



Application of multivariate regression techniques to paint: for the quantitative FTIR spectroscopic analysis of polymeric components

by

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Thesis submitted in fulfilment of the requirements for the degree

Master of Technology Chemistry

in the Faculty of (Science)

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Date submitted: October 2011

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ABSTRACT

It is important to quantify polymeric components in a coating because they greatly influence the performance of a coating. The difficulty associated with analysis of polymers by Fourier transform infrared (FTIR) analysis's is that colinearities arise from similar or overlapping spectral features.

A quantitative FTIR method with attenuated total reflectance coupled to multivariate/chemometric analysis is presented. It allows for simultaneous quantification of 3 polymeric components; a rheology modifier, organic opacifier and styrene acrylic binder, with no prior extraction or separation from the paint. The factor based methods partial least squares (PLS) and principle component regression (PCR) permit colinearities by decomposing the spectral data into smaller matrices with principle scores and loading vectors.

For model building spectral information from calibrators and validation samples at different analysis regions were incorporated. PCR and PLS were used to inspect the variation within the sample set. The PLS algorithms were found to predict the polymeric components the best. The concentrations of the polymeric components in a coating were predicted with the calibration model.

Three PLS models each with different analysis regions yielded a coefficient of correlation R^2 close to 1 for each of the components. The root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) was less than 5%. The best out-put was obtained where spectral features of water was included (Trial 3). The prediction residual values for the three models ranged from 2 to -2 and 10 to -10. The method allows paint samples to be analysed in pure form and opens many opportunities for other coating components to be analysed in the same way.

ACKNOWLEDGEMENTS

I wish to thank:

God for allowing me the strength and dedication

My husband Angus Phala

Freeworld coatings for the financial support

Ancke Hector, Edith April, Khuluwa Mathole and Milicent Matuera for their laboratory assistance.

Professor T.N. van der Walt, my internal promoter.

Plascon colleagues: Jaylin Simpson and Dr. Christo Terblanche

Plascon managers: Y. Koen and J Mcleary



DEDICATION

I dedicate this to my **Son Alec Reed Phala (age 2)** and **Daughter Amber Lee Phala (6 months)**; you can do anything, dream and be “big” but remain humble and love life. Remember mommy loves you very much!!

Glossary

EDX	Energy dispersive x-ray
GC	Gas chromatography
FTIR	Fourier Transform Infrared
ATR	Attenuated total reflectance
NIR	Near infrared spectroscopy
IR	Infrared
HPLC	High performance liquid chromatography
HMPOE	hydrophobically modified polyoxyethylene
HUER	hydrophobically urethane ethoxylated thickener
HASE	hydrophobically modified anionic alkali swellable emulsion
Ps	Polystyrene
MMA	Methylmethacrylate
CLS	Classical least squares
ILS	Inverse least squares
PLS	Partial least squares
PCR	Principle component regression
RMSEC/P	Root mean square error of Calibration/ Prediction
Chemometric	Mathematical computational chemistry

Index

DECLARATION.....	2
ABSTRACT	3
ACKNOWLEDGEMENTS	4
DEDICATION	5
Glossary	6
Index	7
1 Introduction.....	13
1.1 Significance of the Research:.....	14
1.2 Objectives:	15
2 Polymers.....	16
2.1 Polymers for water based coatings	16
2.1.1 Classification according to synthetic procedure.....	17
2.1.1.1 Synthesis performed in water:.....	17
2.1.1.2 Polymer synthesized in bulk or in solution in an organic solvent and subsequently added to water:.....	18
2.1.2 Classification according to physical state	19
2.2 Overview of acrylic polymers in acrylic paints.....	20
2.3 Analysis of polymers.....	21
2.4 Instrumental Techniques for the analysis of polymeric components.....	22
2.4.1 UV – Visible spectroscopy	22
2.4.2 Nuclear magnetic resonance spectroscopy	23
2.4.3 Mass spectroscopy	24
2.4.4 Pyrolysis:	25

2.4.5	Chromatography.....	25
2.4.6	High performance liquid chromatography (HPLC)	26
2.5	Fourier transforms infrared spectroscopy (FTIR).....	26
2.5.1	Quantitative FTIR analysis general methods.....	27
2.5.1.1	Direct calculation:	27
2.5.1.2	Working curve method:	28
2.5.1.3	Standard addition method:	29
2.5.1.4	Absorbance ratio method:	30
2.5.1.5	Internal standard method:	31
2.6	Multivariate analysis	34
2.6.1	Chemometrics	35
2.6.2	Chemometric techniques	37
2.6.2.1	Discriminant analysis.....	37
2.6.2.2	Classical Least squares Method	38
2.6.2.3	Inverse least squares method (ILS).....	38
2.6.2.4	Partial least squares and principle component models	39
2.6.3	Multivariate methods for quantitative spectral analysis:.....	42
3	Experimental: Analysis of the three polymeric components in paint by FTIR and partial least squares.	49
3.1	Introduction:.....	49
3.2	Materials	50
3.3	Equipment	49
3.4	Method Parameters	52
3.4.1	TQ analyst: PLS overview	53

3.5	Experimental procedure	53
3.6	Results & Discussion.....	55
3.6.1	Calibration	57
3.6.1.1	The calibration results discussion	61
3.6.2	External Validation and quantification.....	66
3.6.2.1	The validation discussion	72
3.7	Conclusion.....	74
4	General discussion and conclusion.....	75
4.1	Limitations' of the FTIR-PLS model.....	76
4.2	Conclusion.....	76
4.3	Recommendations.....	77

Figures

Figure 2.1.	H ¹ NMR spectrum of copolymer methylmethacrylate and hexyl methacrylate.....	23
Figure 2.2.	Mass spectrum of polypropylene containing Irgafros168 and Irganox 1330.....	25
Figure 2.3.	HPLC chromatogram of PS/MMA copolymer ranging in composition from 11.4% to 88.54% MMA	Error! Bookmark not defined.
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Figure 2.4.	Graphical presentation of the standard addition method.....	30
Figure 2.5.	Working curve of the ratio method	31
Figure 2.6.	31
Figure 2.7.	Calibration curve of absorbance of the vinyl acetate peak at 1020cm ⁻¹ versus percentage of vinyl acetate in the copolymer.....	33
Figure 2.8.	Spectrum reconstruction	36
Figure 2.9.	Example of data reduction from 500 points to 15 factor loadings and 1 residual.....	37
Figure 2.10.	Summary of the nine cases studied	42
Figure 3.1	Overlay of FTIR spectra of 3 components; Component A –purple, B- green and C – red, showing the spectral differences in the fingerprint region.....	57
Figure 3.2	Actual versus calculated plot (left) and percent difference plots (right) for trial 2: For component A, B & C	59
Figure 3.3	Actual versus calculated plot (left) and percent difference plots (right) for trial 3: For component A, B & C	60
Figure 3.4	Pure component spectra obtained from PLS calibration relative to the Pathlength.....	61
Figure 3.5	Example of principle component spectra (vectors) in a dimensional space .	62
Figure 3.6	Principle components are used to reconstruct a spectrum with the factors which contain the % variance.....	63
Figure 3.7	Component A-1: showing residual values between 5 and -5	67

Figure 3.8 Component B-1: showing residual values between 1 and -2	67
Figure 3.9 Component C-1: showing residual values between 5 and -5	67
Figure 3.10 Component A-2: showing residual values between 10 and -10.....	68
Figure 3.11 Component B-2: showing residual values between 10 and -10.....	68
Figure 3.12 Component C-2: showing residual values between 5 and -5	68
Figure 3.13 Component A-3: showing residual values between 2 and -2	69
Figure 3.14 Component B-3: showing residual values between 2 and -2	69
Figure 3.15 Component C-3: showing residual values between 1 and -1	69

Tables

Table 3.1. FTIR Instrument parameters.....	51
Table 3.2. TQ analysts PLS - Method parameters: showing the parameters used for each trial.....	52
Table 3.3. Calibration results for the PLS model: showing the performance index, Coefficient of variation, standard deviations and the factors calculated for each trial. ..	58
Table 3.4. “PRESS” value for the selected component: changes as the number of factor increases. PRESS value for component A during Trial 3 selected as an example.....	64
Table 3.5. Example of the principle components: for component “A” showing contribution of each PC in concentration, full spectrum and analysis region.....	65
Table 3.6. Mean values of the standard error of prediction (SEP) and % relative error are shown; for each component for the three trials.	66
Table 3.7. The expected error with probability of 68% = a range of mean \pm SEP, which means 68% of data for the application, should fall in this range: Table showing the percentage of data in the range for each component in each trial.....	66
Table 3.8. the quality output for the un-used set; coefficient correlation, regression equation and number of outliers for each component.	70
Table 3.9. Reproducibility; showing the mean, SD and % RSD for component A, B and C during trial 3.....	71
Table 3.10. Residual and %RSD data for components quantified in the simple paint formulation using equation obtained by PLS calibration curve.....	71

1 Introduction

Paint is considered merely for decorative purposes by the general public. Paint systems are very complex and presents analytical chemist in the coating industry with many headaches. The complexities are due to the combination of several inorganic, organic and volatile components. The paints final composition and application may it be for exterior or interior use depends on the specific type of binders, solvent, pigment, extenders and additives. Durability is influenced by having a high molecular weight polymer that forms the final film. In order to analyse paint a thorough knowledge on the use of analytical methodology is imperative.

Separation methods of the various components of paint are easily achievable and analytical methods are documented in standards (such as ASTM) methods as well as in polymer handbooks. Many of the methods described require the paint to first be separated into its individual components, either by laborious extraction or centrifugation before analysis of the individual components. Solvents are currently being analysed after extraction by direct chromatography (GC) injection, headspace analysis as well as with solid phase micro extraction (SPME) Pigments and extenders are usually separated by centrifugation with highly volatile solvents or by ashing the paint samples. The inorganic matter are then analysed by EDX, Inductive coupled plasma (ICP) or atomic absorption spectroscopy (AA) (Ledger, 2002). Organic components (such as binder and additives) can first be separated by multistage extraction (e.g. ASTM D-3618). Presently Fourier transform infrared (FTIR) spectroscopy is used for qualitative identification of paint and paint components. Molecules have specific characteristic frequencies at which they absorb or transmit infrared radiation (Vandenberg, 1980). At present FTIR as well as many other analytical techniques are coupled with computer assisted software which enables one to manipulate and extract desired information. FTIR compared to other techniques, such as High Performance Liquid Chromatography and GC-pyrolysis presents an advantage in terms of cost effective operation and maintenance, as well as the minimum sample preparation especially with the use of an attenuated total reflectance (ATR) accessory.

Spectroscopy with computer assisted software and mathematical processing (chemometrics) is becoming very popular and is being used in a variety of industries. In the Polymer industry the technique has been used to follow; the monomer conversion under different conditions during a solution polymerization of styrene and butyl acrylate (Hong. Hua, 2003), the analysis of styrene copolymer composition by HPLC coupled to FTIR (Zengrong, et al., 2007), and copolymer characterization by UV spectroscopy, (Ulka, 1986).

Literature is filled with FTIR coupled with chemometric techniques for the analysis of copolymers and monomers. Thus the analysis of polymers is clear; however the technique has not been used for the quantification of polymers in paint. The binder content which is normally the main polymeric component in paint is usually asked for and presently industry has no means for quantifying the polymeric components in paint. Difficulties arise especially if more than two components are present. Polymeric components are also very complex, they have low to high molecular weights, they exist in many forms and many are being developed. Polymeric components are also known to form associations with other components, have different solubilities and some with insoluble fractions (Ledger, 2002). The latter makes them difficult to have them in solution all at the same time.

1.1 Significance of the Research:

The aim of this study is to develop a FTIR method; using chemometrics for the polymeric quantities in paint. The availability of such a method will be beneficial for production scrutiny and quality control. It will also be a first step in realizing our analytical capabilities for analysing and understanding our in house products and a gradual improvement to have well defined and cost effective in house methods.

The main focus of the study will be the quantification of three water soluble or dispersible polymeric components in emulsion paint. The polymeric components are a

rheology modifier, a styrene acrylic binder and an organic opacifier, each component contributing significantly to the paint system.

1.2 Objectives:

Use FTIR with chemometric processing software in order to simultaneously evaluate and quantify the three polymeric components in the paint, using the relevant chemometric technique.

The following chapters will deliver the following:

Chapter 2: will cover literature review which includes an overview of polymers and the analysis of polymers, Fourier transform infrared spectroscopy and the use of the chemometric techniques applied to FTIR.

Chapter 3: will outline the experimental chapter, where the use of FTIR and chemometrics will be demonstrated and discussed.

Chapter 4: will contain the general findings and conclusions

Chapter 5 contains the recommendation for future work

2 Polymers

Polymers are described as high molecular weight species or classically termed as macro molecules which consist of repeating unit of the same molecule. The repeating units are typically homopolymers (in the case of one monomer) and copolymers when more than one monomer is present. The monomers impart their own specific functionality for example flexibility, high gloss, hardness, chemical resistance and durability. The polymeric binder in a waterbased coating is typically a copolymer. Polymers can be synthetic, natural or chemically modified, branched or crosslinked. The synthesis and chemistry plays a vital role for their end use. A monomer present in a copolymer has a distinct bearing on the properties of the polymer, thus the major factor that needs to be controlled and monitored in order to produce a satisfactory copolymer for a particular use (Crompton, 1993).

2.1 Polymers for water based coatings

Environmentally friendly coatings, more specifically known as waterborne coatings, have set forth many opportunities for polymer chemist and continues to do so. Advances have been made in terms of polymeric binders, dispersants, rheology modifiers and polymeric colloid stabilizers. The usefulness of polymers in waterborne coatings is due to certain functional groups, which gives a function of water solubility or dispersibility to a water insoluble polymer. The well known functional groups are carboxylic acid, sulphonic acid and tertiary amine groups. The concentration of the functional groups influences the state of the final polymer, for example at high concentration of functional groups the polymer may be water soluble and at low it might only be water dispersible. The classification of aqueous polymers is very difficult due to the fact that there is no clear differentiation between the various polymer types. Polymers can be classified according to its synthetic procedure or according to its physical state (Padget, 1994).

2.1.1 Classification according to synthetic procedure

Two main categories are discussed: 1. Polymer synthesized in the presence of water and 2. Polymer synthesized in bulk or in solution in an organic solvent, polymerization can occur by free radical or step growth polymerization.

