การตรวจวัดสารระเหยง่ายในบรรจุภัณฑ์อาหารชนิดโฟมพอลิสไตรีนโดยสเปกโทรสโกปีย่านอินฟราเรดใกล้

นางสาวศศิธร หอมดำรงค์วงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ปีการศึกษา 2553

DETERMINATION OF VOLATILE SUBSTANCES IN POLYSTYRENE FOAM FOOD PACKAGING BY NEAR INFRARED SPECTROSCOPY

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2010

Thesis Title	DETERMINATION OF VOLATILE SUBSTANCES IN POLYSTYRENE FOAM FOOD PACKAGING BY NEAR INFRARED SPECTROSCOPY
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ศศิธร หอมดำรงค์วงศ์ : การตรวจวัดสารระเหยง่ายในบรรจุภัณฑ์อาหารชนิดโฟมพอลิสไตรีนโดยสเปกโทรสโกปีย่านอินฟราเรดใกล้ . (DETERMINATION OF VOLATILE SUBSTANCES IN POLYSTYRENE FOAM FOOD PACKAGING BY NEAR INFRARED SPECTROSCOPY.) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. อรวรรณ ชัยลภากุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร. สนอง เอกสิทธิ์, 83 หน้า.

เทคนิคสเปกโทรสโกปีย่านอินฟราเรดใกล้สามารถนำมาใช้ในการตรวจวัดสารระเหยได้ในบรรจุภัณฑ์อาหารชนิดโฟมพอลิสไตรีนได้ วัดสเปกตรัมของตัวอย่างในช่วงเลขคลื่นตั้งแต่ 10000 ถึง 4000 เซนติเมตร$^{-1}$ ค่าการแยกเป็น 8 เลขคลื่น จำนวนการสแกนเท่ากับ 30 ใช้โหมดการวัดตัวอย่างแบบ diffuse reflectance สเปกตรัมที่ได้ทำการปรับแต่งด้วยวิธี multiplicative signal correction (MSC) และอนุพันธ์อันดับสอง แล้วใช้เทคนิค partial least squares regression (PLSR) วิเคราะห์ผลสเปกตรัมที่ได้และใช้ค่าอ้างอิงจากวิธีแก๊สโครมาโทกราฟีโดยมีหัวตรวจวัด แบบเฟลมไอออไนเซชัน สร้างกราฟเทียบมาตรฐาน จากสมการได้ค่าสัมประสิทธิ์สหสัมพันธ์ (r) 0.9815 ค่าความคลาดเคลื่อนของสมการเทียบมาตรฐาน (RMSEC) 26.2 มิลลิกรัม/ กิโลกรัม ความเอนเอียง (bias) -2.26 ค่าความคลาดเคลื่อนของการทำนาย (RMSEP) 26.7 มิลลิกรัม/ กิโลกรัม และ ค่า residual predictive deviation (RPD) 5.7

ภาควิชา......เคมี.................. ลายมือชื่อนิสิต..
สาขาวิชา......เคมี.................. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..
ปีการศึกษา.....2553.............. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..

5072625523: MAJOR CHEMISTRY
KEYWORDS : POLYSTYRENE / NIR / PLSR / RMSEC / RMSEP

SASITORN HOMDUMRONGVONG : DETERMINATION OF VOLATILE SUBSTANCES IN POLYSTYRENE FOAM FOOD PACKAGING BY NEAR INFRARED SPECTROSCOPY. ADVISOR: ASSOC.PROF. ORAWON CHAILAPAKUL, Ph.D., CO-ADVISOR: ASSOC.PROF. SANONG EKGASIT, Ph.D., 83 pp.

NIR spectroscopy was employed to determine volatile substances in polystyrene foam used for food packaging. The spectra of samples were scanned in the range 10000 to 4000 cm^{-1}, 30 scans per spectrum at a resolution of 8 cm^{-1}, using diffuse reflectance mode for measured samples. The raw spectra were preprocessed by multiplicative signal correction (MSC) and second derivative. Partial least squares regression (PLSR) was used to construct calibration model. Gas chromatography with flame ionization detector was used to determine actual concentration of volatile substances for constructing calibration model. The correlation coefficient (r) 0.9815, root mean square error of calibration (RMSEC) 26.2 mg/kg, bias -2.26, root mean square error of prediction (RMSEP) 26.7 mg/kg and residual predictive deviation (RPD) 5.7.

Department : Chemistry	Student's Signature
Field of Study : Chemistry	Advisor's Signature
Academic Year : 2010	Co-advisor's Signature

ACKNOWLEDGEMENTS

The success of this research can be attributed to the extensive support and assistance from my advisor, Associate Professor Orawon Chailapakul, Ph.D., for suggestions, assistance, constructive criticism, inspiration, and encouragement. I would also like to thank my co-advisor, Associate Professor Sanong Ekgasit, Ph.D., for all the valuable suggestions, assistance, strong support which helped in the completion of this work. In addition, I would like to extend my appreciation to the members of my thesis committee; thanks to Assistant Professor Aroonsiri Shitangkoon, Ph.D., Passapol Ngamukot, Ph.D., Winai Oungpipat, Ph.D., for all their valuable comments, corrections, and offered suggestions for improvement.

I sincerely thank the Department of Medical Sciences, Ministry of Public Health and Center for Petroleum, Petrochemicals and Advanced Materials for financial support. Special thanks to Mrs.Uma Booriboon and all members of the Food Container Unit at the Bureau of Quality and Safety of Food.

Finally, I would like to express my deepest gratitude to my family for their love, care, kindness, encouragement and other assistance through out my life.

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LIST OF ABBREVIATIONS

FID	flame ionization detector
FT-NIR	Fourier transform near infrared
GC	gas chromatography
MSC	multiplicative signal correction
NIR	Near-infrared
PLS	partial least squares
PLSR	partial least squares regression
PS	polystyrene
RMSEC	root mean square error of calibration
RMSEP	root mean square error of validation
RPD	residual predictive deviation
RSD	relative standard deviation
SD	standard deviation
SEP	standard error of prediction
SNV	standard normal variate correction
nm	nanometer
μL	microliter
mg/kg	milligram per kilogram
mg/L	milligram per liter
mg	milligram
min	minute
g	gram
hrs	hours
mL	milliliter
mm	millimeter
R	reflectance
^{o}C	degree celsius
r	correlation coefficient
df	degree of freedom

CHAPTER I

INTRODUCTION

1.1 Polystyrene food packaging

There are many types of plastic used for food packaging such as polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride, polycarbonate, polystyrene and others. Polystyrene (poly (1-phenylethane-1, 2-diyl), PS) is one of the most widely used plastics in food packaging applications [1] which comes into direct contact with food i.e., foam food packaging, yogurt tubs, biscuit trays, candy boxes, beverage cups and others [2-3]. Currently, foam packaging used as food containers has gained popularity because it is light-weight, easy to use and convenient especially for take away goods.

Polystyrene produced from styrene monomer as shown in Figure 1.1 and styrene is a product of catalytic dehydrogenation of ethylbenzene as shown in Figure 1.2 [4]. Ethylbenzene is generally synthesized from raw material such as petroleum, so the quality of polystyrene is directly affected by the impurity of organic compounds present in the raw material [5-6].

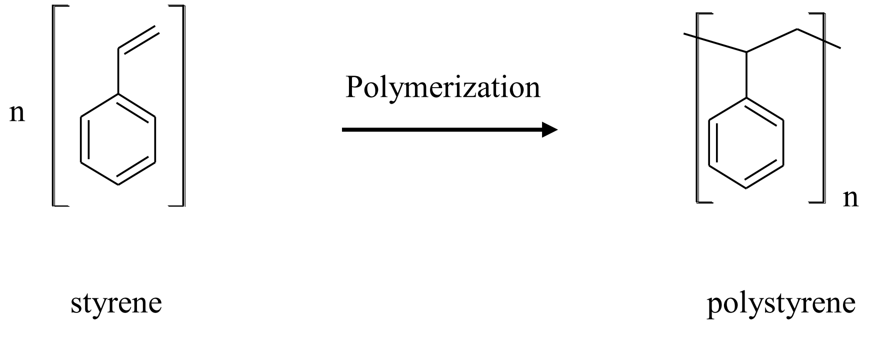


Figure 1.1 Schematic representation of polystyrene polymerization

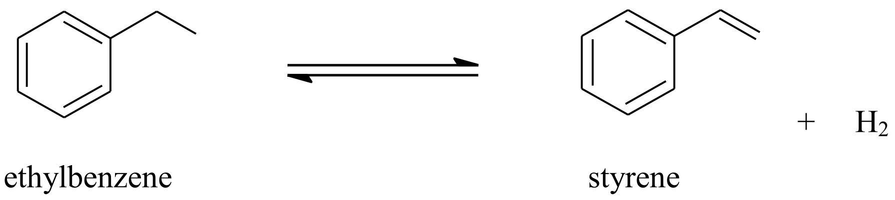
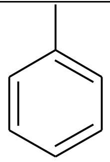
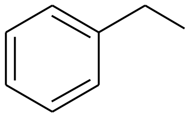
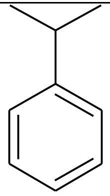
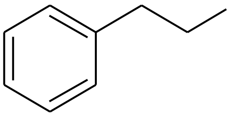
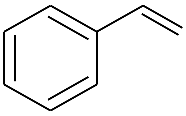


Figure 1.2 Schematic representation of styrene synthesis

The impurity is a group of compounds which have benzene ring as a component such as ethylbenzene, toluene, benzene, etc. often found in polystyrene have two main sources, either the impurity which exists in the raw material or during the production process of the polystyrene [7]. In Notification of the Ministry of Public Health No.295, Thailand (2005 (B.E.2548)) [8] regulated for the maximum accepted content of volatile substances (toluene, ethylbenzene, isopropylbenzene, n-propylbenzene and styrene) in polystyrene packaging is not more than 5,000 milligram/ kilogram (part per million, ppm). Toxicity of volatile substances was shown in Table1.1.

Table 1.1 Structure and toxicity of volatile substances

Volatile compound	Structure	Toxicity
Toluene		effects the central nervous system and causes abnormality of intrauterine , kidney and skeleton of rodents [9-10]
Ethylbenzene		causes carcinogen in kidneys, lungs, livers of rodents and may be carcinogenic to humans [11-14]
isopropylbenzene		Causes irritation upon contact with areas such as skin, nose, mouth and throat [15].

Volatile compound	Structure	Toxicity
n-propylbenzene		The U.S. Environmental Protecting Agency (US.EPA) has determined it a Class D carcinogen in class D (not classifiable) [16].
styrene		- Causes to carcinogenic in humans [7]. - Causes irritation upon contact with areas such as eyes and mucous membranes [17].

1.2 Literature Review

Several procedures used to determine volatile substances were listed in the literature. Ahmad and Bajahlan [7] determined the styrene and aromatic compound leaching from polystyrene bottles using the purge and trap technique and carried out an analysis using gas chromatograph – mass spectrometer (GC – MS). Buchalla et al. [18] studied the analysis of low – molecular weight radiolysis products in extracts of gamma-irradiated polymers using developed solvent extraction and dissolution – precipitation followed by an analysis using gas chromatography and high performance liquid chromatography. Garrigos et al. [19] studied extraction methods using supercritical fluid extraction (SFE), microwave – assisted extraction (MAE), soxhlet extraction, headspace emission and dissolution precipitation and compared the determination of residual styrene monomer using a gas chromatograph – mass spectrometer. Varner and Breder [20] studied the migration of polystyrene into beverages and food simulates with various types polystyrene cups using headspace sampling and carried out an analysis using gas chromatography. Varner et al. [21] studied the migration of styrene from polymer into fatty foods using azeotropic distillation and carried out an analysis using headspace gas chromatography. Nerin et al. [22] did a study to determine the amount of styrene in olive oil using co evaporation and cold trap technique and carried out an analysis using GC-MS. Ragelis et al. [23] compared the gas chromatography and polarography techniques for determining the amount of styrene monomers in polystyrene resin. Geraldo et al. [24] used a rapid electrochemical method to determine residual styrene in food packaging. Chai et al. [25] did a study using the headspace gas chromatographic technique to determine the amount of residual monomers in methyl methacrylate (MMA) polymer. Lehr et al. [26] studied the migration of styrene from polystyrene food packaging into cooking oil using GC-MS. Varner and Breder [27] determined the amount of residual styrene in food packaging using liquid chromatography. The classical methods described above are time consuming, require expensive reagents and sometimes produce hazardous wastes.

1.3 Fourier transform near infrared (FT-NIR) spectroscopy

Fourier transform near infrared (FT-NIR) spectroscopy is one of the techniques that have been applied to analytical techniques in many fields such as agricultural, food and pharmaceutical industries, nutrition evaluation and many others. This technique has been used to determine the fermentation of volatile compounds in aged red wines [28].

FT-NIR spectroscopy technique is being more widely used for analysis because it is fast, accurate, non-destructive, and environmentally friendly since it reduces the use of chemical reagents and eliminates the cost for hazardous waste treatment.

1.4 Objectives

The objective of this research was to apply FT-NIR spectroscopy to determine the amount of volatile substances in polystyrene foam food packaging. The study was carried out within the following scopes.

1. To collect polystyrene samples and determine volatile substances using the reference method [29]
2. To optimize the FT-NIR spectroscopy data collection in terms of the resolution and number of spectrum scanned
3. To construct a calibration model by using partial least square regression (PLSR)
4. To validate the optimized calibration model
5. To study the effect of temperature during the measurement of volatile substances by FT-NIR spectroscopy.

CHAPTER II

THEORY

2.1 Electromagnetic radiation

Electromagnetic radiation is composed of electric and magnetic field components [30]. Electric and magnetic fields are in planes perpendicular to each other as shown in Figure 2.1. The wavelength range of the electromagnetic spectrum varies ranging from radio waves to gamma rays. The infrared region is located between the visible region and the microwave region shown in Figure 2.2 [30].

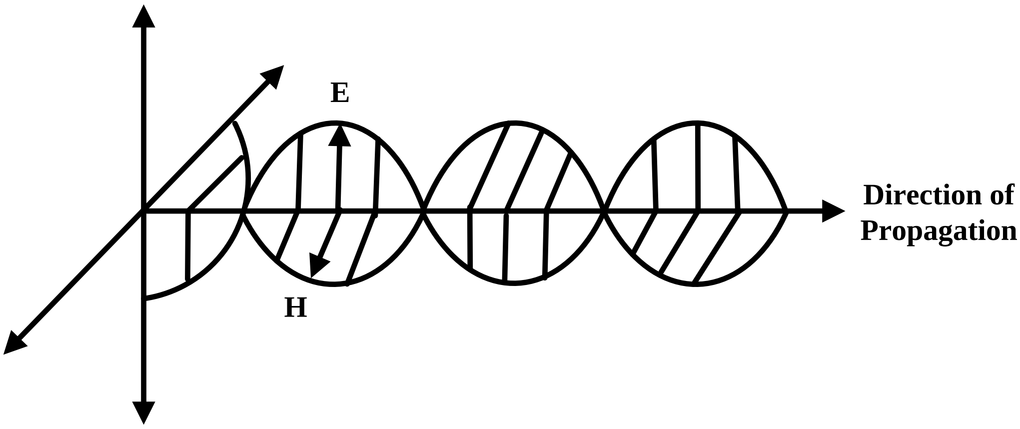


Figure 2.1 Propagation of a linearly polarized electromagnetic wave in space. Electric (E) and magnetic (H) vectors are always perpendicular to each other and to the direction of propagation

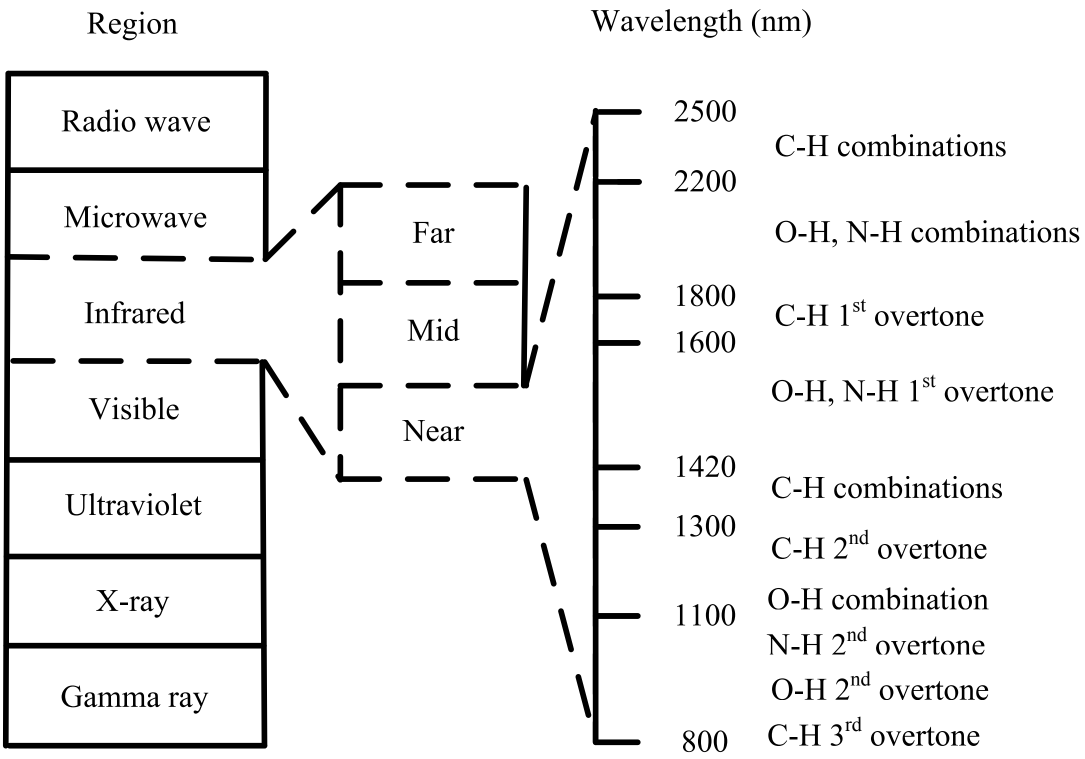


Figure 2.2 The electromagnetic spectrum

2.2 Interaction of light and matter

When electromagnetic radiation travels though a sample, various types of interaction occur such as absorbed, transmitted, scattered and reflected shown in figure 2.3 [30].

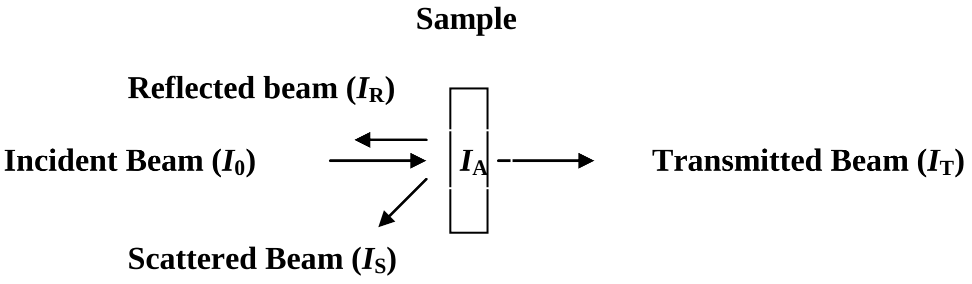


Figure 2.3 Interaction of light with matter.

