การหามวลสมมูลอิพ็อกไซด์ของเรซินอิพ็อกซีโดยใช้ฟูเรียร์แทรนส์ฟอร์มเนียร์อินฟราเรดสเปกโทรสโกปี

นางสาวขนิษฐา เดชขันธ์

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DETERMINATION OF EPOXIDE EQUIVALENT WEIGHT OF EPOXY RESIN USING FOURIER TRANSFORM NEAR INFRARED SPECTROSCOPY

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	DETERMINATION OF EPOXIDE EQUIVALENT WEIGHT OF EPOXY RESIN USING FOURIER TRANSFORM NEAR INFRARED SPECTROSCOPY
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ขนิษฐา เดชขันธ์ : การหามวลสมมูลอิพ็อกไซด์ของเรซินอิพ็อกซีโดยใช้ฟูเรียร์แทรนส์ฟอร์มเนียร์อินฟราเรดสเปกโทรสโกปี. (DETERMINATION OF EPOXIDE EQUIVALENT WEIGHT OF EPOXY RESIN USING FOURIER TRANSFORM NEAR INFRARED SPECTROSCOPY) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.อรุณศิริ ชิตางกูร, 64 หน้า.

มวลสมมูลอิพ็อกไซด์ (EEW) ของเรซินอิพ็อกซีคือน้ำหนักของเรซินในหน่วยกรัมที่มีหมู่อิพ็อกซีหนึ่งกรัมสมมูล ในการประยุกต์ใช้เรซินอิพ็อกซี จำเป็นต้องทราบค่า EEW ที่แน่นอนเพื่อใช้ในการคำนวณหาปริมาณสารทำแข็งที่เหมาะสมที่จะเกิดการเชื่อมขวางในโครงสร้างพอลิเมอร์ เพื่อให้มีสมบัติตามต้องการ ในงานวิจัยนี้ ได้พัฒนาวิธีการหาค่า EEW โดยใช้ฟูเรียร์แทรนส์ฟอร์มเนียร์อินฟราเรดสเปกโทรสโกปีและ partial least squares regression ในการสร้างแบบจำลองเพื่อการทำนาย เมื่อเปรียบเทียบค่า EEW ของเรซินอิพ็อกซีตัวอย่างที่คำนวณได้จากแบบจำลองและที่ได้จากวิธีอ้างอิง ซึ่งใช้การไทเทรตเรซินอิพ็อกซีด้วยไฮโดรเจนโบรไมด์ที่เกิดขึ้นในปฏิกิริยา พบว่าทั้งสองวิธีให้ค่า EEW ที่ใกล้เคียงกัน ดังค่า RMSEC, RMSEP และ R เท่ากับ 0.4265 g/eq, 0.4131 g/eq และ 0.9580 ตามลำดับ วิธีที่พัฒนาขึ้นใหม่นี้ สามารถนำไปใช้กับงานที่วิเคราะห์ค่า EEW เป็นประจำได้ เนื่องจากเป็นวิธีที่ง่าย รวดเร็ว ถูกต้อง ไม่ทำลายสารตัวอย่าง และเป็นมิตรกับสิ่งแวดล้อม

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KANITTHA DETKHAN : DETERMINATION OF EPOXIDE EQUIVALENT WEIGHT OF EPOXY RESIN USING FOURIER TRANSFORM NEAR INFRARED SPECTROSCOPY. ADVISOR : ASST. PROF. AROONSIRI SHITANGKOON, Ph.D., 64 pp.

The epoxide equivalent weight (EEW) of epoxy resin is the weight of resin in grams which contains one gram equivalent of epoxy groups. The EEW values must be accurately determined in order to calculate the exact amount of the hardener that will react with the epoxide group leading to cross-linked polymer of the desired properties. In this study, a method for determination of EEW values was developed using Fourier transform near infrared (FT-NIR) spectroscopy and partial least squares (PLS) regression to construct a prediction model. The predicted EEW values of unknown epoxy resins were compared with EEW values obtained from a reference method, based on titration of epoxy resin with hydrogen bromide generated in situ. The EEW values of both methods agreed well as shown by performance parameters RMSEC, RMSEP, and R values of 0.4265 g/eq, 0.4131 g/eq, and 0.9580, respectively. The newly developed method could be applied for routine analysis of EEW values of epoxy resin as it is simple, fast, accurate, non-destructive and environmental friendly.

Department : .... Chemistry.... Student's Signature ....
Field of Study : .... Chemistry.... Advisor's Signature ....
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CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE **PAGE**

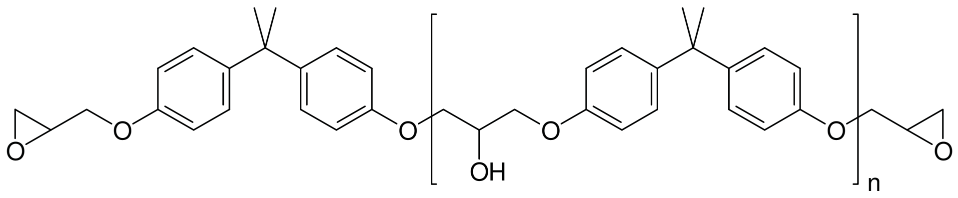
LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
°C	degree Celsius
CCD	charge coupled device
DGEBA	diglycidyl ether of bisphenol A
DTGS	deuterated triglycine sulfate
EEW	epoxide equivalent weight
FIR	far infrared spectroscopy
FT-NIR	Fourier transform near infrared spectroscopy
g	gram
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
InGaAs	indium gallium arsenide
IR	infrared spectroscopy
K	Kelvin
KHP	potassium hydrogen phthalate
L	litre
M	molar
MCT	mercury cadmium tellurium
MIR	mid infrared spectroscopy
mL	millilitre
NIR	near infrared spectroscopy
NMR	nuclear magnetic resonance
PCA	principal component analysis
PLS	partial least squares regression
R	correlation coefficient
RMSEC	root mean square error of calibration
RMSEP	root mean square error of prediction
RSD	relative standard deviation
SD	standard deviation
TEAB	tetramethylammonium bromide

CHAPTER I

INTRODUCTION

Epoxy resin has several trade names, e.g. diglycidyl ether of bisphenol A (DGEBA), Araldite 6010, Epi-Rez 508, Epon 826, Epon 828 and Epon 834. It can be prepared from the reaction of epichlorohydrin and bisphenol A. It is classified as polyether consisting of epoxide groups.



epoxy resin

Currently, epoxy resins have been used widely in various technologies and industries. Moreover, they have been broadly used for daily life, e.g. electronic components and parts, adhesive glue, laminating industry equipments for corrosion protection, laminating food cans, mixing in house paint, laminating boats for rust protection, mixing in car paint, laminating floor of laboratories, or laminating basketball court, etc. [1].