2.1.1.1 Synthesis performed in water:

Emulsion polymerization (oil in water) is the most widely used accomplished procedure for producing water borne polymers. In emulsion polymerization a free radical water soluble initiator is typically used to polymerize a free radical polymerizable monomer (s) to give a water dispersible polymer. Particles of diameter 50 to 500nm can be accurately obtained and easily controlled. The particle stability is achieved by adsorbed surfactants (usually anionic) which have a stabilizing effect, Suspension polymerization also commonly uses monomer soluble free radical initiators to polymerize water insoluble monomers. The polymerizations take place in each monomer droplet. The molecular weight is inversely proportional to the initiator concentration and polymerization rate. Particles are stabilized through the use of adsorbed water soluble polymers like acrylic acid copolymers and partially hydrolyzed polyvinyl acetate. The particle size is generally in the range 0.01-0.1mm. Large particle size suspension polymers are not usually used in the form of aqueous dispersion due to settlement and film forming problems that would be expected as a result.

Free radical solution polymerization is the process whereby the monomers, initiator and polymer are soluble in the continuous phase which may be water or a water and organic solvent mixture. This procedure is used for the preparation of dispersants and thickeners. Dispersants absorb onto the pigment surface and impart a stabilizing effect (avoiding the pigment particles from deflocculating) by introducing an electrical charge or steric hindrance on the pigment surface. Thickeners are rheological (flow behaviour) additives and provide the balance for in can, applicator, spatter, flow and levelling as well as anti-settling properties for the paint (Padget, 1994).

Inverse emulsion polymerization entails the emulsification of an aqueous monomer solution in a bulk oil medium and making use of water in oil emulsifier and an oil-in-water soluble initiator which gives sub-micron swollen water polymer particles in oil. The process is widely used for high molecular weight flocculants. A flocculant also has a deflocculating effect like dispersants (keeps pigment particles apart). The flocculants additive molecule has pigment affinic groups at either side of the molecule, which forms a bridge between the pigment particles. The additive also increase the structure build up in the liquid which reduces sagging and settling (Scholtz, 1993 cited in Padget, 1994).

Micellular polymerization is a process in which a surfactant is used to solubilise a water insoluble monomer to assist its copolymerization with a water soluble monomer (Turner, 1985 cited in Padget, 1994) have studied a polymerization reaction in which sodium laurel sulphate was used to solubilise a hydrophobic monomer butyl phenyl acryamide in a dissolved aqueous phase. Polymers made by this process are known as associative thickeners. Associative thickeners are molecules with hydrophobic elements and tend to interact with other hydrophobic elements in the paint, especially latex binders and opaque polymers; therefore the rheology of paint with these systems is influenced by a whole range of factors (Padget, 1994).

2.1.1.2 Polymer synthesized in bulk or in solution in an organic solvent and subsequently added to water

Binders for surface coatings are preparation as follow (Padget, 1994):

- Free radical addition in the bulk to give a low or medium molecular weight polymer and the water solubilising groups are incorporated via one or more of the co-monomers, then followed by the addition of water or vice versa.
- Free radical addition in the bulk with the introduction of the water solubilising group followed by the addition of water.

- Free radical addition in a water –miscible co-solvent or water co-solvent mixture with incorporation of the water solubilising group via one or more comonomers, followed by the addition of water.
- Free radical addition, step-growth, or ionic polymerization in a solvent, with introduction of a water-solubilising group, followed by the addition of water.

2.1.2 Classification according to physical state

Polymers can be classified in terms of their physical state for example a system in which the polymer is highly water soluble in an entire pH range or a system in which the polymer is highly water in soluble. The polymer can exist as an aqueous dispersion because of its water solubilising group. The difference between polymers is due to smaller functional groups and molecules and it are these essential features that impart their unique characteristics (Hansen, 1996).

The exact physical nature of the polymer systems obtained by the synthesized procedure is very dependent on a number of variables and can be related to the following:

Polymer: Molecular weight, concentration and nature of solubilising groups

Synthetic process: Shear and surfactant content

Solution/ dispersion: pH. Polymer concentration and ionic strength

Associating polymers are polymers with lyophilic and lyophobic groups in the chain; they may form associating structures in solution, are water soluble and consist mainly of hydrophilic groups with a low percentage of associating hydrophobic groups.

Associating polymers are very prone towards surface active agents and additives, and the associating properties of the polymers give solutions with completely different properties from soluble polymers. Associations can be ascribed to a model where the polymer chains are thought to be linked in a dynamic network of mixed micelles of surfactants and parts of one or several polymers. Associating polymers of the water soluble type are used as traditionally as rheology modifiers by the coating industry. They exhibit good flow and good gloss properties. As the coating industries become

more environmentally conscious water base paints are more sought after. (Hansen et al. 1996)

Associating polymers are sub-divided into several main groups, according to their chemical composition. (Hansen, 1996)

1. Hydrophobically modified poly(oxyethylene) (HMPOE) is prepared by the reaction of poly(oxyethylene) or ethylene oxide with aliphatic or aromatic isocyanates that contain a hydrophobic end group. The products are hydrophobically modified urethane ethoxylated (HUER) thickeners.

2. Hydrophobically modified polyacrylic acid is produced by the free radical copolymerization of acrylic acid or methacrylic acid and a hydrophobically modified polyacrylic acid and a hydrophobically modified monomer. This substance is influenced by the electro-viscous effect and by the hydrophobic associations. The products are hydrophobically modified alkali swellable emulsion thickener (HASE).

3. Hydrophobically modified cellulose compounds, commonly known as hydroxyethyl cellulose (HEC), are prepared by reacting alcohol groups in cellulose with alcohols or amines; (HEC) precipitates in hydrophobic associations and in traditional network formation because cellulose is high in molecular weight and a rigid polymer.

2.2 Overview of acrylic polymers in acrylic paints

Acrylic polymers are colourless, thermoplastic solids and are soluble in ketones, esters and aromatic solvents, and generally insoluble in aliphatic hydrocarbons. The acids acrylic, $\text{CH}_2=\text{CH}, \text{COOH}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$, and their esters can be polymerized to form long thermoplastic chains. Hydroxy functional acrylics are widely used in high performance coatings; these acrylic polymers offer exterior durability, very good light fastness and adhesion. Polyacrylate binders consist of copolymers of acrylate and methacrylate esters. The choice of additional monomers offers a wide variation of the physical and chemical properties of the resulting polymer property. Methyl methacrylate promotes weather resistance, light fastness, hardness, gloss and gloss retention. Styrene improves hardness and resistance to water and chemicals but was found to

reduce light fastness and gloss retention while methacrylates promote flexibility and adhesion to metals. (Dieter, 1998)

2.3 Analysis of polymers

From an analytical standpoint the composition of the polymer is usually requested. The analysis of a polymer is quite complex and polymers are available in a wide range of compositions. The synthesis of many new polymers has become more complex with the different types and the increased number of new copolymers. Due to this, Analysis by pyrolysis which was able to give us lots of information is still possible; however interpretation has become more complicated.

However pyrolysis is still described as the sought after technique for polymer analysis and many still find it suitable for characterizing insoluble polymers like cross linked material like used in lacquers. Some polymers are insoluble and non volatile which makes them unsuitable for their analysis by HPLC or GC (Bart, 2000.58-59).

Many polymer analysis books contain analysis for the characterization of the different class of polymers namely. The different classes of polymers include condensation polymers, formaldehyde copolymers, natural resins or ether resins as well as for addition polymers. They do not describe the separation as well as the analysis of the same and different classes from one another (Ledger, 2002).

Many techniques require the polymers to be present in pure form for the exact identification of the polymer. Chemical analysis was first used to determine monomer ratios of copolymers trace concentration of polymers and end group of polymers (Critchfield, 1961). The application of chemical methods to analyse polymers is made difficult by their limited solubility and chemical resistance. When Union Carbide chemicals Pty Ltd[®] introduced the ethylene – ethyl acrylate copolymer a saponification method was developed to determine how much of the ethyl acrylate was introduced into the polymer structure. After trial and error experiments and considerable investigation a solvent system was successfully developed in order to get both the polymer and KOH alkali in solution. The solution consisted of 2% water, 13% triethylene glycol, 30%

hexanol and 55% xylene. The technique was later used to calibrate a much easier Infrared method (Critchfield, 2002).

2.4 Instrumental Techniques for the analysis of polymeric components

The following paragraphs explain the existing analytical techniques which could be used to analyse polymeric components.

2.4.1 UV – Visible spectroscopy

UV spectroscopy based on the principle of absorption spectrophotometry, which involves the determination of a substance from its ability to absorb UV and Visible light at specific wavelengths. UV-Vis light is passed through the test sample and the amount of light absorbed by the sample is recorded against the wavelength. The above is in accordance with Beer-Lambert law which illustrates the linear relationship between light absorption and concentration:

The adsorption by UV requires polymers to have chromophoric groups (double bonds). Chromophores are responsible for electronic absorptions undergoing transition from the ground state to the excited state. UV analysis has found application in analysis of residual monomer remaining in a polymer sample (Painter, 1997).

Individual UV absorption spectra are taken for the styrene monomer, the monomer free polystyrene and the monomer-polymer mixture.

This methodology was further applied to a styrene methyl methacrylate copolymer. A range of styrene/methyl methacrylate copolymer solutions were prepared in chloroform and a wavelength at which the copolymer and one homopolymer showed characteristic peaks at the same wavelength was sought after. A calibration curve was obtained by plotting the absorbance values versus the % concentrations of the homopolymer solutions. The concentrations values of the unknown copolymer solutions were obtained from the spectra. Only two monomer systems could be determined (Ramelow, 1986).

2.4.2 Nuclear magnetic resonance spectroscopy

With NMR analysis a sample is placed in a magnetic field and irradiated with radiofrequency. The absorption's are due to transitions from quantized energy states. Atoms have atomic nuclei and these nuclei have a residual magnetic moment which allows them to react with an applied magnetic field. The frequency, at which the nuclei absorb, depends on the magnetic field and neighbouring nuclei and the relative shielding or de-shielding effect. The chemical environment of the nuclei can alter the frequency and this change is known as the chemical shift, and structural data can be obtained from it. The most important nuclei for the chemical Industry are the hydrogen and carbon, but silicone, fluorine and phosphorous are also useful in special circumstances (Ledger, 2002).

The technique is commonly used to identify and characterize copolymers; the HNMR has been used to study the copolymer methyl methacrylate (MMA) and hexyl methacrylate (HMA). Peaks were assigned to the alkyl methylene and methyl protons in the copolymer from range 0.5 to 2.5ppm and 3.6 and 3.9ppm to the three protons on the OCH₃ group of the MMA and the two protons of the OCH₂ of the HMA selectively.

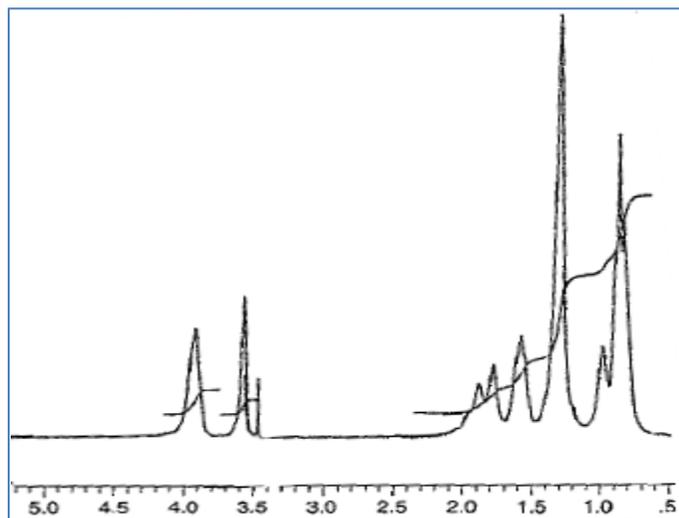


Figure 2.1. ¹H NMR spectrum of copolymer methyl methacrylate and hexyl methacrylate

(Painter,, 1997)

The % MMA in the copolymer was then determined by the expression: Where A is the area under the specific peak.

$$\%MMA = 100 \times \frac{\left(\frac{A_{3.6}}{3}\right)}{\left(\frac{A_{3.6}}{3} + \frac{A_{3.9}}{2}\right)} \quad 1$$

2.4.3 Mass spectroscopy

Ions are formed by bombardment of electrons, and introduction of sample molecules of methane occurring in a gas phase. Two ionization methods namely, electron impact and chemical ionization mechanisms exist, but the chemical ionization method is a softer technique for polymers because it produces less fragmentation. A number of mass fragmentation data are available on software libraries, or sample composition can be deduced from knowledge of elementary principles for interpretations. The technique relies on the reproducibility of the fragmentation and has

proven to be reliable for the identification of polymer additives and copolymer composition determination (Ledger, 2002).

The following is an example of a polymer polypropylene containing additives Irganox 1330 and Irgafros 168 of about 0.15% and 0.05% respectively. The molecular ions for Irganox $m/z=774$ and for Irgafros $m/z=646$ attributed to the oxide and $m/z=441$ side group.

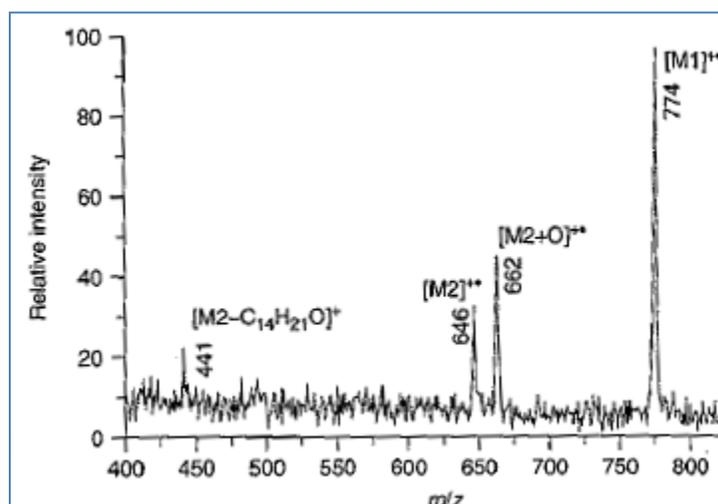


Figure 2.2. Mass spectrum of polypropylene containing Irgafros168 and Irganox 1330
(Painter, 1997)

2.4.4 Pyrolysis

Pyrolysis creates volatile components from high molecular weight and opaque particles. The process is based on free radical induced degradation, and the pyrolysis products are indicative of the original polymer. The polymers in the coating industry consist of monomers and small oligomers upon pyrolysis, which make the polymer easy to characterize. The procedure involves heating a small piece of solid or injection of a liquid into the pyrolyser and heating the sample rapidly to a high temperature usually between 600-800°C. The sample is degraded to smaller compounds which can generally be analysed by an additional analytical technique like GC-MS or FTIR (Wampler, 2009).