The total amount of incident radiation is the sum of reflected, scattered, transmitted, and absorbed light. The process is as follows [30]:

$$I_0 = I_R + I_S + I_T + I_A \qquad (2.1)$$

Where I_0 is the intensity of the incident radiation.

I_R is the reflected radiation.

I_S is the scattered radiation.

I_T is the transmitted radiation.

I_A is the radiation absorbed by matter.

The intensity of each type of radiation depends on the intensity and wavelength of the incident radiation. The fraction of incident radiation absorbed by the sample, the ratio of the sample attenuated (I) and not attenuated (I_0) intensities of the radiation are measured. The ratio is proportional to the transmittance of the sample which can be quantitatively related to the chemical composition of the sample by the Beer-Lambert law as [30]:

$$\frac{I}{I_0} = e^{-A(\bar{v})} = e^{-C_2\varepsilon(\bar{v})l} \qquad (2.2)$$

Where $A(\bar{v})$ is the absorbance at a given wavenumber $\bar{v}$

C_2 is the concentration of the absorbing functional group

$\varepsilon(\bar{v})$ is the wavenumber - dependent absorption coefficient

and l is the film thickness for the infrared beam at a normal incidence to the sample surface

2.3 Near infrared spectroscopy

Infrared spectroscopy is based on the absorption of electromagnetic radiation. The infrared region is commonly classified into three regions near, mid and far infrared show in table 2.1.

Table 2.1 Classified of infrared region [31]

Region	Wave number (cm^{-1})	Wavelength (nm)
Near Infrared	12500 - 4000	800 - 2500
Mid Infrared	4000 - 400	2500 – 25000
Far Infrared	400 -10	25000 – 100000

Table 2.1 shows that the infrared region of the electromagnetic spectrum can be divided into three regions, namely: near, mid and far infrared. The region of mid- infrared region, near-infrared region and far-infrared region was 12500 - 4000 cm^{-1} (800 - 2500 nm), 4000 - 400 cm^{-1} (2500 - 25000 nm) and 400 - 10 cm^{-1} (25000-100000 nm), respectively.

Molecules which contain functional groups such as O-H, C-H, N-H and C-O response to NIR radiation. The spectrums of NIR region are overtones and combinations. Absorption bands of overtones and combinations are weaker and broader than absorption bands of fundamental vibration which is region of mid infrared region.

The vibration frequency of the molecule depends on the mass, the length and the strength of the bond. When the molecule absorbs the infrared radiation, it changes in dipole moment during the vibration which have must heteronuclear diatomic molecules (i.e., carbon monoxide CO, hydroxide OH) commonly refers as IR active molecule. And homonuclear diatomic molecule (i.e., oxygen O_2, hydrogen H_2) which absent in the changes of dipole moment so calls IR inactive molecule.

Near infrared spectrometric (NIR) is a spectroscopic technique used in analytical chemistry for qualitatively and quantitatively analysis. This technique is based on the interaction of electromagnetic radiation with the matter.

2.3.1 NIR measurement mode

The mode of measurement depends on the characteristics of the material of the sample. An NIR spectrometer can measure in transmission and reflection mode. The transmission mode is used for liquid samples and the reflectance mode for solid samples.

Figure 2.4 and 2.5 shows the basic instrumental design of the transmittance and diffuse reflectance modes. In the transmittance mode, the detector is placed between the samples but the reflectance mode sets the detectors at 45 ° for the reflected light. Two detectors at a 45 ° angle can be used [32].

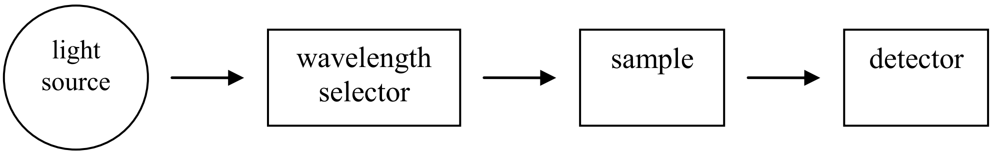


Figure 2.4 Near-infrared transmittance

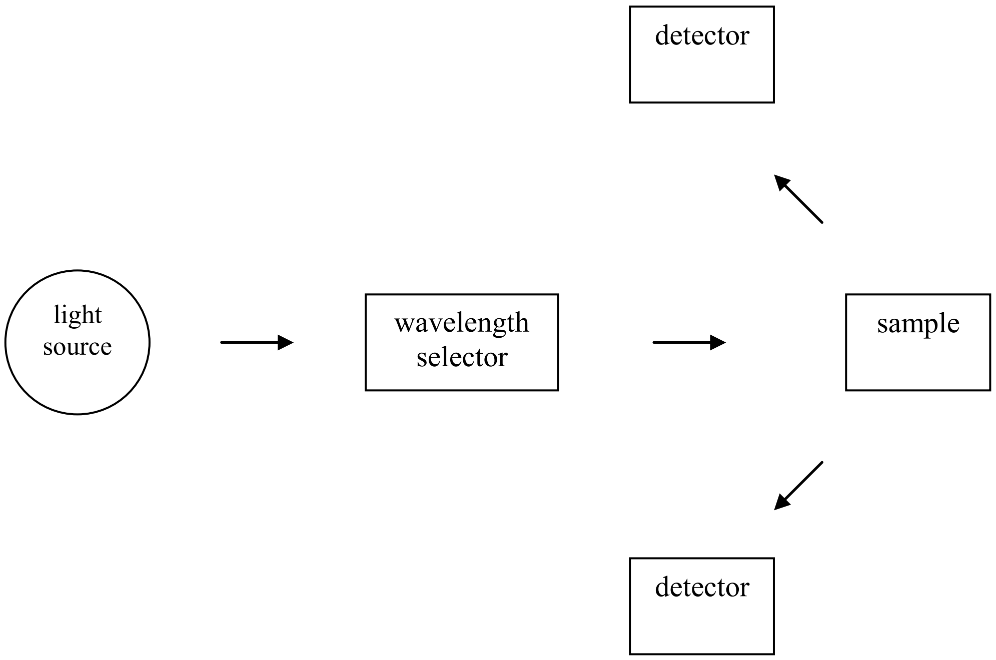


Figure 2.5 Near-infrared diffuse reflectance

Reflectance measurements penetrate the front surface of the sample. This small penetration of energy into a sample brings about greater variation when measuring non homogeneous samples than with the transmittance mode [32].

2.3.2 Instrument

The components of FT-NIR Spectrometer

2.3.2.1 Light source

Most of NIR source utilizes white light from a tungsten halogen lamp because it is cheap, small and has high intensity [33-34]. The white light from the tungsten halogen lamp is a continuous radiation. Light emitting diodes (LEDs) have a limited number of waves and the price is high so it not popular [34-35].

2.3.2.2 Wavelength selector

There are many types of wavelength selectors such as prisms, grating, filter and interferometer. The interferometer shown in figure 2.6, is popular because it is fast, provides the best resolution and improves the signal-to-noise ratio.

The interferometer contains a fixed mirror, a moving mirror and a beam splitter. White light from the tungsten halogen source travels into a beam splitter and separates into two beams. One of the two beams travels to the fixed mirror and the second beam travels to the moving mirror. When the moving mirror is moving make not equal of moving mirror and fixed mirror so give the two waves in the interferometer. The difference in the pathlengths is called the retardation, δ. A plot of light intensity versus retardation is called an interferogram. Interferogram is changed to spectrum by the mathematics of the Fourier transform.

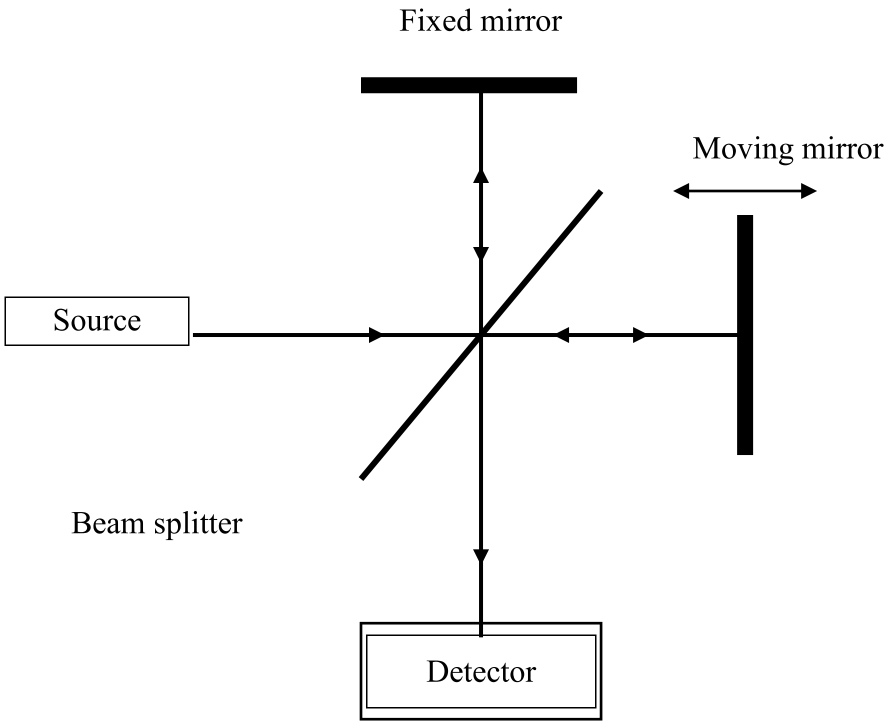


Figure 2.6 Schematic representation of Michelson interferometer

2.3.2.3 Sample holder

The sample holder is designed according to the type of sample used such as liquid samples use quartz cells, solid or powder samples use sample cups.

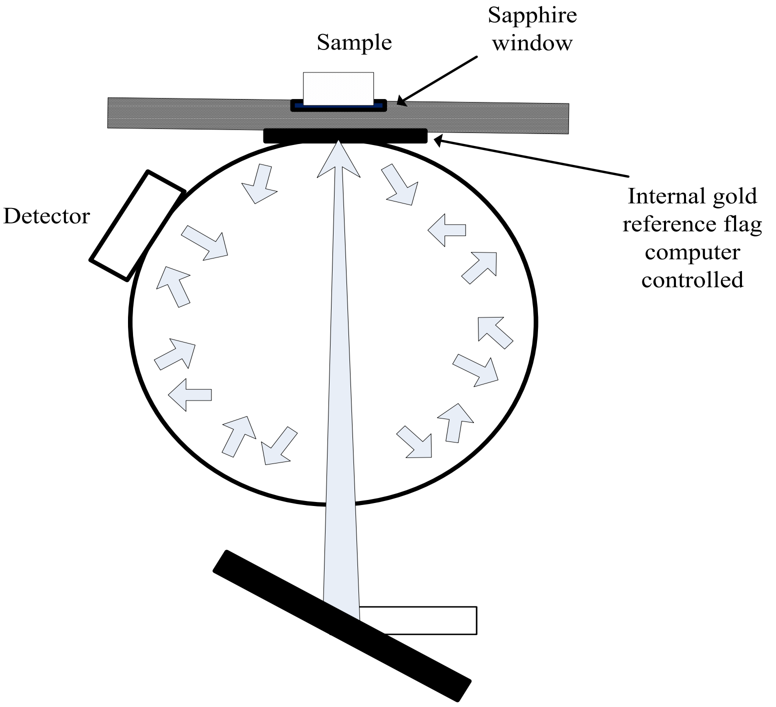


Figure 2.7 Diffuse reflectance using an integrating sphere [36]

Figure 2.7 shows an integrating sphere used to measure solid samples and powder samples. The integrating sphere is based on the standard diffuse reflection sampling technique with a unique optical design, called an integrating sphere [36]. The incident beam travels into the sphere directly through the center of the sphere into the sample. The beam scatters off the sample and the reflected light beam within the sphere which is coated with diffused gold collects the reflected beams and directs it to the detector [36].

2.3.2.4 Detector

Light from the wavelength selector onto the sample and focused onto the detector which produces an electrical signal in response to the energy which attacks it [36-37].

The Silicon detector is small; it is short with a sensitivity around 1100 nm [37-38]. Lead Sulfide (PbS) detector has a cover range 1100 to 2500 nm, it is slower but good for signal-to-noise ratio [34]. And Indium gallium arsenide (InGaAs) detector which is small and fast with a wavelength from 1100 to 2500 nm but it is expensive [34].

2.4 Chemometrics

Chemometrics are mathematical and statistical; it is used to extract related information [34], and must be used with modern computer software for processing.

2.4.1 Preprocessing methods

Effect from light scattering, path length differences, random noise, physical characteristics of samples and instruments whereby this irrelevant information can be removed by using preprocessing methods such as a standard normal variate (SNV), multiplicative signal correction (MSC), first and second derivation.

2.4.1.1 Standard normal variate (SNV)

Standard normal variate is a mathematical transformation method which is used to remove the effects of slope variation and light scattering. The SNV centers each spectrum and then scales it by its own standard deviation [39-41]:

$$X_{ij}(SNV) = \frac{X_{ij} - \overline{X}_i}{SD} \tag{2.1}$$

Where i mean the wavelength counter, j is the intensity value counter

X_{ij} *(SNV)* is the corrected intensity value at the wavelength counter

X_{ij} is the intensity value (raw data) at the wavelength counter

$\overline{X}_i$ is the mean value of the intensity value (for all wavelengths)

SD is the standard deviation of the intensity value (for all wavelengths)

2.4.1.2 Multiplicative signal correction (MSC)

MSC is used to remove additional (the chemical absorption) and multiplicative (light scattering and sample thickness) effects which result from baseline shifts of the original spectra [41-42].

The MSC is stated below [43-44]:

$$X_{ij}(MSC) = \frac{X_{ij} - a_i}{b_i} \tag{2.2}$$

Where $X_{ij}(MSC)$ is the corrected spectrum value at the wavelength counter

X_{ij} is the intensity value (raw data) at the wavelength counter

a and b are estimated by ordinary least square regression of spectrum versus y_{Aver} over the available wavelengths counter

2.4.1.3 Derivative transformations

The original spectrum intensity has broad bands. The first and second derivative spectrum which is shown in figure 2.2 can be used to enhance the intensity, resolution of overlapping bands and remove baseline drifts [39, 42]. The higher order derivatives are very sensitive to random error [45].

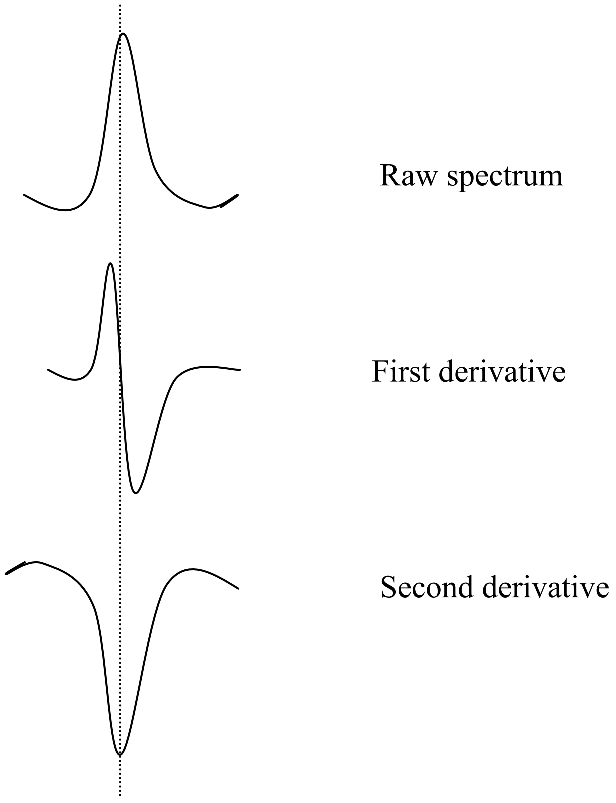


Figure 2.8 Schematic representation of raw spectrum, first and second derivatives spectrums

2.4.1.4 Smoothing

The Savitzky-Golay algorithm is aimed to reduce the effect of noise on a spectrum by removing small variations in absorbance. It improves the visual aspect of the spectrum [37, 46]

2.4.2 Partial least squares regression (PLSR)

PLSR method is most widely used in chemometrics for constructing a calibration model between chemical composition and NIR spectra. PLSR method is a bilinear regression method. The PLSR decomposes X and Y, matrix X is the independent data and the dependent data is matrix Y. The formulas can be written as:

$$X = TP + E \qquad (2.5)$$

$$Y = UQ + F \qquad (2.6)$$

Where T and U are the score matrices of X matrix and Y matrix

P and Q are the loading matrices of X matrix and Y matrix

E and F are errors which come from the process of PLSR

Two formulas are processed by linear regression. A correlation between X and Y must be built using the following linear correlation:

$$U = bt + e \qquad (2.7)$$

The best PLS model was evaluated in terms of root mean square error of calibration (RMSEC), the root mean square error of prediction (RMSEP), bias and the correlation coefficient (r) between NIR predict and reference method [40, 47 - 48]. The best model should have a low RMSEC, RMSEP, bias and high correlation coefficient (r) [48]. The RMSEC was calculated as follows:

$$RMSEC = \sqrt{\frac{\sum_{i=1}^{n}(\hat{x}_i - x_i)^2}{n}} \tag{2.8}$$

Where x_i is the chemical reference value provided by the reference method

$\hat{x}_i$ is the value of the NIR predicted value for the model building

n is the number of calibration samples

For the validation set, the RMSEP was calculated as follows:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n}} \tag{2.9}$$

Where y_i is the chemical reference value provided by the reference method

$\hat{y}_i$ is the NIR predicted value.

n is the number of validation samples.

The standard error of prediction (SEP) is the square root of the prediction variance and is computed as

$$SEP = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i - Bias)^2}{n}} \tag{2.10}$$

Where *Bias* is estimated by

$$Bias = \frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i) \tag{2.11}$$

Correlation coefficients between the NIR predictive and the reference measurement value are calculated for both the calibration set and the validation set, which is calculated as follows:

$$r = \sqrt{1 - \frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}} \qquad (2.12)$$

Where $\bar{y}$ is the mean of the reference results for all samples in the calibration and validation set.

CHAPTER III

EXPERIMENTAL

3.1 Instruments and equipments

1. Fourier transform near infrared (FT-NIR) spectrometer with an integrating sphere equipped with a Indium gallium arsenide (InGaAs) detector (Antaris II Analyzer, Thermo electron Corporation, USA)
2. Gas chromatography (GC) with flame ionization detector (FID)
   (GC 17-A gas chromatography, Shimadzu, Japan)
   Column HP-Wax (Cross linked Polyethylene Glycol) 30 m x 0.32 mm x 0.50 μm, HP part no. 19091x-213, USA
3. Analytical balance (4 digits), Model ED 224S, Max 210 g, Sartorius, AG Gottingen, Germany
4. Autopipettes 10-100 μL and 100-1,000 μL
5. Polystyrene film 0.05 mm, part no.0457 5131 (Perkin-Elmer)

3.2 Chemicals and reagent

1. Toluene 99.8% (Wako Pure Chemical Industries, Japan)
2. Ethylbenzene 99.0% (TCI Tokyo Kasai, Japan)
3. Isopropylbenzene 99.0% (TCI Tokyo Kasai, Japan)
4. n-Propylbenzene 99.0% (TCI Tokyo Kasai, Japan)
5. Styrene 99.0% (TCI Tokyo Kasai, Japan)
6. p-Diethylbenzene 99.8% (Wako Pure Chemical Industries, Japan)
7. Tetrahydrofuran (Merck)

3.3 Samples and sample preparation

A total of polystyrene foam food packaging samples were purchased from the local market in Khet Don Mueang, Bangkok and Amphoe Mueang, Nonthaburi Province.

