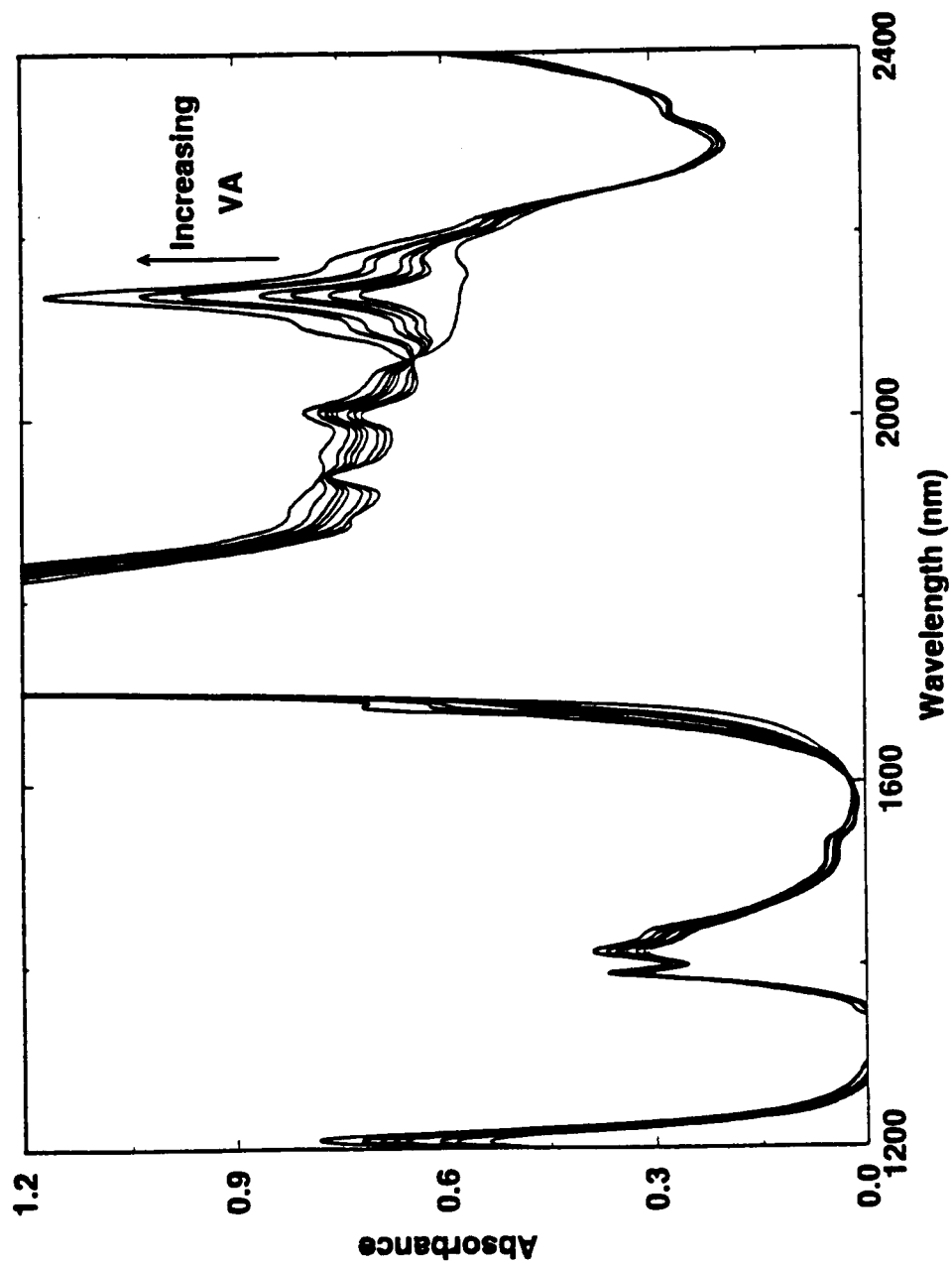


Figure 7.14 Spectra of EVA polymers, in the wavelength range 1200-2400 nm, and using 9.5 mm pathlength.

Fig. 7.15, the above region has been blown up. It can be noticed that other minor peaks (in the 1900-2000 nm range) due to the second overtone of the carbonyl group in vinyl acetate, etc., have also been amplified. Thus, even by visual examination it can be concluded that the 9.5 mm pathlength is more suitable for the analysis of the EVA samples in the 2000-2200 nm region. However, it was interesting to compare the performance of the region using the expanded pathlength, versus the 2.5 mm pathlength, for quantification of the VA content.

In order to avoid redundancy, the quantitative analysis of the above data set was restricted to first derivative data in the 2040-2160 nm range. This data set had outperformed the baseline-corrected data by a factor of 2. Also, in this study, only PLS based regression was used for calibration purposes. Ten spectra, corresponding to each of the eleven samples were chosen for modeling. The first derivative data for each of the spectra were computed, following which the spectra were smoothed. The data set of 110 spectra was divided into two sets of 55 spectra (five spectra for each sample) each, one for calibration and the other for validation. PLS calibration model of the calibration set yielded that more than 98.5% of the variance was accounted by one factor. The robustness of the calibration model was tested on the Class I validation set. A SEP value of 0.33 wt.% was obtained using one factor. This SEP value is slightly lower than the SEP value for the 2.5 mm data set, thereby indicating that the results are comparable and marginally better at this increased pathlength.

The robustness of the calibration model was further verified by tests against external data sets. In this respect, the external set was created by using five spectra each of the four Class II samples. The spectral data were subjected to first derivatives and smoothing. The PLS calibration model, as described above, was used to predict the VA concentration in all the 20 spectra, and the SEP was calculated

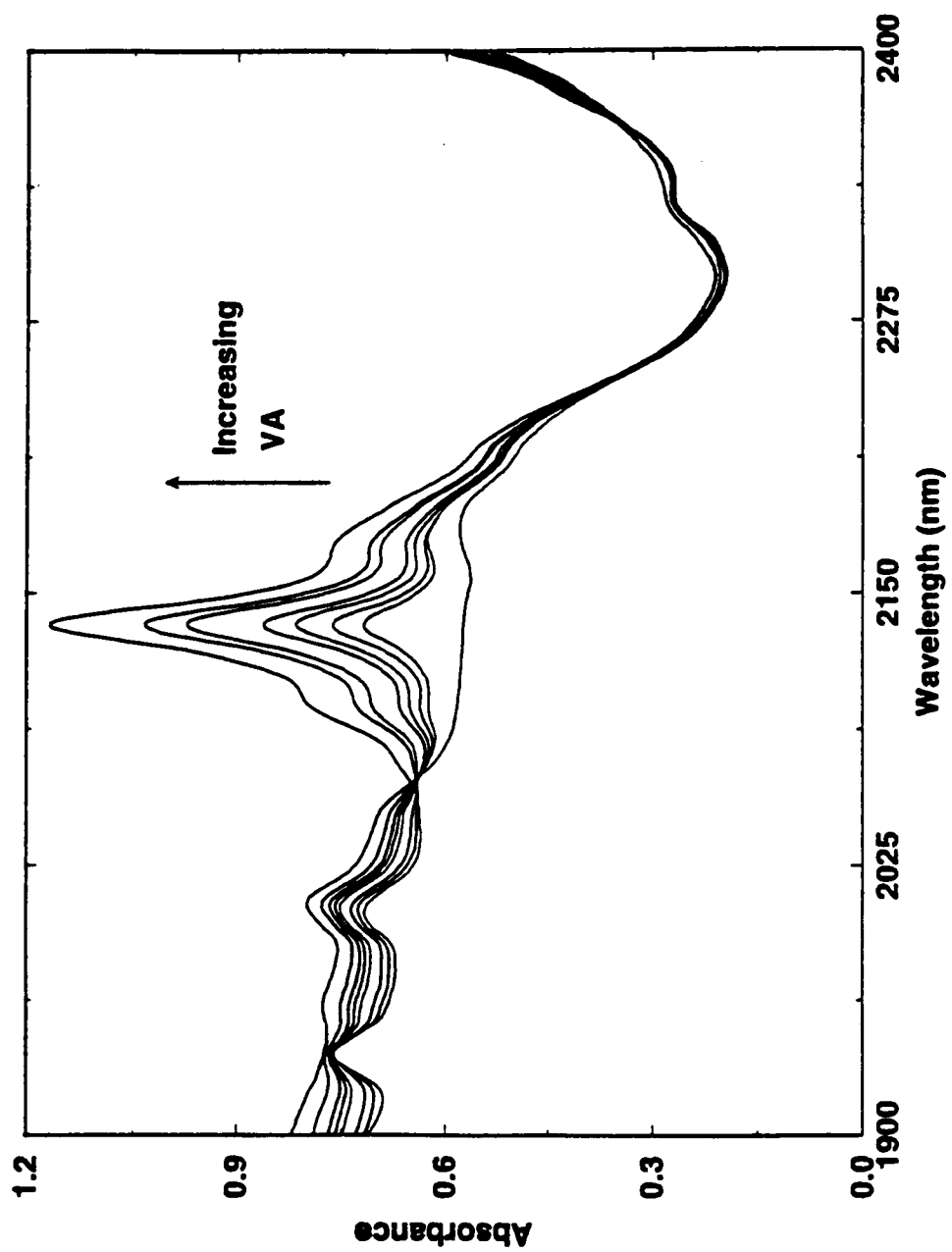


Figure 7.15 Magnified view of spectra in Fig. 7.14, in the 1900-2400 nm range.

using one factor. The SEP for this data set was 0.48 wt.% which is almost identical to the SEP value obtained for the Class II samples in the previous study. This result proves that although there is no marked improvement in the prediction results by utilizing the expanded pathlength, the reliability of the NIR results is certainly obvious. Figure 7.16 shows the scatter plot of predicted versus actual concentrations for both the calibration and validation sets.