2.4.5 Chromatography

A chromatographic separation method can be used to separate mixtures especially those of being chemically similar. It involves partitioning a sample between moving fluids or gas phase and a stationary phase within a column. There are a wide number of techniques suitable for polymer analysis and the methods all involve the separation of sample components. Current Plascon[®] test methods include quantification of polymer additives and monomers, as well as determining the volatile organic components from

emulsions by GC analysis. GC can be coupled with other analytical techniques which can strengthen the identification of the eluted components (Ledger, 2002).

2.4.6 High performance liquid chromatography (HPLC)

HPLC involves injecting a sample into a mobile phase where it interacts with a stationary phase, as it flows down the column. The retention of the components depends on the components interaction with the stationary phase due to the different polarity. The eluted components are then detected commonly by ultraviolet or refractive detector. Two modes for analysis exist namely the reverse phase and normal phase. The reverse phase requires a stationary phase to be non polar and the mobile phase polar, the reverse is true for normal phase (Glockner, 1989).

Size exclusion chromatography (SEC) also called gel permeation chromatography (GPC) is a chromatographic technique that provides valuable information regarding the molecular weight distribution of a polymer. The columns used for SEC are defined in terms of the molecular weight exclusion limit and are normally soft, semi rigid or rigid gels with varying porosity (Ledger, 2007).

2.5 Fourier transforms infrared spectroscopy (FTIR)

A molecule absorbs electromagnetic radiation and therefore the increase in total energy is due to vibrational, rotational and translational motions. The atom in the molecule has three degrees of freedom which corresponds to motions along the perpendicular x, y and z coordinates in space. Infrared spectroscopy is a study of transitions within these energy levels of a molecule, due to absorption of the infrared radiation. Vibrational modes are classified as stretching and deformation modes, which correspond to changes in bond length and bond angles respectively. When a heteronuclear molecule absorbs energy it vibrates which results in a change in dipole moment because the inter-atomic distance between atoms changes. When this occurs the molecule is said to be infrared active, which is not the case in analysis of a homonuclear molecule because of its symmetry. When molecules, atoms or groups absorb at the same frequency the

vibrations are said to be degenerated because absorption bands overlap with the bands of atoms having identical frequencies and therefore the spectra of polymers may appear simple. The vibrational energy of functional groups in a molecule is unaffected by surrounding functional groups and each functional group has specific frequencies also known as characteristic frequencies (Vanderberg, 1980).

Attenuated infrared spectroscopy (ATR) is a different measuring technique and accessory for infrared spectroscopy, it measures what happens with a totally reflected infrared beam through a multi-bounce or single-bounce crystal when it comes in contact with a sample. The infrared interacts with the sample through a series of waves and these waves can penetrate the sample from 1 to 4 micrometers in distance.

Infrared analysis can be a great utility in quantitative analysis and literature is filled with references for quantitative analysis employed in the coating industry. FTIR is used in the quantitative infrared analysis of polymers, inorganic pigments, solvents and additives frequently found in coatings.

2.5.1 Quantitative FTIR analysis general methods

The following procedures discuss the current quantitative methods that can be used, for the analysis of polymer components in paint.

2.5.1.1 Direct calculation:

The method is used when you have the concentration of one sample and would like to know the concentration of an unknown sample with the same sample matrix:

$$C = \frac{A}{ab} \quad 2$$

The absorptivity (a) can be calculated from a known sample concentration with known sample concentration and known cell thickness (b). The concentration of the unknown

can be determined directly from knowing the absorbance of the unknown and dividing the equation from the unknown by the known.

$$C = \frac{AuCk}{Ak} \quad 3$$

Au = Absorbance of unknown

Ak = Absorbance of Known

CK = Concentration of Known

The method is limited to samples that can be measured in a liquid cell with constant path length, the absorption law is obeyed and there is a linear relationship between absorbance and concentration (Vanderberg, 1980).

2.5.1.2 Working curve method:

A calibration curve method is used when the concentration of an unknown sample concentration is expected over a wide range of concentration. The calibration curve is a function of concentration versus absorbance of known samples. The absorbance of the sample is then measured and the concentration read from the working curve (Vanderberg, 1980).

In an infrared method, with a solution of St-co-BA in toluene, was analysed off-line in order to evaluate the ability of infrared analysis to determine the monomer conversion and polymer composition from spectral changes. According to Beer's law the concentration of the various reaction components are proportional to the absorbencies measured from the corresponding peak heights. In applying Univariate analysis, characteristic absorbance bands for both monomers were identified and were used to track the reaction. The individual conversion rates of each monomer were determined by calculating the ratio of the absorbance's (peak heights at a certain time over the peak height initially at their respective wavelengths. The monomer conversion was monitored by following the change of certain characteristic peaks because it was assumed that the component concentration is proportional to the absorbance peak heights. (Hong. Hua, 2003)

$$x(\text{mol } \%) = 1 - \frac{\text{peak height at time } t}{\text{peak height at } t = 0} \times 100 \quad 4$$

The overall weight percentage conversion, X of the copolymer was also calculated using:

$$X(\text{wt}\%) = \frac{w_i}{w_i + w_j} x_i(\text{mol}\%) + \frac{w_j}{w_i + w_j} x_j(\text{mol}\%) \quad 5$$

X (wt%) = overall conversion X of the copolymerization

Where $\frac{w_i}{w_i + w_j}$ is the weight fraction of monomers i fed into the reactor at time t = 0

And

$\frac{w_j}{w_i + w_j}$ Is the weight fraction of monomers j fed into the reactor at time t = 0

2.5.1.3 Standard addition method:

An analytical band for the compound to be quantified is measured. Known amounts of the compound are added to the sample and the absorbance is measured after each addition. A plot of absorbance versus the amount of component added is constructed

The curve is extrapolated to zero absorbance. The intersection of the curve with the concentration axis indicates the original amount of the component present. The technique is most useful with samples that, obey the absorption law and when components are present in low concentration. The methods discussed above can be used for multicomponent analysis. Large errors may occur, if there are component interaction or when the wrong spectral bands are measured (Vanderberg, 1980).

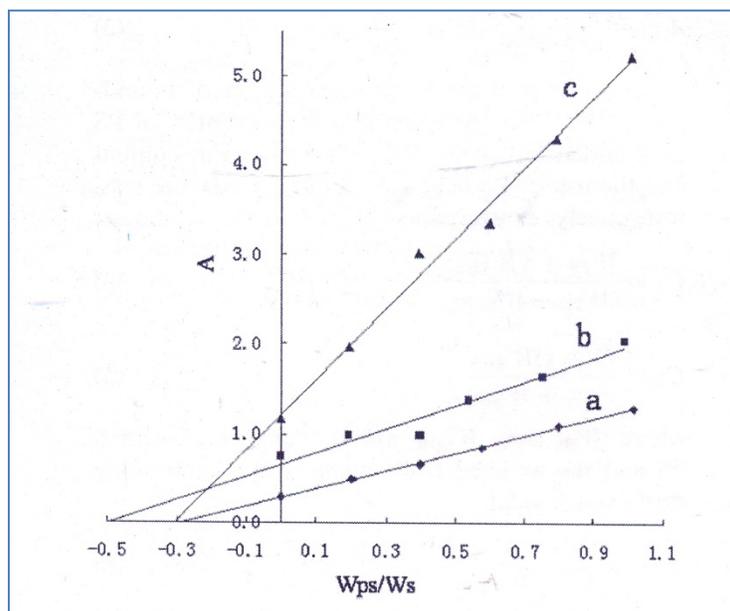


Figure 2.3. Graphical presentation of the standard addition method
(Zengrong, 2007)

In Zengrong (2007) the standard addition method was applied to the quantification of bound styrene in copolymers. The quantification of bound styrene is important because it greatly affects the performance of the styrene-butadiene rubber with regards to friction, aging and decomposition. Prior to this method the bound styrene was measured by the refractive index, but the method is limited for 55% bound styrene copolymers (ASTM D5775-95, 2004 and ISO 2453:1991, 2003).

Different quantities of polystyrene (Ps) were added to the sample in separate aliquots to obtain a series of mixtures with ratios of Ps to sample at 0/5 to 5/5. The samples were cast onto a KBR disc and the chloroform which was used to dissolve the samples was evaporated under an infrared light. The thickness of the film was controlled using the strongest peak height at a selected wave number (Zhang, 2007).

2.5.1.4 Absorbance ratio method:

The sample must meet the following criteria in order for the method to be successful:

The components in the sample must obey Beer's law.

Absorbivity for each component must be known.

Analytical band for each component must be known and must be free of interference from other components.

Considering a three component system, the following equations can be applied:

$$C_2 = \frac{A_2}{a_2b_2} \quad C_1 = \frac{A_1}{a_1b_1} \quad C_3 = \frac{A_3}{a_3b_3} \quad 6$$

The three components must be the sum total of all components present in the system:

$$C_1 + C_2 + C_3 = 1 \quad 7$$

The concentration of each component can be calculated by using the following expression and substituting equation 12:

$$\% C_1 = \frac{C_1 (100)}{C_1 + C_2 + C_3} \quad 8$$

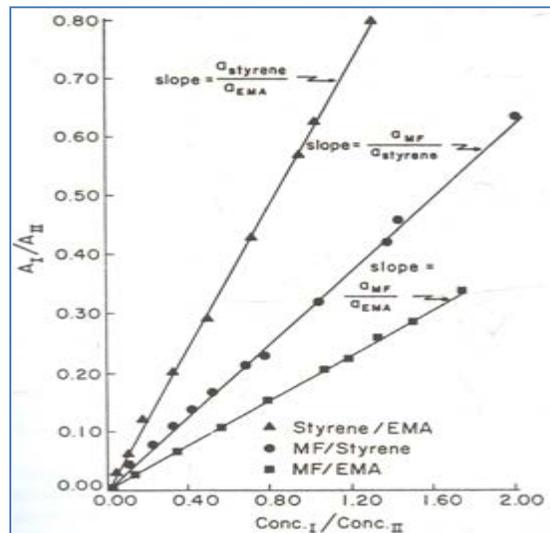


Figure 2.4. Working curve of the ratio method

(Vandenberg, 1980)

2.5.1.5 Internal standard method:

The method is used to determine only one component in a multi component system; a known amount of material (internal standard) is added to a known amount of sample. A

band for the internal standard and the component to be quantified must be obtained. The absorbance ratio is obtained from the working curve. The working curve is constructed by measuring the absorbance ratio for a number of samples with known concentration ratios. The following expressions can be used to determine the component of interest:

$$A_u = a_u b_u C_u \quad 9$$

$$A_s = a_s b_s C_s \quad 10$$

$$\frac{A_u}{A_s} = K \frac{C_u}{C_s} \quad 11$$

Cu = Concentrate of unknown

Cs = Concentration of sample

a = Absorbance activity

b = path length

An internal standard must have the ability to not interact with the components in the sample; the absorbance bands should be strong and apparent and must not overlap or interfere with the component to be measured. The internal standard must be available in pure form (Vanderberg, 1980).

The following is an example where the height of C-O peak at 1020 cm^{-1} due to the presence of vinyl acetate copolymer was divided by the height of C-H peak at 720 cm^{-1} due to the presence of polyethylene (Bellamy, 2010).

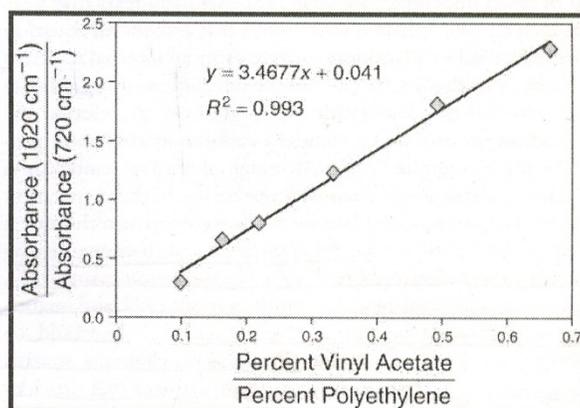


Figure 2.5. Calibration curve of absorbance of the vinyl acetate peak at 1020 cm⁻¹ versus percentage of vinyl acetate in the copolymer.

A plot of the absorbance ratio versus the concentration ratios from the analyte and standard are also useful when the internal standard concentration is not constant.

2.6 Multivariate analysis

The following is an introduction to multivariate analysis and its application to FTIR spectroscopy as well as an overview of the different techniques.

In order to consider a cause and effect relationship, where the independent variable is the cause and the dependent variable the effect, least squares linear regression comes to mind. This is a method for predicting the value of a dependent variable Y from an independent variable X . In the case where there is only one independent variable it is called simple least squares regression. This is a mathematical model for the data when the variable y has a linear relationship to the independent variable x , when a xy scatter plot is linear residual (is the difference from the observed y and the predicted y) plot shows a random pattern. Linear regression analyses yield the straightest line that best represents observation in a bivariate data set.

The regression line formulae are given by:

$$Y = B_0 + B_1X$$

12

B_0 is the constant

B_1 the regression coefficient

X and Y previously defined.

The coefficient of determination (denoted by R^2) is a key output of the regression analysis, it indicates the extent to which the dependent variable is predictable. The standard error is another important parameter, which measures the average amount that the regression equation over or under predicts. The standard error is found to be lower with the closer R^2 is to 1 and then more accurate prediction is likely to be made. A software package like i.e. Microsoft excel[®] or a graphing calculator are used to compute the analysis, but can be done manually as well.

Multiple linear regressions are an extension of linear regression to several dimensions.

Multivariate calibration enables rapid and simultaneous determination of each component in a complex mixture (Maggio, 2009).

Chemometric techniques like classical least squares, inverse least squares, partial least squares (PLS) and principle component regression (PCR), are commonly used multivariate techniques. A required exercise in multivariate analysis is to thoroughly investigate the entire quantitative spectrum. Each wavelength element or digitized data point can be considered as a separate variable. The process is called chemometrics or computational chemistry.

2.6.1 Chemometrics i.e. computational chemistry

Spectroscopic data can generally be very complex due to the multitude of molecular absorbencies. Differences in similar chemical spectra often consist of merely a slight shift or small change in shape which makes it visually impossible to distinguish. It is for this reason that spectra are complimented with the aid of mathematical methods.

Chemometric is a mathematical and statistical application for processing and interpreting large amount of chemical data (e.g. FTIR spectra). It finds a statistical correlation between spectral data and the known property using calibration. It allows one to predict desired parameters of unknowns if the correlations between calibration sets are systematic. It utilizes a feature known as principle component analysis in which a large number of data is compressed without losing any important information, principle components are extracted which are statistically independent from one another and orthogonal relative to each other and can be imagined to be a point in space. In mathematical terms the point is equivalent to a vector with (l_1, \dots, l_{500}) .

$$l_n(k) = \langle l_n(k) \rangle + \sum_{i=1}^{max.i} v_{in} \cdot (U_i(k)) + R_n$$

13

$\langle I_n(k) \rangle =$ mean spectrum

$U_i(k) =$ factors

$V_{in} =$ loadings which are weightings for each factor, describes the % variance from that factor

$R_n =$ Residuum which is the difference between the pre-treated and reconstructed spectrum.