3.4 Chemical analysis

Volatile substances in polystyrene foam used for food packaging were determined by gas chromatography as shown in figure 3.1.

Figure 3.1 GC 17-A gas chromatography (Shimadzu, Japan**)**

3.4.1 Preparation of chemical solution

3.4.1.1 Stock standard solution

3.4.1.1.1 Stock standard toluene solution

2,000 mg/L of the stock standard toluene solution was prepared by weighing 50.0 mg of toluene and dissolving it with tetrahydrofuran and diluting the solution in a 25 mL volumetric flask.

3.4.1.1.2 Stock standard ethylbenzene solution

2,000 mg/L of the stock standard ethylbenzene solution was prepared by weighing 50.0 mg of ethylbenzene and dissolving it with tetrahydrofuran and diluting the solution in a 25 mL volumetric flask.

3.4.1.1.3 Stock standard isopropylbenzene solution

2,000 mg/L of the stock standard isopropylbenzene solution was prepared by weighing 50.0 mg of isopropylbenzene and dissolving it with tetrahydrofuran and diluting the solution in a 25 mL volumetric flask.

3.4.1.1.4 Stock standard n-propylbenzene solution

2,000 mg/L of the stock standard n-propylbenzene solution was prepared by weighing 50.0 mg of n-propylbenzene and dissolving it with tetrahydrofuran and diluting the solution in a 25 mL volumetric flask.

3.4.1.1.5 Stock standard styrene solution

2,000 mg/L of the stock standard styrene solution was prepared by weighing 50.0 mg of styrene and dissolving it with tetrahydrofuran and diluting the solution in a 25 mL volumetric flask.

3.4.1.2 Internal standard solution (ISTD)

Internal standard solution was prepared by pipetting 1 mL of p-diethylbenzene into a 100 mL volumetric flask and making up to 100 mL with tetrahydrofuran. After that, pipetting 1 mL in a volumetric flask and making up to 100 mL with tetrahydrofuran.

3.4.1.3 Intermediate standard volatile substances solution

The intermediate mixed standard of volatile substances solutions of 250 µg/mL was prepared by pipetting 6.25 mL each of toluene, ethylbenzene, isopropylbenzene, n-propylbenzene and styrene of stock standard solution in a volumetric flask and adjusting to 50 mL with tetrahydrofuran. This intermediate standard solution was kept in a brown glass bottle and stored in the refrigerator.

3.4.1.4 Working standard volatile substances solution

Working standard solution of volatile substances of 5, 10, 15, 20, 25 and 30 µg/mL were made from the intermediate mixed standard volatile substance solution of 250 µg/mL. A 200, 400, 600, 800, 1000 and 1200 µL of the intermediate solution were transferred into six 10 mL volumetric flasks respectively and then, the volumes were made up to the mark with tetrahydrofuran.

3.4.2 GC parameter

The GC conditions followed in Table 3.1

Table 3.1 The GC conditions for determination of volatile substances

GC Parameter	Conditions
Column	Capillary column, HP-Wax (30 m x 0.32 mm x 0.5µm)
Carrier gas	Helium, 3.2 mL/min
Oven program	50 ^{o}C (1 min) rate 50 ^{o}C/min to 100 ^{o}C (2 min) rate 20 ^{o}C/min to 200 ^{o}C (1 min)
Injection	Split (1/100), Inlet 220 ^{o}C
Detector	FID 250 ^{o}C

3.4.3 Preparation of test solution

The samples were prepared by cutting the samples to small pieces and weighing 0.5 g into Erlenmeyer flask with cap, adding 1mL of internal standard and 19 ml of tetrahydrofuran, mix, shake gently, keep in refrigerator for 24 hrs. until completely dissolved.

3.5 FT-NIR spectroscopy

In this study, the samples were measured using FT-NIR Spectrometer (Antaris II Analyzer) as shown in Figure 3.2.

Figure 3.2 FT-NIR Spectrometer (Antaris II Analyzer, Thermo Electron Corporation, USA)

3.5.1 Default spectral acquisition

Instrument setup

Source	High intensity halogen NIR
Detector	Indium gallium arsenide (InGaAs)
Wavelength selector	Interferometer
Mode	Integrating sphere
NIR range	10000 - 4000 cm^{-1}
Spectral format	$\log \frac{1}{R}$

3.5.2 Sample preparation

NIR spectra were measured using a FT-NIR spectrometer. In this study, all polystyrene foam food packaging samples were cut into 2 cm x 2 cm before analysis. The samples were placed on the integrating sphere and covered with aluminium foil and then a weight was placed on the aluminium foil; shown in Figure 3.3.

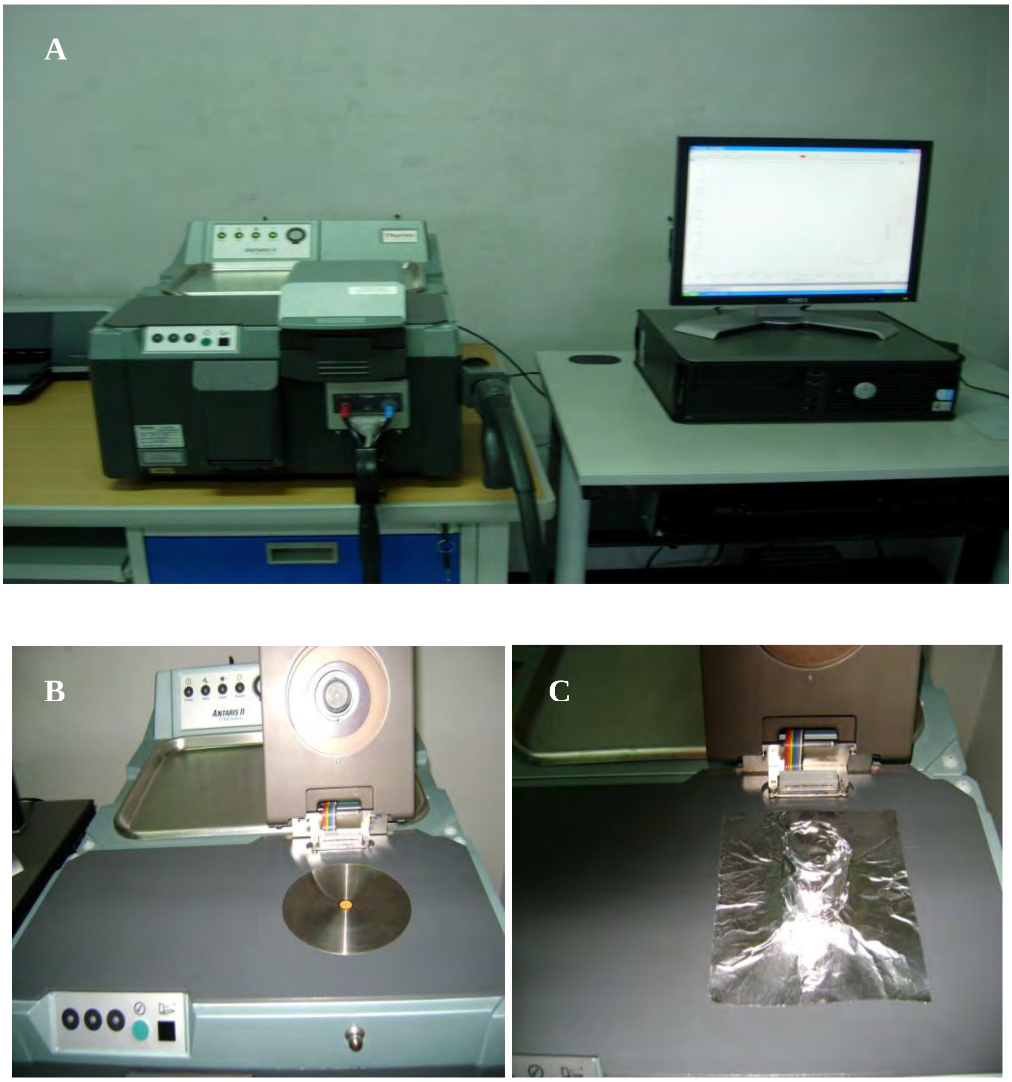


Figure 3.3 A) FT-NIR spectrometer B) Integrating sphere and C) measured sample

3.5.3 Identification of polystyrene

Figure 3.4 Food packaging

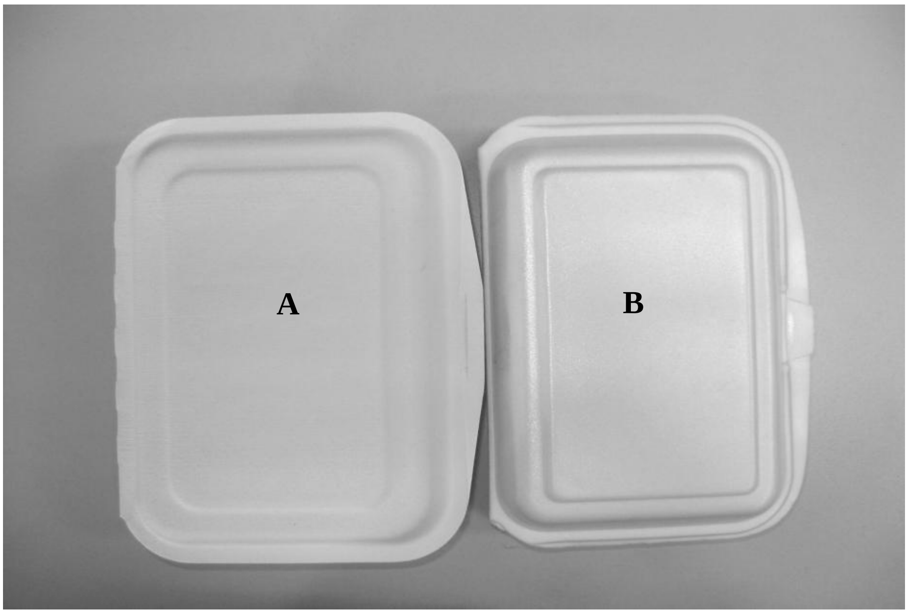


Figure 3.4 A) Biodegradable packaging B) Polystyrene packaging

Using FT-NIR spectrometer (Antaris II Analyzer, Thermo Electron Corperation, USA) equipped with an integrating sphere using a halogen light source and InGaAs detector the food packaging was identified by comparing the spectrum of transparent standard polystyrene film with biodegradable packaging and polystyrene packaging. The samples measured in a diffuse reflectance mode using by integrating sphere were scanned in 10000 to 4000 cm^{-1} range at 30 scans and the resolution was 8 cm^{-1}. The samples spectrum was average of three times.

3.5.4 Optimized resolution and the number of scans

The polystyrene foam food packaging samples were scanned with a FT-NIR spectrometer (Antaris II Analyzer, Thermo Electron Corperation, USA) equipped with an integrating sphere using a halogen source and InGaAs detector. All of the samples were analyzed in the diffuse reflectance mode at a range from 10000 to 4000 cm^{-1} using a resolution of 4, 8, 16 and 32 cm^{-1}. 16 and 30 scans were made. Each sample spectrum was collected twenty times. The samples spectrum was an average of twenty spectra. The background spectrum used the same conditions as the sample and a new background was scanned every time before measuring the sample. The background spectrum measures the signal of the instrument and the environment. All spectrums were recorded as log (1/R), where R is the relative reflectance. The sample was tested at room temperature (23-26 ^{o}C).

3.5.5 Spectra preprocessing

This study was done to test mathematical preprocessing to improve the prediction of calibration models by comparing the raw spectrum and four data preprocessing namely: multiplicative signal correction (MSC), standard normal variate correction (SNV), first derivative and second derivative. The smoothing is done by using the Savizky-Golay filter and variables for data point and polynomial order.

3.5.6 Construct calibration and validation model

In this thesis, chemometric analysis used was TQ Analyst Version 7.2 under Windows XP. Calibration set (n=50) using partial least square regression (PLSR) to construct the equations. A good calibration model should have a high correlation coefficient (r) between the predicted NIR value and the reference value, low bias and RMSEC. In this study, the correlation coefficient (r) of calibration curves and root mean square of calibration (RMSEC) and bias were presented. Validation set (n=20) using a test calibration equation which should have a low root mean square error of prediction (RMSEP). In this study, RMSEP was present.

3.5.7 Comparison of FT-NIR and chemical analysis

Using twenty concentrations to compare using the FT-NIR and chemical analysis with a statistic paired t-test at 95% confidence.

3.5.8 Study the effect of the environmental condition on the analysis

Using one concentration to measure different temperatures of the environment by measuring twenty replicates.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Chemical analysis

The volatile substances analysis was performed using GC (GC17-A gas chromatography, Shimadzu, Japan) with an FID detector. GC parameters were as followed; the GC column used was a capillary column HP-Wax (30 m x 0.32 mm x 0.5 μm), the carrier gas was helium: 3.2 mL/min, Oven program: 50 ^{o}C (1 min), rate 50 ^{o}C/min. to 100 ^{o}C (2 min), rate 20^{o}C/min to 200 ^{o}C (1 min), Injection: split (1/100), inlet 220 ^{o}C, Detector: FID 250 ^{o}C. Injection volume: 1 μL. The chromatogram of standard volatile substances is shown in figure 4.1

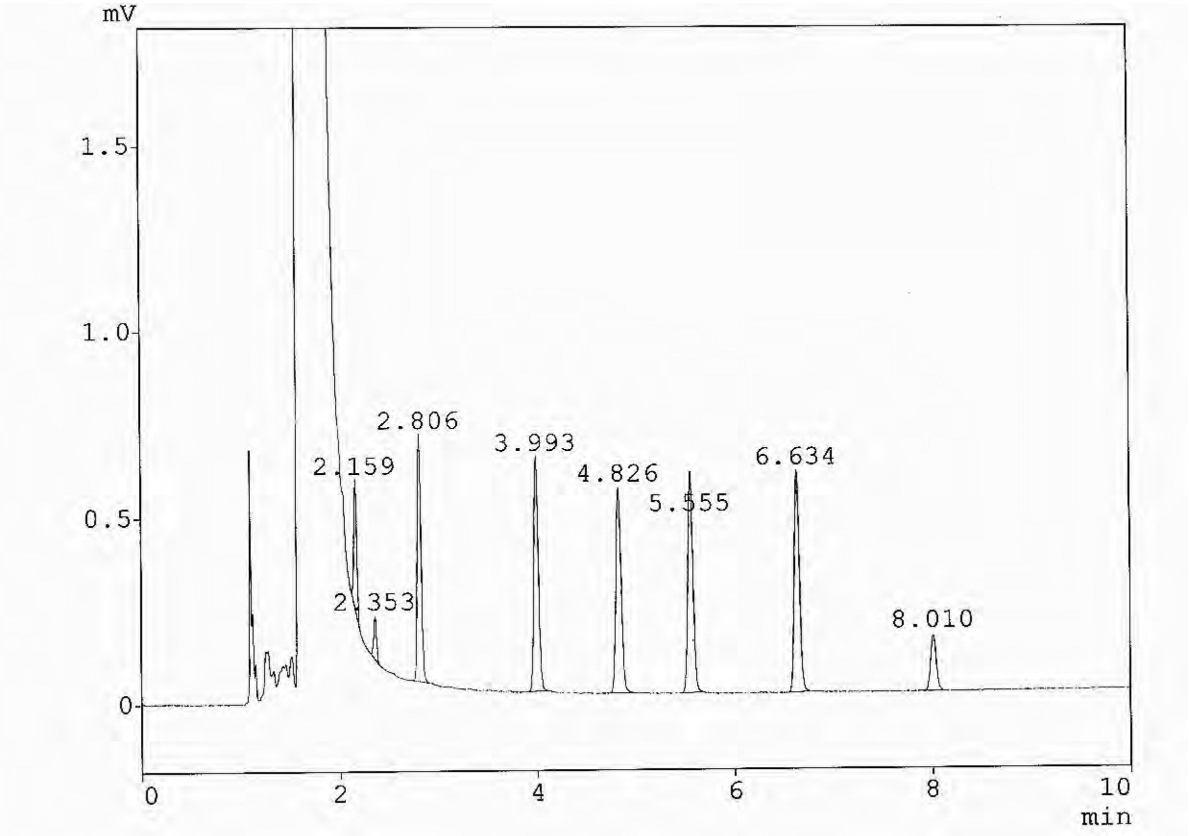


Figure 4.1 The chromatogram of standard mixture solutions of volatile substances

The separation of volatile substances namely; toluene, ethylbenzene, isopropyl benzene, n-propylbenzene and styrene are as follows:

Table 4.1 Resolution of volatile substances by GC

Time (min)	Volatile substances
2.806	toluene
3.993	ethylbenzene
4.826	isopropylbenzene
5.555	n-propylbenzene
6.634	styrene
8.010	ISTD

4.1.1 Standard calibration curve

The calibration curve of volatile substances (toluene, ethylbenzene, isopropylbenzene, n-propylbenzene, styrene) at concentration 5, 10, 15, 20, 25 and 30 µg/mL were displayed in Appendix A. The results of the coefficient of determination (R^2) and equation were summarized in Table 4.2. The corresponding coefficient of determination (R^2) in Table 4.2 were more than 0.9500.

Table 4.2 Equation and coefficient of determination from standard calibration curve of volatile substances.

No.	Compound	Equation	(R^2)
1.	Toluene	Y=10443X+25.267	0.9971
2.	Ethylbenzene	Y=10679X+22.267	0.9977
3.	isopropylbenzene	Y=10206X+33.333	0.9977
4.	n-Propylbenzene	Y=10819X+18.2	0.9970
5.	Styrene	Y=11060X+51.467	0.9973

Volatile substances of all samples were determination by GC. Table 4.3 shows information about the reference data.

Table 4.3 Volatile substances in polystyrene foam food packaging from GC

Component	Units	Numbers	Range	Mean	SD
Volatile substances	mg/kg	70	355-852	581	150

4.2 NIR analysis

The steps used in the NIR analysis to determine the volatile substances in foam food packaging can be summarized in Figure 4.2 [49].