One of the properties of epoxy resin is epoxide equivalent weight (EEW), which is the weight of the resin per one epoxide group [1]. High EEW resin is a brittle solid as it has long polymer chain, high molecular weight and high melting point. While low EEW resin is a viscous liquid as it has short polymer chain and low molecular weight. The accurate EEW of epoxy resin is an important value and must be known in order to calculate appropriate quantity of hardener to form crosslink between polymers to achieve materials of desired properties.

Standard method for the determination of EEW of epoxy resin is based on the titration of resin solution with hydrogen bromide either directly or generated in situ [2]. Hydrogen bromide reacts stoichiometrically with epoxy group, thus epoxy content can be achieved. However, this method is time-consuming and sample-destructive. In addition, chemical waste is also produced. Fourier transform near infrared spectroscopy (FT-NIR) is a versatile analytical technique as it is simple to use, non-destructive, and requires no (or minimal) chemical reagents. There were reports on the use of near infrared (NIR) spectroscopy to analyze sugar content in fruits [3] or to identify pharmaceutical raw materials [4]. In addition, the ASTM standard method for determination of hydroxyl number of polyols by near infrared spectroscopy was approved [5].

The objective of this study is to develop a quick, easy, and nondestructive method for determination of EEW of epoxy resins using mathematical technique to correlate the absorbance values obtained from FT-NIR to the EEW of epoxy resins obtained from titration (the ASTM standard method).

CHAPTER II

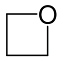
THEORY

2.1 Epoxy resin

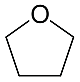
The term “*epoxy*” refers to a chemical group consisting of oxygen atom bonded with two carbon atoms already united in some way. The simple epoxy is a three-membered ring to which the term α-epoxy or 1,2-epoxy- is applied such as ethylene oxide. The term 1,3-epoxy- and 1,4-epoxy- are applied to trimethylene oxide and tetrahydrofuran, respectively.

For this work, the resins containing the three-membered rings (e.g., ethylene oxide derivatives) are of interested. There is no universal agreement on the nomenclature of the three-membered epoxy ring. The European generally preferred the term epoxide, while the American preferred the term epoxy. Other common names may be used to refer to epoxy such as oxirane (for ethylene oxide), epichlorohydrin, glycidic acid, and glycidol.

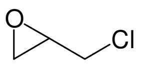
ethylene oxide (oxirane)



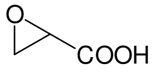
trimethylene oxide



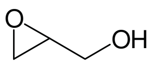
tetrahydrofuran



epichlorohydrin



glycidic acid



glycidol

Epoxy resin has several commercial names, e.g., diglycidyl ether of bisphenol A (DGEBA), Araldite 6010, Epi-Rez 508, Epon 826, Epon 828, and Epon 834. Epoxy resin is a polymer that contains epoxide functional group and can be prepared from the reaction of epichlorohydrin and bisphenol A (Figure 2.1).

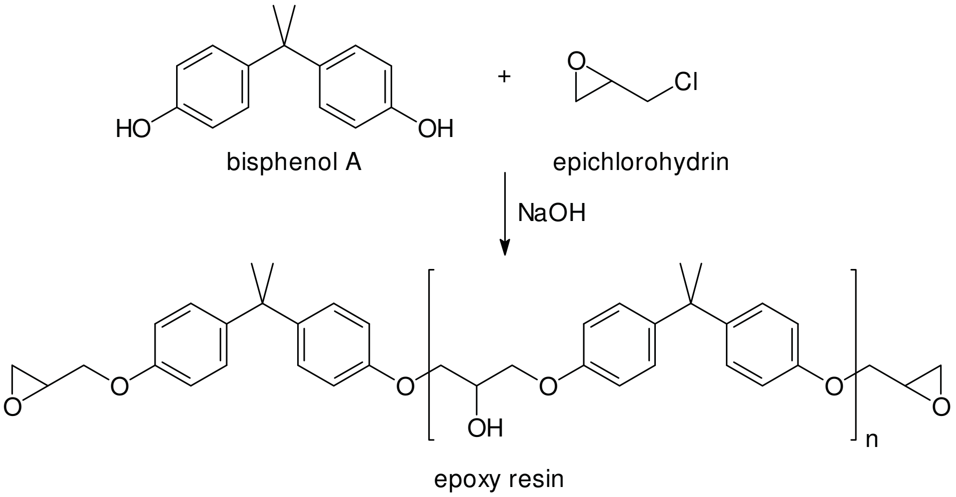


Figure 2.1 Preparation of epoxy resin

The process for the preparation of epoxy resin contains six major steps [1].

1. Pre-reactor

Bisphenol A, excess epichlorohydrin, and sodium hydroxide were mixed in the pre-reactor under the atmospheric condition for the reaction to form intermediates. The reaction is an exothermic process; thus, the cooling system is needed to control the reaction temperature at around 62 ± 3 °C. Then, the intermediates were transferred to the main reactor.

2. Main reactor

Sodium hydroxide solution was added into the main reactor to react with the intermediates from the pre-reactor step to complete the epoxy resin formation reaction. The epoxy resin produced from the main reactor not only contained sodium chloride and water residue from the reaction, but also some excess starting material, epichlorohydrin. All three undesired compounds must be separated from the epoxy product.