The loadings and the residuum are variables for each spectrum. The following figure shows the reconstruction of the spectrum and data reduction example.

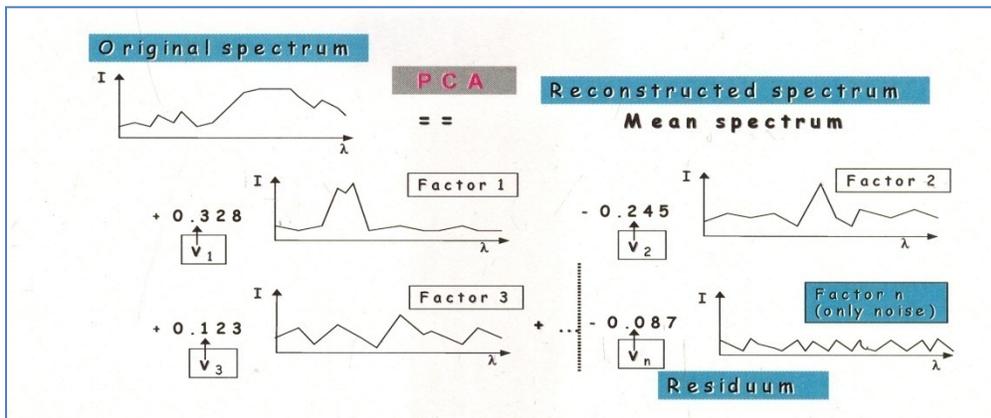


Figure 2.6. Spectrum reconstruction

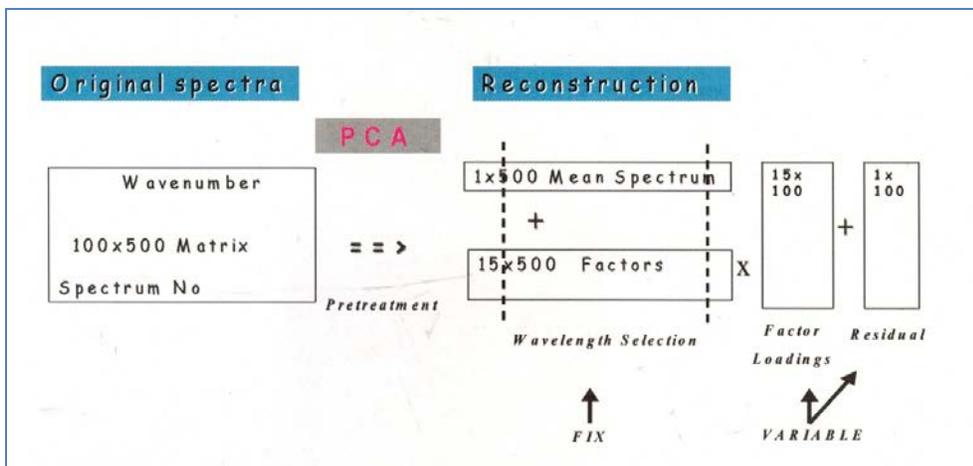


Figure 2.7. Example of data reduction from 500 points to 15 factor loadings and 1 residual

(Figure 4 & 5 Adapted from Buchi NIR training manual)

In layman's terms it creates artificial spectra from the principle components or factors. This is done by creating a mean spectrum by averaging the intensity values at each wavelength. The mean centre of the new artificial coordinate system gets shifted to this point. The following equation is used for the reconstruction of the spectrum:

2.6.2 Chemometric techniques

The following is an overview on the different chemometric techniques

2.6.2.1 Discriminant analysis

The Discriminant analysis technique is used to determine a class or classes of known materials which are similar to unknown materials by computing the mahalanobis distance units. The mahalanobis distance is an algorithm for calculating the distance of a sample from the mean of a set of standards using the following equation.

The method is typically used to screen incoming materials to determine if they are compound a, b or c. The method typically specifies at least two classes of known materials, but the method also works with only one class. Multiple standards may be used to describe each class and multiple regions of the spectrum may be used for the analysis.

During calibration the software computes a mean spectrum and then generates a distribution model by estimating the variance at each frequency in the analysis range. When the method is used to analyse an unknown sample, the software performs a principle component analysis (one or more orthogonal vectors that describe spectral concentration variation in the Discriminant method) on the spectra of the standards and uses the results to determine score values (a measurement of the distance a standard projects onto a principle component) for the unknown sample spectrum. The score plots are then used to determine the mahalanobis distance values. The results of the method

is the name of the class that are most similar to the spectrum of the unknown, the closer the distance is to zero the better the match.

2.6.2.2 Classical least squares (CLS) method

The CLS method follows Beer's law in which it assumes that the absorbance at each frequency is equal to the component concentration. In matrix notation assume m calibration standards which contain L chemical components with spectra of n digitized absorbance are given by:

New coordinate systems are formed from the calibration spectra which is the pure component spectra l rather than the spectral frequencies n . The spectral intensities for each mixture in the new coordinate of the pure component is the concentration of the components, because the component concentration represent the amount (intensities) of the pure component spectra which make up any given mixture spectrum (Haaland, 1980).

Advantages of the CLS method:

- Improvements in precision

- Allows simultaneous fitting of baselines

- Pure component spectrum and full spectrum residuals are made available for interpretation.

Disadvantages of CLS method:

- Method cannot handle unexpected impurities or components in a sample matrix

2.6.2.3 Inverse least squares (ILS) method

The (ILS) method also assumes that concentration is a function of absorbance, the inverse of the Beer's law with m calibration standards with spectra of n amounts of digitized absorbance's is given by:

Advantages of ILS method

Spectral analysis can be performed if only one component is known in the calibration mixtures. The components not included in the model must be present and totally modelled during calibration.

Disadvantage of ILS method

Analysis regions restricted; equation 12 has the dimensions equal to the frequencies which cannot exceed the number of calibration mixtures used in the analysis.

When frequencies becomes too large the precision of the results degrades, but sub optimal frequencies can result in poor baseline modelling, noise inflation and over fitting (Haaland, 1980).

2.6.2.4 Partial least squares (PLS) and principle component analysis (PCA) models

The general goals for PLS and PCA are similar, PCA is just a simple principal component analysis followed by a regression step. They are both factor analysis methods and they have the full spectrum advantage of the CLS method and the ILS advantage for being able to perform the analysis of only one chemical component at a time. PLS and PCA provides outlier detection from spectral residuals (difference between measured and estimated spectra) and limited chemically interpretable spectral information. PLS also has the advantage in the number of spectral frequencies that can be included in the analysis (Haaland, 1988).

The role of PLS is to form principle components that capture most of the information from the x variables that will help in the prediction of y_1 y_2 . In doing so it also reduces the dimension in regression by using fewer components than the number

of x variables. A new full spectrum coordinate system is obtained from principle component and loading vectors. The prediction step involves calculating the spectral intensities of the new coordinate system and can be related to analyte concentration just like in the ILS method.

2.6.2.4.1 Principle component analysis

In principle component analysis each sample can be represented as a vector or point in multidimensional space. A principle component describes the most spectral variation and it can be seen as independent sources of variation. The approach can be expressed mathematically as the decomposition of the data matrix, \mathbf{D} into the product of the two matrices \mathbf{P} for scores and \mathbf{T} for the transpose of the loadings.

$$D = PT^t \quad 14$$

D describes dimensions of samples by wavelengths, T is the loading matrix which and describes the dimensions of wavelength by principle components and contains the information from which it was constructed from. P is the score matrix and has dimensions of the samples by principle components and represents the samples in a new principle component space. The first three PC selected are said to contain most of the variation in the spectra and the others can be regarded as to contain minor characteristics or noise and thus can be ignored. PCA is used to make more defined groupings of the samples (Wold,1987).

2.6.2.4.2 Qualitative information from PLS and PCA:

First weight loading vector \hat{w} contains qualitative spectral information due to it being the first order approximation to the pure component spectrum of the analyte. It can be used to for making band assignments as well as to determine which regions of the spectrum are most relevant to a particular analyte. Vector of final calibration regression coefficient b_f may contain interpretable information. It can be used to indicate which spectral regions are important for prediction related to pure component spectra it takes into account all interfering information, molecular interactions and baseline variation. Spectral residuals can provide chemical info and outlier detection.

PLS and PCR can model the number of new components necessary for predicting and are therefore called soft modelling systems (Haaland, D.M.1985).

The following reviews are examples of how multivariate methods are used in combination with spectral analysis in the food industry, medicine and biological samples.

2.6.3 Multivariate methods for quantitative spectral analysis

The following sections are examples of how multivariate methods are used in combination with spectral analysis.

PCA and PLS have found their way into academics and various industries and for purpose of spectrometer calibrations, process modelling and quality control. Available software packages make the data analysis very easy, but it remains far from easily understood. Textbooks and journal articles give frequent explanations with a large amount of mathematics. The following paragraphs give an overview of the technique used in various other industries.

A submitted tutorial by the Department of Chemical and Biological Engineering of Dublin City University provides non experts with a practical understanding by using simple examples and a few equations. Nine virtual calibrations were used to study how factor analysis can be used when dealing with signal drift, random noise, interaction between compounds & non linear responses. The virtual mixtures were three hypothetical compounds and artificially assumed spectra (Jonas Schenk et al cited in Breton. RG, 2007).

Case No	Linear	Interactions	Noise	Drift	Explained variance by factor [%]				
					1	2	3	4	5
1	Y	N	N	N	78.6	14.7	6.7	0.0	0.0
2	Y	N	N	Y	74.8	14.3	7.1	3.8	0.0
3	Y	N	n = 1	N	11.0	3.2	3.0	3.0	3.0
4	Y	N	n = 1/3	N	25.4	5.0	2.9	2.5	2.4
5	Y	N	n = 1/10	N	48.3	9.1	4.2	1.4	1.4
6	Y	Y*	N	N	77.2	14.4	7.3	1.0	0.0
7	Y	Y**	N	N	77.2	14.4	7.3	1.0	0.0
8	Y	Y***	N	N	72.6	14.0	8.5	2.5	0.0
9	N	N	N	N	80.1	13.2	6.7	0.0	0.0

Figure 2.8. Summary of the nine cases studied

The examples studied have shown that factor analysis is superior to normal least squares regression methods in terms when the spectrometer signal is subjected to predictable drift and when compounds interact with each other, both methods performed

similar when facing random noise and none of them was able to predict the case in which absorbance was not linear with respect to concentration. Signal drift can also be overcome by correction methods like anchoring of Savitzky-golay filtering. The additional learning's from the tutorial suggest that before setting up a calibration model one has to determine the validity of the samples in terms of lamberts beers law, and to determine the independence of the species present. Checking for linearity and interactions will also lead to a significant reduction in the calibration set and a simplified modelling approach (Brereton, 2007).

The fundamental relationship between UV and IR spectral response and concentration is described by the Beers Lambert law.

If more absorbing species are present it becomes

$$A_{tot} = \varepsilon_1 \lambda C_1 b + \varepsilon_{12} \lambda C_2 b + \varepsilon_n C_n b \quad 15$$

Absorbitivity can be measured by measuring the absorbance of standard solutions of pure components at each wavelength. By applying simple matrix components the concentration of the pure component can be estimated. (Clark, 1993)

The following mathematical illustration is an example of how simple least squares regression was used to determine the unknown concentration of UV spectral data. 10 points was observed between 570 and 300 nm at two variables pH 2.2 and pH 2.5.

$$A = EC \quad 16$$

With standards having a concentration of 1:

$$A = E \quad 17$$

E' is the transpose of Absorbitivity E

$$E'A = E'EC \quad 18$$

$$(E'E)^{-1}E'A = (E'E)^{-1}E'EC \quad 19$$

The concentration can be given by:

$$C = (E'E)^{-1}E'A \quad 20$$

The synthetic spectrum (B) is calculated from:

$$B = EC \quad 21$$

The residual spectrum is given by:

$$R = A - B \quad 22$$

The residual variance is expressed by:

$$S^2 = \frac{R'R}{M - 2} \quad 23$$

The estimate of error is valuable because it is used as a weighting function allowing better estimate of the calculated concentration.

The variance estimates of each concentration are given by the covariance matrix:

$$V = (E'E)^{-1}S^2 \quad 24$$

Partial least squares analysis (PLS) was applied to the analysis of fecal fat. Fecal fat were normally determined by a three stage principle: saponification, acid hydrolysis and extraction and then finally a titrimetric assay (Polonovski, Kumagawa and Manual cited in Franck et al, 1996), which was found to be very time consuming. FTIR measurements were done on a Mattson Galaxy FTIR 5020 spectrophotometer, 24 scans per interferograms were accumulated at a 4 cm^{-1} resolution. The samples were first applied

to a transparent plate and then measured using an ATR accessory equipped with a zinc selenide (ZnSe) crystal. After data acquisition of the spectra, using adapted software (Win first v2.1 1994, ATI Mattson which have PLS-Quant v1.1 1993), PLS analysis a multicomponent method was applied.

Analysis was conducted on standard stools used for calibrations and another set of 91 independent stools were used as validations. A calibration matrix was built using lipid specific wave numbers from natural fatty solutions like butter, olive and sunflower oil. The performance of calibration was checked by cross validation which involves each standard in the calibration to be successively removed from the matrix calibration and considered as an unknown. External validation (accuracy) was based on the criteria to predict the concentration of the unknown sample and comparing the results with those obtained with the reference method. Repeatability, reproducibility and linearity were also studied. The choice of spectral regions for analysis included other spectral regions besides for the ones identified by the natural oils to better cope with variations in fecal matrix. A total of seven analytical regions were selected for analysis. The cross validation yielded coefficient of variation of ($r=0.996$), the standard error of calibration (SEC) was found to be 0.352%, the linearity range was 1-15% and the standard error of prediction is 1.07%. The reproducibility of samples which contained a lot of water was not good, due to water being a major interference in FTIR spectra (Franck, et al., 1996).

Edible vegetable oils are predominantly mixtures of triglycerides, which differ only in relative amounts of each. Small differences in their composition can lead to large differences in the cost and health properties (Dupont, et al., 1991). Many patented and expensive analytical techniques exist for the classification and quantification of these oils, namely gas chromatography (GC) and high-performance liquid chromatography (HPLC), and they do not lend themselves to on-line analysis. Drifting temperature is known to be a problem with both FTIR and NIR spectroscopy, often requiring careful thermostating of either the sample or the spectrometer. Chemometric classification and calibration techniques are very sensitive to instrumental variations and can therefore to greatly improve the robustness of the technique (Wang, 1992).