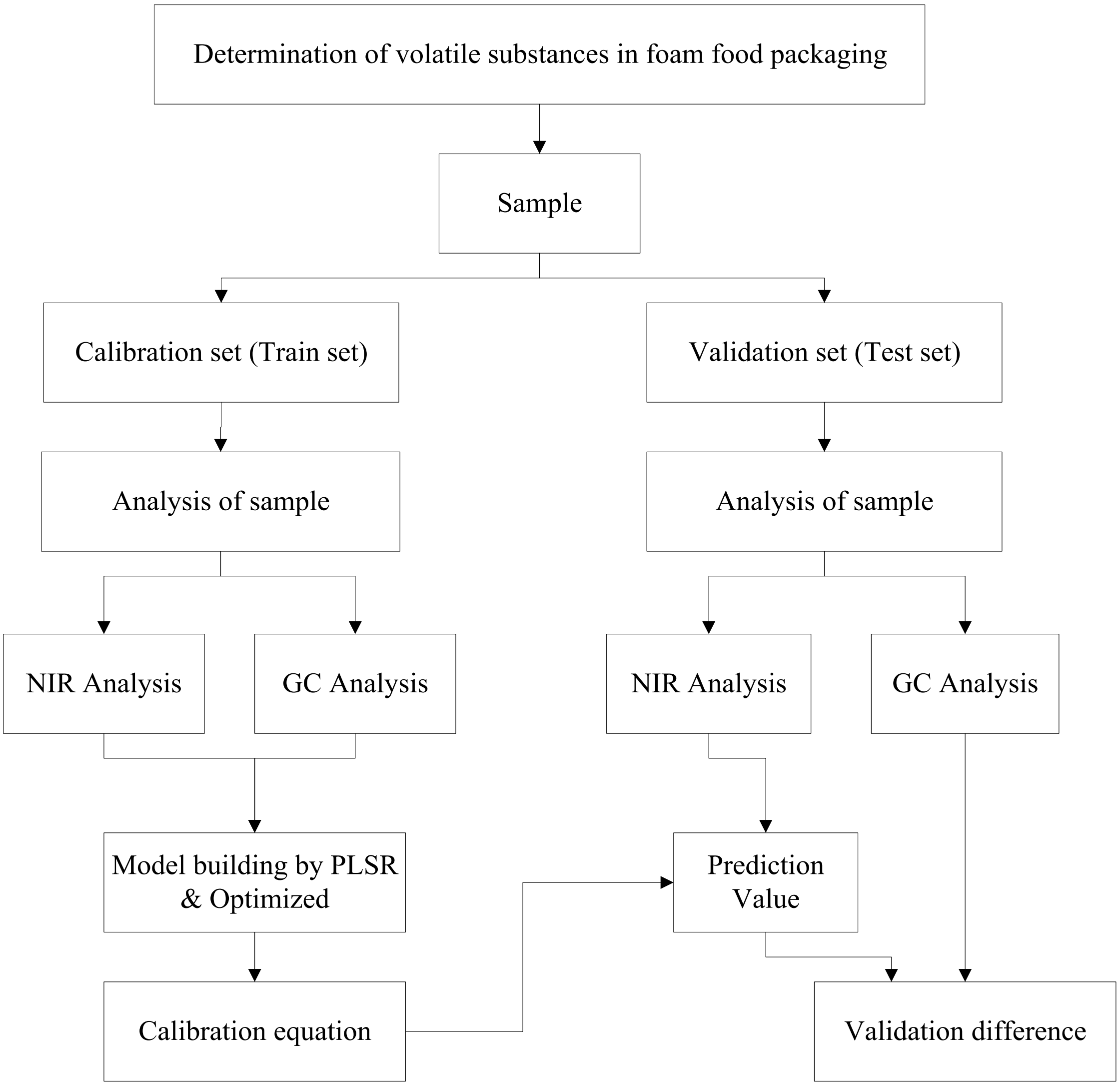


Figure 4.2 Schematic diagram of NIR analysis

4.2.1 Identification of polystyrene

Three samples namely: standard transparent polystyrene film, polystyrene packaging and biodegradable packaging were performed in diffuse reflectance mode using FT-NIR equipped with integrating sphere. 30 scans were made in the ranges from 10000 to 4000 cm^{-1} at resolution of 8 cm^{-1}. All spectra were recorded as log 1/R.

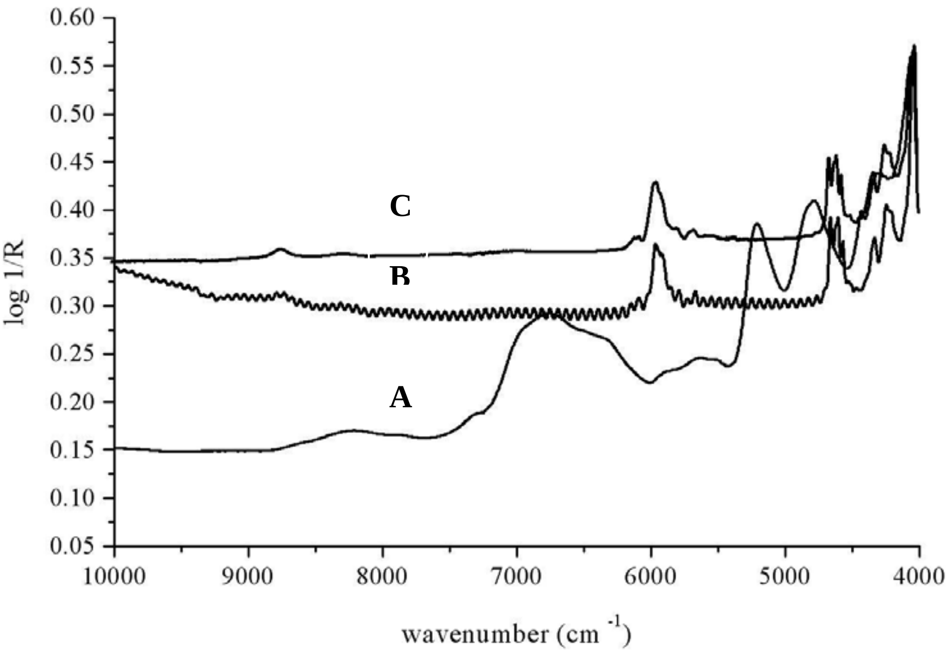


Figure 4.3 Spectra of A) biodegradable packaging B) standard polystyrene film and C) polystyrene packaging

Figure 4.3 shows the spectrum of standard transparent polystyrene film, biodegradable packaging and polystyrene packaging. A FT-NIR spectrum of transparent polystyrene film and sample polystyrene packaging has a similar band around 6200 cm^{-1} to 5900 cm^{-1} and 4700 cm^{-1} to 4000 cm^{-1} but the spectra of the biodegradable packaging is different. In this study, the FT-NIR spectrometer can identify the type of packaging.

4.2.2 Optimizing the resolution and number of scans

All of the samples were analyzed by a diffuse reflectance mode in the range from 10000 to 4000 cm^{-1} at resolution 4, 8, 16 and 32 cm^{-1}. 16 and 30 scans were prepared in total. Each sample spectrum was collected twenty times using the same conditions for the background spectrum as the sample. Before measurement of the sample were taken, a new background spectrum was scanned every time.

. Selected band in range 4750-4050 cm^{-1}, 6205-5575 cm^{-1}, 7455-6880 cm^{-1}, and 8800-8655 cm^{-1} which were refer to band assignment shown in Table 4.4. Spectra were preprocessing by using MSC and first derivative, MSC and second derivative and smoothing by Savitzky-Golay (SG) filter. Partial least squares regression (PLSR) was used to construct calibration models. The samples were tested at room temperature (23-26 ^{o}C). The samples were divided into two groups. The first group consisted of 50 samples used for developing the calibration model. The second group consisted of 20 samples used for prediction models.

Table 4.4 Band assignment

Wavelength (nm)	Wavenumbers (cm^{-1})	Assignment	Reference
1100-1300	9090-7692	C-H second overtone	31
1300-1420	7692-7042	C-H combination	31
1600-1800	6250-5555	C-H first overtone	31
~ 2,126	~ 4703	C=C combination, aromatic ring	35
2200-2500	4545-4000	C-H combination	31

The results from optimizing the resolution and no. of scans are shown in Appendix B. Appendix B shows the correlation coefficient (r), RMSEC and RMSEP on different resolutions. The result of 8 cm^{-1} resolution and the number of scans 30 gave a better trend of high correlation coefficient (r), low RMSEC and RMSEP than 4, 16 and 32 cm^{-1} resolution. The high resolution (16 and 30 cm^{-1}) provided the broad feature band resulting in the low signal to noise ratio. For low resolution (4 cm^{-1}), the sharpest feature band was obtained and the signal to noise ratio was improved. However, the results showed the higher noise interference. 30 scans at 8 cm^{-1} resolution gave the better results than 16 scans at 8 cm^{-1} resolution. Noise was reduced and signal to noise ratio was improved. Therefore, 30 scans with a resolution of 8 cm^{-1} were selected. Figure 4.4 shows spectra of polystyrene packaging at 8 cm^{-1} resolution with 30 scans. All of the spectra are shown in Appendix C.

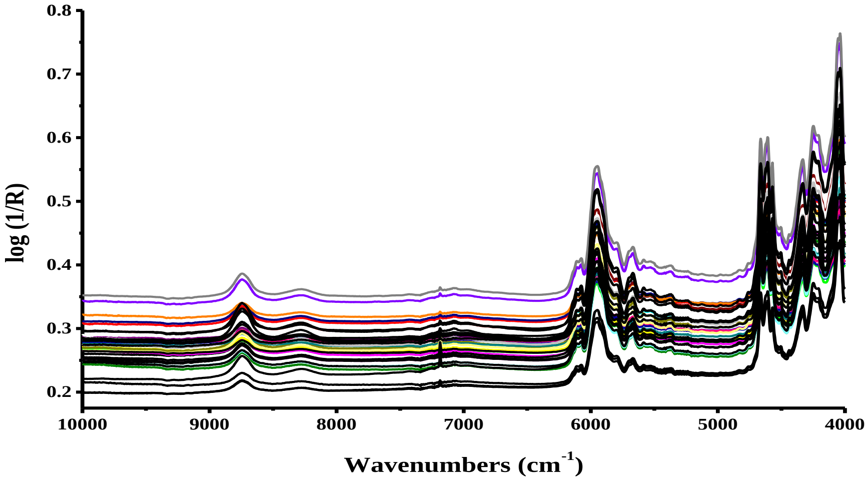


Figure 4.4 Raw spectra of polystyrene packaging at 8 cm^{-1} resolution, 30 scan

4.2.3 Preprocessing and construction of calibration model

All of the samples were analyzed by diffuse reflectance mode using thirty scans in a range from 10000 to 4000 cm^{-1}at resolution 8 cm^{-1}. Each sample spectrum was collected twenty times. The background spectrum obtained from conditions which were the same as the sample. Before measurement, a new background of the sample was scanned every time. Partial least squares regression (PLSR) was used to construct calibration models. The samples were tested at room temperature (23-26 ^{o}C). The samples were divided into two groups. The first group consisted of 50 samples used for developing the calibration model. The second group consisted of 20 samples used for the prediction models. The calibration set will be used to calibrate the NIR spectral response against the reference data, and should be selected to cover the full variation in the sample set as a whole in order to ensure that the calibration covers the full range of interest for the analysis. Spectra were optimizing preprocessing shown as follows in Table 4.5.

Table 4.5 Optimize preprocessing

Preprocessing parameter		
Resolution, no. of scan	Smoothing	Preprocessing
8, 30	Savitzky-Golay (SG) filter	MSC and first derivative MSC and second derivative SNV and first derivative SNV and second derivative

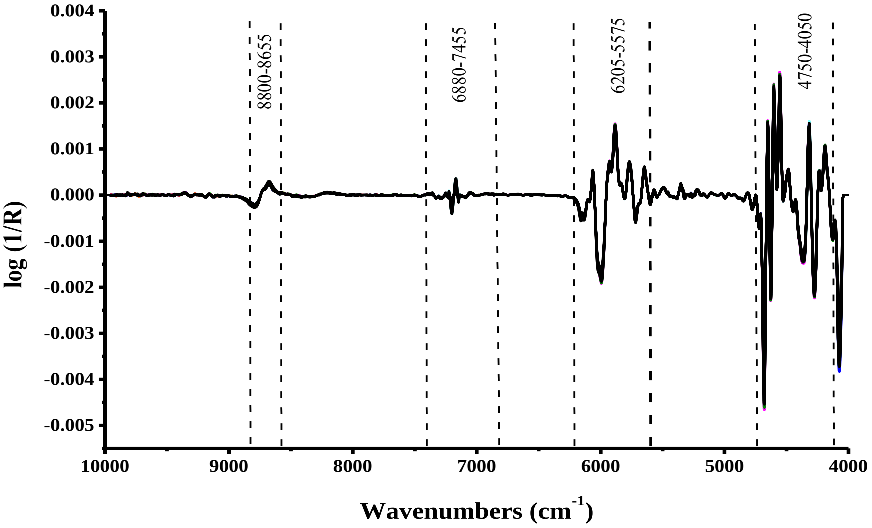


Figure 4.5 Spectra preprocessing by MSC and first derivative of polystyrene packaging at 8 cm^{-1} resolution, 30 scan

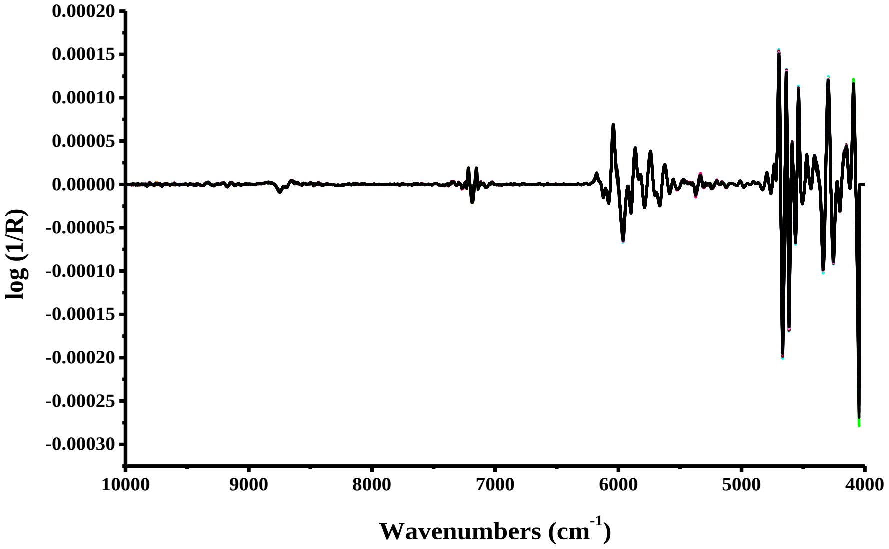


Figure 4.6 Spectra preprocessing by MSC and second derivative of polystyrene packaging at 8 cm^{-1} resolution, 30 scan

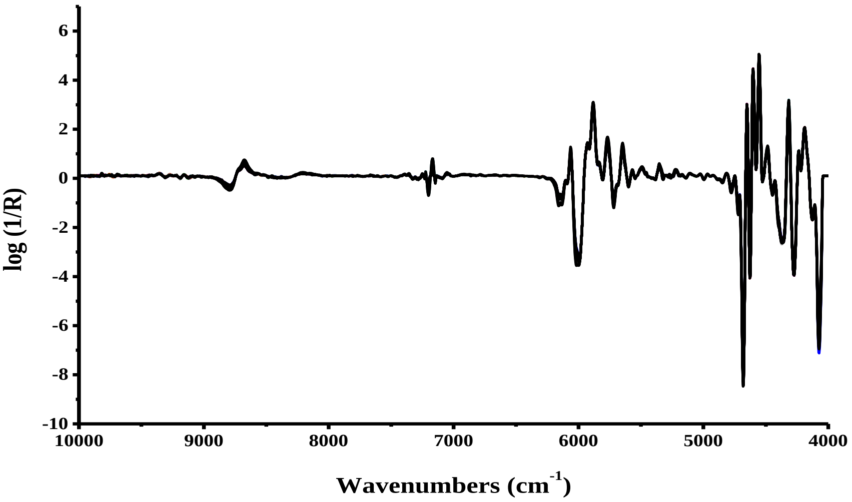


Figure 4.7 Spectra preprocessing by SNV and first derivative of polystyrene packaging at 8 cm^{-1} resolution, 30 scan

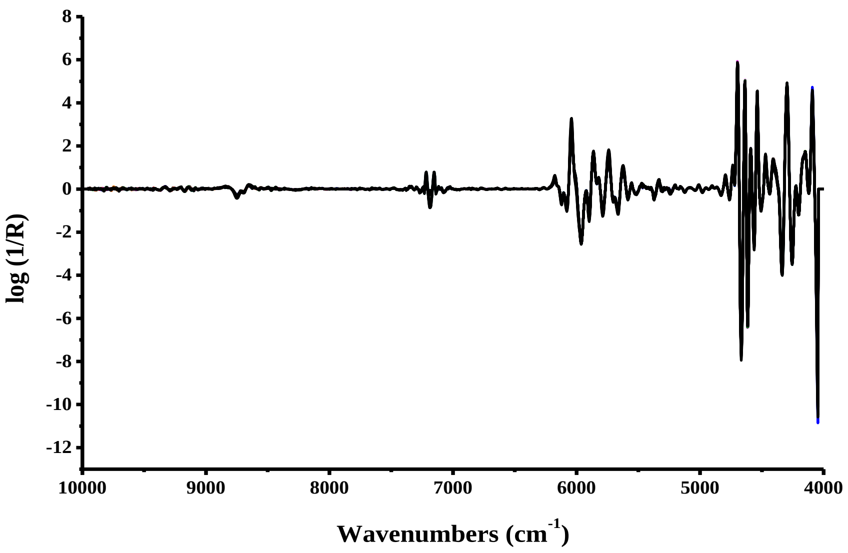


Figure 4.8 Spectra preprocessing by SNV and second derivative of polystyrene packaging at 8 cm^{-1} resolution, 30 scan

Figure 4.5 to Figure 4.8 shows spectra preprocessing of polystyrene food packaging by MSC and first derivative, MSC and second derivative, SNV and first derivative, and SNV and second derivative, respectively.

Selected bands in range 4750-4050 cm^{-1}, 6205-5575 cm^{-1}, 6880-7455 cm^{-1}, and 8800-8655 cm^{-1} which were refer to band assignment shown in Table 4.4.

The performance of the final PLSR model was evaluated in terms of the root mean square error of calibration (RMSEC), the root mean square error of prediction (RMSEP), the correlation coefficient (r) and bias.

Table 4.6 Results for the final PLSR model without preprocessing

r	RMSEC	Bias	RMSEP
0.6807	104 mg/kg	-28.6	119 mg/kg

Results of PLSR models by optimized preprocessing parameter shown in Appendix D show the results of the calibration models using different spectral preprocess methods for determining volatile substances. Compared with others, preprocessing by multiplicative signal correction (MSC) and second derivative and smoothing by Savitzky-Golay filter at data points 25, polynomial order 5 presented the lowest values of the root mean square error of calibration (RMSEC). The multiplicative signal correction (MSC) path length treatment may also be used to compensate for variations in sample thickness that is caused by particle size and scattering. Also, transformation with Savitzky-Golay second derivative (Data points 25, polynomial order 5) was used to remove the baseline shift, overlapping peak and resolution broad absorbance band on the reflectance spectra. The results indicate that the PLS models developed on the second derivative spectra showed better statistics compared with no preprocess and first derivative.

Table 4.7 showed that the characteristics of the sample in the calibration and validation set to the reference method and NIR method are relatively similar in mean and standard deviation.