The above results reinforce our initial inference that one-factor calibration models on derivative data in the combination region are the most adequate for quantification of the VA content in EVA copolymers. Furthermore, it must be reiterated that the advantage of a much lower prediction error in the combination region certainly makes the combination region more attractive for plant-wide process control. Also the expanded pathlength of 9.5 mm is certainly more desirable than the 2.5 mm pathlength because it provides a much larger window into the process stream. Also, in some industrial processes, a single-insertion transmission probe with a reflective tip at the far end of the probe, is utilized for data acquisition. The utility of the single-insertion transmission probes over the dual-transmission probes lies in the fact that two transducer ports facing each other may not be present in a process stream, and in such a case, the single-insertion probe can be easily mounted by removing any pressure transducer. However, with a single-insertion transmission probe the effective pathlength is twice the flow path because the optical beam traverses the flow path twice. Thus 2.5 mm and 9.5 mm pathlengths for dual-transmission probes are equivalent to 1.25 mm and 4.75 mm wide flow channels for single-transmission probes, respectively. Thus, for single insertion transmission probes the expanded pathlength would undoubtedly be preferred, in order to avoid any remote possibility of clogging that may occur with a 1.25 mm wide flow channel. Another pertinent reason, which would be described in

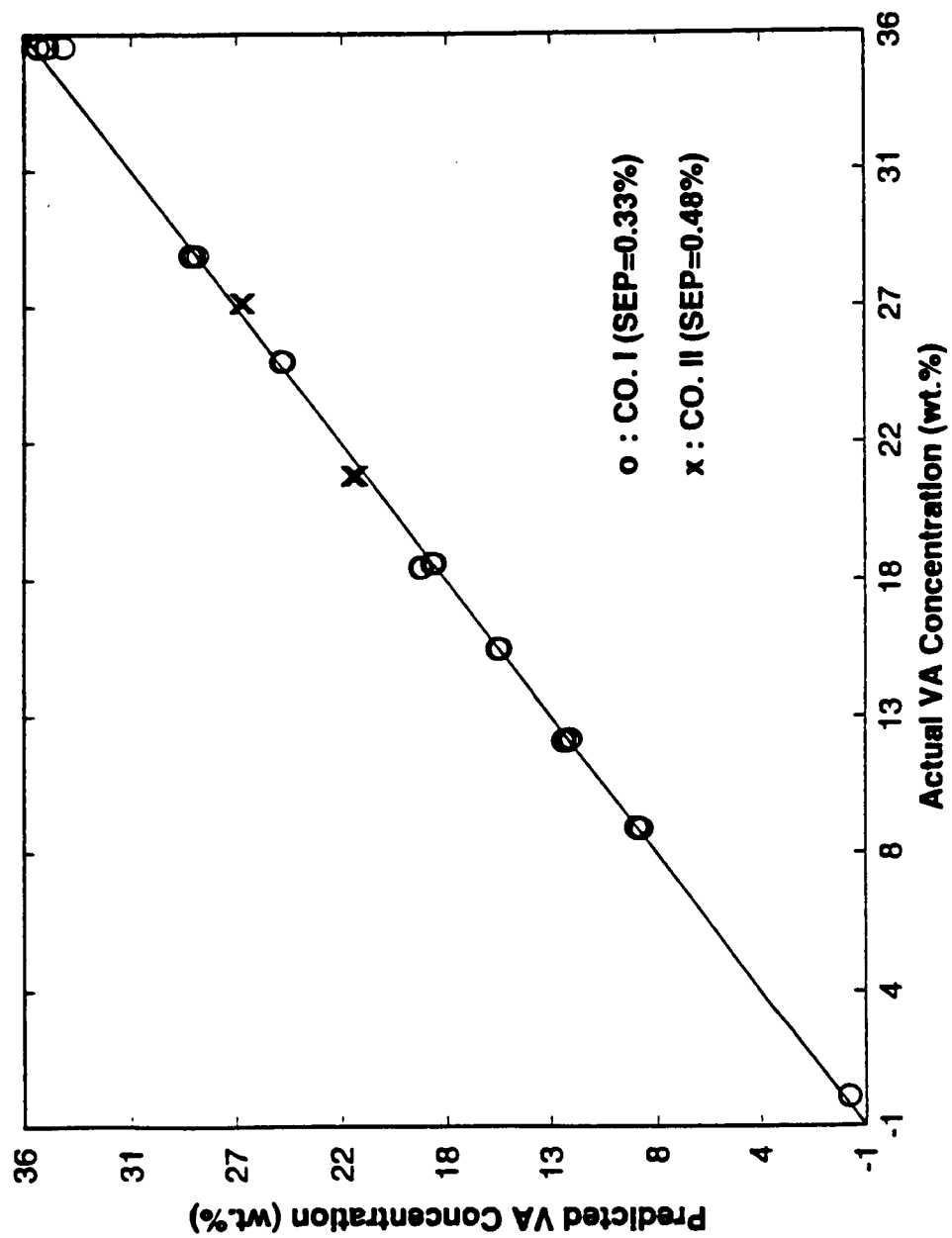


Figure 7.16 Scatter plot showing predictions of calibration model for Class I and Class II validation sets.

detail in the next study, is that the 9.5 mm pathlength is the most adequate for quantification of trace-level additives in EVA copolymers. In that case, the same probe setup could be interchangeably used for both VA and additive quantification, without any perturbation and process shutdown.

Having discussed both the performance and the utility of the expanded pathlength, the real-time monitoring of the Class II EVA copolymers shall be described. As compared to the previous study, a slightly different approach was adopted in this study. In the previous study, the calibration model was utilized for real-time in-line predictions of the VA concentration, but the actual spectra corresponding to each prediction point were not saved. In this case, the actual spectra during real-time monitoring were saved in order to enable diagnostic studies on outliers and scores. These diagnostic studies shall be described following the discussion of the real-time monitoring results.

For real-time monitoring, two samples of Class II, containing 26.87% and 21.01% VA were used, followed by flushing out the extruder with low density polyethylene (LDPE) of MI equal to 1g/10 min. The LDPE was supplied by a third source and is routinely used in the lab for purging the extruder following each set of experiments, and before shutdown. This high-viscosity LDPE helps to flush out the various types of polymer that are used for experimental purposes, some of which crosslink if they are left in the extruder. The upper and lower control limits were fixed as the SEP value of 0.48 wt.%, that was obtained by the PLS calibration model for the Class II samples. Since the LDPE was not previously used in any data analysis, its prediction error was not available. However, as a test, the same Class II control limits were used on the LDPE samples, to check their performance. Furthermore, this sample provided another important test to check the robustness of the calibration model, especially considering the facts that the sample had not

previously been used in any data analysis and that it was available from an independent source. Figure 7.17 shows the real-time monitoring results of the three samples. It can be seen that all three samples lie within the control limits, with a very few samples falling out of range. The transition from one sample to another is very smooth, and represents the residence time of the extruder. The performance of the LDPE sample is very promising and proves that the extrusion of the EVA samples could be monitored very effectively within an accuracy of less than 0.5 wt.%.

The spectra acquired during real-time predictions were used for diagnostic studies on outliers and scores. According to Kaspar and Ray [93], the scores values can be used for real-time monitoring, in a way similar to a statistical process control (SPC) chart. One distinct advantage of using scores values, is that the outliers can be easily identified even before the model is utilized for prediction purposes. This procedure thus reduces the computation time involved in calculating the concentrations of the outlier samples, and would trigger off the warning alarms more expeditiously. In the present case, in order to create the scores chart, the scores values corresponding to the actual concentrations and the respective upper and lower control limits had to be calculated. This calculation required back calculation of the scores values using the concentration values and some existing model parameters. The procedure developed for a one-factor model is described in the following equations.

In the prediction step of PLS regression the spectrum of an unknown sample is first scaled and then the scores value for the first factor are calculated by projecting the scaled spectrum (x) along the vector containing the loadings weights for the first factor.