3. Epichlorohydrin separation

The excess epichlorohydrin that still remained from the reaction was separated from the epoxy resin using rotary evaporator. The evaporated epichlorohydrin was collected as the condensed liquid for future re-use.

4. Epoxy resin purification

The epoxy resin, obtained after the separation of an excess epichlorohydrin, was reacted with sodium hydroxide once again to purify the resin to ensure a desired quality before separation of sodium chloride. Then, toluene was added to dissolve epoxy resin and clean the residue off. In this step, the mixture separated into three phases that are

a. toluene-resin solution phase
b. waste polymer phase
c. sodium hydroxide and aqueous solution phase

5. Filtration

Toluene-resin solution from the purification step may contain some waste polymer. Hence, the waste polymer had to be separated out with filter paper.

6. Toluene separation

At this step, toluene solvent was separated from the epoxy resin. The toluene-resin solution was passing through the falling thin film evaporator under vacuum to evaporate toluene out. Toluene separation was repeated again to finally obtain a pure epoxy resin product.

To apply epoxy resin in various applications, some properties of epoxy resin must be taken into account such as viscosity, ability to set or solidify, low contraction rate, thermosetting property, cohesion property and high adhesion property, and epoxide equivalent weight (EEW).

2.2 Epoxide equivalent weight

Epoxide equivalent weight (EEW) is the weight of resin in grams which contains one gram equivalent of epoxy groups [1]. The polymer with high EEW value has long chain, high molecular weight, and high melting temperature. It is in a solid state and fragile. The polymer with low EEW value has short chain and low molecular weight. It is a highly viscous liquid. For the application of epoxy resin, to achieve the material that contains the properties that appropriate for the specific task, it is important to know the exact value of EEW to calculate the exact amount of the hardener that will react with the epoxide group leading to cross-linked polymer structure.

ASTM Standard method for the determination of the EEW of epoxy resin usually performs by titration, manually or automatically, with hydrogen bromide generated in situ by the addition of perchloric acid to an excess amount of tetraethylammonium bromide [2]. Other methods for the determination of EEW of epoxy resin were also reported.

Garcia and Soares [6] determined EEW of liquid epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) from different companies (with reported EEW values ranged from 182–560) using proton nuclear magnetic resonance (^{1}H-NMR). The results obtained from ^{1}H-NMR agreed well with those obtained from the classical titration procedure with HBr in glacial acetic acid.

Garea and coworkers [7] used ^{1}H-NMR and gel permeation chromatography (GPC) to characterized and determine EEW of epoxy resins from various companies (with reported EEW values ranged from 120–192). Different chemical structures of liquid and solid epoxy resins were used, such as bis-(3-glycidyloxy)phenylphosphine oxide, resorcinoldiglycidyl ether, Epon 154, diglycidylether of bisphenol A, diglycidylether of bisphenol F, and triglycidylether of triphenylol methane. Good correlations between GPC and ^{1}H-NMR data were obtained.

These reported techniques are usually time consuming, create waste chemicals, damage the sample, or involve with high-cost equipments. Therefore, this work focuses on the development of the method to determine the EEW of epoxy resin in a fast and simple way to analyze the sample without damaging the sample by using easily accessible equipments.

2.3 Near infrared spectroscopy [8]

Near infrared (NIR) region of the electromagnetic spectrum ranges from 780 to 2500 nm (12820 to 4000 cm^{-1}), but the region commonly used is between 1100 to 2500 nm (10000 to 4000 cm^{-1}). NIR spectroscopy provides much more complex structural information related to the vibration behavior of combinations of bonds. When the sample is exposed to the NIR radiation, molecules at the vibrational ground state can absorb the energies at certain frequencies, and then be induced to populate the vibration excited states corresponding to various vibrational modes, which occur at different frequency depending on the functional group. Vibrational modes are often given descriptive names, such as stretching and bending. The vibrational absorption of several functional groups, i.e., O-H, C-H, C-O, and N-H, which is usually found in the organic compounds, could be observed at close by regions. Then the combination tones and overtones complicate the spectrum, especially for the sample with complicated structure. To analyze these spectra, mathematic and statistical methods are used to help distinguish their specific features.

The advantage of the NIR technique is that only a small amount of sample is required and the technique is non-destructive and required minimal or no sample preparation. The NIR technique is also environmental friendly as no reagent is required and no chemical waste is produced [9]. Moreover, one can acquire the real time NIR analysis and the process can be done in a short period time. One can analyze multiple samples at a time and measure other factors at the same time. It is simple for regular use.

Instrumentation

The components of FT-NIR instrument can be described as follows.

Source

Source is heated to temperature of 1500-2000 K to release electromagnetic wave in the infrared region. There are several kinds of source.

a) Nernst glower – The Nernst glower can be heated to 2200 K. It has long lifetime but it is unstable at high temperature. Because its resistance decreases when the temperature increases, the current needs to be under control.

b) Globar source – The Globar source can be heated to 1500 K. It is more stable and can emit higher intensity electromagnetic wave than the Nernst glower.

c) Incandescent wire source – The incandescent wire source use Nichrom wire that can be heated to 1100 K. This kind of source uses lower current and voltage and longer lifetime than the other two sources.

Interferometer

The light signal passing through the interferometer is called interferogram, which has to be transformed to spectrum by Fourier transform, which the computer is used for calculation. The interferometer is better than monochromator, which filters light with continuous wavelength for a single wavelength, thus can be used in each wavelength only one at a time. The interferometers can analyze data faster because it can be used to measure different wavelengths at the same time.

Sample

The sample to use for analysis can be solid, liquid, or gas. Different procedures for sample preparations are applied, e.g., KBr disk for solid sample, liquid cell for liquid sample, and gas cell for gas sample, etc.