Table 4.7 Characteristics of the sample in calibration set and validation set compared to the reference method and NIR method

Variable	Calibration set		Validation set	
Method	GC	NIR	GC	NIR
Mean	587 mg/kg	585 mg/kg	585 mg/kg	590 mg/kg
Standard deviation	138 mg/kg	135 mg/kg	138 mg/kg	147 mg/kg

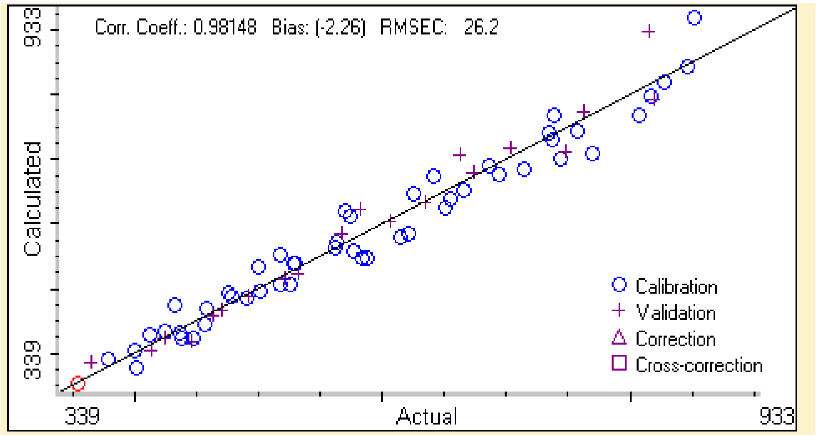


Figure 4.9 Correlation statistics between the measured values and calculated values of volatile substances in polystyrene foam. (O calibration, + validation)

Figure 4.9 shows the correlation between the values determined by the reference analysis method and the values predicted by the NIR spectroscopy technique. The cycle points refer to calibration samples, and the plus points refer to validation samples. Results are summarized in Table 4.7.

Table 4.8 Calibration and validation resulting from PLSR models

Component	Calibration set			Validation set			
	r	RMSEC mg/kg	Bias	RMSEP mg/kg	SEP mg/kg	RPD	PLS
Volatile substances	0.9815	26.2	-2.26	26.7	24.1	5.7	11

Table 4.8 shows the values of r and RMSEC indicating the precision achieved in calibration. On the other hand, the correlation coefficient (r), root mean square error of calibration (RMSEC), bias, root mean square error of prediction (RMSEP), standard error of prediction (SEP) and the residual predictive deviation (RPD) was found to be 0.9815, 26.2 mg/kg, -2.26, 25.4 mg/kg, 5.4, respectively. The PLSR factor was 11 for the construct calibration model. From the results, the correlation coefficient (r) was 0.9815 which was considered as excellent [50]. A

good model could give a low value of root mean square error of calibration (RMSEC) value , bias, root mean square error of prediction (RMSEP) and standard error of prediction (SEP). The residual predictive deviation (RPD) is a simple statistic that enables the evaluation of an SEP in terms of the SD of the reference data. It is calculated by dividing the SD of reference values used in the validation by the SEP. If the RPD value is high it indicates that the model can give a good prediction. Generally, an RPD above 3 is considered very good for prediction [50-51]. However, the RPD was 5.7 which indicate that the predictive quality of this model is considered very good.

4.2.4 Comparison of FT-NIR and chemical analysis

Using twenty values to compare by FT-NIR and chemical analysis with statistic paired t-test at 95% confidence.

Table 4.9 Comparison between the chemical method and the FT-NIR method using paired t-test at 95% confident (degree of freedom, df = 19)

Method	Mean (mg/kg)	SD	t-value
GC	585	138	$t_{crit} = 2.09$
FT-NIR	590	147	$t_{exp} = 0.82$

Results of comparing the paired t-test statistics between the chemical method and the NIR method are shown in Table 4.9. The critical value 19 degree of freedom at 95% confidence was 2.09. If $t_{exp} > t_{crit}$, the null hypothesis will be rejected but $t_{exp} < t_{crit}$ the null hypothesis will be accepted. In this study $t_{exp} = 0.82$ was lower than the $t_{crit,}$ so this hypothesis proved that the chemical method and the NIR method were not significantly differences.

4.2.5 Effect of the environmental condition on the analysis

This was determined by varying room temperatures

Table 4.10 Effect of environmental condition on the analysis

Temperature	N	Mean value (mg/kg)	%RSD
25 °C	20	433 (424)	4.63
32 °C	20	436 (424)	4.74

As shown in Table 4.10, the concentration at 424 mg/kg was used for the test. The effect of the environmental condition on the analysis by varying the room temperature showed no difference.

CHAPTER V

CONCLUSION

FT-NIR spectroscopy in diffuse reflectance mode selected wave numbers in the range of 8800 - 8655, 7455 - 6880, 6200 - 5195 and 4750 - 4050. The PLSR for the constructed calibration model and validation model preprocessing by MSC and second derivative, Savitzky-Golay smoothing at 25 data point, 5 polynomial gave the best model. The best model showed the correlation coefficient, RMSEC, bias, RMSEP were 0.9815, 26.2, -2.26 and 26.7, respectively. From comparing the chemical method and the FT-NIR method to determine volatile substances in polystyrene foam food packaging, it was found that it was not significantly different from using the pair t-test method.

The results of this study indicated that NIR spectroscopy was employed for the determination of volatile substances in foam food packaging. This technique was cost effective convenient and avoided the use of chemical reagents, was environmentally friendly and left no waste from the reagent.

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APPENDICES

APPENDIX A

APPENDIX A Calibration curve

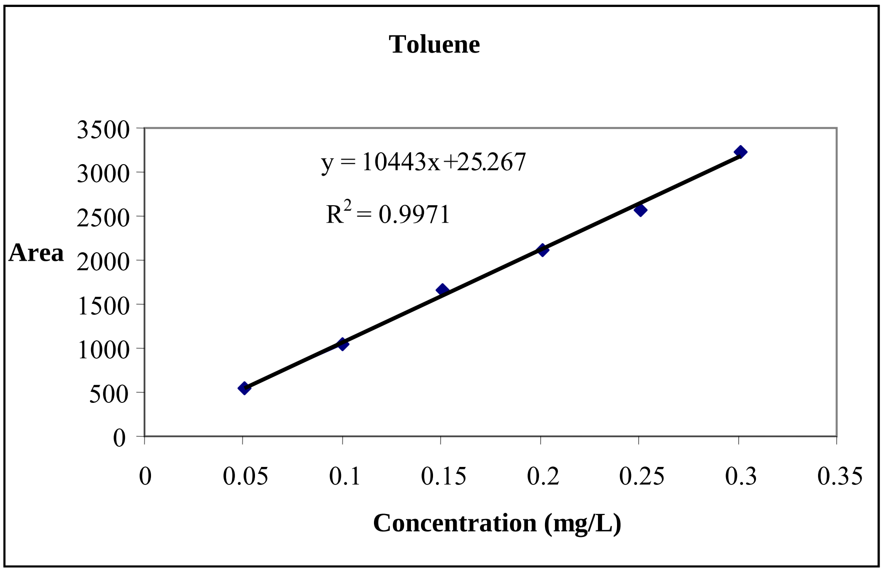

Figure A.1 Standard calibration curve of toluene

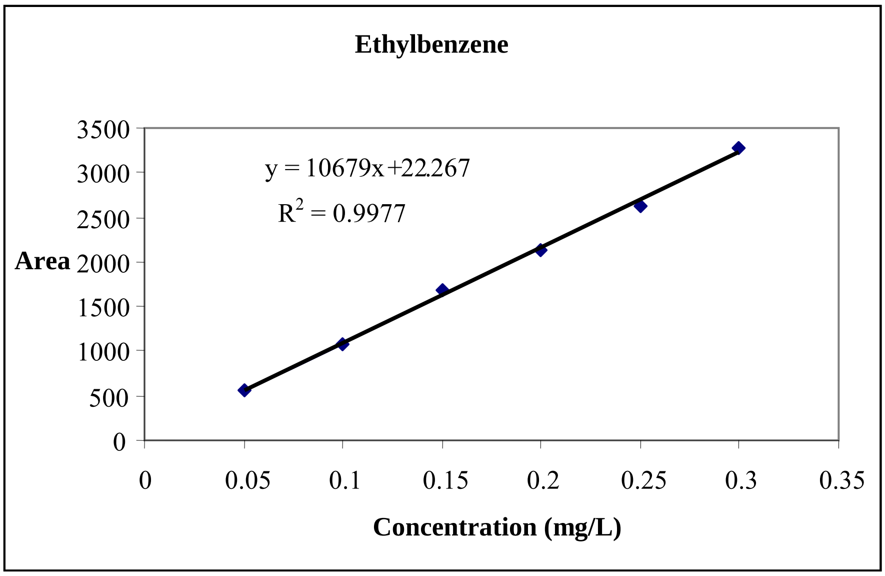

Figure A.2 Standard calibration curve of ethylbenzene

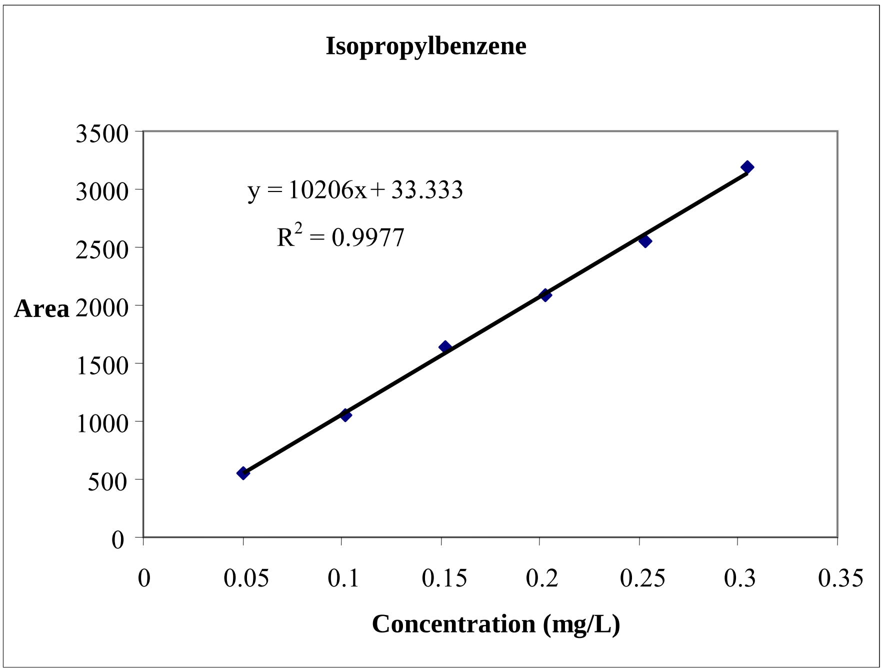

Figure A.3 Standard calibration curve of Isopropylbenzene

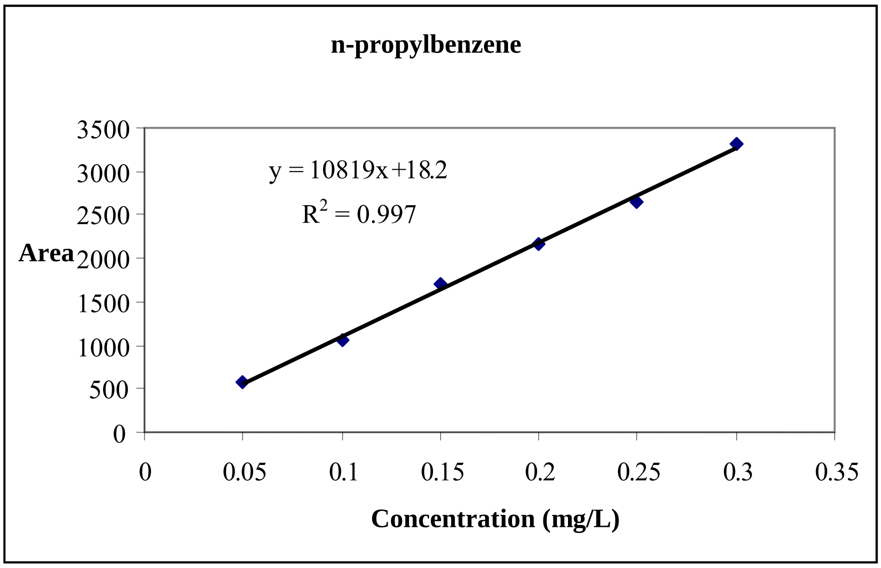

Figure A.4 Standard calibration curve of n-propylbenzene

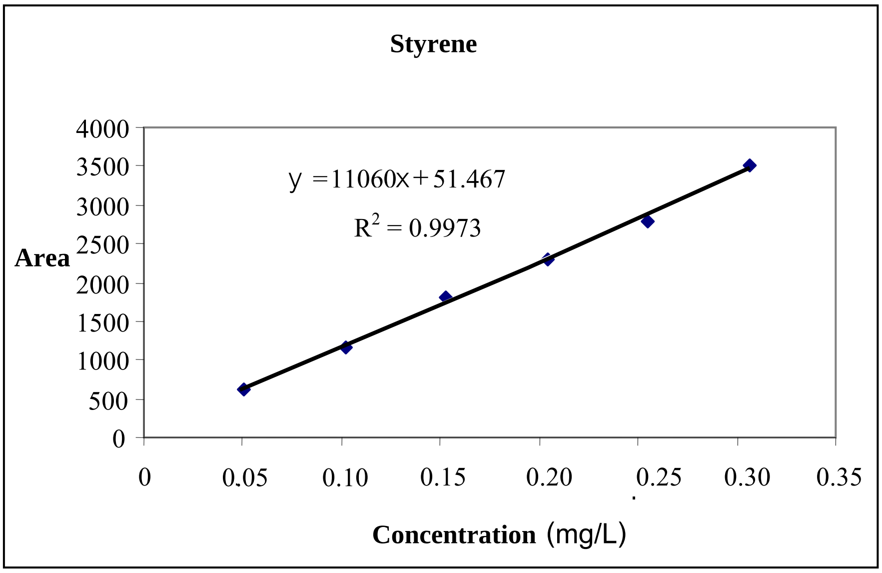

Figure A.5 Standard calibration curve of styrene

APPENDIX B

APPENDIX B show results of optimized resolution and no. of scan

Table B.1 Results obtained using 4 cm^{-1} resolution, no. of scan was 16 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9854	19.9	104	0.9927	14.0	116
5	2	0.9761	25.4	95.3	0.9885	17.6	130
7	2	0.9639	31.1	107	0.9835	21.1	111
9	2	0.9530	35.6	118	0.9778	24.4	105
11	2	0.9478	37.6	118	0.9815	22.4	108
13	2	0.9432	39.1	104	0.9745	26.3	114
15	2	0.9510	36.5	106	0.9738	26.7	114
17	2	0.9181	46.8	102	0.9828	21.6	103
19	2	0.9341	42.2	111	0.9675	29.6	110
21	2	0.9434	39.2	101	0.9570	34.0	100
23	2	0.9324	42.7	95.7	0.9631	31.6	99
25	2	0.9136	48.0	101	0.9791	23.8	108
27	2	0.9200	46.2	107	0.9680	29.4	95.2
29	2	0.9225	45.6	108	0.9684	29.1	97.6
31	2	0.9133	48.1	107	0.9691	28.7	103
33	2	0.9275	44.2	112	0.9656	31.0	96.4
35	2	0.9191	46.5	134	0.9652	30.7	90.3
37	2	0.9099	49.1	128	0.9523	35.8	111
39	2	0.9145	47.8	119	0.9574	34.0	110
41	2	0.9261	44.7	112	0.9548	35.3	108
43	2	0.1723	47.1	118	0.9528	35.7	94.6
45	2	0.9215	45.9	122	0.9484	35.8	127
47	2	0.9166	47.3	115	0.9591	33.3	103
49	2	0.9231	45.4	120	0.9513	36.2	102
51	2	0.9030	50.7	121	0.9607	32.7	105

Table B.2 Results obtained using 4 cm^{-1} resolution, no. of scan was 16 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9758	25.6	111	0.9846	20.4	114
5	2	0.9789	24.5	114	0.9781	24.5	109
7	2	0.9724	27.4	96.5	0.9791	23.8	112
9	2	0.9732	26.9	111	0.9662	30.1	112
11	2	0.9535	35.4	113	0.9512	36.2	113
13	2	0.9275	44.0	113	0.9612	32.5	114
15	2	0.9432	45.3	120	0.9456	37.2	128
17	2	0.9398	40.4	119	0.9410	39.9	123
19	2	0.9426	39.4	117	0.9487	37.3	109
21	2	0.9342	42.1	119	0.9187	47.8	110
23	2	0.9096	49.3	106	0.9228	45.7	114
25	2	0.9234	45.4	112	0.9397	40.5	121
27	2	0.9265	44.2	111	0.9262	44.7	113
29	2	0.9162	47.3	109	0.8929	53.4	98.3
31	2	0.9147	47.8	111	0.9101	49.1	103
33	2	0.9046	50.4	110	0.8960	52.6	111
35	2	0.9052	50.3	114	0.9027	51.1	109
37	2	0.9089	49.3	114	0.9244	45.3	93.2
39	2	0.8923	53.5	102	0.9090	49.5	101
41	2	0.8842	55.2	105	0.8812	56.1	117
43	2	0.8923	51.8	111	0.8806	56.0	116
45	2	0.8856	55.1	118	0.8819	55.7	99.5
47	2	0.8863	54.9	109	0.8655	55.3	109
49	2	0.8909	53.8	109	0.8695	58.6	109
51	2	0.8709	58.4	110	0.8773	51.7	103

Table B.3 Results obtained using 4 cm^{-1} resolution, no. of scan was 30 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9837	21.0	99.5	0.9934	13.4	117
5	2	0.9723	27.3	92.3	0.9879	19.3	127
7	2	0.9568	34.0	103	0.9835	21.1	110
9	2	0.9518	36.0	116	0.9768	25.0	105
11	2	0.9472	37.6	112	0.9815	22.4	105
13	2	0.9469	37.8	111	0.9759	25.5	114
15	2	0.9555	34.7	118	0.9732	27.0	110
17	2	0.9235	45.2	106	0.9857	19.7	106
19	2	0.9428	39.2	121	0.9763	25.3	109
21	2	0.9436	39.0	113	0.9749	26.0	102
23	2	0.9519	36.1	99.5	0.9661	30.3	98.6
25	2	0.9408	39.9	101	0.9833	21.2	107
27	2	0.9253	44.5	114	0.9702	28.3	91.6
29	2	0.9202	46.0	114	0.9674	29.6	104
31	2	0.9200	46.2	119	0.9686	29.3	100
33	2	0.9401	40.1	118	0.9647	31.4	95.0
35	2	0.9244	45.0	148	0.9740	26.6	91.6
37	2	0.9119	48.4	139	0.9507	36.5	109
39	2	0.9061	50.0	120	0.9619	32.4	105
41	2	0.9361	41.3	117	0.9920	35.1	102
43	2	0.9278	43.8	126	0.9570	34.2	93.2
45	2	0.9262	44.2	122	0.9522	35.8	124
47	2	0.9184	46.5	115	0.9675	29.7	102
49	2	0.9281	43.8	121	0.9552	34.8	101
51	2	0.9069	49.4	126	0.9624	32.0	105