In one study the effectiveness of multiplicative signal correction (MSC) in correcting FTIR spectra for environmental variations was tested to see whether FTIR is capable of classifying edible oils according to their vegetable source, MSC was used to make corrections for temperature variations experienced while spectrum data were acquired (Donald, 1997). The calibration model was based on the assumption that the pathlength through the sample is constant, because PLS and principle component regression (PCR) techniques will fail when this assumption fails (Martens, 1989). Samples of oils were obtained from local suppliers in Anville Pennsylvania; spectra were acquired by FTIR on a Nicolet 5-Dx system at 4 cm^{-1} resolution, three to seven replicas were taken in a sealed NaCl cell with a fixed pathlength of 0.015mm. After each analysis the cells were cleaned with dichloromethane and dried with air.

The resulting spectra were combined to form a data matrix by using algebraic MAT-LAB software package. The data contained of 1556 measurements in the region from 3600 to 600 cm^{-1} . The pre-treatment with MSC has resulted in the separation of most of the oils according to plant origin by using two principle components. Most of the resolution was due to PC1 which contained 79% of the variance in the system and was obtained through a negative relationship with the absorbance in the 3005 cm^{-1} region which was caused by the cis-vinyl C-H stretch. The second principle contained 16% of the variance and it was negatively correlated with the trans-vinyl C-H in-plane bend at 967 cm^{-1} . The third principle component was responsible for separating the sesame oils from the canola oils and it contained 3.6% variance. The same frequencies were used for the Discriminant analysis. Frequencies corresponding to the cis-double bond content were predominantly responsible for this discrimination of the oils. (Donald, 1997).

Several studies exist concerning the characterization, classification and authentication of edible fats and oils by using FTIR (Dobson, 2001), but in combining them with chemometric techniques, FTIR is proving to become an emerging analytical technique

The PLS and PCR calibration model was built using 27 samples containing extra virgin olive oil and palm oil mixed in accurately weighted proportions of 1:50 wt/wt in chloroform, and an additional set of 32 prepared samples was used for validations. For

the Discriminant analysis extra virgin olive oil and palm oil mixtures were prepared; 15 pure extra virgin olive oil standards and 27 mixed with palm oil. The samples were measured using an FTIR Nicolet 6700 from Thermo Nicolet® Corporation equipped with an attenuated total reflectance (ATR) accessory. FTIR spectra were recorded from 4000 to 650 cm^{-1} , co-adding 32 interferograms at a resolution of 4 cm^{-1} .

The analysis was performed using software TQ analyst TM version 6. Upon analysing the pure spectra of extra virgin olive oil and palm oil, their entire spectra looked very similar with the naked eye which is due to similar chemical composition of the two oils which showed typical characteristics for common triglycerides. In closer examination of the spectra minor differences were found between the spectra which were observed at frequencies of 1402 cm^{-1} caused by =C-H bending vibration and 1030 cm^{-1} attributed to the C-O stretching. The spectral region, where most of the variations were, was in the finger print region and this region was chosen for the analysis. In fats and oils most of the peaks and shoulders are attributable to the specific functional groups (Bendini, et al., 2007). The optimum number for PLS and PCR factors was determined by cross validation, cancelling one standard at a time and plotting the number of factors against the root mean square. The predictability was tested by the root mean square of error. PLS and PCR calibration in the first derivative spectra yielded the highest R2 with a value of 0.999 and the lowest RMSECV of 0.285 and RMSEP of 0.616 (Rhoman, et al., 2010).

A multivariate calibration model combined with IR spectroscopy was set up to follow the monomer concentration changes under different conditions during a solution polymerization of styrene and butyl acrylate in toluene (50 to 65 wt %). A calibration model was built from twenty nine samples. Spectral regions from 1800 to 700 cm^{-1} were included in the analysis. PLS in linear combination approximated the original spectra by reducing the calibration spectra to a smaller number of key spectra called factors; factor analysis was used to determine the optimal number of factors (In this study 4) which explained most of the variance. The PLS model was used to establish the predictive relationship between the spectral data set and the monomer concentrations. The correlation coefficient for the model predictions for styrene and butyl acrylate was found

to be 0.9966 and 0.9961 respectively suggesting a good agreement between the model prediction and actual measurements (Hong, 2003).

The use of chemometrics techniques to analyse FTIR (Zhang, 2007) was once again demonstrated with the analysis or the determination of styrene copolymer concentration & composition. A method was demonstrated whereby SEC is coupled to an on line Fourier transform infrared detector and an on line viscometer detector. The method was applied to several types of styrene copolymers. Styrene, methyl methacrylate and butadiene were considered the three components. The training set was composed of 27 standards ranging 0 to 100% styrene weight fraction and 24 standards with different concentration was used as validation standard. As a full spectrum method they have found that PLS gives better predictions when you narrow the spectrum down to a few absorption bands.

This chapter has described the standard analytical methods and techniques that are commonly used to determine polymers. The same applications were applied to the analysis of the three polymeric components. The features that stood out was the fact that the predictions with the PLS method was very close to the original values. The commonality between these methods was that great care has been taken to prepare accurate calibration and validation standards. The FTIR coupled to chemometric technique have shown to be successful in various applications. The combination of FTIR with chemometrics makes it possible to analyse multicomponent with severe spectral overlapping and component interactions. The former will be applied to a pigment extender (PE) free coating, in hope of quantifying three polymeric components. The experimental will be outlined in the following chapter.

3 Experimental: Analysis of the three polymeric components in paint by FTIR and partial least squares.

3.1 Introduction:

Paint is a complex system consisting of organic and inorganic materials offering special challenges to the analytical chemist. It consists of many opaque and very high molecular weight constituents. The identification and quantification of the polymeric component for example the binder, organic opacifiers, dispersant or rheology modifiers in a coating are usually required for analytical scrutiny, quality assurance or competitor analysis. Many polymers are also very complex and many industrial synthesized polymers exist, they are also known to form associations with other components.

A variety of analytical techniques has been applied to the identification and classification of polymers; the techniques include GC - pyrolysis and HPLC, but are very costly and time consuming. Infrared spectroscopy is widely used as an analytical tool for the qualitative and quantitative analysis of materials. The development in recent years gave FTIR spectrometers a significant advantage over traditional dispersive instruments. FTIR coupled with computerized techniques allowed the manipulation of digital data and access to more information which was previously not possible. Researchers' has applied the techniques of differentiation and regression analysis to infrared analysis in order to obtain more information on component analysis and to predict significant properties of samples. (Osborne, 1981). The methods are based on multivariate statistical analysis or more specifically factor analysis. It has found numerous uses, which includes the determination of the number of components in a sample, the separation of the pure component spectra from spectra of a mixture, spectral identification of unknown mixtures, signal drift, random noise, interaction between components and non linear responses (Malinowski, 1980).

FTIR based on computerized data processing like chemometric classification and calibration techniques has found application in many fields, such as medical, petroleum and agricultural industries. Applications in the coatings industry are very limited. This study reports a multicomponent technique whereby the quantification of the polymeric

can be determined without extraction and the quantity predicted to a good degree of accuracy.

3.2 Materials

Biocide: Ammonia

Three polymeric components consisting:

- a polymeric opacifier (Plascon),
- Styrenated Acrylic emulsion
- HASE – polyurethane anionic rheology modifier from Rohm & Haas,

The three polymeric components will be named component A, B and C respectively.

Component A: The organic opacifier is a spherical polymer particle that has a multitude of aerated micro voids within the polymer shell. The voids cause effective light scattering comparable to that of TiO_2 – pigment, the polymer particles can successfully replace TiO_2 for this reason (Stewart, 1993). They are produced by emulsification whereby an organic phase containing an unsaturated polyester resin and styrene monomer is emulsified with an aqueous phase. A polyamine is added to achieve absorption of water inside the organic phase and this water is replaced with air when it evaporates (Gous, 2003)

Component B: The polymeric binder is a styrene acrylic binder, prepared by suspension polymerization. It is one of the major components in paint which forms a tough coherent film when the solvent evaporates.

Component C: The rheology modifier is an anionic thickener or better known as a hydrophobic modified alkali swellable emulsion. It influences the low shear viscosity properties of paint.

The extraction solvent was a mixture of 1:1 by volume. Dimethyl formamide and Tetrahydrofuran. The former as well as Heptane obtained from Sigma chemicals.

3.3 Equipment

Oven maintained at 105°C for 2 hrs, data obtained by Nicolet® 380 FTIR spectrometer equipped with Omnic® 6 and TQ analyst professional® edition 8 and software for data capturing and processing. Transmission spectra were obtained with FTIR by using Silver bromide (AgBr) halide discs and ATR spectra were obtained with a diamond crystal.

Table 3.1. FTIR Instrument parameters used in experimental work

No of scans:	128
Resolution:	4 cm ⁻¹
Spectral range:	400 – 4000 cm ⁻¹
Gain parameter:	1
Gain velocity	0.416
Background correction:	subtracted after each run

3.4 Method Parameters

The parameter selected provides the optimal performance index (how well a calibrated method can quantify the validation standards).

Table 3.2. TQ analysts PLS - Method parameters: showing the parameters used for each trial

TQ analyst set up tabs	Trial 1	Trial 2	Trial 3
Description	PLS - by transmission FTIR	PLS by ATR	PLS by ATR
Pathlength	assumed to be constant	Constant	Constant
Components	Analysis limits – on	Analysis limits – on	Analysis limits – on
Spectra	no subtraction	no subtraction	no subtraction
Data Format	Original spectra	Original spectra	Original spectra
Smoothing	none	none	none
Regions and type	Spectrum range /cm ⁻¹ 2761.73 – 3393.17 1687.41 – 938.76 1687.41 – 1677.41 1074.32 – 678.34 1687.41 – 1834.19	Spectrum range /cm ⁻¹ 1051.01 - 662.43 1746.71 – 1057.28	Spectrum range /cm ⁻² 1773.64 - 999.39 3720.05 - 2832.87
Fit value algorithm	simple	simple	simple
concentration weighted PLS	No	Yes Yes	Yes
PLS factors	No		yes

3.4.1 TQ analyst: PLS overview

The PLS method was applied to the raw data. PLS is a statistical and quantitative technique, it examines the specified region/ regions of the calibration spectra to determine which areas are varying statistically as a function of component concentration. The calibration model uses spectral and concentration information from the standards as well as intensity and wavelength information. PLS was used because the measurable peak of the pure components overlaps severely. PLS is capable of quantifying sample components when the correlation between concentration and absorbance is very complex. PLS is also good when there are interactions between component peaks in the mixture, which causes the peaks to broaden or shift or when component are present when concentrations are not known. The method can be set up to measure all components in a region or you can specify which components to measure in which region. Up to 50 components can be specified.

The TQ analyst method development software is very user friendly, and has several tabs in which parameters can be defined for optimum quantification of a method. The software also has a unique suggest wizard, which can be used when the parameter option is not known. The parameters used for the PLS calibration in this study are defined as follows:

- Pathlength: in Trial 1, transmission spectra were collected by using Silver Bromide halide discs. The Pathlength (sample thickness) of the sample could not be verified, and therefore the suggest wizard evaluated the spectra from a zero spectra off which the constant pathlength could be ascribed. A constant pathlength for trail 2 & 3 was selected because ATR was used, and is known to have a constant pathlength.
- Components: Concentration limits affects analysis limits significantly. The upper and lower limits of a component have been specified for both methods. This also affects the performance index and indicates how well the method can quantify the validation standards.

- No spectral subtraction for the two methods was required and the data analysis was done on the original spectra. Data analysis can be conducted by selecting the first and second derivative spectra. The first derivative shows the rate of change across the entire spectrum, which means shoulders on peaks become narrower and is therefore easier to see. The second derivative shows the change in the rate across the spectrum, which result in complex curve with narrower bands. It is useful for finding exact peak locations, but increases baseline noise.
- No smoothing was selected. Spectra smoothing improve spectra that might contain random noise obscurities, which can decrease the error in the method.
- The spectra were corrected with calibration and correction standards to correct the linearity of the method component. Error handling was set on constant across measured range. The first trial was normalized by selecting the mean centering technique. Trial two were normalized by selecting both the mean centering and the variance scaling techniques. Mean centering calculates the average spectrum and subtract it from each calibration spectrum, it also calculates the average concentration value for each component and subtracts the average value from the concentration value of each calibration spectrum. Variance scaling specifies whether the calibration data will be scaled so that all of the data contribute equally to the calibration model. It estimates the standard deviation (SD) at the intensity values and divides each spectral data point by its estimated SD. A simple fit value algorithm was applied to both methods which measures the validation spectrum to a zero spectrum. It is used when the concentration of the standards in a method spans over a large range of concentration relative to the concentration you expect in the samples. A sensitive fit measures the validation spectrum relative to a mean spectrum for all the calibration standards.

- Concentration weighted PLS was applied to trial two, to see whether it can reduce the uncertainty in the lower concentration ranges.

3.5 Calibration and Validation set

Design of calibration set: A full experimental design for 3 components and 3 levels would involve $3^3 = 27$ standards, TQ analyst reduce the number of standards by introducing factors from principle components with variable correlation. Standards were prepared according to the standard matrix that was modelled as required by TQ analyst software after the three polymeric components were specified. Each standard had had the three components in varied amounts but all added up to 100%. Each standard and sample spectrum was evaluated for baseline correction and total absorbing peaks before the spectral data was transferred to the TQ analyst processing methods.

3.6 Samples

The concentration ranges from the three polymeric components in 4 simple PE free formulation are as follows: A 10 – 75%; B 10 -75% and C 0 – 5%, But the calibration model covers the range from 0 to 100% for all components.

3.7 Experimental

- Trial 1: The initial experiment was used to see if one can extract the three polymeric components from the paint and quantifying the extracts via TQ analyst. The PE free paints were formulated varying in three polymeric components three times. Paints with unknown polymeric content were also prepared and used for external validation. The polymeric components were extracted using ASTM method D3168 which requires weighing 1 to 2 g of paint into a glass beaker and allowing the paint to dry in an oven at 105°C for 2hrs. Subsequently, it was washed with water to remove the emulsifiers and protective colloids, 50 ml of heptane was added to remove the emulsified plasticizers' and oils and other insoluble non polymeric organic materials. 10ml of the extraction mixture was added to extract the polymeric from the pigment. The extract was filtered through fine filter paper

and solvent evaporated leaving only the polymeric which could then be applied to a crystal halide and sample and standards were acquired by FTIR transmission.