Detector

The detector is used to measure the energy of electromagnetic wave that transmits through the sample.

a) Pyroelectric detector – The pyroelectric detector transforms the IR signal to conductivity with high sensitivity. Deuterated triglycine sulfate (DTGS) can be used for the frequency range of 400-4000 cm^{-1} and can detect at high intensity. It has been widely used for FT-IR because of the advantage of functioning at room temperature.

b) Semiconductor detector – The mercury cadmium tellurium (MCT) detector can be used for the frequency range of 650-4000 cm^{-1}. The advantage is that it has higher sensitivity than DTGS and it detects fast. There is a limitation that it can be used only at very low temperature. Therefore, it needs to be cool down with liquid nitrogen before use, which is costly. Normally it is used as a detector in FT-IR microscope.

In addition, the manufacturers may use indium gallium arsenide (InGaAs) for the detection at wavelength of 800-1700 nm. The detector that is used in other kind of machines such as diode array is also used in the NIR spectrometer. It is not suitable for portable equipment because it is easy to break. If some parts of spectrometer have to be replaced frequently, the performance of the machine will deteriorate. Therefore, small sized spectrometers use charge coupled device (CCD) for detection, instead. However, there are some limitations in that it can detect the electromagnetic wave only in the region of visible light and NIR in the short wavelength. Generally the results can be 1) the spectrum data which one can use to build calibration curve or to measure data of interest, and 2) the data of interest which the computer and software take a role to collect and manage them.

Advantages and limitations of NIR

Advantages

The advantage of the NIR spectrometry over mid-infrared (MIR) and far-infrared (FIR) is that it requires only minimum or no sample preparation and generates real time data. Moreover, the NIR differs from other analytical method for the fast process, no sample damage, no chemical waste, and no chemical residue. It can measure different compositions and variables at the same time. The machine can be set in any place and easy to use even for non-chemist. It works fine without fume hood and drainage system. The accuracy of NIR spectroscopy depends on the accuracy of standard method as a control set.

NIR has another advantage over MIR and FIR because of fewer problems with thermal noise. Electronic device inside the spectrometer can generate heat noise to disturb the detection of the detectors in MIR and FIR region but it only slightly interferes NIR functioning or does not interfere at all.

Limitations

The limitation of NIR spectroscopy is that it can analyze only organic molecules because the metal, such as silver or lead, and most of inorganic compounds cannot absorb NIR radiation. Since NIR is not a stand-alone system, the calibration of various compositions and variables as well as the analysis of sample with standard method is crucial. To ensure that the calibration is reliable, the calibration needs to be adjusted to keep up-to-date. Although mathematical and statistical methods assist in analysis of important spectrum data that are overlapped, the methods need the computer that is well-developed for finding relationship of spectrum data and compositions or variables such as functional group properties in statistical analysis.

NIR spectroscopy has proved to be a powerful tool for qualitative and quantitative analysis in food, agricultural, pharmaceutical, textile and petrochemical industries [10-18]. Recently, it has gained interest among researcher as it was used together with multivariate calibration to replace other time-consuming or destructive methods. Several studies showed the application of NIR to find the properties and quantities of various compounds as follows.

Aske *et al.* [10] characterized the chemical compositions in crude oils and condensates into four classes: saturate, aromatic, resin and asphaltenic (or called SARA) using infrared (IR) and NIR spectroscopy. Partial least squares (PLS) regression was used to establish the relationship between IR and NIR spectra and SARA components obtained from high performance liquid chromatography (HPLC). The uncertainties in the prediction models based on IR and NIR spectroscopy of SARA were in the range of 1.0 – 2.8 wt % and were in the same range as reported by direct determination with HPLC.

Iñón *et al.* [11] determined the quality of beers in Spain based on the original extract, real extract, and ethanol content values using NIR spectroscopy and PLS calibration. The official methods for the determination of the aforementioned quantities are based on distillation of the beer and density measurement. The use of autoanalyzer reduces sample handling but involves a long analysis time. The method based on NIR and PLS compares favorably with the automatic reference method in terms of speed, reagent consumed and waste generated.

Chen *et al.* [12] used NIR spectroscopy as a rapid method to identify tea varieties from different provinces in China. PLS was used simultaneously to predict the content of caffeine and total polyphenols in tea. The correlation coefficient (R) and the root mean square error of prediction (RMSEP) in the test set were: R = 0.9688, RMSEP = 0.0836 % for caffeine and R = 0.9299, RMSEP = 1.1138 % for total polyphenols.

Liu *et al.* [13] developed a method for quantifying the concentrations of glucose, fructose, and sucrose in apples using FT-NIR spectroscopy. PLS regression was used to construct calibration models. The method was validated according to reference method, HPLC. The best model showed satisfactory results as the R and RMSEP values were: R = 0.950, RMSEP = 0.201 for glucose; R = 0.968, RMSEP = 0.298 for fructose; and R = 0.969, RMSEP = 0.335 for sucrose.

Xie *et al.* [14] applied NIR spectroscopy to determine glucose, fructose, and sucrose concentrations in bayberry juice. HPLC was used to provide the reference values for calibration. Calibration models were constructed using concentration values from reference method (HPLC) and NIR spectral data using PLS regression. The prediction accuracy of models was improved by using second derivative process, especially for sucrose with the determination coefficient (R^2) of 0.993.

Henniges *et al.* [15] developed a method to determine molecular weight, carbonyl group content and carboxyl group content in pulp hand sheets and historic papers using NIR and PLS. Group-selective fluorescence labeling of carbonyl and carboxyl structures followed by gel permeation chromatography (GPC) was used as a reference method to provide reference values to be correlated with NIR data.

However, the drawbacks for the reference method were sample-destructive, time-consuming, and costly. The developed pulp and paper testing method was fast and non-destructive and was preferred in paper conservation.

In addition to the increasing applications of NIR spectroscopy with multivariate calibration for qualitative and quantitative analyses of various samples, ASTM has approved a standard method to determine the hydroxyl number in polyols with NIR [5]. The hydroxyl number of polyols was first determined by a reference method and then analyzed by NIR. Mathematic and statistical analyses were used to find the relationship between the NIR absorption data and hydroxyl number of polyols from the reference method.