Table B.4 Results obtained using 4 cm^{-1} resolution, no. of scan was 30 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9854	19.9	104	0.9938	12.9	119
5	2	0.9861	19.4	109	0.9923	14.4	129
7	2	0.9866	19.0	109	0.9829	21.6	110
9	2	0.9827	21.7	94.8	0.9683	29.1	111
11	2	0.9778	24.4	96.8	0.9674	29.9	106
13	2	0.9798	23.3	113	0.9612	32.5	114
15	2	0.9732	26.9	118	0.9527	35.7	117
17	2	0.9633	31.4	116	0.9699	28.5	103
19	2	0.9516	36.1	116	0.9514	36.1	110
21	2	0.9531	35.6	124	0.9518	36.0	107
23	2	0.9490	37.1	117	0.9583	33.6	99.1
25	2	0.9505	36.5	116	0.9792	23.8	101
27	2	0.9397	40.3	116	0.9632	32.8	97.5
29	2	0.9322	42.7	104	0.9648	31.0	102
31	2	0.9389	40.5	106	0.9644	31.2	99.9
33	2	0.9269	44.4	102	0.9655	30.8	100
35	2	0.9194	46.5	103	0.9727	27.3	93.9
37	2	0.9280	44.0	110	0.9563	34.4	104
39	2	0.9315	42.8	111	0.9638	31.4	115
41	2	0.9148	48.0	112	0.9563	34.6	112
43	2	0.9097	49.3	105	0.9354	41.8	92.6
45	2	0.9165	47.1	103	0.9514	36.3	121
47	2	0.9226	45.3	112	0.9582	33.8	102
49	2	0.8975	52.6	94.4	0.9564	34.1	98.7
51	2	0.9074	50.3	95.1	0.9629	31.8	103

Table B.5 Results obtained using 8 cm^{-1} resolution, no. of scan was 16 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9684	33.8	138	0.9932	15.9	120
5	2	0.9709	32.7	103	0.9911	18.1	108
7	2	0.9378	47.6	103	0.9828	25.2	100
9	2	0.9517	42.1	96.1	0.9824	25.6	99.0
11	2	0.9506	42.5	98.6	0.9852	23.4	95.2
13	2	0.9526	41.6	113	0.9820	25.8	99.3
15	2	0.9344	48.9	98.1	0.9843	24.1	82.9
17	2	0.9311	50.0	80.2	0.9751	30.4	81.3
19	2	0.9461	44.4	112	0.9783	28.3	88.9
21	2	0.9497	42.9	85.5	0.9765	29.5	82.1
23	2	0.9526	41.6	84.4	0.9747	30.6	94.7
25	2	0.9538	41.1	92.6	0.9755	30.1	99.7
27	2	0.9234	52.8	99.7	0.9790	27.9	83.8
29	2	0.9294	50.7	98.1	0.9729	31.7	97.3
31	2	0.9207	53.7	113	0.9730	31.6	97.4
33	2	0.9325	49.6	93.8	0.9661	35.4	92.4
35	2	0.9437	45.3	128	0.9666	35.1	88.1
37	2	0.9468	44.2	117	0.9656	35.6	88.9
39	2	0.9351	48.6	141	0.9699	33.3	99.6
41	2	0.9457	44.6	112	0.9670	34.9	99.8
43	2	0.9332	49.4	97.3	0.9626	37.4	97.0
45	2	0.9346	49.0	129	0.9822	25.9	94.9
47	2	0.9454	45.1	100	0.9700	33.3	101
49	2	0.9637	36.6	117	0.9672	34.8	100
51	2	0.9371	48.0	101	0.9610	38.0	98.6

Table B.6 Results obtained using 8 cm^{-1} resolution, no. of scan was 16 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9880	38.7	121	0.9908	18.5	110
5	2	0.9806	31.7	116	0.9918	17.4	113
7	2	0.9858	29.7	95.5	0.9908	18.6	114
9	2	0.9834	31.5	105	0.9837	24.6	122
11	2	0.9754	32.2	114	0.9822	25.7	99.3
13	2	0.9801	35.9	118	0.9785	28.1	115
15	2	0.9733	40.3	104	0.9727	31.7	91.6
17	2	0.9515	45.6	95.9	0.9787	28.0	85.9
19	2	0.9611	43.5	92.7	0.9812	26.4	87.5
21	2	0.9563	53.6	94.5	0.9800	27.2	96.0
23	2	0.9771	45.3	98.3	0.9858	23.0	88.8
25	2	0.9678	37.9	91.2	0.9666	35.2	88.5
27	2	0.9854	34.9	99.6	0.9669	35.0	81.5
29	2	0.9746	46.2	90.8	0.9692	33.7	94.1
31	2	0.9692	36.8	89.0	0.9758	29.9	97.4
33	2	0.9613	39.5	98.1	0.9423	46.0	111
35	2	0.9561	41.6	111	0.9711	32.7	117
37	2	0.9751	38.9	101	0.9519	42.1	98.7
39	2	0.9710	38.5	99.8	0.9698	33.4	93.7
41	2	0.9567	35.8	97.7	0.9472	44.2	97.7
43	2	0.9634	72.9	87.4	0.9642	36.6	112
45	2	0.9869	37.8	96.5	0.9556	40.5	101
47	2	0.9602	35.9	94.6	0.9673	34.8	120
49	2	0.9599	29.8	92.2	0.9568	40.1	99.5
51	2	0.9675	27.6	110	0.9738	31.1	103

Table B.7 Results obtained using 8 cm^{-1} resolution, no. of scan was 30 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9866	22.3	68.3	0.9947	14.0	128
5	2	0.9772	29.0	86.1	0.9947	14.0	123
7	2	0.9674	34.6	84.9	0.9889	20.2	129
9	2	0.9460	44.6	93.9	0.9788	28.0	89.6
11	2	0.9531	41.6	76.9	0.9909	17.4	88.5
13	2	0.9508	42.7	62.6	0.9779	28.6	74.0
15	2	0.9522	42.0	87.9	0.9841	24.3	76.2
17	2	0.9496	43.1	94.0	0.9821	25.7	49.9
19	2	0.9534	41.4	82.9	0.9810	26.5	66.3
21	2	0.9235	52.9	95.4	0.9827	25.4	61.1
23	2	0.9017	59.8	69.6	0.9803	29.7	79.7
25	2	0.9155	55.6	78.4	0.8773	29.0	51.6
27	2	0.8805	65.9	92.0	0.9737	31.3	77.1
29	2	0.8595	71.3	82.2	0.9811	26.4	81.1
31	2	0.8964	61.4	111	0.9721	32.3	91.9
33	2	0.8809	65.8	123	0.9773	29.0	68.6
35	2	0.8643	69.9	103	0.9652	35.9	93.9
37	2	0.8582	71.6	95.6	0.9796	27.5	81.4
39	2	0.8518	72.9	91.5	0.9580	39.5	84.7
41	2	0.8528	72.7	116	0.9572	39.6	69.9
43	2	0.8519	71.2	125	0.9639	36.6	80.6
45	2	0.8868	64.0	86.7	0.9627	37.1	92.8
47	2	0.8629	70.2	85.2	0.9719	32.2	92.9
49	2	0.8323	77.3	90.9	0.9511	42.4	73.2
51	2	0.8401	75.7	80.3	0.9632	36.9	81.3

Table B.8 Results obtained using 8 cm^{-1} resolution, no. of scan was 30 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9908	18.5	110	0.9935	15.5	133
5	2	0.9837	24.6	86.0	0.9915	17.7	124
7	2	0.9844	24.0	67.2	0.9847	23.8	120
9	2	0.9774	28.9	60.2	0.9811	26.4	96.2
11	2	0.9769	29.2	54.3	0.9815	26.2	72.1
13	2	0.9764	29.5	61.9	0.9691	33.8	78.0
15	2	0.9755	30.1	84.7	0.9704	33.0	71.9
17	2	0.9706	33.0	60.6	0.9742	30.8	61.2
19	2	0.9645	36.1	72.2	0.9704	33.1	70.6
21	2	0.9714	32.5	84.5	0.9650	35.9	58.8
23	2	0.9690	33.9	76.4	0.9699	33.4	78.3
25	2	0.9714	31.9	68.5	0.9764	29.6	52.4
27	2	0.9783	28.4	76.7	0.9620	37.5	67.2
29	2	0.9634	36.8	60.6	0.9802	27.1	92.9
31	2	0.9707	33.0	60.8	0.9519	42.3	99.2
33	2	0.9717	32.3	74.6	0.9726	31.9	65.8
35	2	0.9657	35.6	80.4	0.9669	35.0	92.0
37	2	0.9637	36.6	73.4	0.9757	30.0	85.5
39	2	0.9773	29.0	74.4	0.9510	42.5	71.6
41	2	0.9622	37.3	87.7	0.9499	42.9	81.0
43	2	0.9634	36.8	77.4	0.9614	37.7	76.7
45	2	0.9701	33.2	86.5	0.9616	37.6	83.6
47	2	0.9558	40.3	72.4	0.9614	37.7	79.0
49	2	0.9597	38.5	70.5	0.9603	38.2	81.8
51	2	0.9579	39.4	83.9	0.9653	35.8	73.8

Table B.9 Results obtained using 16 cm^{-1} resolution, no. of scan was 16 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9609	38.0	105	0.9749	30.5	146
5	2	0.9589	39.1	157	0.9566	39.9	139
7	2	0.9342	49.3	120	0.9619	37.5	115
9	2	0.9403	47.0	125	0.9570	40.0	130
11	2	0.8927	62.6	117	0.9440	45.7	150
13	2	0.9173	55.3	129	0.9468	44.2	174
15	2	0.9053	59.3	146	0.9458	45.0	123
17	2	0.9145	55.8	152	0.9467	45.0	120
19	2	0.8961	61.3	154	0.9389	47.3	151
21	2	0.9094	57.7	149	0.9381	47.8	125
23	2	0.8894	63.4	129	0.9416	46.4	150
25	2	0.8479	73.7	133	0.9250	53.1	117
27	2	0.8754	67.2	144	0.9168	56.0	129
29	2	0.8612	70.6	134	0.9190	54.8	159
31	2	0.8823	65.2	142	0.9347	49.0	108
33	2	0.8749	67.3	134	0.9524	42.1	150
35	2	0.8472	74.1	125	0.9461	44.7	121
37	2	0.8438	74.7	130	0.9377	47.8	137
39	2	0.8321	77.2	181	0.9320	50.5	125
41	2	0.8015	83.3	171	0.9576	39.7	118
43	2	0.8364	76.2	175	0.9354	49.6	136
45	2	0.8228	79.2	163	0.9472	54.4	130
47	2	0.8164	80.5	154	0.9193	55.0	102
49	2	0.7797	87.6	173	0.9663	38.6	142
51	2	0.7839	89.9	182	0.9393	47.5	125

Table B.10 Results obtained using 16 cm^{-1} resolution, no. of scan was 16 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9402	30.8	114	0.9723	22.4	101
5	2	0.9415	35.1	109	0.9421	21.7	113
7	2	0.9356	34.7	105	0.9007	33.5	121
9	2	0.9177	35.7	98.6	0.9211	29.9	115
11	2	0.9374	34.1	95.9	0.9187	30.2	88.9
13	2	0.9315	38.7	92.6	0.9309	28.0	99.6
15	2	0.9754	36.2	98.0	0.9218	29.8	89.6
17	2	0.9444	36.1	98.6	0.9161	30.7	95.7
19	2	0.9452	38.3	105	0.9341	27.3	95.8
21	2	0.9171	35.8	99.1	0.9009	33.3	90.1
23	2	0.9358	42.2	96.4	0.9235	29.4	89.4
25	2	0.9045	35.6	111	0.9021	33.1	99.1
27	2	0.9078	37.2	95.4	0.9133	31.2	87.4
29	2	0.9044	30.4	90.1	0.9034	32.8	85.2
31	2	0.9062	28.8	90.4	0.9533	23.0	91.5
33	2	0.9121	33.5	91.3	0.9308	28.0	100
35	2	0.9041	40.9	87.7	09407	25.9	97.1
37	2	0.9015	29.8	80.8	0.9505	23.7	82.1
39	2	0.9120	32.8	82.4	0.9455	24.9	84.7
41	2	0.8986	29.9	80.6	0.9466	24.6	98.7
43	2	0.9052	42.3	99.8	0.9472	24.4	113
45	2	0.9863	34.4	119	0.9505	23.6	95.7
47	2	0.9802	35.6	108	0.9449	25.2	99.5
49	2	0.8749	40.8	102	0.9525	23.2	122
51	2	0.8659	40.8	98.9	0.9668	29.5	113

Table B.11 Results obtained using 16 cm^{-1} resolution, no. of scan was 30 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9764	29.5	148	0.9525	42.1	116
5	2	0.9663	35.2	148	0.9666	35.1	135
7	2	0.9443	45.3	111	0.9709	32.9	112
9	2	0.9496	43.1	114	0.9704	33.1	121
11	2	0.8957	61.8	116	0.9605	38.3	140
13	2	0.9209	54.5	115	0.9629	37.0	151
15	2	0.9043	60.2	121	0.9441	45.4	116
17	2	0.8888	63.6	132	0.9566	40.2	102
19	2	0.8915	62.8	129	0.9438	45.5	136
21	2	0.8937	62.4	121	0.9535	41.4	142
23	2	0.8909	63.3	100	0.9434	45.6	142
25	2	0.8710	68.4	104	0.9402	47.0	111
27	2	0.8743	67.7	78.8	0.9369	48.2	88.2
29	2	0.8672	69.4	99.7	0.9566	40.0	167
31	2	0.8652	69.6	109	0.9441	45.3	113
33	2	0.8560	71.8	111	0.9595	38.9	135
35	2	0.8517	73.0	117	0.9522	41.6	118
37	2	0.8784	66.2	130	0.9537	41.3	130
39	2	0.8580	71.9	123	0.9508	42.6	122
41	2	0.8629	70.4	136	0.9648	36.0	127
43	2	0.8748	67.4	164	0.9499	43.5	123
45	2	0.8519	73.1	163	0.9662	35.6	100
47	2	0.8240	79.2	157	0.9839	24.5	112
49	2	0.8102	82.0	163	0.9734	31.6	129
51	2	0.8054	83.2	165	0.9525	42.1	116

Table B.12 Results obtained using 16 cm^{-1} resolution, no. of scan was 30 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9284	31.9	121	0.9612	34.8	131
5	2	0.9202	32.1	119	0.9586	21.7	129
7	2	0.9158	30.7	114	0.9612	21.0	115
9	2	0.9206	29.8	122	0.9038	32.9	101
11	2	0.9279	28.4	109	0.9122	31.6	98.6
13	2	0.9101	31.8	95.6	0.9019	33.1	87.8
15	2	0.9131	31.2	97.8	0.8905	34.9	83.3
17	2	0.8956	34.1	94.9	0.9179	30.3	96.3
19	2	0.9133	31.3	96.3	0.9124	31.4	84.8
21	2	0.9001	33.6	92.5	0.9229	29.4	94.9
23	2	0.9299	28.2	99.7	0.9022	33.4	82.3
25	2	0.9295	28.3	89.5	0.9035	32.9	97.7
27	2	0.9295	28.2	94.5	0.9128	31.3	98.3
29	2	0.9231	29.4	105	0.9089	32.0	92.4
31	2	0.9149	30.8	99.8	0.9377	26.5	91.5
33	2	0.9241	29.2	86.9	0.9148	30.9	90.2
35	2	0.9308	27.9	96.5	0.9337	27.3	88.6
37	2	0.9335	27.4	92.8	0.9351	27.1	101
39	2	0.9260	28.8	89.2	0.9309	27.8	105
41	2	0.9144	30.9	111	0.9225	29.5	98.9
43	2	0.9062	32.3	93.0	0.9512	23.5	95.6
45	2	0.8929	34.4	104	0.9483	24.2	105
47	2	0.8945	34.2	101	0.9182	30.4	115
49	2	0.8841	35.8	112	0.9319	27.7	98.9
51	2	0.8768	36.8	119	0.9633	20.4	115

Table B.13 Results obtained using 32 cm^{-1} resolution, no. of scan was 16 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9357	30.9	85.3	0.9558	22.4	85.0
5	2	0.9315	27.9	80.2	0.8975	33.9	86.4
7	2	0.9196	30.0	93.9	0.9187	30.1	91.3
9	2	0.9284	28.4	99.8	0.9338	27.3	103
11	2	0.9339	27.3	91.5	0.9436	25.4	96.1
13	2	0.9359	26.9	93.2	0.9124	31.4	82.4
15	2	0.9354	27.0	96.8	0.9362	26.9	90.3
17	2	0.9217	29.6	104	0.9044	32.8	116
19	2	0.9118	31.4	112	0.9224	29.6	88.7
21	2	0.9141	31.0	101	0.9256	28.9	85.0
23	2	0.9218	29.6	102	0.9394	26.2	97.0
25	2	0.9017	33.1	102	0.9561	22.3	113
27	2	0.9080	32.0	96.1	0.9383	26.5	106
29	2	0.9197	30.0	101	0.9311	28.0	104
31	2	0.9221	29.6	95.4	0.9478	24.3	110
33	2	0.9155	30.8	103	0.9475	24.4	101
35	2	0.9025	33.0	104	0.9453	25.0	91.0
37	2	0.8850	35.6	105	0.9674	19.3	104
39	2	0.8971	33.8	97.8	0.9583	21.7	84.2
41	2	0.8706	36.8	91.2	0.9697	18.6	93.9
43	2	0.8816	36.1	96.2	0.9634	20.4	98.0
45	2	0.8944	34.2	86.9	0.9587	21.6	87.9
47	2	0.8908	34.8	81.4	0.9607	21.1	80.9
49	2	0.8930	34.4	81.6	0.9424	25.5	87.9
51	2	0.9045	32.6	89.2	0.9673	19.3	79.4

Table B.14 Results obtained using 32 cm^{-1} resolution, no. of scan was 16 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9308	30.5	83.4	0.9627	24.6	99.8
5	2	0.9312	27.9	79.4	0.9688	36.0	98.5
7	2	0.9196	30.1	73.4	0.9814	32.1	112
9	2	0.9278	28.5	78.7	0.9721	37.4	120
11	2	0.9337	27.4	90.4	0.9742	35.4	115
13	2	0.9353	27.1	92.1	0.9674	34.3	108
15	2	0.9353	27.0	96.3	0.9633	38.6	98.3
17	2	0.9218	29.6	103	0.9450	38.4	117
19	2	0.9118	31.4	112	0.9456	39.5	122
21	2	0.9140	31.0	100	0.9523	38.5	101
23	2	0.9213	29.7	101	0.9475	36.2	115
25	2	0.9015	33.1	102	0.9416	32.4	104
27	2	0.9080	32.0	95.5	0.9334	36.5	99.7
29	2	0.9193	30.0	101	0.9177	37.9	113
31	2	0.9218	29.6	94.8	0.9647	34.5	98.8
33	2	0.9153	30.8	102	0.9862	34.3	101
35	2	0.9004	33.3	105	0.9542	28.9	99.0
37	2	0.8848	35.7	105	0.9415	29.2	103
39	2	0.8962	34.0	94.8	0.9543	31.7	93.1
41	2	0.8762	36.9	90.6	0.9411	28.1	114
43	2	0.8812	36.2	95.8	0.9547	26.5	122
45	2	0.8938	34.3	86.3	0.9144	26.9	124
47	2	0.8907	34.8	90.8	0.9647	31.5	99.9
49	2	0.8928	34.5	81.2	0.9255	24.6	97.0
51	2	0.9047	32.6	89.0	0.9569	39.8	118