$$T_u = x * W(:,1); \dots\dots\dots (7.1)$$

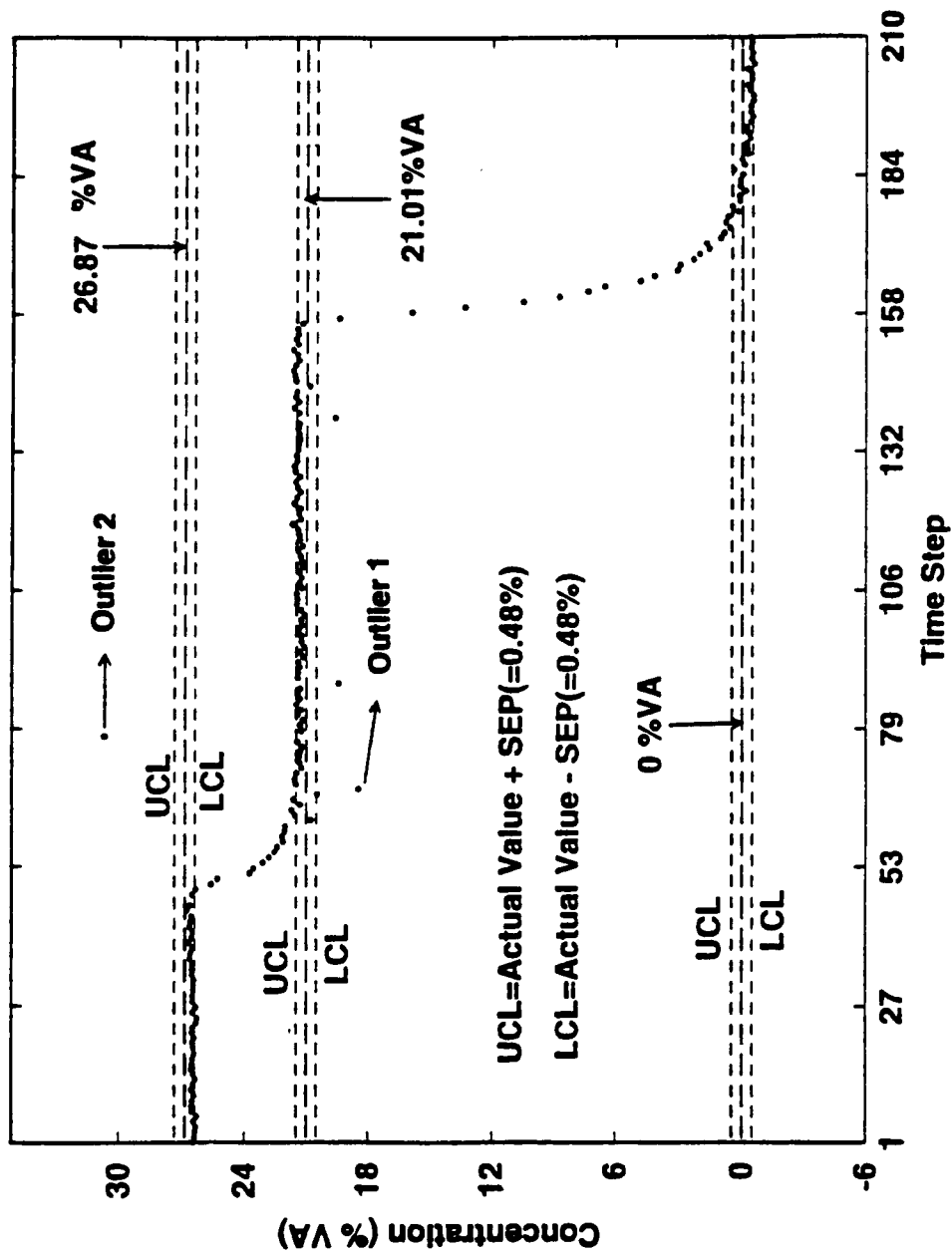


Figure 7.17 Real-time in-line predictions for two samples of Class II, and an LDPE sample from a third source (9.5 mm pathlength).

Here, x is 1 by n , and $W(:,1)$, which is the first column of the matrix of loadings weights, is of size n by 1. Thus, T_u (the scores vector for an unknown spectral observation) is a number. This T_u is used to calculate the predicted y value as

$$\hat{y} = b \cdot T_u \cdot Q; \dots\dots\dots (7.2)$$

where b is the regression coefficient corresponding to the regression of the first scores vector of the X calibration matrix on to the first scores vector of the Y calibration matrix. Q is the vector containing the loadings for the first factor. Since Y has only one variable (the VA concentration), the Q vector has only one entry and is therefore reduced to a number.

Since b and Q are just numbers the back calculation of the T_u values corresponding to the concentrations and the control limits, was very straight forward. Each concentration was scaled with respect to the mean of the Y matrix of the calibration set and divided by the product of b and Q .

$$T_u = y / (b \cdot Q); \dots\dots\dots (7.3)$$

An alternative approach for determining the control limits for the scores values (especially when there is more than one factor) [94], is to determine the scores values for a particular factor, corresponding to both the actual and predicted y values. These scores values can be determined by projecting the actual and predicted y values onto the y loadings vector for the particular factor. The standard deviation of the scores corresponding to actual and predicted y values could then be used as the interval for determining the control limits.

In the present study, the control limits were established for the scores values (eq. 7.3), and the scores chart was created by computing the scores value for each unknown spectral observation using eq. (7.1). This scores chart is illustrated in Fig. 7.18. It can be seen that the scores chart can be easily used to monitor the process and identify perturbations. As seen in both Figs. 7.17 and 7.18, there are a few

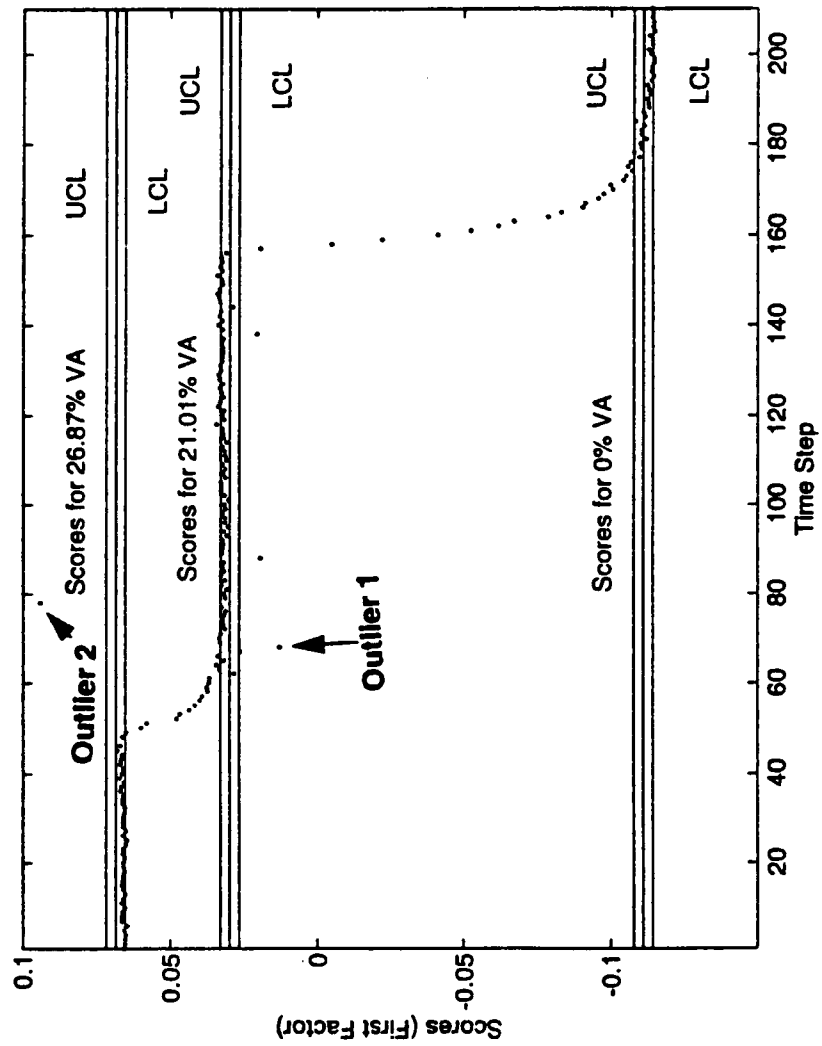


Figure 7.18 Scores chart showing variations of scores in real-time.

spectral points which fall out of range of the control limits. These points are termed as outliers. These outliers could be due to process shifts, bubbles in the flow stream, black particles (due to degraded polymer) in the flow stream, and particulate matter in the flow stream. As seen in Figs. 7.17 and 7.18, two severe outliers have been identified. The spectra corresponding to these outliers have been shown in Fig. 7.19. The spikes in the spectra clearly represent the abnormalities in the spectrum, thereby indicating that the samples are out of specifications and corrective measures should be taken for quality control. These outlier samples can be easily identified in the scores chart, even before predictions.

Conclusions:

This study has demonstrated that an inherent weakness of the NIR region could be exploited as a strength. The weak absorptions could be magnified by increasing the pathlengths, and thus providing a larger flow channel. However, the method does have its limitations and samples of very high melt index could not fully fill up the flow channel and were not used for data acquisition in the continuous monitoring mode. This situation, is however, rarely encountered in a manufacturing process where there would be sudden change of MI from 0.3 g/10 min. to 400 g/10min.

The study has also demonstrated that a calibration model in the combination region is robust enough to monitor a totally unknown LDPE sample from a new source. The utility of using scores charts for monitoring real-time processes has been successfully demonstrated. It has also been shown that the scores charts could be easily used for real-time outlier detection, without using the model for prediction purposes.