2.4 Partial least squares regression [19, 20]

The partial least squares (PLS) regression has been used in many fields such as chemistry, economics, medicine, pharmaceutical science and industrial process control. It is a method that combines features from principal component analysis (PCA) and multiple regression. PLS is useful for constructing predictive models when the explanatory variables are large and highly collinear. In its simplest form, a linear model specifies the linear relationship between a dependent variable (response) Y, and a set of predictor variables, the X's:

$$Y = \mathrm{B}_0 + \mathrm{B}_1 X_1 + \mathrm{B}_2 X_2 + \mathrm{B}_3 X_3 + \ldots + \mathrm{B}_n X_n$$

Where B_0 is the regression coefficient for the intercept

B_i values are the regression coefficient for variable 1 to n

For this study, the PLS is used to construct a calibration curve by matching the spectrum obtaining from FT-NIR with chemical data (i.e. the EEW from titration) known from the experiment. The samples are regrouped by their absorption bands in the range of 10000 to 4000 cm^{-1} and their chemical data from the experiment. Thus, the number of the new group sample decreases because of recruiting for the same features. Therefore, the variables for this study are

Y is the EEW value

B_0 is the regression coefficient for the intercept

B_i values are slopes of the graph at wavelength 1 to n

X_i values are absorbance values at wavelength 1 to n

The performance of the final PLS model was evaluated in terms of root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), BIAS, error and correlation coefficient (R) [9, 12, 19]. For the calibration set, the RMSEC is defined as

$$\mathrm{RMSEC} = \sqrt{\frac{\sum_{i=1}^{n}\left(\hat{y}_i - y_i\right)^2}{n}}$$

Where y_i is the measurement value for sample i obtained from the reference method (from titration)

$\hat{y}_i$ is the estimated value (from NIR) for sample i when the model is constructed

n is the number of calibration samples

For the validation set, the RMSEP and BIAS are calculated as

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

$$\mathrm{BIAS} = \frac{\sum_{i=1}^{n}\left(\hat{y}_i - y_i\right)^2}{n}$$

Where y_i is the measurement value for sample i obtained from the reference method (from titration)

$\hat{y}_i$ is the estimated value (from NIR) for sample i obtained from the developed model

n is the number of validation samples

Correlation coefficient (R) between the predicted and the reference value was calculated for both the calibration and validation samples. R and error are calculated as

$$\mathrm{R} = \sqrt{1 - \frac{\sum_{i=1}^{n} \left(\hat{y}_i - y_i\right)^2}{\sum_{i=1}^{n} \left(y_i - \bar{y}_i\right)^2}}$$

$$\mathrm{error} = \frac{\mathrm{BIAS}}{\left(y_{\max} - y_{\min}\right)}$$

Where $\bar{y}_i$ is mean of the measurement value obtained from the reference method for all samples in the calibration and validation sets

y_{max} is the maximum measurement value obtained from the reference method

y_{min} is the minimum measurement value obtained from the reference method

CHAPTER III

EXPERIMENTAL

3.1 Epoxy resin

Epoxy resins used in this study, prepared from the reaction between bisphenol A and epichlorohydrin, were provided by Aditya Birla Chemicals (Thailand). At least 150 samples of epoxy resins were used as a calibration sample set. Another independent set of samples, known as the validation sample set, contains at least 40 samples.

3.2 Chemicals

- acetic anhydride, 99.5% (Fluka)
- chlorobenzene, ≥ 99.7% (Fluka)
- crystal violet indicator, ≥ 90% (Sigma)
- glacial acetic acid, ≥ 99.85% (Sigma-Aldrich)
- perchloric acid, 60% (Fluka)
- potassium hydrogen phthalate (KHP), ≥ 99.5% (Sigma-Aldrich)
- tetraethylammonium bromide (TEAB), 98% (Aldrich)

3.3 Reagents

- 0.1 % solution of crystal violet indicator in glacial acetic acid
- 0.1 M perchloric acid in glacial acetic acid

  Slowly add 13 mL of 60% perchloric acid and 50 mL of acetic anhydride to 250 mL of glacial acetic acid in 1 L volumetric flask. Dilute to mark with glacial acetic acid and mix well.
- TEAB solution in glacial acetic acid

  Dissolve 100 g of TEAB, with agitation at room temperature, in 400 mL of glacial acetic acid.

3.4 Determination of EEW of epoxy resins by titration

3.4.1 Standardization of 0.1 M perchloric acid

Weigh accurately 0.4 g of KHP and dissolve it with 50 mL of glacial acetic acid. Add 6–8 drops of 0.1 % crystal violet indicator. The KHP solution was titrated with perchloric acid solution. At the end point, the solution changes from blue to green and remains green for at least 2 minutes. Calculate the exact concentration of perchloric acid.

3.4.2 Analysis of EEW of epoxy resin

At least 150 samples of epoxy resins were used as a calibration sample set. Each epoxy resin sample was individually analyzed at least in triplicate. Weigh accurately 0.07–0.15 g of epoxy resin and dissolve it with 20 mL chlorobenzene. Add 10 mL glacial acetic acid and 20 mL of TEAB solution in glacial acetic acid. Add 6–8 drops of 0.1 % crystal violet indicator. Titrate the solution using the autotitrator (model DL15, Mettler-Toledo, U.S.A.) equipped with a pH electrode and a 10 mL burette containing standard perchloric acid solution. At the end point, the solution changes from blue to green and remains green for at least 2 minutes. Calculate the EEW of epoxy resin.

3.5 Analysis of epoxy resin by FT-NIR

All FT-NIR analyses were performed using Fourier transform near infrared spectrometer (NIRFlex N-500, from BUCHI, Switzerland) equipped with a tungsten halogen light source and an InGaAs (indium gallium arsenide) detector. A cuvette of 8 mm pathlength was used. The FT-NIR spectra were measured in a transmittance mode from 10000 to 4000 cm^{-1} with 8 cm^{-1} resolution. The temperature was set at 40.0 °C. Each spectrum corresponded to the average of 64 scans.

The same epoxy resins from a calibration sample set were analyzed by FT-NIR. Each epoxy resin sample was analyzed five times. If the epoxy resin sample contains bubbles, sonication (ultrasonic bath model 8200 from Branson Ultrasonic Corporation, U.S.A.) was performed prior to transferring the sample to a cuvette.