Table B.15 Results obtained using 32 cm^{-1} resolution, no. of scan was 30 and preprocessing using MSC and first derivative, MSC and second derivative

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9216	27.7	115	0.9667	32.4	115
5	2	0.9170	30.5	125	0.9357	32.6	123
7	2	0.9360	26.9	99.7	0.9566	36.9	112
9	2	0.9136	31.2	115	0.9221	37.3	103
11	2	0.9185	30.2	94.6	0.9631	35.6	99.8
13	2	0.9088	32.0	95.4	0.9413	34.1	94.9
15	2	0.9238	29.4	96.2	0.9699	29.6	93.7
17	2	0.9328	27.5	120	0.9571	38.9	116
19	2	0.9278	28.6	114	0.9422	29.9	124
21	2	0.9301	28.1	95.6	0.9652	35.3	96.8
23	2	0.9154	30.8	97.4	0.9496	22.9	112
25	2	0.9170	30.5	98.4	0.9988	35.1	113
27	2	0.9242	29.2	122	0.9835	36.5	104
29	2	0.9224	29.5	115	0.9111	38.0	117
31	2	0.9170	30.5	99.8	0.9758	34.3	124
33	2	0.9082	32.0	97.5	0.9745	32.9	111
35	2	0.9149	30.8	95.3	0.9653	35.0	99.8
37	2	0.9070	32.2	100	0.9785	29.6	114
39	2	0.9230	29.6	95.3	0.9854	27.1	98.9
41	2	0.9028	32.9	99.7	0.9758	28.6	99.3
43	2	0.9087	31.9	113	0.9588	30.4	98.7
45	2	0.9203	29.9	99.5	0.9603	31.6	87.9
47	2	0.9240	29.2	121	0.9777	35.3	96.3
49	2	0.9199	30.0	117	0.9874	35.5	117
51	2	0.9066	32.3	116	0.9764	29.3	121

Table B.16 Results obtained using 32 cm^{-1} resolution, no. of scan was 30 and preprocessing using SNV and first derivative, SNV and second derivative

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9212	29.7	84.5	0.9556	22.4	84.7
5	2	0.9167	30.5	81.0	0.8967	34.0	85.8
7	2	0.9361	26.8	84.5	0.9184	30.2	71.1
9	2	0.9134	31.2	76.8	0.9337	27.4	102
11	2	0.9182	30.3	72.8	0.9437	25.4	95.4
13	2	0.9082	32.1	80.5	0.9122	31.4	81.7
15	2	0.9229	29.5	89.8	0.9363	26.8	89.1
17	2	0.9332	27.4	79.2	0.9045	32.8	115
19	2	0.9275	28.7	86.0	0.9229	29.5	77.2
21	2	0.9299	28.1	86.9	0.9254	28.9	74.0
23	2	0.9153	30.8	105	0.9393	26.2	95.9
25	2	0.9172	30.5	105	0.9556	22.4	111
27	2	0.9242	29.2	91.4	0.9384	26.5	104
29	2	0.9224	29.5	92.7	0.9318	27.9	103
31	2	0.9169	30.5	96.6	0.9468	24.5	108
33	2	0.9084	31.9	99.3	0.9487	24.3	101
35	2	0.9148	30.8	105	0.9452	25.0	90
37	2	0.9070	32.2	96.9	0.9675	19.2	103
39	2	0.9219	29.6	102	0.9583	21.7	83.1
41	2	0.9029	32.9	91.6	0.9699	18.6	92.8
43	2	0.9087	31.9	92.3	0.9643	20.1	96.6
45	2	0.9205	29.8	92.5	0.9590	21.6	86.7
47	2	0.9238	29.3	96.1	0.9612	21.0	79.9
49	2	0.9199	30.0	101	0.9420	25.6	87.0
51	2	0.9069	32.3	106	0.9659	19.8	79.8

APPENDIX C

APPENDIX C show raw spectra of polystyrene food packaging

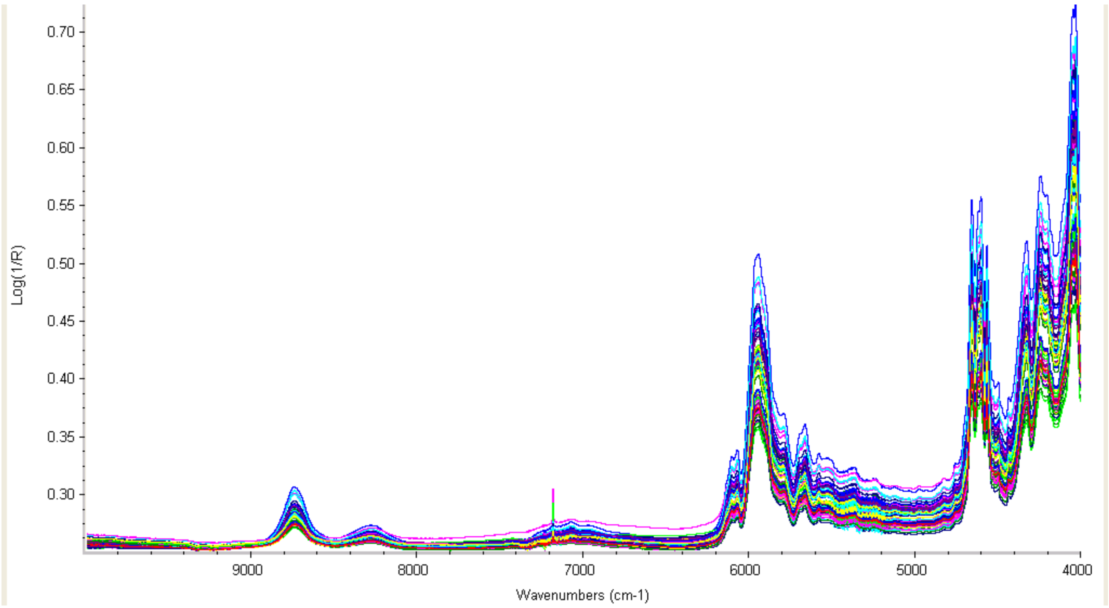

Figure C.1 show raw spectra of polystyrene food packaging at resolution 4 cm^{-1} and 16 scans

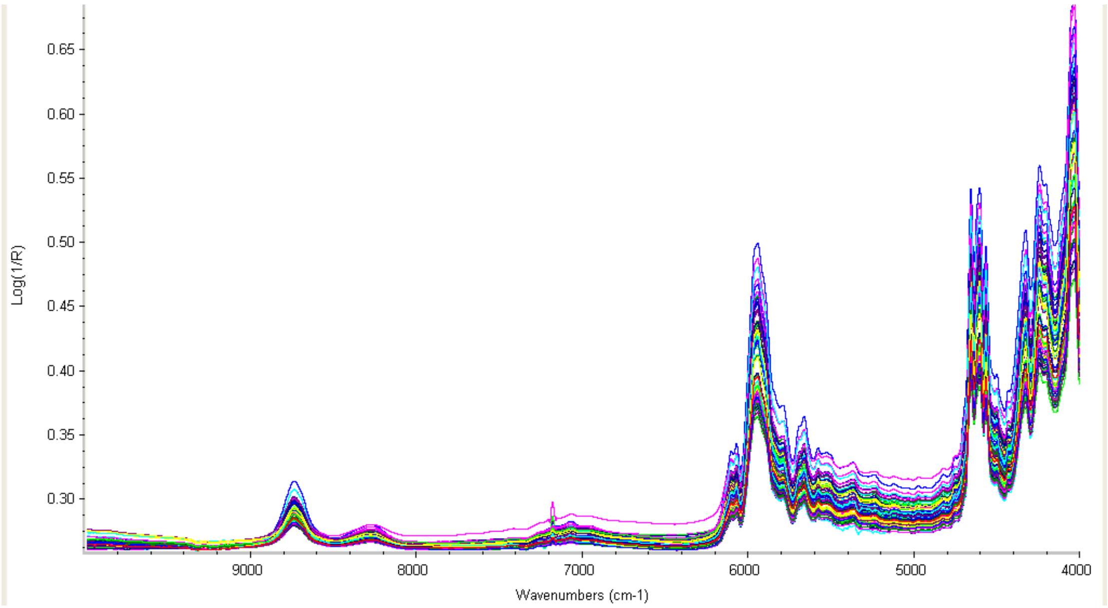

Figure C.2 show raw spectra of polystyrene food packaging at resolution 4 cm^{-1} and 30 scans

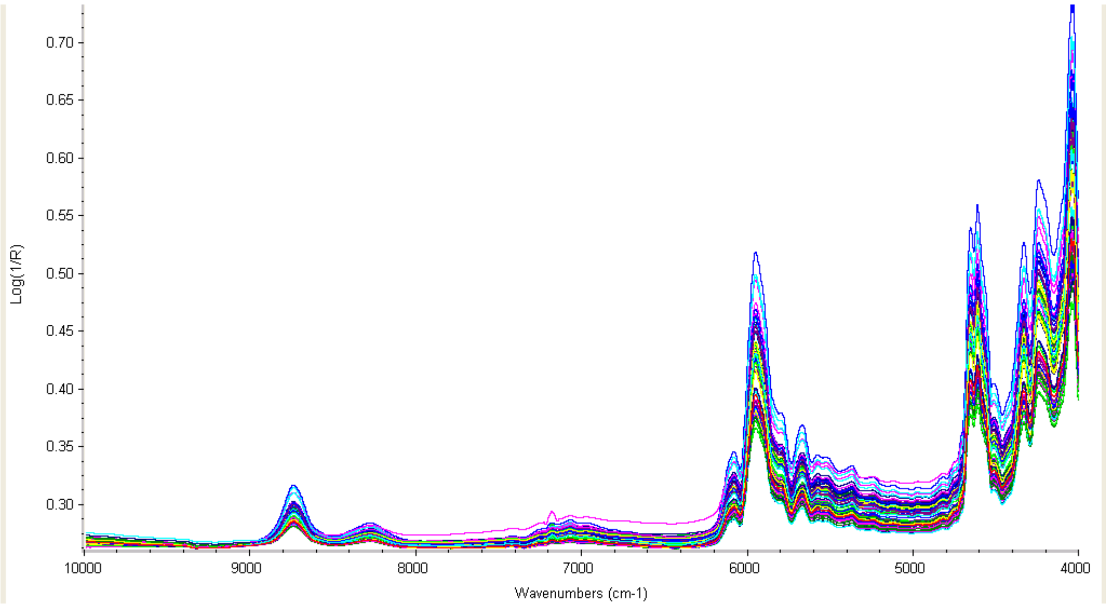

Figure C.3 show raw spectra of polystyrene food packaging at resolution 8 cm^{-1} and 16 scans

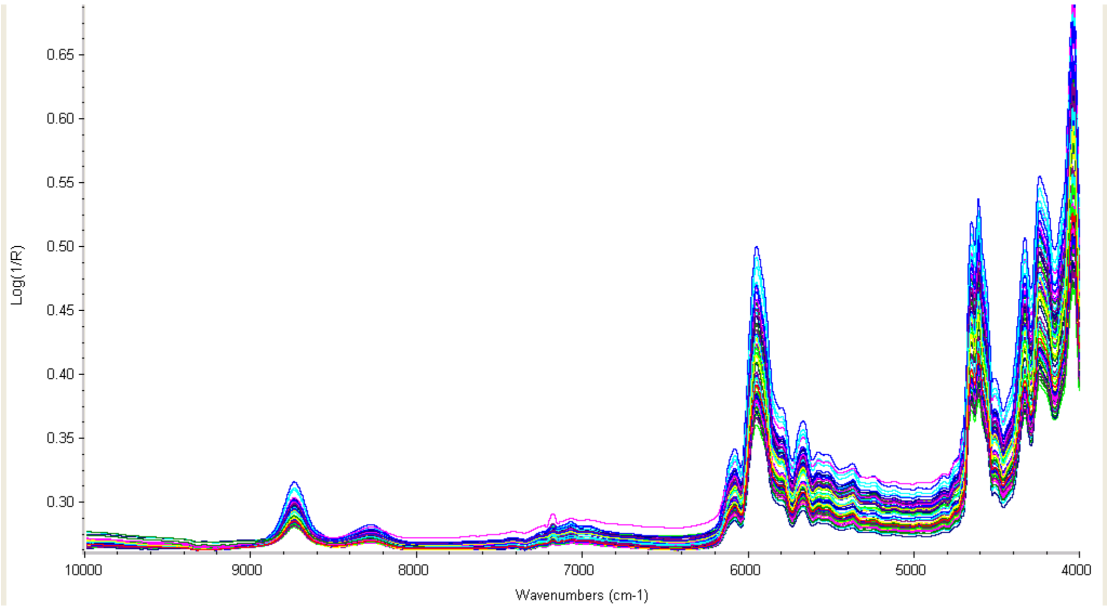

Figure C.4 show raw spectra of polystyrene food packaging at resolution 8 cm^{-1} and 30 scans

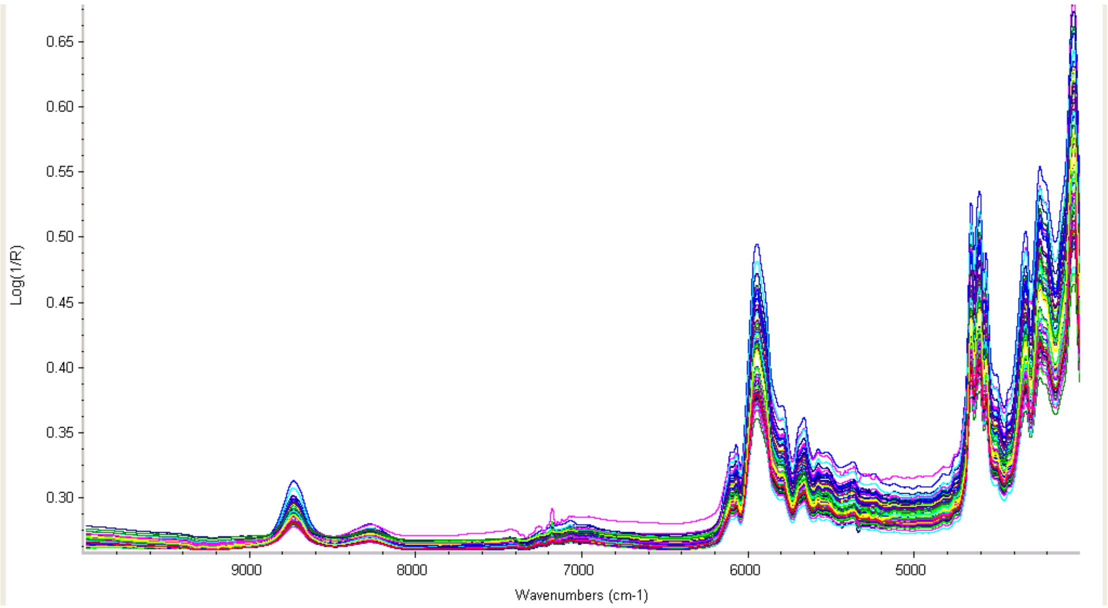

Figure C.5 show raw spectra of polystyrene food packaging at resolution 16 cm^{-1} and 16 scans

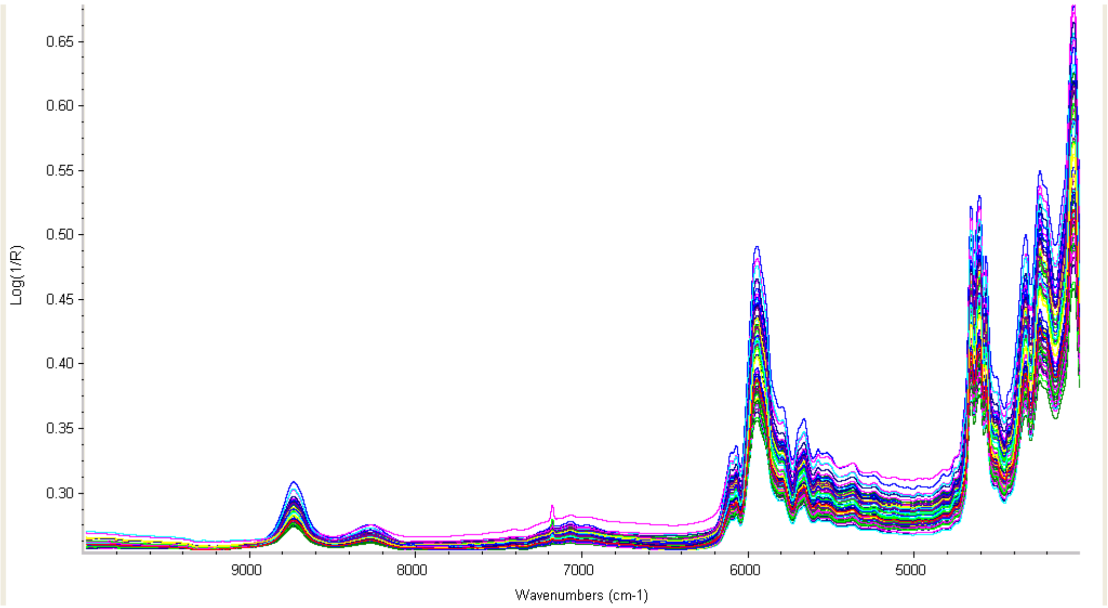

Figure C.6 show raw spectra of polystyrene food packaging at resolution 16 cm^{-1} and 30 scans

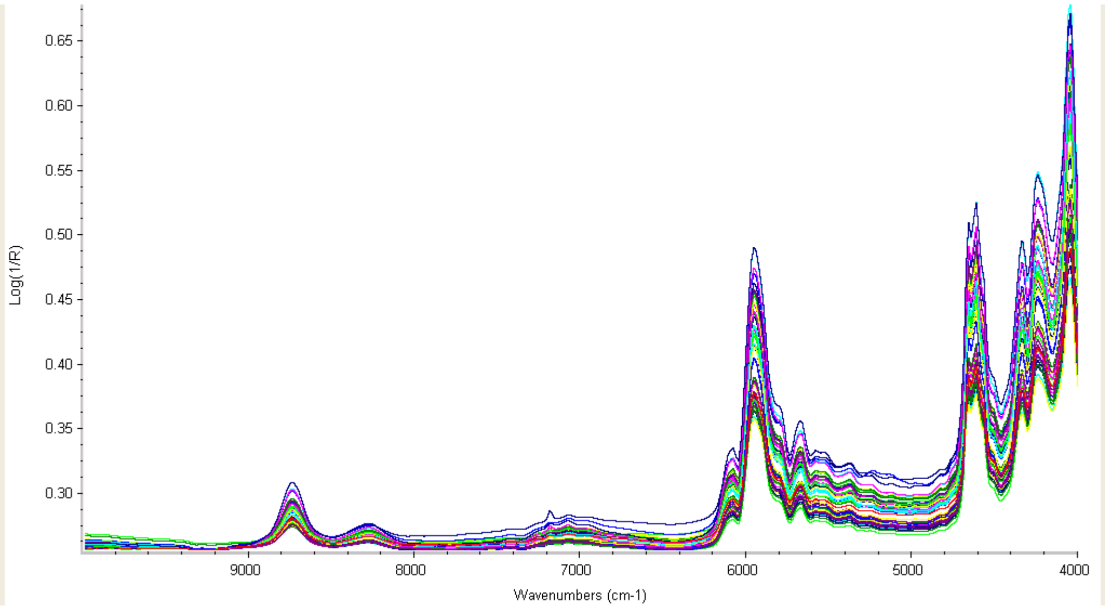

Figure C.7 show raw spectra of polystyrene food packaging at resolution 32 cm^{-1} and 16 scans