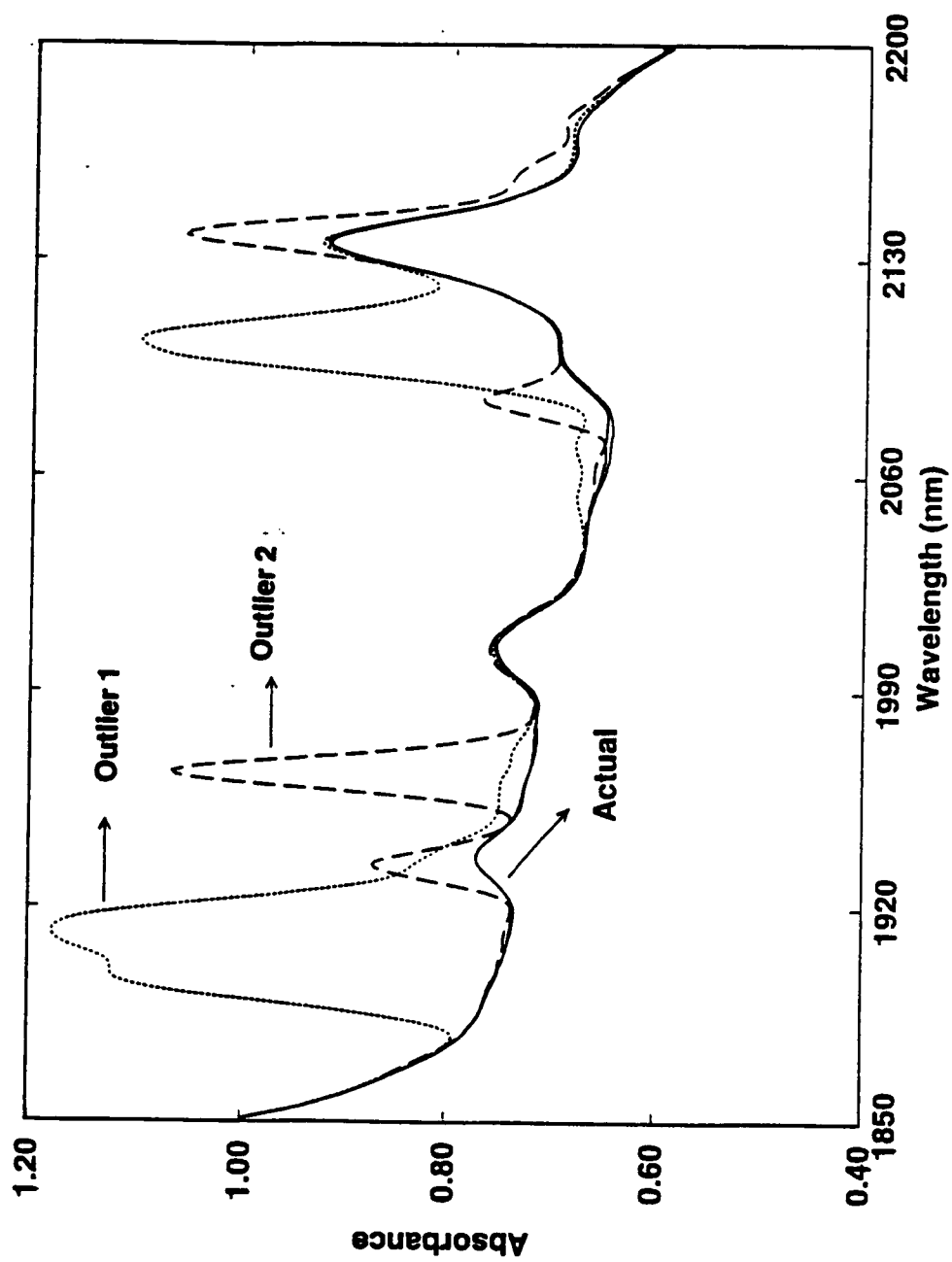


Figure 7.19 Spectra corresponding to the two outliers identified in Figs. 7.17 and 7.18.

7.3 Experiments - EVA copolymer with varying concentration of additive

Introduction:

The most common additive in EVA copolymers is a slip agent or lubricant, by the name erucamide, which is an amide of erucic acid, a fatty acid. This additive is used to lower the viscosity of the EVA copolymers and also to prevent the molten polymer from sticking to metal surfaces in extruders and other processing equipment. Very low concentrations, in the ppm range, of the additive are incorporated in commercial resins.

The objective of this study was to analyze the suitability of the NIR region for quantification of the erucamide concentration in molten EVA copolymers. Owing to its trace-level concentration, the monitoring of the additive in the NIR region was a challenging task. In the past, the NIR region has been used for trace-level additive quantification [45]. However, not much work has been done with additives in the NIR region. Fidler *et al* [86] have previously reported analysis of erucamide in high density polyethylene, using FT-IR spectroscopy, on a slip stream from the extruder.

Experimental:

Five samples of EVA (12 wt % VA) copolymer, with erucamide concentration in the range 0-2300 ppm were obtained from the same source as that of the Class I samples. Apart from these samples, one more sample containing erucamide as a 7.25 wt.% concentrate was provided for diagnostic studies. The details of the six samples have been tabulated in Table 7.3.

Initially, the EVA sample containing 7.25% erucamide was extruded to identify the regions where erucamide had distinct absorption peaks. Since the concentrations of erucamide were very low, the full pathlength of the flow cell was

Table 7.3 **Details of varying erucamide concentrations in six
EVA (12 % VA) samples.**

Sample No.	Erucamide Content
1	0 ppm
2	363 ppm
3	729 ppm
4	1114 ppm
5	2295 ppm
6	7.25 %

utilized. The experimental conditions were the same as that of the previous study. Thus, the temperature setpoint in the flow cell was fixed at 200 °C. The screw speed was fixed at 20 rpm, and the mass flow rate fixed at 1.2 lb./hr. Using the 7.25 % sample, it was found that the 1850-2400 nm wavelength range was only susceptible to the presence of erucamide. For all experiments on the other five erucamide samples, the 1850-2400 nm range was only used. Before running these samples, the whole flow cell was fully purged with polyethylene and the flow cell was dismantled and fully cleaned by pyrolysing the polymer in a furnace. Such extra precautions were necessary, especially considering the low concentrations of the additive. Also, all the polymers were purged with dry nitrogen prior to extrusion and also in the feed hopper during extrusion.

Results and Discussion:

Figure 7.20 shows the chemical structure of erucamide. The structure of the compound suggests that the spectrum of erucamide in the NIR regions would contain peaks due to the overtones of the C-H and N-H vibrations, and combinations thereof. However, the intensity of the peaks would be very low, considering the trace level concentrations of the additive. As mentioned earlier, the 7.25% erucamide concentrate was used for diagnostic studies to identify the spectral regions that were the most sensitive to the presence of erucamide in EVA copolymers.

Figure 7.21 shows a plot of an EVA sample containing 12% VA and 7.25% erucamide, on a spectrum of EVA sample containing only 12% VA. Since the full pathlength of the flow cell (9.5 mm) was used, the absorbances in the first overtone region were very high and were not considered for the study. In the 1850-2400 nm wavelength range, erucamide was found to have some distinct peaks and the most intense peak was at 1960 nm (Fig. 7.21). Goddu [9] had reported that primary