- Trial 2: After a good correlation of the calibration model for trial 1 (R^2 close to 1) and realizing one cannot extract all of the polymeric components with the ASTM 3618 method. The FTIR spectra of the extract were that of styrene acrylic only, regardless of the concentration used in the formulation. set; TQ analyst PLS was applied to analyse the paint for quantification of the polymeric components without prior extraction. The polymeric was not extracted; the standards and sample spectra were obtained by ATR using a diamond crystal.
- Trial 3: The following trial was conducted to determine reproducibility of the lower end concentration for component C. Following a similar route to trial 1, standards and validation samples were prepared by rationing the components to add up to 5. The unit required by the component tab was left out, and the decimal places were reduced to 2. Furthermore different analysis region compared to trial 1 and 2 were selected for processing.

3.8 Results & Discussion

The results of the PLS calibration and validation results for each trial are displayed, followed by a discussion of the calibration results and validation results respectively.

3.8.1 Calibration

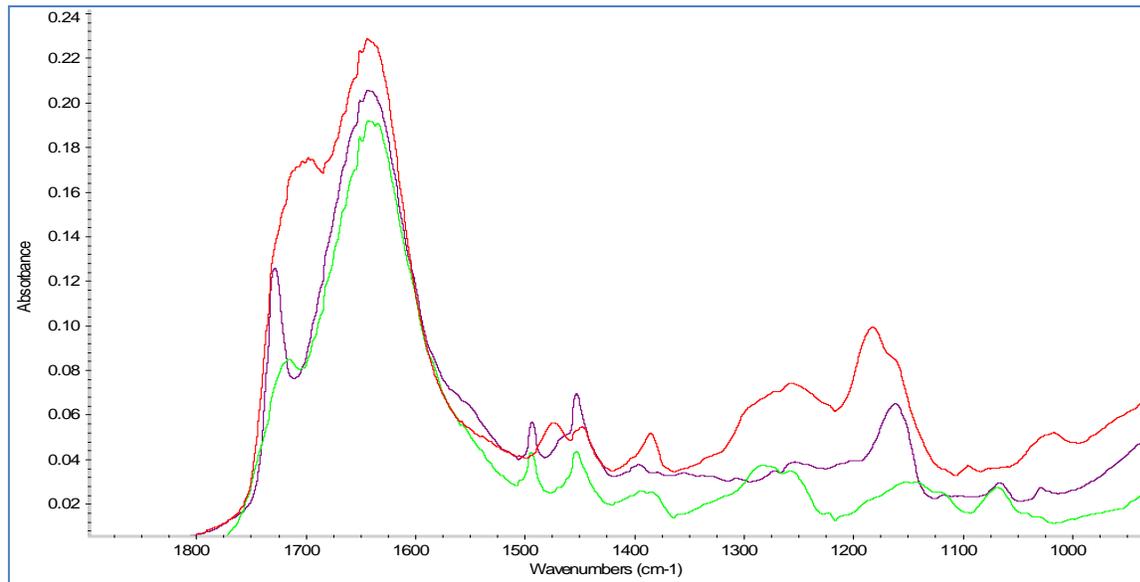


Figure 3.1 Overlay of FTIR spectra of 3 components; Component A –purple, B- green and C – red, showing the spectral differences in the fingerprint region.

The entire range of the calibration spectra looks very similar for the standards containing the three polymeric components because of highly overlapping and associating peaks. But on closer inspection of the spectra one notices minor differences associated with spectral shifts of the shoulder bands. Figure 3.1 shows the minor differences. The spectral regions where the differences occurred were chosen for the analysis region.

Table 3.3. Calibration results for the PLS model: showing the performance index, Coefficient of variation, standard deviations and the factors calculated for each trial.

			EQUATION				
Trial	P-INDEX	COMP	CAL	R 2	RMSEC	RMSEP	FACTORS
1	81.2	A	$Y = 1x + 0$	0.9973	2.41	6.53	4
		B	$Y = 1x + 0$	0.9998	0.58	4.42	5
		C	$Y = 1x + 0$	0.9933	3.94	2.02	3
2	79.9	A	$Y = 0.98x + 1.88$	0.9927	4.24	5.63	4
		B	$Y = 0.99x + 0.9$	0.9916	4.29	6.21	5
		C	$Y = 0.9x + 0.94$	0.9901	4.47	2.33	5
3	N/A	A	$Y = 1x + 0$	1.0000	1.85E+05	2.52	10
		B	$Y = 1x + 0$	1.0000	4.82E+05	0.843	10
		C	$Y = 1x + 0$	1.0000	3.65E+05	0.593	10

The following figures are example of the calibration output for Trials 2 and 3; data presented in Table 3.3, were obtained from the figures below (TQ analyst 8).

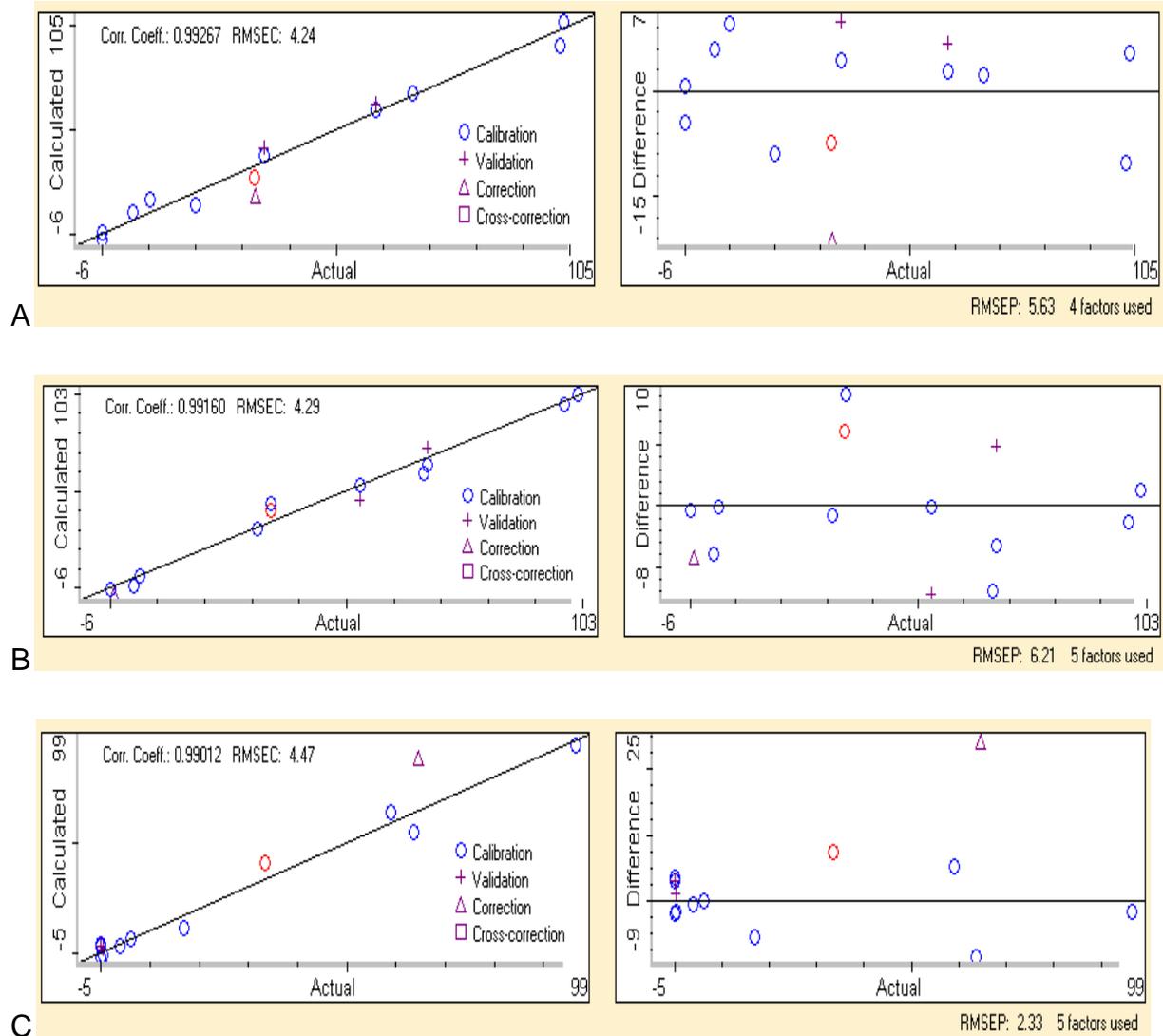


Figure 3.2 Actual versus calculated plot (left) and percent difference plots (right) for Trial 2: For component A, B & C

TQ analyst® 8

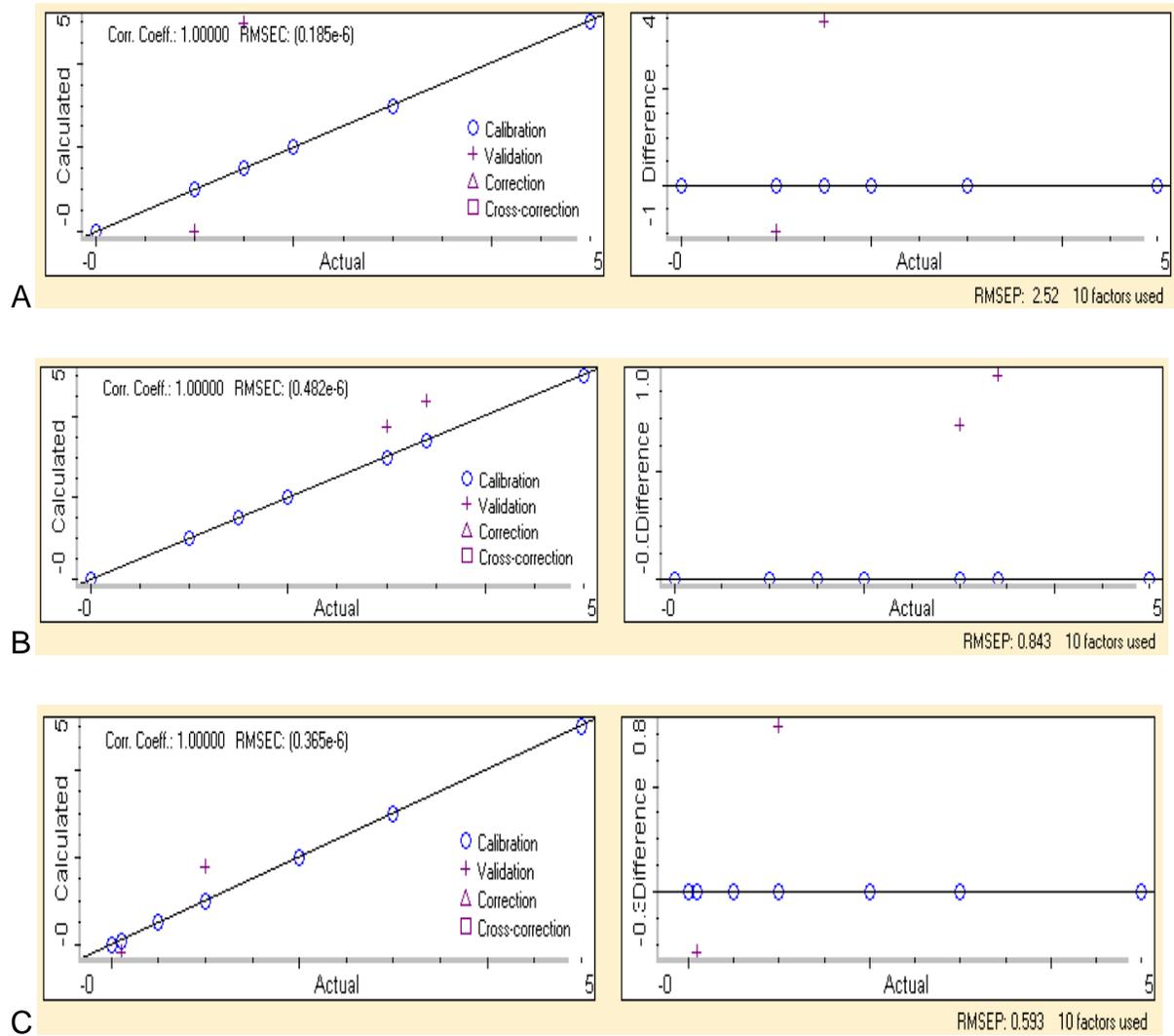


Figure 3.3 Actual versus calculated plot (left) and percent difference plots (right) for Trial 2: For component A, B & C

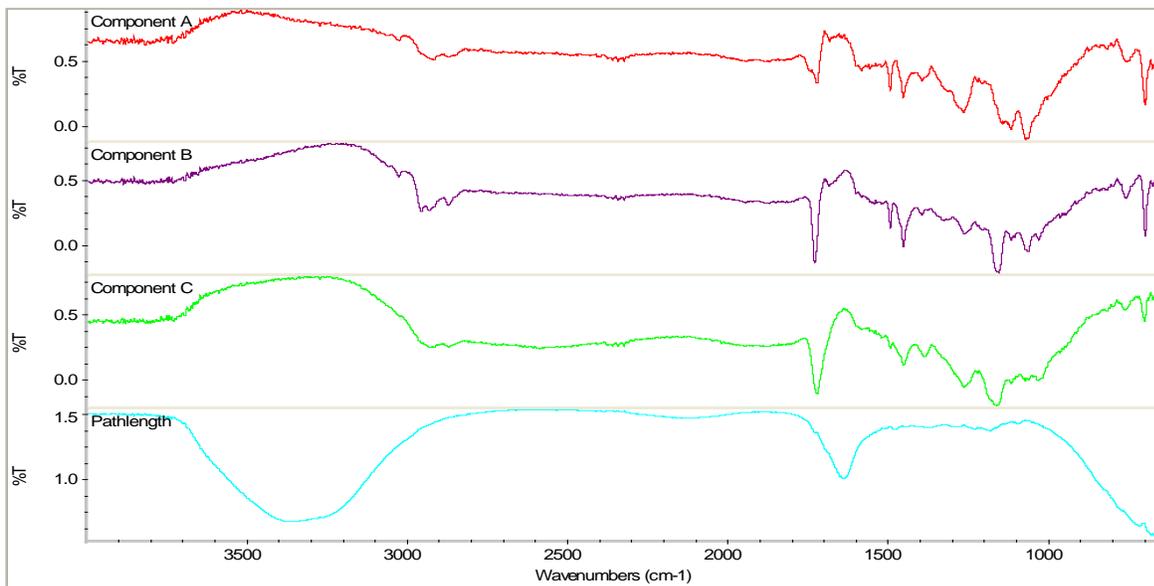


Figure 3.4 Pure component spectra obtained from PLS calibration relative to the Pathlength

PLS can also be used to evaluate the pure spectra from a mixture of spectra

3.8.1.1 The calibration results discussion

The calibration sets consisted of 16 samples and 2 validation samples. The PLS method displays the calibration and validation results such as in figure 3.2 and 3.3. The calculated versus the actual plot compares the concentration value to the actual concentration value for each standard that contains the selected component. The % difference plot shows the differences between the calculated and the actual concentration, relative to the actual values. A typical % difference plot shows data points randomly distributed around the zero lines similar to figure 3.2. The plots are characteristic of a good calibration output. An ideal output displays the data points for the calculated versus the actual concentrations on an exact 45° line from both axes and the percent difference plot will form a horizontal line at exactly zero, obtained by trial 3 see figure 3.3.