3.6 Data analysis

FT-NIR spectra were recorded using NIR Flex N-500 software (BUCHI, Switzerland). NIR Flex N-500 software comprises three subgroups: Operator software, NIRWare Management Console, and NIRCal. Operator software is responsible for measuring reference spectra and routine spectra. NIRWare Management Console is an application designer, sample management, and security management. NIRCal is a chemometric tool responsible for graphical visualization, quantitative and qualitative calibration. Prior to calibration, the FT-NIR transmittance data were mean centered, smoothed with a 25 point Savitzky-Golay function [21]. The processed spectral data were transformed by Savitzky-Golay first and second derivatives. Partial least square regression (PLS) was applied to generate calibration models using a NIRCal software system.

3.7 Validation of the method

At least 40 samples from the validation sample set were analyzed for their EEW values by FT-NIR and titration, respectively according to the procedures described in 3.4-3.5.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination of EEW of epoxy resins by titration

At least 150 samples of epoxy resins were used for determination of their EEW values by a reference method according to ASTM 1652-04 [2]. Each epoxy resin sample was dissolved in chlorobenzene. Excess amount of tetraethylammonium bromide (TEAB) in acetic acid was added and the mixture was autotitrated with standard perchloric acid. The added standard perchloric acid reacted with TEAB to generate HBr in situ, which then reacted stoichiometrically with epoxide group of epoxy resins (Figure 4.1). At the endpoint, EEW could be calculated from the volume of standard perchloric acid used (Figure 4.2). Each epoxy resin sample was individually analyzed at least three times. The EEW values of all tested samples ranged from 181–194 g/eq.

$$\text{EEW} = \frac{\text{weight of epoxy resin (g)}}{\text{volume of } HClO_4 \text{ (L)} \times \text{concentration of } HClO_4 \text{ (mol/L)}}$$

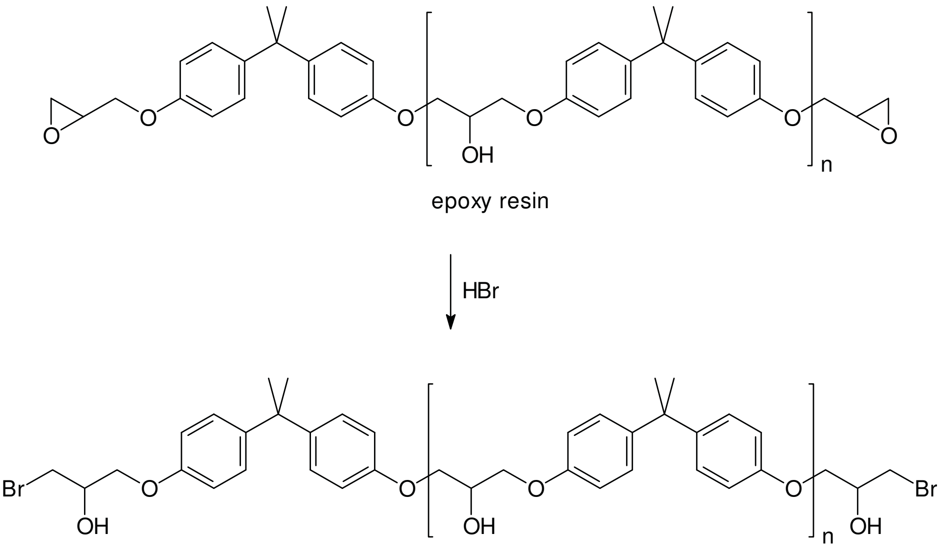
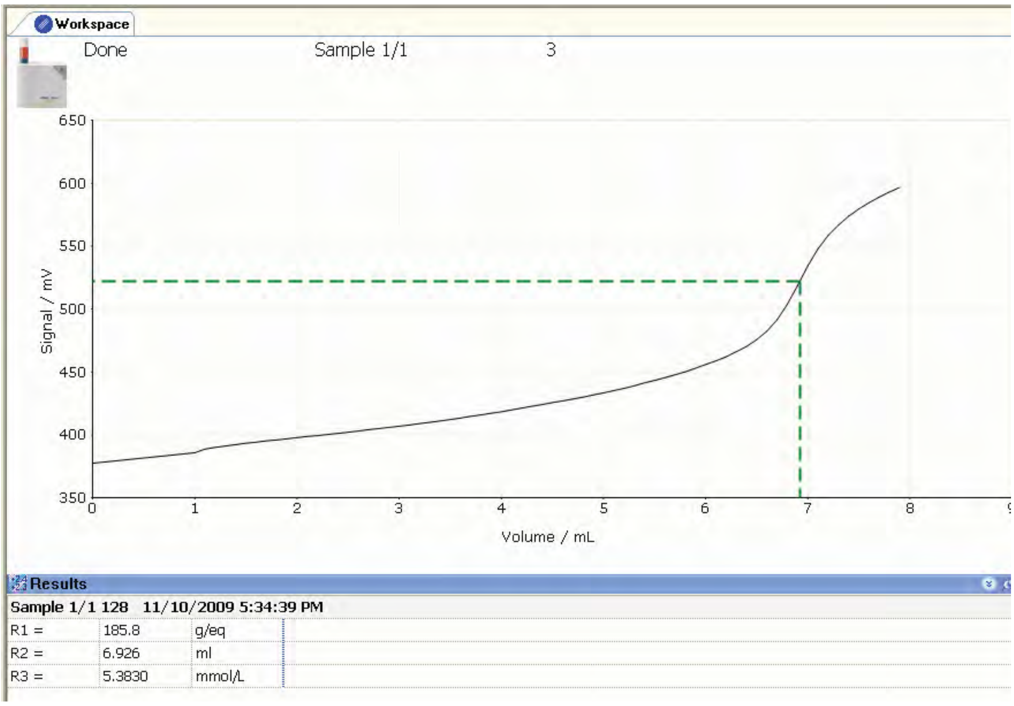