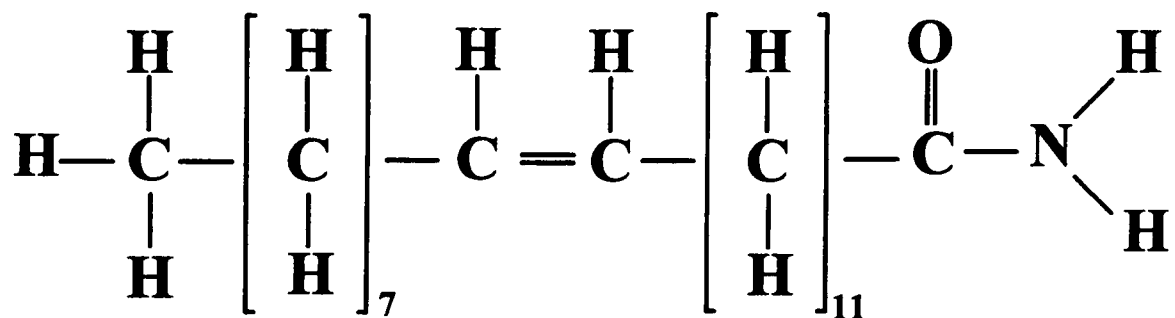


Figure 7.20 Chemical Structure of erucamide

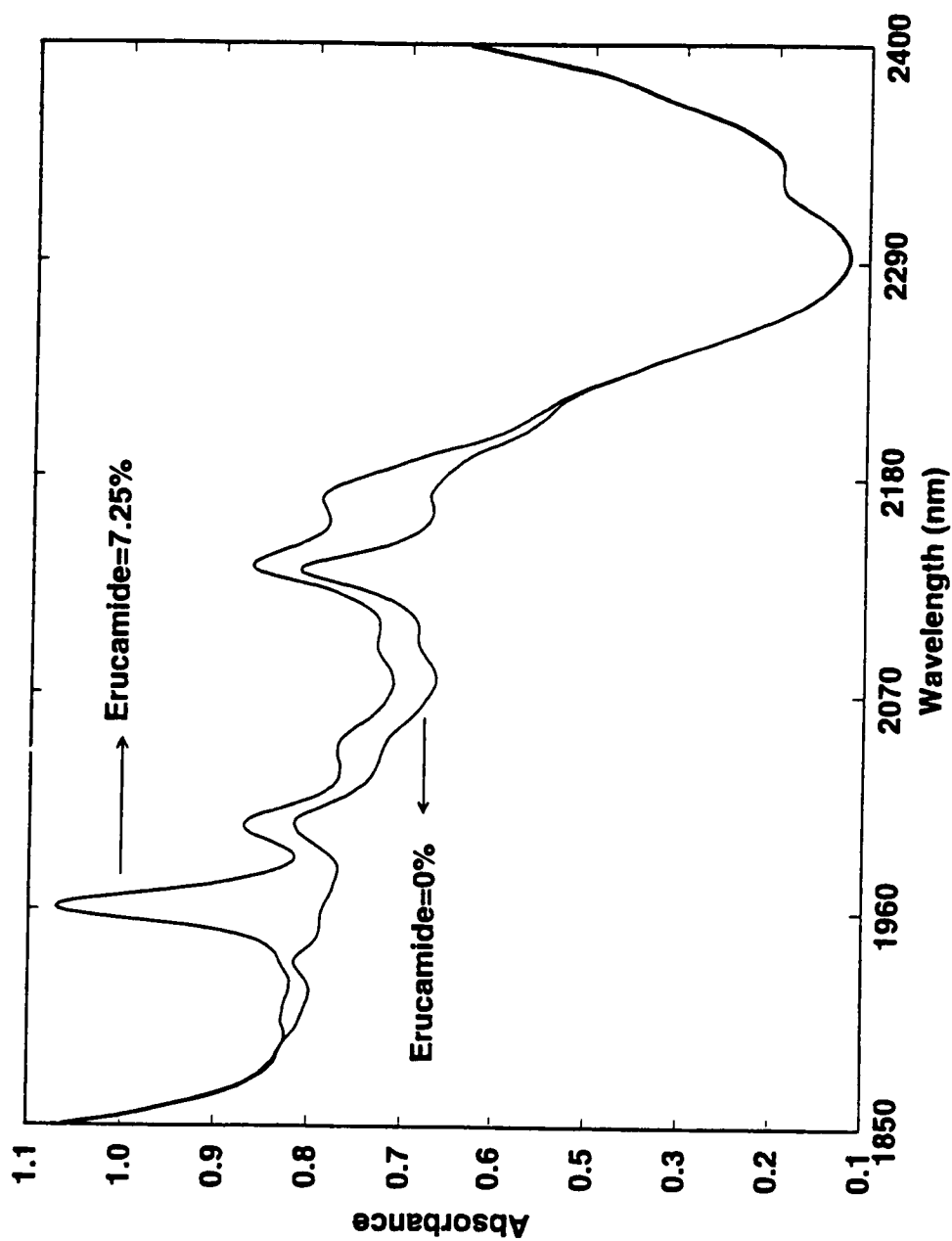


Figure 7.21 Overlaid spectra of EVA (12% VA) sample and EVA (12% VA) sample with 7.25 % erucamide.

amides have a strong and unique band at 1960 nm, which was tentatively assigned to a combination of the fundamental asymmetric N-H stretching vibration at 2820 nm, and the N-H deformation band at 6400 nm. The 1960 nm erucamide peak is therefore the same strong combination band that was described by Goddu. This 1960 nm band was used in studying the effects of trace-level erucamide content in molten EVA copolymer.

Figure 7.22 shows the baseline corrected spectra (1950-1983 nm) of the EVA copolymer containing 0, 1114, and 2295 ppm of the additive, respectively. Only three samples have been overlaid so as to clearly illustrate the differences due to such low concentrations of the additive. It can be seen that the spectral variations are really very subtle, and that the maximum absorbance is less than 0.02 AU. Such low intensity of the erucamide peak suggests that the quantification of erucamide content would have its limitations with the present experimental system.

Owing to the limited number of erucamide samples (five in all), all the samples were used for calibration. Out of an initial set of seventy-five spectra for the five samples, sixty-six spectra were chosen to constitute the spectral data set, after eliminating serious outliers. All the spectra were baseline-corrected in the 1950-1983 nm range, using a 2-point baseline correction. The spectra were smoothed to increase the signal-to-noise ratio. The data set was divided into two sets of thirty three samples each, one for calibration and the other for validation. PLS modeling showed that the validation set had minimum SEP (194 ppm) with 2 factors.

The quantitative analysis of the erucamide content was by no means exhaustive. The basic idea was to examine the suitability of the NIR region for trace-level additive quantification. The results show that the SEP of 194 ppm, would make it difficult to distinguish among samples containing concentration differences of less than 500 ppm of erucamide. Thus, 500 ppm could be established as the

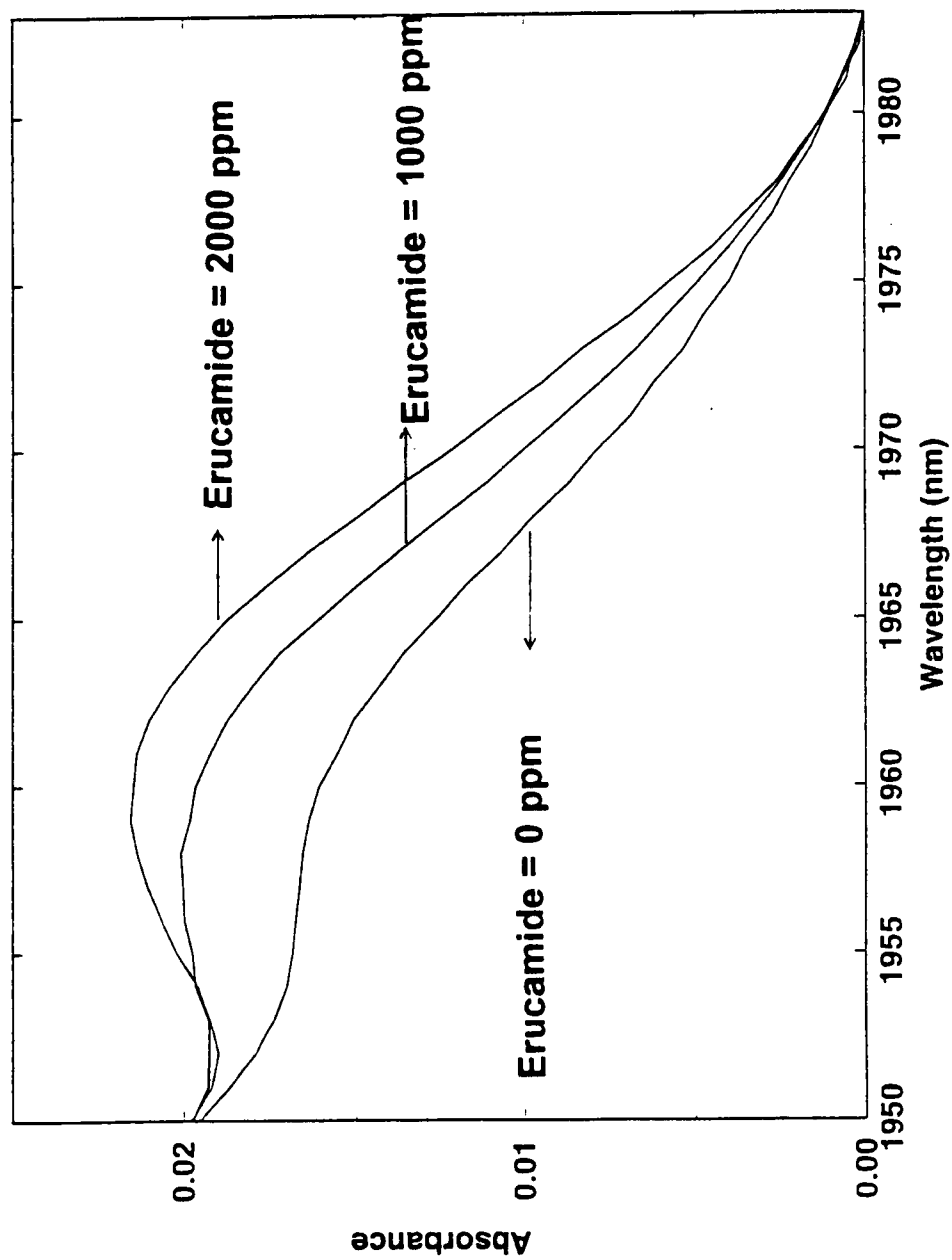


Figure 7.22 Spectra of EVA (12% VA) copolymer showing variations in erucamide content.

resolution capability of this method. Figure 7.23 shows a scatter plot of the predicted and actual concentrations of the samples in the validation set.

Conclusions:

The feasibility study described above proves that the NIR region has limited utility in the quantification of trace-level additives in polymers. The study established that a resolution of 500 ppm and a standard error of 200 ppm are possible using this technique. It must be mentioned here that the limitations of the dispersive NIR instrument were also a factor in the performance of the technique. Recently, interferometric instruments based on the FT-NIR technique have become available. These instruments offer other advantages and are much faster than the dispersive NIR instruments, as well as providing a higher signal to noise ratio. It is expected that the FT-NIR technique [95-103] would considerably improve the results obtained with erucamide samples. Also, a higher number of samples should be utilized in these experiments.