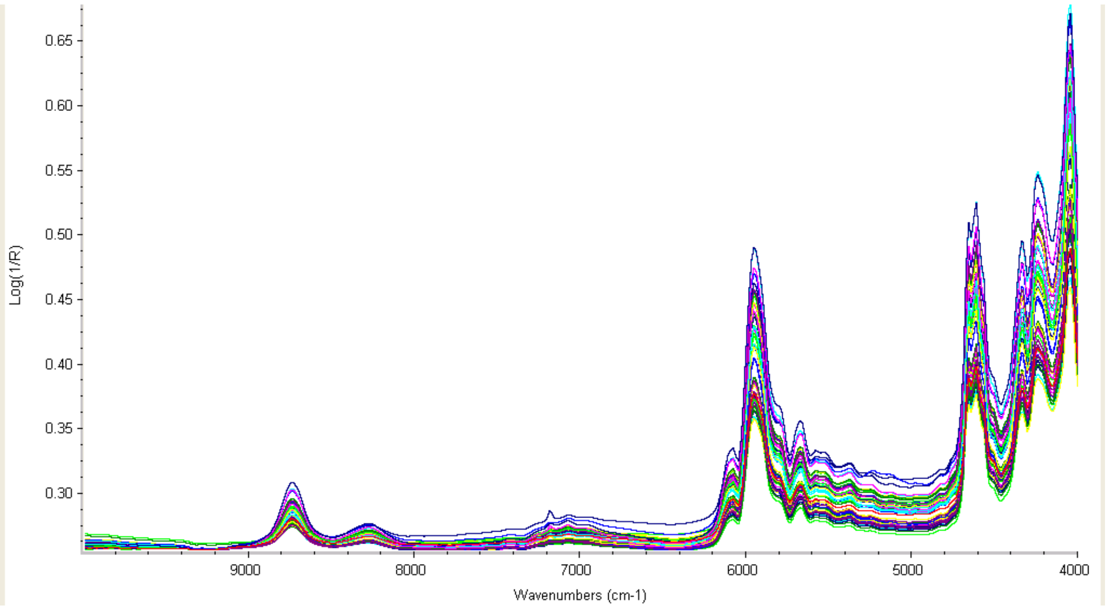

Figure C.8 show raw spectra of polystyrene food packaging at resolution 32 cm^{-1} and 30 scans

APPENDIX D

APPENDIX D show results of optimized preprocessing at 8 resolution, 30 scan

Table D.1 Results obtained MSC, derivative preprocessing and smoothing at 2 polynomial order

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9866	22.3	68.3	0.9947	14.0	128
5	2	0.9772	29.0	86.1	0.9947	14.0	123
7	2	0.9674	34.6	84.9	0.9889	20.2	129
9	2	0.9460	44.6	93.9	0.9788	28.0	89.6
11	2	0.9531	41.6	76.9	0.9909	18.4	88.5
13	2	0.9508	42.7	62.6	0.9779	28.6	74.0
15	2	0.9522	42.0	87.9	0.9841	24.3	76.2
17	2	0.9496	43.1	94.0	0.9821	25.7	49.9
19	2	0.9534	41.4	82.9	0.9810	26.5	66.3
21	2	0.9235	52.9	95.4	0.9827	25.4	61.1
23	2	0.9017	59.8	69.6	0.9803	79.7	79.7
25	2	0.9155	55.6	78.4	0.8773	29.0	51.6
27	2	0.8805	65.9	92.0	0.9737	31.3	77.1
29	2	0.8595	71.3	82.2	0.9811	26.4	81.1
31	2	0.8964	61.4	111	0.9721	32.3	91.9
33	2	0.8809	65.8	123	0.9773	29.0	68.6
35	2	0.8643	69.9	103	0.9652	35.9	93.9
37	2	0.8582	71.6	95.6	0.9796	27.5	81.4
39	2	0.8518	72.9	91.5	0.9580	39.5	84.7
41	2	0.8528	72.7	116	0.9573	39.6	69.9
43	2	0.8591	71.2	125	0.9639	36.6	80.6
45	2	0.8868	64.0	86.7	0.9627	37.1	92.8
47	2	0.8629	70.2	85.2	0.9719	32.2	92.9
49	2	0.8323	77.3	90.9	0.9511	42.4	73.2
51	2	0.8401	75.7	80.3	0.9632	36.9	81.3

Table D.2 Results obtained MSC, derivative preprocessing and smoothing at 3 polynomial order

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	3	0.9932	15.9	120	0.9947	16.8	122
5	3	0.9921	17.2	125	0.9951	13.5	123
7	3	0.9877	21.4	102	0.9906	18.7	131
9	3	0.9862	22.6	99.1	0.9814	26.2	88.7
11	3	0.9832	25.0	101	0.9902	19.0	85.0
13	3	0.9837	24.6	61.4	0.9777	28.7	68.1
15	3	0.9826	25.4	73.1	0.9845	24.0	73.4
17	3	0.9739	31.1	67.8	0.9828	25.2	47.8
19	3	0.9745	27.8	75.9	0.9800	27.2	66.1
21	3	0.9754	30.1	81.1	0.9778	28.6	52.9
23	3	0.9826	25.4	37	0.9797	27.4	79.8
25	3	0.9775	28.8	59.4	0.9759	29.8	54.5
27	3	0.9708	32.8	71.4	0.9741	31.1	74.0
29	3	0.9883	29.3	69.9	0.9817	26.0	90.4
31	3	0.9773	29.0	72.0	0.9672	35.0	95.5
33	3	0.9615	38.0	102	0.9762	29.7	66.4
35	3	0.9700	33.0	65.2	0.9603	38.2	99.3
37	3	0.9683	34.3	85.8	0.9776	28.8	85.6
39	3	0.9684	34.1	79.7	0.9602	38.5	83.7
41	3	0.9655	35.9	66	0.9545	40.8	69.6
43	3	0.9461	44.7	82.8	0.9854	35.8	75.0
45	3	0.9526	41.8	73.8	0.9573	29.6	89.3
47	3	0.9562	40.1	63.1	0.9656	35.6	84.0
49	3	0.9731	31.5	76.3	0.9530	41.5	70.8
51	3	0.9991	47.3	69.9	0.9635	36.7	75.1

Table D.3 Results obtained MSC, derivative preprocessing and smoothing at 4 polynomial order

Preprocessing							
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	4	0.9954	19.6	124	0.9953	17.2	110
5	4	0.9902	17.8	115	0.9940	15.0	133
7	4	0.9886	24.3	102	0.9958	12.4	104
9	4	0.9876	26.3	101	0.9857	23.0	103
11	4	0.9878	25.0	101	0.9857	23.1	105
13	4	0.9877	26.4	69.5	0.9810	26.5	67.1
15	4	0.9812	24.9	78.1	0.9827	25.3	71.8
17	4	0.9723	32.1	68.3	0.9816	26.1	67.8
19	4	0.9764	28.9	79.3	0.9863	22.6	70.9
21	4	0.9714	31.0	86.5	0.9824	25.5	74.5
23	4	0.9835	28.5	77.0	0.9789	27.9	47.1
25	4	0.9777	28.8	89.4	0.9811	26.5	67.8
27	4	0.9785	38.2	71.4	0.9794	27.6	79.7
29	4	0.9843	401	65.3	0.9729	31.7	73.1
31	4	0.9699	39.0	77.0	0.9649	36.1	75.3
33	4	0.9655	37.0	102	0.9778	28.6	104
35	4	0.9744	34.3	75.2	0.9578	39.4	68.7
37	4	0.9611	34.7	95.8	0.9817	26.1	78.6
39	4	0.9674	34.1	89.7	0.9732	31.5	75.5
41	4	0.9742	39.6	68.0	0.9714	32.6	84.6
43	4	0.9633	47.2	82.8	0.9708	32.8	89.9
45	4	0.9475	42.3	78.3	0.9746	30.7	65.8
47	4	0.9632	44.1	71.1	0.9589	39.1	71.8
49	4	0.9701	35.1	79.3	0.9461	44.6	78.4
51	4	0.9377	47.3	70.1	0.9630	41.5	76.6

Table D.4 Results obtained MSC, derivative preprocessing and smoothing at 5 polynomial order

		Preprocessing					
Smoothing (SG)		MSC and first derivative			MSC and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	5	0.9973	23.9	69.7	0.9962	18.0	121
5	5	0.9903	18.9	74.9	0.9953	17.2	117
7	5	0.9918	17.5	80.0	0.9957	12.7	132
9	5	0.9782	28.4	87.5	0.9839	24.4	133
11	5	0.9815	26.2	97.6	0.9897	19.7	116
13	5	0.9735	31.3	98.0	0.9868	22.1	100
15	5	0.9706	32.9	122	0.9797	27.4	100
17	5	0.9670	34.9	121	0.9790	27.8	85.5
19	5	0.9527	41.8	110	0.9864	22.5	58.3
21	5	0.9486	43.7	104	0.9830	25.1	51.0
23	5	0.9452	45.1	78.7	0.9798	27.3	67.3
25	5	0.9267	51.8	92.9	0.9815	26.2	26.7
27	5	0.9334	49.6	73.1	0.9799	27.3	57.8
29	5	0.9338	49.3	59.1	0.9736	31.3	62.9
31	5	0.9327	49.7	94.1	0.9654	35.8	63.0
33	5	0.9164	55.5	107	0.9775	28.8	67.0
35	5	0.9224	53.3	92.7	0.9618	37.5	79.1
37	5	0.9209	53.8	94.3	0.9803	27.1	66.9
39	5	0.8926	62.5	127	0.9691	33.8	97.6
41	5	0.8909	63.0	121	0.9730	31.6	68.0
43	5	0.8763	68.5	87.3	0.9661	35.5	97.9
45	5	0.8533	72.7	106	0.9733	31.5	107
47	5	0.8583	71.5	106	0.9588	39.1	84.2
49	5	0.8820	66.2	119	0.9374	48.0	73.5
51	5	0.8981	61.7	108	0.7509	42.5	93.9

Table D.5 Results obtained SNV, derivative preprocessing and smoothing at 2 polynomial order

Smoothing (SG)		Preprocessing					
		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	2	0.9908	18.5	110	0.9935	15.5	133
5	2	0.9837	24.6	86.0	0.9915	17.7	124
7	2	0.9844	24.0	67.2	0.9847	23.8	120
9	2	0.9774	28.9	60.2	0.9811	26.4	96.2
11	2	0.9769	29.2	54.3	0.9815	26.2	72.1
13	2	0.9764	29.5	61.9	0.9691	33.8	78.0
15	2	0.9755	30.1	84.7	0.9704	33.0	71.9
17	2	0.9706	33.0	60.6	0.9742	30.8	61.2
19	2	0.9645	36.1	72.2	0.9704	33.1	70.6
21	2	0.9714	32.5	84.5	0.9650	35.9	58.8
23	2	0.9690	33.9	76.4	0.9697	33.4	78.3
25	2	0.9724	31.9	68.5	0.9764	29.6	52.4
27	2	0.9783	28.4	76.7	0.9620	37.5	67.2
29	2	0.9635	36.8	60.6	0.9802	27.1	92.9
31	2	0.9707	33..0	60.8	0.9519	42.3	99.2
33	2	0.9717	32.3	74.6	0.9726	31.9	65.8
35	2	0.9657	35.6	80.4	0.9669	35.0	92.0
37	2	0.9637	36.6	73.4	0.9757	30.0	85.5
39	2	0.9773	29.0	74.4	0.9510	42.5	71.6
41	2	0.9622	37.3	87.7	0.9499	42.9	81.0
43	2	0.9634	36.8	77.4	0.9614	37.7	76.7
45	2	0.9702	33.2	86.5	0.9616	37.6	83.6
47	2	0.9558	40.3	72.4	0.9614	37.7	79.0
49	2	0.9597	38.5	70.5	0.9603	38.2	81.8
51	2	0.9579	39.4	83.9	0.9653	35.8	73.8

Table D.6 Results obtained SNV, derivative preprocessing and smoothing at 3 polynomial order

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	3	0.9938	19.8	130	0.9914	16.7	128
5	3	0.9901	18.5	124	0.9899	19.2	114
7	3	0.9897	27.0	127	0.9810	24.9	101
9	3	0.9974	26.1	103	0.9870	28.8	97.8
11	3	0.9854	28.7	111	0.9984	28.2	92.1
13	3	0.9874	29.6	76.1	0.9961	34.1	88.0
15	3	0.9712	28.9	78.3	0.9854	33.4	73.9
17	3	0.9608	34.1	68.2	0.9741	32.8	62.2
19	3	0.9841	31.0	71.4	0.9787	34.1	77.6
21	3	0.9840	32.4	75.0	0.9419	35.1	65.8
23	3	0.9738	35.6	49.3	0.9775	34.5	72.5
25	3	0.9774	31.1	65.7	0.9747	31.2	62.1
27	3	0.9745	31.6	71.4	0.9701	37.7	69.1
29	3	0.9545	44.4	72.3	0.9877	27.1	90.2
31	3	0.9756	31.9	74.3	0.9629	44.3	97.1
33	3	0.9798	42.9	89.2	0.9806	40.9	61.2
35	3	0.9669	31.3	65.7	0.9709	34.7	82.0
37	3	0.9500	39.3	77.4	0.9771	33.0	84.5
39	3	0.9854	33.0	65.5	0.9630	42.5	77.9
41	3	0.9585	38.6	84.6	0.9549	40.9	71.0
43	3	0.9375	48.0	89.9	0.9734	37.0	72.4
45	3	0.9504	44.9	64.5	0.9744	36.9	82.4
47	3	0.9687	34.9	69.8	0.9584	36.1	69.0
49	3	0.9602	42.4	65.4	0.9733	34.2	79.8
51	3	0.9388	42.6	66.0	0.9693	33.9	70.8

Table D.7 Results obtained SNV, derivative preprocessing and smoothing at 4 polynomial order

Preprocessing							
Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	4	0.9958	18.9	130	0.9941	16.3	130
5	4	0.9919	17.4	133	0.9935	15.5	132
7	4	0.9798	27.3	104	0.9930	16.1	132
9	4	0.9874	21.6	103	0.9767	29.3	121
11	4	0.9774	28.8	105	0.9889	20.3	114
13	4	0.9794	27.6	67.1	0.9716	32.3	94.2
15	4	0.9786	28.1	71.8	0.9745	30.7	100
17	4	0.9698	33.4	67.8	0.9791	27.8	83.7
19	4	0.9726	32.0	70.9	0.9811	26.5	51.2
21	4	0.9680	34.3	74.5	0.9764	29.6	59.9
23	4	0.9700	33.2	47.1	0.9686	34.1	52.4
25	4	0.9737	31.1	67.8	0.9617	37.6	42.6
27	4	0.9718	32.2	79.7	0.9657	35.5	69.9
29	4	0.9445	45.2	73.1	0.9679	34.4	82.3
31	4	0.9725	31.9	75.3	0.9623	37.5	87.8
33	4	0.9528	41.9	104	0.9745	30.7	61.1
35	4	0.9623	37.3	68.7	0.9706	32.9	82.6
37	4	0.9590	38.9	78.6	0.9771	29.1	80.9
39	4	0.9724	32.0	75.5	0.9693	33.7	89.2
41	4	0.9595	38.6	84.5	0.9624	37.3	58.4
43	4	0.9375	48.0	89.9	0.6726	31.9	89.0
45	4	0.9405	46.8	65.8	0.9680	34.4	95.9
47	4	0.9666	35.1	71.8	0.9427	45.9	92.5
49	4	0.9512	42.4	78.4	0.9345	49.0	91.2
51	4	0.9385	47.4	76.6	0.9522	41.9	85.6

Table D.8 Results obtained SNV, derivative preprocessing and smoothing at 5 polynomial order

Smoothing (SG)		SNV and first derivative			SNV and second derivative		
Data points	Polynomial order	r	RMSEC (mg/kg)	RMSEP (mg/kg)	r	RMSEC (mg/kg)	RMSEP (mg/kg)
3	5	0.9786	28.1	87.8	0.9942	14.7	134
5	5	0.9831	25.0	96.1	0.9943	14.5	133
7	5	0.9848	23.7	99.9	0.9928	16.3	131
9	5	0.9678	34.5	94.2	0.9744	30.7	124
11	5	0.9771	29.2	100	0.9824	25.5	100
13	5	0.9741	31.0	116	0.9737	31.1	94.5
15	5	0.9669	35.0	130	0.9755	30.1	104
17	5	0.9436	45.6	121	0.9755	30.1	90.5
19	5	0.9490	43.3	135	0.9811	26.4	56.5
21	5	0.9392	47.7	98.6	0.9778	28.6	62.5
23	5	0.9299	51.0	68.8	0.9719	32.3	52.8
25	5	0.9019	59.8	87.8	0.9596	38.5	36.2
27	5	0.9135	56.3	63.2	0.9663	35.2	69.3
29	5	0.9146	56.0	61.3	0.9674	34.7	77.8
31	5	0.9046	59.1	93.5	0.9649	36.2	74.6
33	5	0.8893	63.6	100	0.9685	34.1	64.2
35	5	0.9141	56.0	93.6	0.9616	37.6	73.2
37	5	0.9075	58.1	99.8	0.9825	25.5	79.9
39	5	0.8920	62.6	136	0.9630	37.0	93.3
41	5	0.8709	68.4	122	0.9676	34.6	58.9
43	5	0.8731	68.0	88.9	0.9618	37.5	96.2
45	5	0.8582	71.6	97.0	0.9685	34.1	95.6
47	5	0.8515	73.4	93.9	0.9578	39.6	85.4
49	5	0.8736	68.6	104	0.9299	50.7	78.0
51	5	0.8862	65.4	91.1	0.9516	42.2	88.6

Preprocessing

VITA

Miss Sasitorn Homdumrongvong was born on Semtember 3, 1971 in Khonkaen, Thailand. She received a Bachelor’s degree of Science in Chemistry from Ramkhamhaeng University in 1995. Subsequently, she has been a graduate student at the Department of Chemistry, Chulalongkorn University. At present, she has been working for Bureau of Quality and Safety of Food (BQSF), Department of Medical Sciences, Ministry of Public Health, THAILAND