Figure 4.1 Reaction between epoxy resin and HBr



Sample 1/1 128 11/10/2009 5:34:39 PM

R1 =	185.8	g/eq
R2 =	6.926	ml
R3 =	5.3830	mmol/L

Figure 4.2 Titration curve of epoxy resin obtained from autotitrator

Table 4.1 Repeatability of the EEW values (g/eq) of epoxy resin obtained from autotitration

entry #	EEW value
1	185.69
2	185.80
3	185.79
4	185.69
5	185.81
6	185.81
7	185.70
8	185.78
9	185.79
10	185.73
average	185.76
SD	0.05
% RSD	0.03

As seen from Table 4.1, the same epoxy resin sample was individually autotitrated with standard perchloric acid ten times according to the reference method. The repeatability of the titration was excellent as the standard deviation (SD) of 0.05 and % relative standard deviation (% RSD) of 0.03 were quite low.

4.2 Analysis of epoxy resin by FT-NIR

4.2.1 Construction of the prediction model

At least 150 samples of epoxy resins from the same calibration set were analyzed by FT-NIR. If the epoxy resin sample received from the company contained small bubbles, it was subjected to sonication until clear liquid was achieved (Figure 4.3) prior to NIR analysis.

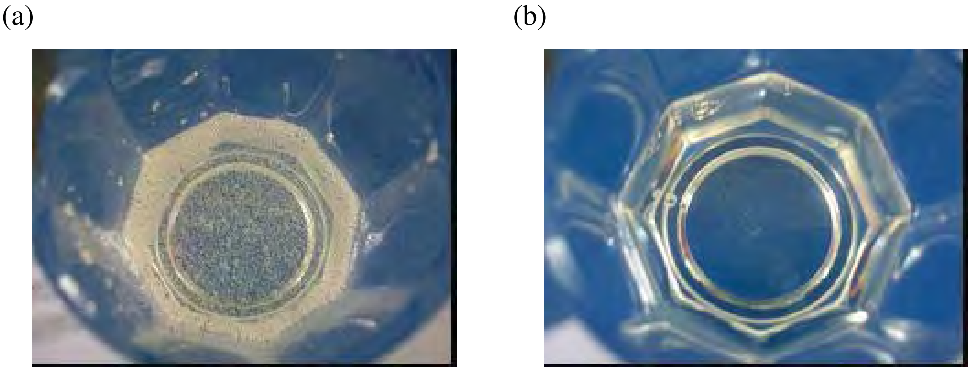


Figure 4.3 Epoxy resin (a) with small bubbles; (b) after sonication

FT-NIR spectra of all samples from the calibration set, with known EEW values from titration, were then collected in a transmittance mode from 10000 to 4000 cm^{-1} as shown in Figure 4.4. The spectra of all samples were homogeneous and no outlier was observed by naked eyes. The original NIR spectra were smoothed with a 25-point Savitzky-Golay function as illustrated in Figure 4.5. The spectra were then transformed through the first and second derivatives to extract useful band information (Figure 4.6) before creating regression equation.

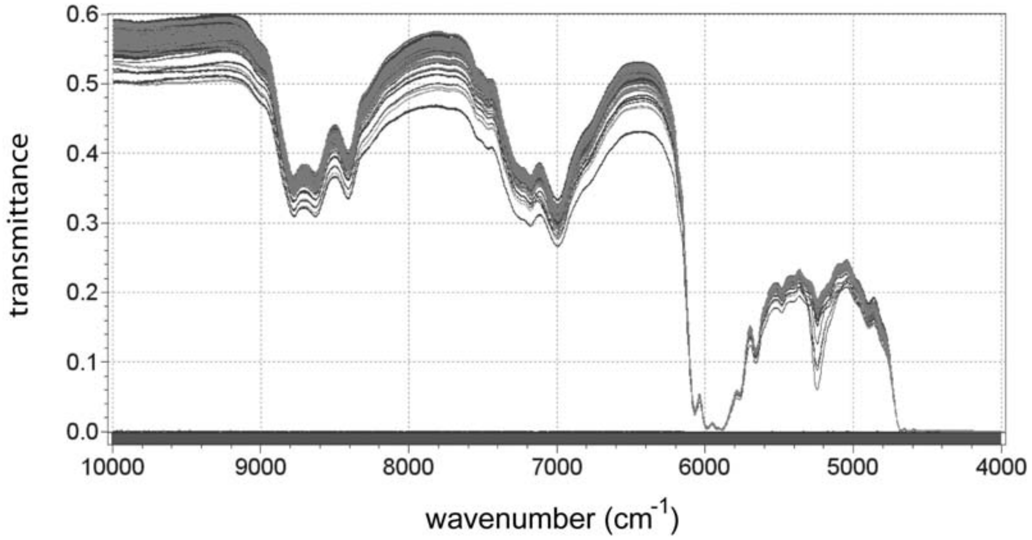


Figure 4.4 Untreated original FT-NIR spectra of all samples from the calibration set

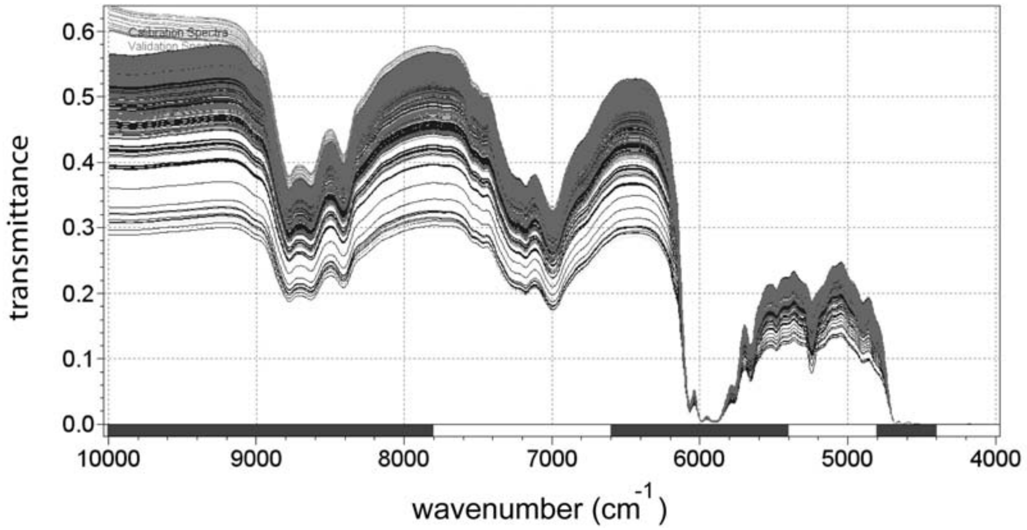


Figure 4.5 Smoothed spectra of all samples from the calibration set with a 25-point Savitzky-Golay function