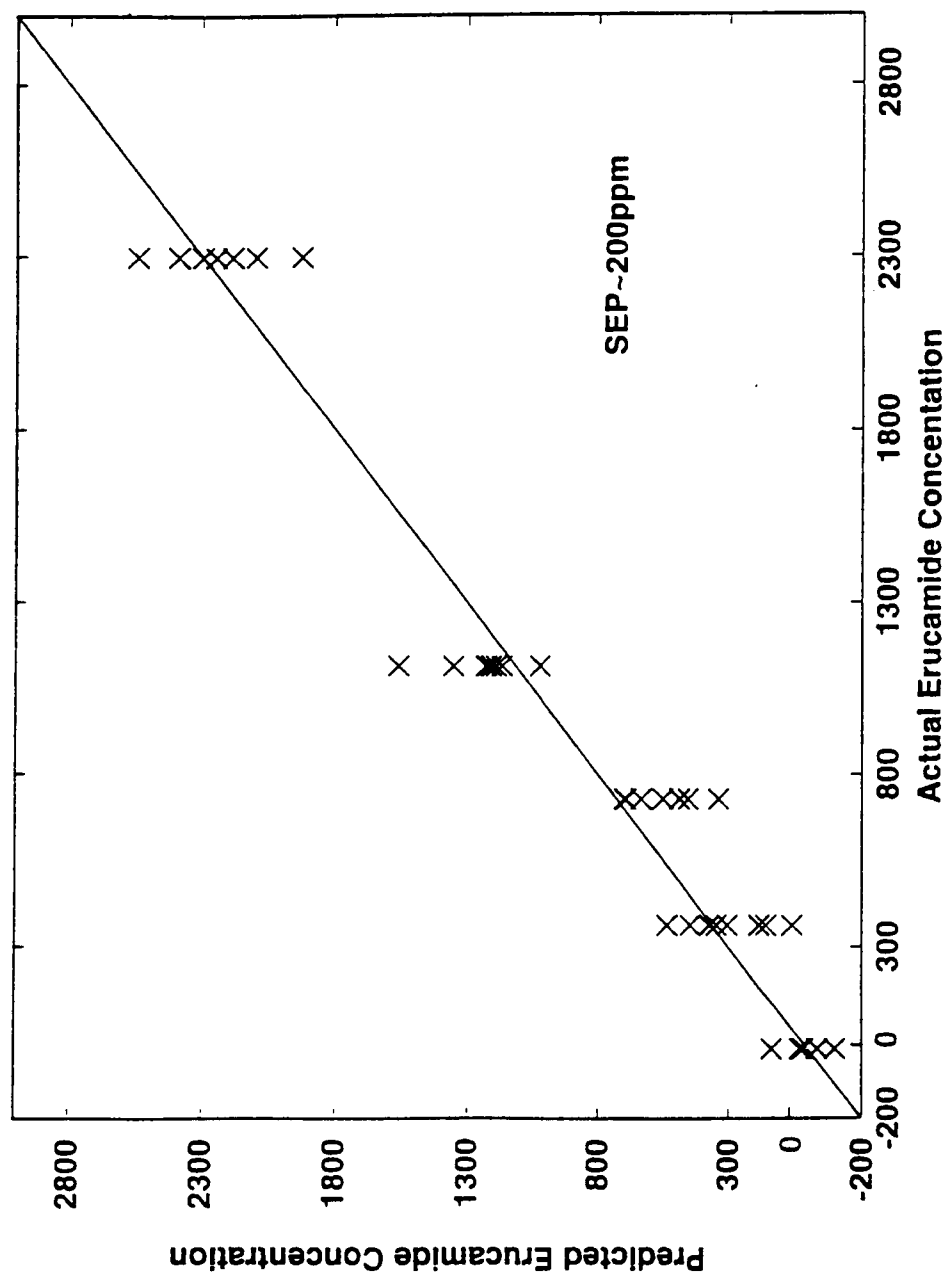


Figure 7.23 Scatter plot showing predictions of erucamide levels in the validation set.

8. CONCLUSIONS AND FUTURE DIRECTIONS

This research in the use of NIR spectroscopy for in-line composition analysis of molten polymers has made a significant contribution in demonstrating the potential of a technique which is rapidly gaining acceptability for plantwide process control.

The studies have demonstrated that transmission spectroscopy in the NIR region is suitable for in-line analysis of miscible polymer blends and random copolymers. The development and evaluation of rugged fiberoptic probes was another objective of this research. The probes play a crucial role in the transition from bench-top analysis to in-line analysis of molten polymers. The evolution of different types of probe designs, throughout this research, have helped to elucidate and address the problems associated with their use in a polymer process line.

The applications of chemometrics tools in the development and optimization of calibration models was thoroughly demonstrated. The studies have shown that there are numerous approaches in making the important distinction between information and noise, while extracting the useful information from large data sets. In this respect, the limitations of using commercial data packages were obvious, particularly with respect to speed and data exploration.

The miscible blends of PS and PPO provided the initial trial set, to test both the experimental system and the probes. The results showed that even with the variability associated due to the mixing of two polymers, the standard errors of predictions were less than 1%. This polymeric system provided the main motivation for the development of rugged fiberoptic probes, because commercial fiberoptic probes that were used initially had succumbed to the demands of the harsh process environment.

The system of random copolymers provided a complete sample set for an exhaustive study, particularly from a quantitative perspective. The studies established the utilities of different spectral regions, different pathlengths, and different modeling procedures, for monitoring the comonomer concentration in random copolymers. The availability of sample sets from two sources provided the opportunity to verify the robustness of the calibration models against independent data sets. The precision and the robustness of the calibration models can be judged from the fact that they were successful in monitoring the comonomer concentration in samples: (i) from an independent source; (ii) in real-time; and (iii) on a different day (than the calibrations).

The real-time monitoring of molten polymers was a major step in demonstrating the utility of the NIR technique for feedback process control. The real-time predictions provided an important test to verify the robustness of the calibration models. The real-time predictions showed that an interval of $\pm$ SEP value, that was used to establish the upper and lower control limits was sufficient for the data sets. The fact that the real-time results conformed to this interval proves the precision of the calibration models. In many industrial processes, deviations as high as three times the SEP values are used to determine the control limits [104].

The study on additives in EVA copolymers, in the NIR region, was to examine the suitability of the NIR region for the analysis of the additives and to determine the limitations of such an approach. The results showed that the precision of the NIR region is about 500 ppm. The results exposed the limitation of scanning dispersive type instruments in the above situations, where high signal to noise ratios are extremely important.

Although this research has contributed in the advancement of the overall research on in-line composition analysis of molten polymers, there are many areas that are still unexplored. These areas are the possible directions for this research, in the future.

The in-line studies using NIR transmission spectroscopy are useful for polymeric systems that do not scatter light significantly. For polymeric systems, such as immiscible blends or polymers containing high concentrations of fillers, in-line Raman spectroscopy could be a viable alternative. For quantification of trace-level additives in polymers, the ultraviolet region has tremendous potential. As far as the NIR region is concerned, fast instruments should be used in future, because of the high signal to noise ratios that are possible. Moreover, fast chemometrics algorithms warrant that the data acquisition should be as fast as the analysis, especially for real-time control. A variety of new (fast) instruments, such as FT-NIR instruments, instruments based on acousto-optical-tunable-filter (AOTF) technology, instruments containing charge-coupled-device (CCD) based detectors, and instruments containing diode array based detectors, are currently entering the market. The utility of these instruments shall be based on a number of factors, such as speed, cost, resolution, wavelength stability, etc.

In future, the real-time monitoring of molten polymers can be further advanced, to incorporate feedback process control. The idea of optical multiplexing can also be evaluated to simultaneously monitor different processes, or different regions in one process. The chemometrics algorithms would also need certain modifications to address this issue. Future research on probes could be aimed at developing single-insertion probes, and probes for in-line ultraviolet and Raman analyses.

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APPENDICES

APPENDIX A: NOMENCLATURE

SYMBOL - ABBREVIATION	DESCRIPTION
A	Absorbance
a	Absorptivity at a particular wavelength
B	Matrix of regression coefficients
c	Concentration of absorber
E	Matrix of residuals of X
E_v	Energy of vibration
F	Matrix of residuals of Y
h	Planck's constant
I	Intensity of light with the sample in the path of beam
I_0	Intensity of light without the sample in the path of beam
IR	Mid Infrared
k	Force constant
l	Pathlength of sample
MLR	Multiple linear regression
N	Total number of samples in the prediction set during cross-validation
NC	Number of samples in the calibration set
NIPALS	Nonlinear Iterative Partial Least Squares algorithm for eigenvector estimation
NIR	Near Infrared

NP	Number of samples in the test set
P	Matrix of loadings of X
PCA	Principal Component Analysis
PCR	Principal Component Regression
PLS	Partial Least Squares
m x n	Size of X matrix - m rows and n columns
PRESS	Predicted Residual Sum of Squares
Q	Matrix of loadings of Y
R	Diffuse reflectance from the sample
R ₀	Diffuse reflectance from a background
RNR	Residual-norm-ratio
SEC	Standard Error of Calibration
SEP	Standard Error of Prediction
SVD	Singular Value Decomposition
T	Matrix of scores of X
T _u	Scores vector for an unknown spectral observation
U	Matrix of scores of Y
v	Vibrational quantum number
X	Matrix of absorbance data
x _e , y _e	Anharmonicity constants
Y	Matrix of concentration data
$\hat{t}_1$	First scores vector of X
$\hat{p}_1$	First loadings vector of X
y _i	Actual value of concentration of sample i in the prediction set during cross-validation

$\hat{y}_i$	Predicted concentration of sample i in the prediction set during cross-validation
$y_{i,c}$	Actual concentration of sample i in the calibration set
$\hat{y}_{i,c}$	Predicted concentration of sample i in calibration set
$y_{i,p}$	Actual value of concentration of sample i in the test set
$\hat{y}_{i,p}$	Predicted concentration of sample i in the test set
%T	Percent transmittance
μ	Reduced mass of two vibrating masses
ν_j	Frequency of j th harmonic
ν_o	Frequency of fundamental vibration
ν_{osc}	Frequency of vibration of oscillator
ν	Frequency of vibration of two atoms joined together
$'$	Transpose of matrix or vector

APPENDIX B: DATA ANALYSIS

The following description is intended to provide a synopsis of the procedure used for the multivariate analysis of NIR spectral data in MATLAB environment. The description coupled with a flow chart (Figure B.1 on the next page) provides the basic framework for the multivariate techniques used in this research. Furthermore, the codes for the MATLAB programs have also been included in this appendix.

The Guided Wave Model 260 stores each spectral data file in ASCII format, with the absorbance spectral values stored as a column of data. Each file has about 15 lines of headers, describing information such as starting wavelength, end wavelength, wavelength increment, data of experiment, etc. The spectral data files are first preprocessed to remove baseline offsets by one of four methods: (i) one-pt. baseline correction; (ii) two-pt. baseline correction; (iii) computing first derivatives of spectra; (iv) computing second derivatives of spectra [step 1]. The preprocessed data files are transported to a Sun Sparcstation. A C-shell file is run to strip off the headers and to store the remaining lines under the same filename, but with a .mat extension [step 2].