Validation standards represent the accuracy of the method better than the calibration set, because the calibration set is used to create the model and validations are not. The root mean square error of prediction (RMSEP) is determined by the validation standards and it is the standard deviation for each measured component (). Coefficient correlation

values close >0.9 and 1 were obtained with trial 1, 2 and 3 respectively. This is an indication of the linear relationship between the actual and calculated values. The root mean square error of calibration (RMSEC) shows the uncertainty of the calibration. The RMSEC was found to be below 5% and RMSEP was found to be below 7% for trial 1 and 2. Trial 3 yielded RMSEC and RMSEP below 3%. The results obtained from PLS calibration models are presented in table 3.3.

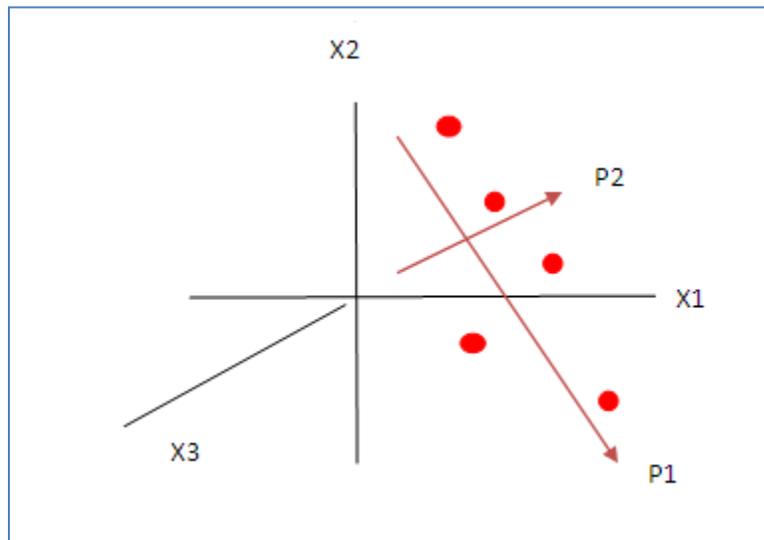


Figure 3.5 Example of principle component spectra (vectors) in a dimensional space

Principle component (PC) is one or more vectors in a multidimensional space at right angles to each other which explains much of the variation in that space. The software condenses the concentration and spectral information into a set of factors and therefore each factor represents an independent variation.

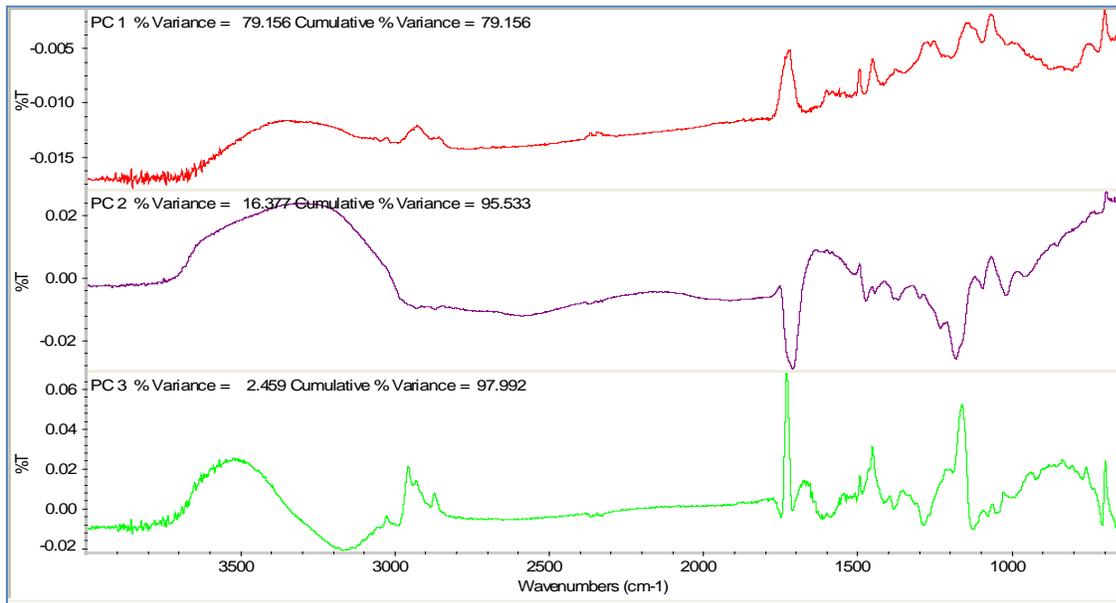


Figure 3.6 Principle components are used to reconstruct a spectrum with the factors which contain the % variance

Factors are ranked by the amount of variance they describe, therefore the first factor contains most of the variance and the ones that follow are more specific to small variations (see Figure 3.6).

The predicted residual square sum error (PRESS) The PRESS value for a factor is the sum of the (residual values)² over the removed standards. The PRESS changes as the number of factors used to calibrate each component in the active method increase It is a measure on how well the calibration predicts the concentration left out during cross validation, an indication of the calibration error. In order to validate the method, cross validation using leave one out technique was used. Cross validation evaluates the data by excluding selected samples in the regression model and then constructing a model for the remaining samples

Increasing a factor reduces the error and the PRESS value decrease at some point where the PRESS reaches a minimum. The PRESS plot flats off or increase more factors are added at this flat off point and the model becomes an over fit.

Table 3.4. "PRESS" value for the selected component: changes as the number of factor increases.
PRESS value for component A during Trial 3 selected as an example

Factor	PRESS	RMSECV
0	27.43827	1.65645
1	25.00983	1.58145
2	20.9393	1.44704
3	31.76976	1.78241
4	17.8287	1.33524
5	18.00691	1.3419
6	8.20821	0.90599
7	3.53608	0.59465
8	3.67108	0.60589
9	3.67837	0.6065
10	3.66982	0.60579

Table 3.4 shows no clear minimum it continues to decrease as soon as another factor is added. The factors used for trial 3 were 10, but from the table above the optimum number one can use is the first minimum which is 8. After 8 factors the model flats off and when more factors are added after this point the model may become an over fit. The RMSECV limits the number to require a specified level of error, in other words it is the minimum uncertainty value you require. For this study the RMSECV was left on default which is zero because of the not so stringent uncertainty requirements for each component. The relative estimated precision for each factor is given by the RMSECV.

Table 3.5. Example of the principle components: for component “A” showing contribution of each PC in concentration, full spectrum and analysis region.

Eigen values			
Principal Component	Concentration	Full Spectrum	Analysis Region
1	53.9129	84.7338	83.0193
2	98.4419	94.8564	93.4721
3	100	97.6897	97.1285
4	100	99.2393	99.0806
5	100	99.7089	99.6882
6	100	99.8451	99.8531
7	100	99.9602	99.9757
8	100	99.9883	99.9891
9	100	99.9946	99.9948
There is sufficient variability for this method			

The Eigen value diagnostic showed that the component concentrations of the standards are evenly distributed over the analysis range and that the principle components' have enough spectral variation

3.8.2 External Validation and quantification

During each model a few samples were left out namely “unused set”. The Accuracy and precision of the model were tested with the unused set and paint samples prepared.

Table 3.6. Mean values of the standard error of prediction (SEP) and % relative error are shown; for each component for the three trials.

Trial	<u>Component A</u>		<u>Component B</u>		<u>Component C</u>	
	% Relative error	SEP	% Relative error	SEP	% Relative error	SEP
1	12.6	1.07	2.68	0.18	14.97	4.25
2	13.33	16.95	18.41	13.07	12.85	0.18
3	19.38	0.17	19.99	0.12	27.91	0.1

Table 3.7. The expected error with probability of 68% = a range of mean \pm SEP, which means 68% of data for the application, should fall in this range: Table showing the percentage of data in the range for each component in each trial.

Component	Trial 1	Trial 2	Trial 3
A	60%	75%	55%
B	60%	75%	55%
C	60%	62%	55%

The following nine illustrations are % difference plots; showing the residual values for each component for the three trials for each component relative to the actual value.

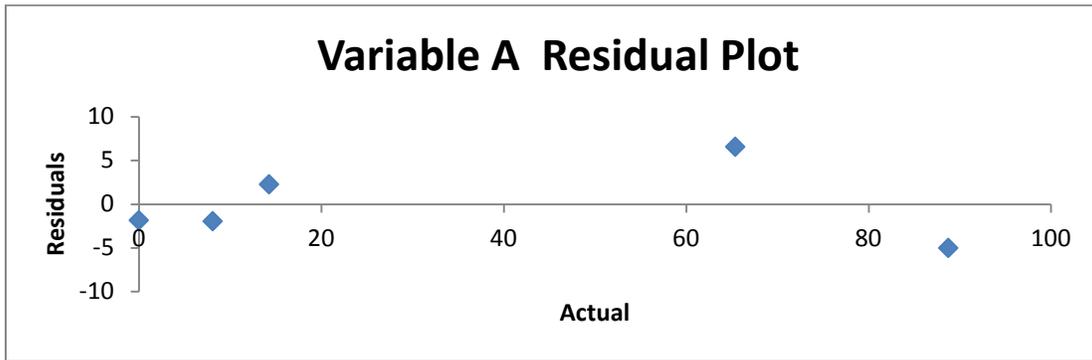


Figure 3.7 Component A-1: showing residual values between 5 and -5

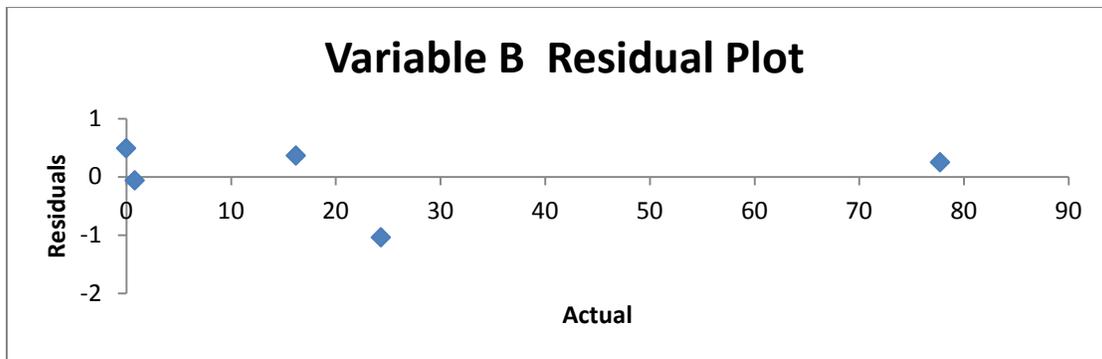


Figure 3.8 Component B-1: showing residual values between 1 and -2

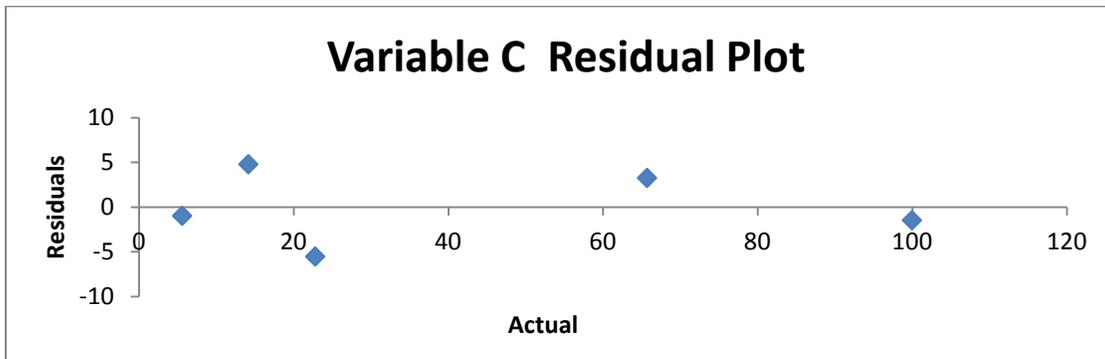


Figure 3.9 Component C-1: showing residual values between 5 and -5

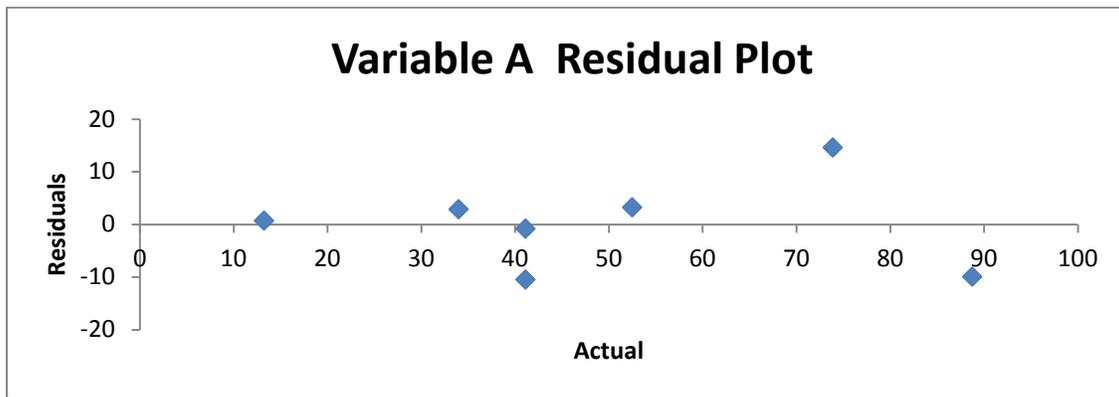


Figure 3.10 Component A-2: showing residual values between 10 and -10

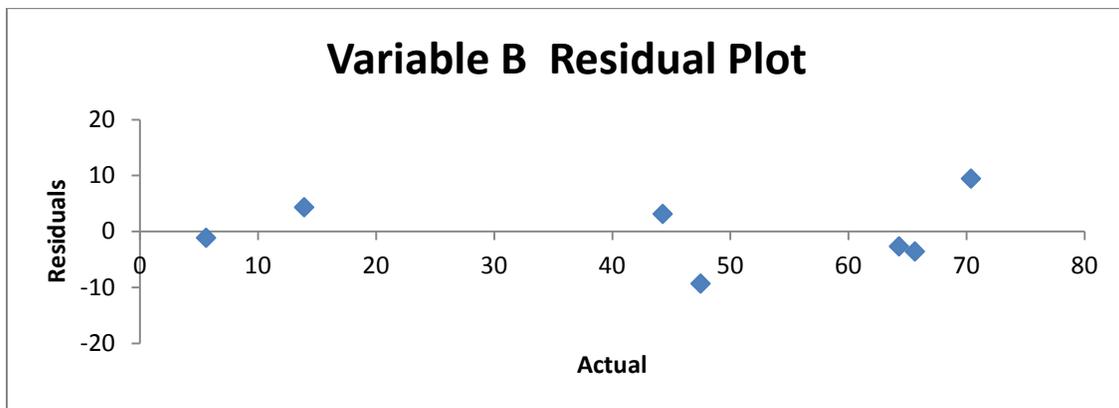


Figure 3.11 Component B-2: showing residual values between 10 and -10

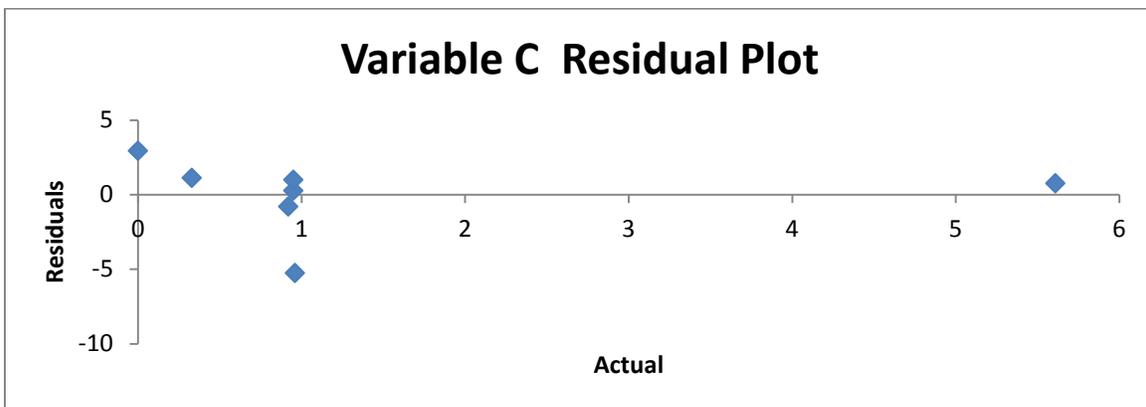


Figure 3.12 Component C-2: showing residual values between 5 and -5

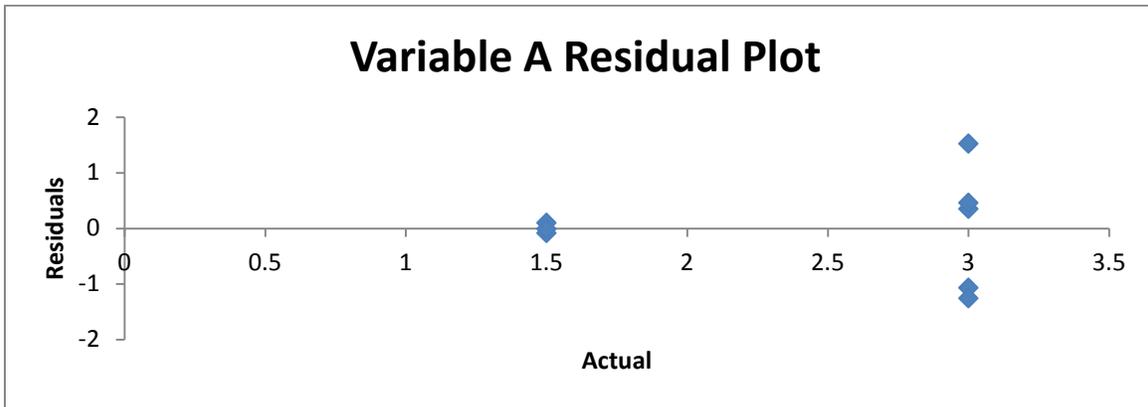


Figure 3.13 Component A-3: showing residual values between 2 and -2

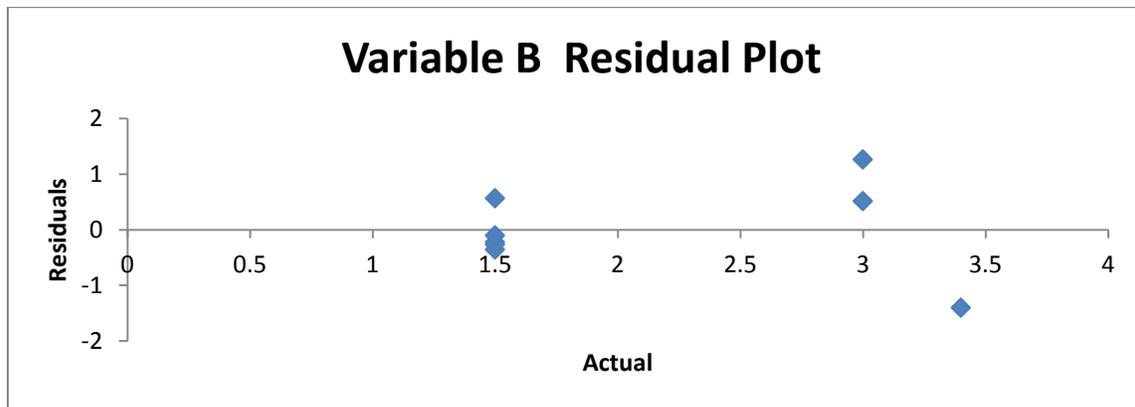


Figure 3.14 Component B-3: showing residual values between 2 and -2

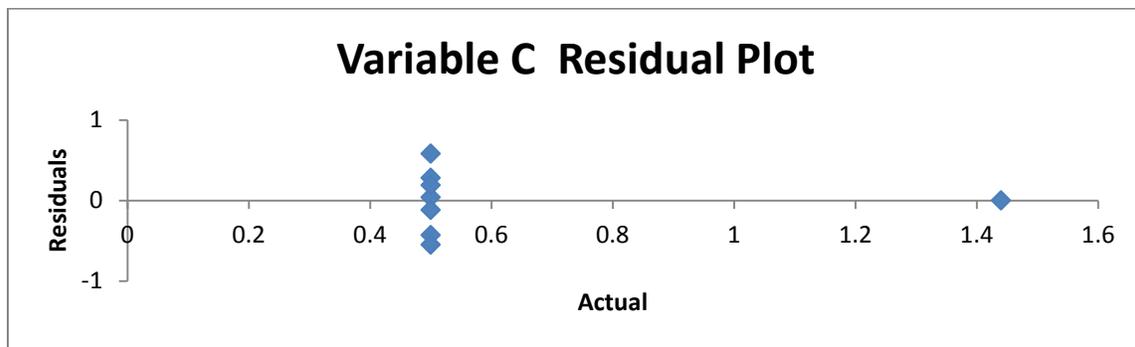


Figure 3.15 Component C-3: showing residual values between 1 and -1

Table 3.8. The quality output for the un-used set; coefficient correlation, regression equation and number of outliers for each component.

	Trial	R ²	Equation	no obs	no outliers
A	1	0.9819	$y=0.841x + 0.783$	5	2
	2	0.919	$y=1.14x - 0.338$	8	2
	3	0.715	$y=1.791x + 1.3$	9	4
B	1	0.9996	$y=1.01x - 0.817$	5	2
	2	0.958	$y=1.13x + 0.985$	8	2
	3	0.712	$y=1.46x - 0.46$	9	4
C	1	0.9906	$y=1.05x - 2.5$	5	2
	2	0.334	$y=0.95x + 0.13$	8	3
	3	0.642	$y=-1.48 + 1.2$	9	4

Table 3.9. Reproducibility; showing the mean, SD and % RSD for components A, B and C during Trial 3

	Component A	Component B	Component C
No observations	10	10	10
mean	4.3375	1.66	0.44
SD	0.99	0.38	0.28
% RSD	22.90	23.15	63.49
True value	3	1.5	0.5

Table 3.10. Residual and %RSD data for components quantified in the simple paint formulation using equation obtained by PLS calibration curve.

	Component A $Y=0.98x+1.88$			Component B $Y=0.99x+0.9$			Component C $Y=0.9x+0.94$		
	Actual	Residual	% RSD	Actual	Residual	% RSD	Actual	Residual	% RSD
1	73.88	0.40	0.38	13.91	0.76	3.76	0.96	0.84	43.18
2	41.14	1.06	1.79	64.30	0.26	0.28	0.96	0.84	43.18
3	41.14	1.06	1.79	44.30	0.46	0.72	0.95	0.85	43.53
4	52.50	0.83	1.11	47.50	-0.46	0.71	0	0.94	141.42

3.8.2.1 The validation discussion

Additional samples were left out during each trial and were later used for external validation to test for precision and accuracy of the technique. The samples were quantified by the relevant method for each trial.

Table 3.16 shows the relative error and standard error of prediction (SEP) obtained by subtracting the predicted concentration from the real concentration divided by the number of samples subtracted by one sample. It was found that the components can be quantified with a relative error of below 20%, except for component C measured during trial 3 which gave an error of 27%. Trial 3 contained significantly lower concentration because it was originally included to test the reproducibility of the lower end concentration of C. Component B showed an error of 2.68% which were significantly lower than the rest. The majority of the error lies between 12 to 20%. The standard error of prediction for trial one and three were found to be lower than 2% The SEP for trial 2 was significantly higher. It was found when quantifying samples left out during trial two an error message appeared stating that the spectral parameters for the standards and samples were not the same.

One can never be certain of the accuracy of any method therefore an acceptable allowable error must be stated beforehand, For any application the expected error with a probability of 68% are mean \pm SEP. Table 3.7 indicates the amount of data found in the range for the different trials. The amount of data outside the range was, considered as outliers. 75% of the trial 2 data fell into the range, even though its prediction error was very weak. Only 60% and 55% of trial 1 and 3 data were found to be in the range of mean \pm SEP, respectively. When the outliers are excluded the SEP and %relative errors was significantly reduced.

Figure 3.7 to figure 3.15 are the residual plots showing the difference relative to the actual components A, B and C for trial 1 – 3 respectively. These plots gave an idea of the accuracies that can be obtained with the technique.

The regression line was calculated for each of the components. Trial 1 showed good correlation with R^2 of 0.9818 for A, 0.9996 for B and 0.9906 for C. Trial 2 also had good linear correlation with R^2 of 0.919 and 0.958 for components A and B respectively. The regression was not so good for component C as well as for trial 3. A less accurate regression was expected with trial C due to the non-linear range of the samples tested. As mentioned previously trial C was done to check the reproducibility of the method at the lower end concentration of C. The samples for trial C was prepared to represent the concentration of the components found in the paint. The rheology modifier – component C is normally present in concentration lower than 1%.

Three simple paint formulations with known polymeric concentration and one blind unknown formulation were quantified using the regression equation obtained from PLS in trial 1. The paints and blind samples were predicted with a %RSD of less than 5% for component A and B. Component C had concentration ranges of less than 1% and could therefore not be accurately calculated and gave a %RSD of 40 (refer to Table 3.10).

3.9 Conclusion

The calibration models for all three trials were very good with R^2 close to 1 and RMSEC and RMSEP of less than 5%. The best calibration model was trial 3 with all points lying on zero in the percentage difference plot. Actual versus predicted value plots resulted in an exact 45 degrees line running through 0 on both axes. Two analysis regions were selected for trial 3, which were the finger print region as well as the region where water absorbs. The styrene acrylic had a solid content of 50% and therefore the 50% water in the component played a crucial role in the quantification of the standards to its degree of accuracy. The external validations for trial 1 and 3 were found to be significantly better with R^2 close to 1 and a slope of 1, intercepting at 0. The analysis regions for trial 1 and 3 were found to be optimum for the quantification of polymeric components in paint. The accuracy and precision of the method can be further increased with the meticulous development of the calibration and validation set as well as increasing the linear range of the external validation. The reproducibility will also be better with a higher concentration mean. The PLS method could predict the higher concentration components A and B better than the lower (less than 1%) component C in trial 3.

4 General discussion and conclusion

Fourier transform infrared spectroscopy has been used as the technique of choice, although it has its limitations. Spectroscopy i.e. FTIR coupled with computer assisted software enables one to manipulate and extract the desired information. It is also a very cost effective technique, fast and requires minimal sample preparation especially with the ATR accessory and allows for on line investigation

The development of the method involved in accurately preparing calibration and validation standards of the three components as well as a simple paint formulation. Before, only classification of the binder could be ascertained, by FTIR (using functional group analysis) after extraction by ASTM D3168 standard method for the polymeric extraction from paint. At the time it was believed that all polymeric can be extracted using this method, but from Trial 1 we learned that only the binder gets extracted, which is true cause one cannot expect all the polymeric to be extracted due to their different polarities.

Initially transmission spectra were taken and later ATR was conducted because the Pathlength through the sample could not be established and is important to know for quantification. Having the polymers extracted in different solvents was soon proposed, but realized that by doing this was only going to complicate the model.

The next objective was soon realized, to have the polymeric components in the paint analysed as is. The use of ATR and the Strength of PLS made the analysis possible, because for ATR one can apply the paint sample and PLS model can handle unexpected components and when chemical matrices are not well known.

Chemometric models were set-up via CLS, PCR and PLS. The standards were entered and calibrated. PLS was found to yield the best performance index off all with prediction errors of less than 6%. CLS and PCR gave poorer prediction equations. CLS requires one analysis region for each component and with the case of severe overlapping in this study that was not possible. In PCR the regression step is done after the principle components is selected and therefore not weighed towards the concentration information.

4.1 Limitations of the FTIR-PLS model

The method is limited to sub micro concentration, not as sensitive as GC-MS or HPLC. It requires careful preparation of calibration and validation samples. It cannot be used to quantify a total unknown, unless all the components in the sample has been previously been analysed and set-up as standards. Component regions and Pathlength must be well defined.

4.2 Conclusion

A cost effective technique capable of analysing complex multicomponent infrared spectra with good precision and accuracy for samples higher than 1% was achieved. The PLS model can be used to predict polymeric components in a coating without prior extraction and an acceptable degree of error must be established beforehand.

4.3 Recommendations

With the advent of proper data base building of all the raw materials available by ATR, will benefit the further development of the method for the quantification of all components in paint. This will allow discriminant methods to be used in conjunction with Partial least squares methods for qualification as well as quantification of unknowns. Thorough analysis that expands deeper into the Binder or polymeric systems can also be investigated using these techniques. The possibility seems endless, but one has to weigh the possibility of what's important in terms of cost effectiveness for the company and the possibility of success.

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