As mentioned in the dissertation, the program for PLS based on singular value decomposition, was created in MATLAB, where it along with some files from a chemometrics toolbox created by Wise [27], forms a framework for chemometrics. The relevant codes from Wise's toolbox shall also be included in this appendix. In the program for SVD, the terminology used is similar to that of Wise's toolbox, so as to avoid any inconsistencies.

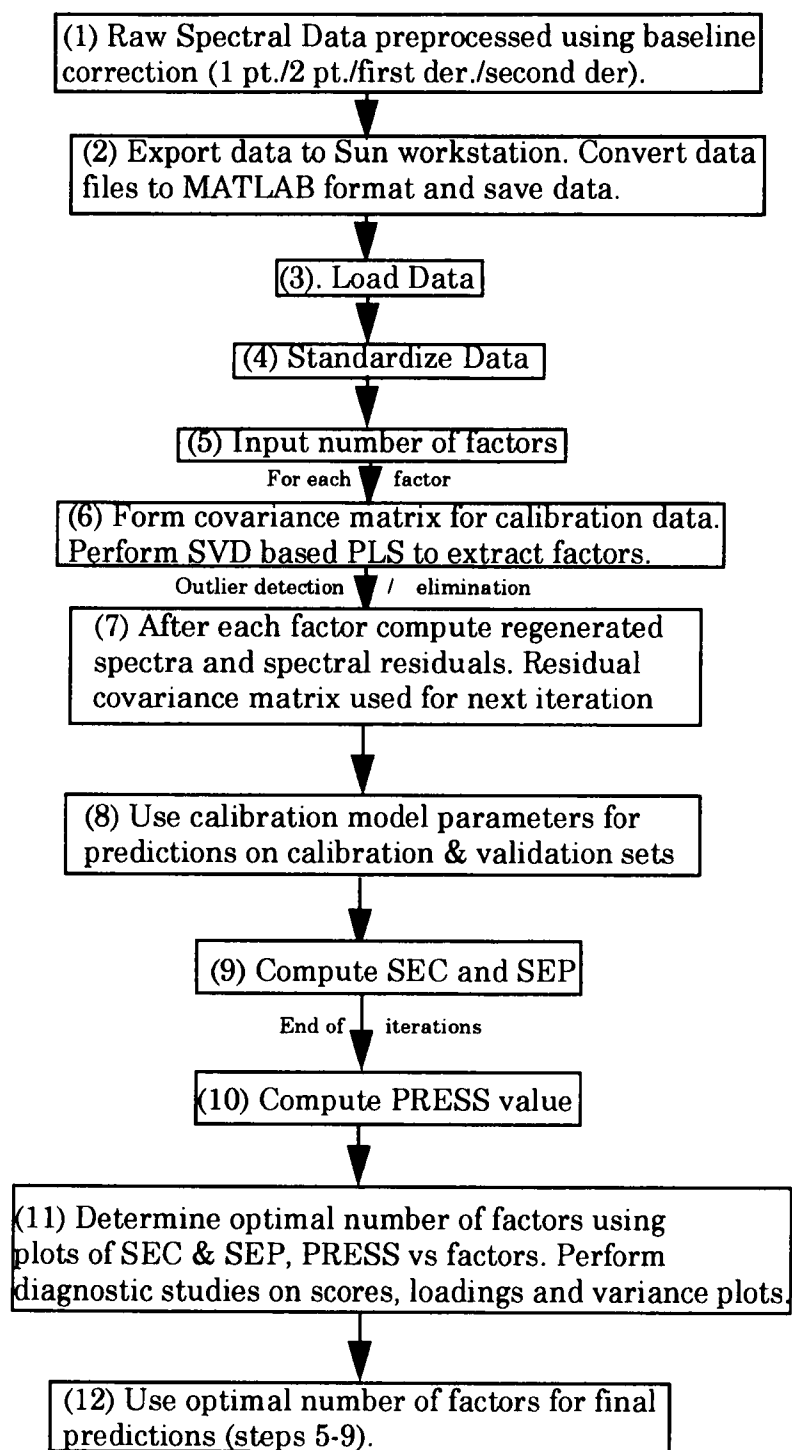


Figure B.1 Flow chart for multivariate analysis.

In MATLAB, all the data files for a particular set (calibration or validation) are loaded individually. Thus, each spectral file appears as a variable (i.e., a column of data) in the workspace. The variables are then transposed (so that each spectral data file corresponds to a row in the absorbance matrix) and appended together to constitute the absorbance data matrix (X) whose rows correspond to the number of spectral data files and the columns correspond to the number of wavelengths in each data file (further details of the sizes of the matrices are included in Section 2.3.2). The concentration matrix (Y) corresponding to each X matrix is created manually by inputting the concentration values corresponding to each spectrum. Thus, the rows of the Y matrix are equal to the number of the rows in the X matrix, while the columns correspond to the different constituents whose concentrations have to be calibrated. The above procedure is used to create the X and Y matrices for calibration (stored under names xc and yc, where c implies calibration) and validation (stored as xp and yp, where p implies prediction). All the four variables are then stored in a file data.mat [step 2], so that they can be retrieved during data analysis.

The names and descriptions of the MATLAB programs used for multivariate analysis are given below:

- (i) pn.m: main executable file that performs PLS analysis on a data set.
- (ii) spls.m: subroutine to extract the loadings and scores matrices for the calibration data, and the regression coefficients of concentration data versus absorbance data.

- (iii) `plssvd.m`: subroutine that is called within `spls.m`. It extracts eigenvectors of the residual covariance matrix during each iteration.
- (iv) `auto.m`: subroutine to extract the column mean and standard deviation of any given data matrix.
- (v) `scale.m`: subroutine to mean-center a given data matrix and, if required, normalize it with respect to the standard deviation of each column.
- (vi) `rescale.m`: subroutine to descale a given data matrix by de-centering it and de-normalizing (if required) with respect to the column standard deviation.
- (vii) `pls_pred.m`: subroutine to compute the values of concentration from the absorbance data and the calibration model parameters.

The main executable file in MATLAB is called `pn.m`. In this program, the file `data.mat` is loaded [step 3]. Each matrix is standardized [step 4] by mean centering and (if required) normalizing with respect to the column standard deviation. Standardization is a term used in chemometrics to describe the mean centering and normalization (with respect to column standard deviation) of data. The column mean and standard deviation are obtained using the subroutine `auto.m`, while the standardized matrices are obtained using subroutine `scale.m`. The standardized matrices (`xcc` and `ycc`, for the calibration set, and `xpc` for the spectral data in validation set) are subsequently used for PLS modeling. The next step in the program `pn.m` is to input the maximum number of factors [step 5], that are to be used in the cross-validation step. For each factor, the program uses the subroutine

spls.m [step 6] and the standardized calibration data matrices (xcc and ycc) to determine: the scores matrix (T), the loadings weight matrix (W) and the loadings matrix (P) for xc; the scores matrix (U) and the loadings matrix (Q) for yc; the vector (b) of regression coefficients of the scores vectors in U against scores vectors in T; the matrix (called ssqdif) that contains the residual variance in xcc and ycc after each factor; the matrix of regression coefficients (Beta) between the Y and X matrices. The subroutine spls.m uses another routine plssvd.m, which extracts the singular vectors of the residual covariance matrix after each factor. In the main program (pn.m), the scores and loadings matrices (T and P) for xcc are used to regenerate the data [step 7] using the specified number of factors, which is then descaled with respect to the mean and standard deviations. The spectral residuals are calculated [step 7] by subtracting the regenerated spectra (xnew) from the original calibration spectra (xc). The predicted concentration values (ypc) for the calibration set are computed using the subroutine plsprod.m [step 8]. These predicted values are then descaled (stored under name sypc in program pn.m) with respect to the mean of the concentration data in the calibration set (yc). The standardized spectral data for the validation set (xpc) are used in the subroutine plsprod.m to obtain the predicted concentration values (ypred) for the validation set [step 8]. These predicted values are then descaled (stored under name syprd in program pn.m) to obtain the predicted concentration values in the original reference frame. The series of steps described above are carried out for each factor. In all the studies during this research, the y matrix had only one column, and so the calculation and storage of sec, sep, and PRESS values are based on this particular

case only. For each factor the standard deviation of the predicted concentration values from the actual values, is calculated and stored as sec (standard-error-of-calibration, for calibration set) and sep (standard-error-of-prediction, for validation set) [step 9]. (Note: In the program pn.m, sec and sep are defined in lowercase. They are the same as uppercase SEC and SEP defined in Section 2.2). The predicted concentration values of the validation set, and at each factor are stored in a separate matrix (BB) whose columns correspond to the number of factors, and rows correspond to the number of samples. Another matrix (AA) of the same size as BB is also constructed, where each column contains the actual values of concentration in the validation set (i.e. all columns are identical). Using, AA and BB matrices, the PRESS (predicted residual sum of squares) is calculated for each factor [step 10], by subtracting the BB matrix from AA, and squaring and summing the individual values. At the end of the run (of file pn.m), the PRESS values are plotted against the number of factors [step 11]. The number of factors at which the PRESS value is a minimum, is considered to provide an estimation of the optimal number of factors. However the decision about the optimal number of factors is very subjective one, and requires that the number of factors should be enough that there is neither underfitting nor overfitting of the data. The sec and sep values can also be plotted against the number of factors [step 11]. The sec values always decrease with the increase in the number of factors, because the model is built on the calibration set and therefore by increasing the number of factors more and more information of the calibration set is accounted for. However, the SEP behaves similar to the PRESS plot, and that it exhibits a minimum for the optimal number of factors. It should be

mentioned here, that the SEP and the PRESS plots may not exhibit a sharp minimum. A judicious choice of the number of factors, is to include factors to a point that an inclusion of an extra factor does not produce a significant improvement in the prediction results (i.e. SEP and PRESS).

After determining the optimal number of factors, the file pn.m is executed again, and the optimal number of factors is input [step 12]. The prediction results for the calibration sets and the validation sets are then stored as sypc and sypred, respectively. The plots of sypc versus yc, and sypred versus yp are the scatter plots for the calibration and validation.

```

% Program pn.m
% This is the main executable file used to perform PLS modeling on absorbance and
% concentration data sets.

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% 1993
% Acknowledgment : Barry Wise

% clears all variables from the workspace

clear
load data.mat

% Standardization of data sets

mxc = min(size(xc));
mxp = min(size(xp));
[xcc,mx,stdx] = auto(xc);
xpc = scale(xp,mx,stdx);
[ycc,my] = auto(yc);

lv=input('No. Of factors?');

% Loop in which factors are succesively determined

for j=1:lv
    [P,Q,W,T,U,b,ssqdif,Beta]=splsc(xcc,ycc,lv);

    xnew = zeros(size(xc));
    for i = 1:lv,
        xnew = xnew + T(:,i)*P(:,i)';
    end

    xnew = rescale(xnew,mx,stdx);           % Regenerated data
    residuals=xc-xnew;                     % Spectral Residuals

    ypc = plspspred(xcc,b,P,Q,W,lv);
    sypc = rescale(ypc,my);                % Predicted values for calibration

    ypred = plspspred(xpc,b,P,Q,W,lv);
    sypred = rescale(ypred,my);            % Predicted values for validation

    sec(j) = sqrt(sum((sypc - yc).^2)/(mxc-1)); % Std. Error of Calibration
    sep(j) = sqrt(sum((sypred - yp).^2)/mxp); % Std. Error of Prediction

    AA(jj,j)=yp;

```

```

        BB(jj,j)=sympred;
    end
end

PRESS=sum((AA-BB).^2); % Predicted Residual Sum of Squares

```

```

function [P,Q,W,T,U,b,ssqdif,Beta] = spls(x,y,lv)
% This PLS program calculates the P, Q, W, T, and U matrices
% for the given x and y blocks and the number of latent
% variables specified: 1 <= lv <= dim(x); using the SVD method
% It also outputs the fraction of variance used in the x and y matrices;
% the equivalent LSR coefs (Beta).
% Input format is as follows:
% function [P,Q,W,T,U,b,ssqdif,Beta,ypred] =spls(x,y,lv);

```

```

% Adapted from program pls.m
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% Barry M. Wise
% 1991

```

```

[mx,nx] = size(x);
[my,ny] = size(y);

```

```

if (nx < lv)
error('No. of LVs must be <= no. of x-block variables')
end

```

```

X = x;
Y = y;
P = zeros(nx,lv);
Q = zeros(ny,lv);
W = zeros(nx,lv);
T = zeros(mx,lv);
U = zeros(my,lv);
b = zeros(1,lv);
ssq = zeros(lv,2);
ssqx = 0;

```

```

for i = 1:nx
    ssqx = ssqx + sum(x(:,i).^2);
end;

```

```

ssqy = sum(sum(y.^2));
for i = 1:lv
    [p,q,w,t,u,SR] = plssvd(x,y);

```

```

SR;
b(1,i) = u'*t/(t'*t);
x = x - t*p';
y = y - b(1,i)*t*q';
ssq(i,1) = (sum(sum(x.^2)))*100/ssqx;
ssq(i,2) = (sum(sum(y.^2)))*100/ssqy;
T(:,i) = t(:,1);
U(:,i) = u(:,1);
P(:,i) = p(:,1);
W(:,i) = w(:,1);
Q(:,i) = q(:,1);
end; % for

```

%This step computes the regression coefficients Beta's

% and the predicted y-block

```

Beta = W*pinv(X*W)*Y;
ypred = X*Beta;

ssqdif = zeros(lv,2);
ssqdif(1,1) = 100 - ssq(1,1);
ssqdif(1,2) = 100 - ssq(1,2);
for i = 2:lv
    for j = 1:2
        ssqdif(i,j) = -ssq(i,j) + ssq(i-1,j);
    end; % for
end; % for
disp(' ')
disp('    Percent Variance Captured by PLS Model') disp(' ')
disp('          ----X-Block-----          ----Y-Block-----')
disp('    LV#          This LV    Total          This LV    Total ')
disp([(1:lv)' ssqdif(:,1) cumsum(ssqdif(:,1)) ssqdif(:,2) cumsum(ssqdif(:,2))])

```

```

function [p,q,w,t,u] = plssvd(x,y);

```

```

% This program executes the SVD based algorithm for PLS. It runs as a
% subprogram of a main program as it calculates only one latent variable or factor.
% The format to invoke in the main program is: [p,q,w,t,u] = plssvd(x,y)
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% A. Khettry, J. Batra, P. Sarma, M. G. Hansen, and T. W. Wang
% 1993

```

```

% This step calculates the covariance between x and y
RY = x'*y;

```

```

[my,ny] = size(y);

% If number of y variables is equal to one, svd step is not required. The
% normalized covariance matrix is used to compute the principal component.
    if (ny == 1)
% The loadings weight for X in this case, is the covariance matrix normalized with
% respect to the norm of the covariance matrix. The scores (t) for x are the
% projection of the x matrix on to the loading weight.
        w = RY/norm(RY);
        t = x*w;
        q = 1;
    end; % if
% If there are more than one y variables, svd of the covariance matrix yields the
% principal component.
    if (ny ~= 1)
        [UR,SR,VR] = svd(RY,0); % svd of the covariance matrix
% The loadings weight corresponds to the first left singular vector. The scores (t) for
% x are the projection of x onto the loadings weight vector.. The loadings (q) for y are
% obtained by first regressing the scores (t) against y, followed by normalization
% w.r.t. to its norm.
        w = UR(:,1);
        t = x*w;
        q = (t'*y)';
        q = (q'/norm(q'))';
    end; % if
% The loading vectors for x are obtained by the regression of x against the scores
% vectors of x, followed by normalization. The scores vectors and the loadings weight
% vectors of x are multiplied by the norm of the corresponding p vector. The scores
% vectors for y are obtained by the regression of y against the corresponding
% loadings vectors.
        p = (t'*x/(t'*t))';
        p_norm = norm(p);
        t = t*p_norm;
        w = w*p_norm;
        p = p/p_norm;
        u = y*q;

```

```

function [ax,mx,stdx] = auto(x)
% autoscales matrix x and returns a vector of means (mx) and
% standard deviations (stdx) used in the scaling. I/O format
% is: [ax,mx,stdx] = auto(x)
[m,n] = size(x);

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% Barry M. Wise

```

```
% 1991

% Calculate the mean and standard deviation of the input data.
% Open a matrix with zeros for the scaled data (this makes
% the function faster since it doesn't have to resize y)
```

```
mx = mean(x);
stdx = std(x);
ax = zeros(m,n);
for i = 1:m
    ax(i,:) = (x(i,:) - mx)./stdx;
end
```

```
function sx = scale(x,means,stds)
% Scales matrix x using means (mx) and standard deviations (stds)
% specified. I/O format is: sx = scale(x,means,stds);
% If only two input arguments are supplied then the function
% will not do variance scaling, but only vector subtraction.
% I/O format is: sx = scale(x,means);
```

```
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% Barry M. Wise
% 1991
```

```
[m,n] = size(x);
sx = zeros(m,n);
if nargin == 3
    for i = 1:m
        sx(i,:) = (x(i,:)-means)./stds;
    end
else
    for i = 1:m
        sx(i,:) = (x(i,:)-means);
    end
end
```

```
function rx = rescale(x,mx,stdx)
% Rescales matrix x using the means (mx) and standard deviation
% (stdx) vectors specified. I/O format is:
% rx = rescale(x,mx,stdx);
% If only two input arguments are supplied the function rescales
% the means only. The I/O format is then:
```

```

% rx = rescale(x,mx);

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% Barry M. Wise
% 1991

[m,n] = size(x);
rx = zeros(m,n);
if nargin == 3
    for i = 1:m
        rx(i,:) = (x(i,:).*stdx)+mx;
    end
else
    for i = 1:m
        rx(i,:) = x(i,:)+mx;
    end
end
end

```

```

function ypred = plspred(x,b,P,Q,W,lv)
% This program uses pls model parameters to predict the
% responses to an new x block. Input/output sequence is:
% ypred = plspred(x,b,P,Q,W,lv);

```

```

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% 1991

```

```

[mx,nx] = size(x);
[mq,nq] = size(Q);
that = zeros(mx,lv);
ypred = zeros(mx,mq);

```

```

for i = 1:lv
    that(:,i) = x*W(:,i);
    x = x - that(:,i)*P(:,i)';
end

```

```

for i = 1:lv
    ypred = ypred + b(1,i)*that(:,i)*Q(:,i)';
end

```

VITA

Atul Khettry was born in Lucknow, India on June 11, 1968. He attended high school at St. Francis College, Lucknow, India. He joined Institute of Technology, Banaras Hindu University, Varanasi, India in August 1986, where he received the Bachelor of Technology degree in Chemical Engineering in June 1990. In January 1991, he joined The University of Tennessee, Knoxville and received the Doctor of Philosophy degree in Chemical Engineering in May 1995.