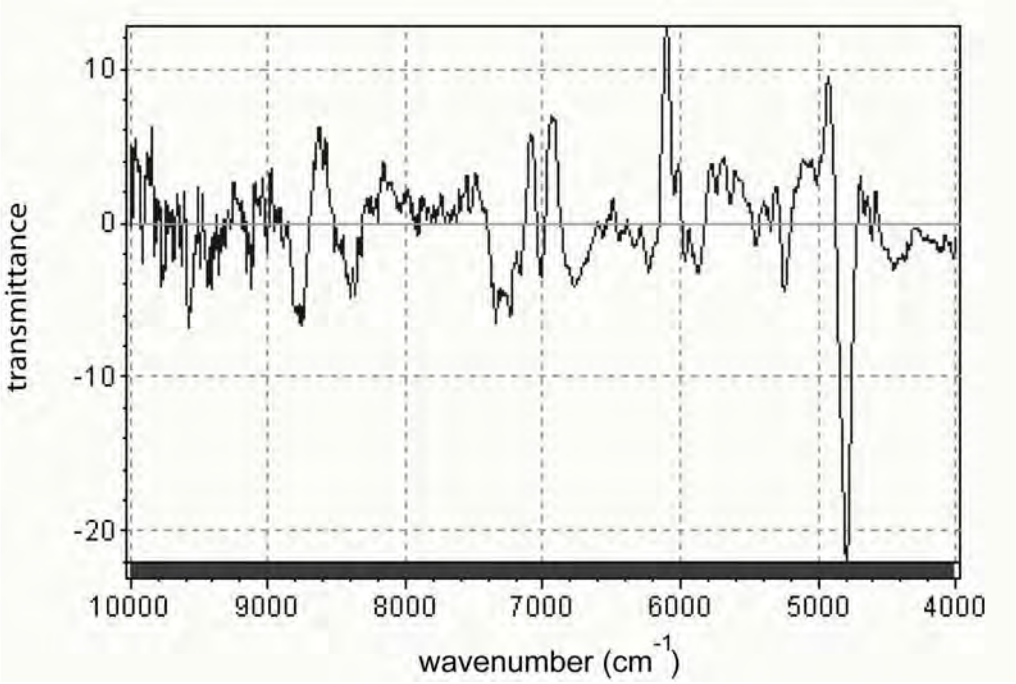


Figure 4.6 Spectra of sample from the calibration set after the first and second derivatives

A calibration curve was constructed which correlate the measured EEW values obtained from the reference method (titration) to the EEW values predicted by FT-NIR (Figure 4.7). This calibration curve could be applied to provide EEW values of unknown epoxy resins under the same experimental conditions.

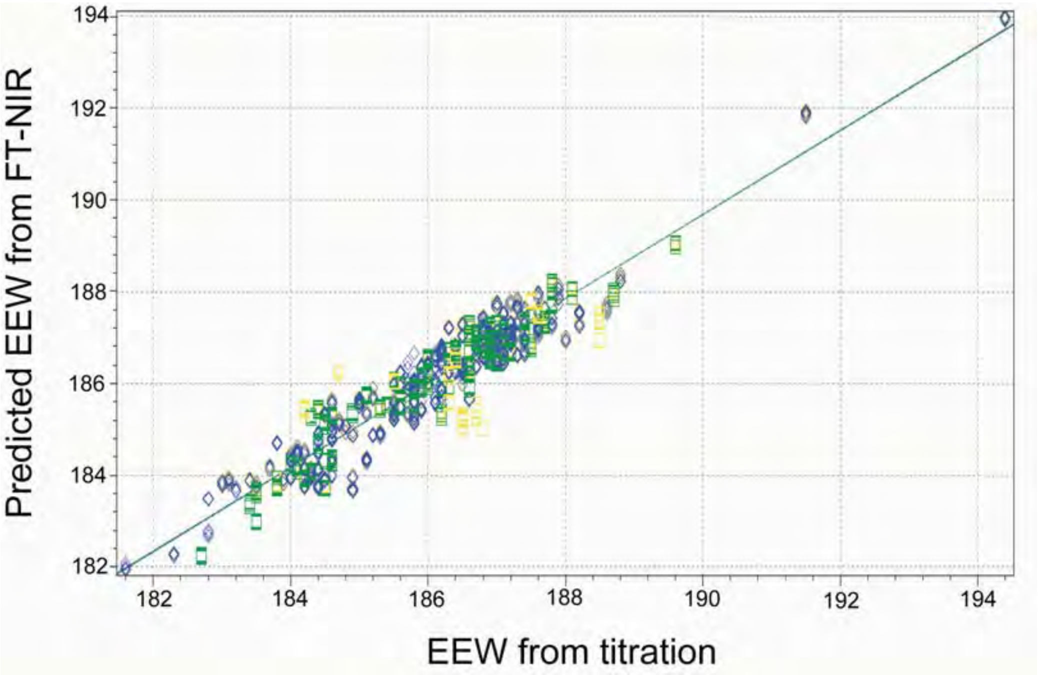


Figure 4.7 Calibration curve for determination of EEW values of epoxy resins. Blue dots and green dots represent the samples used by the instrument to predict the equation for the calibration curve and to verify the accuracy of the predicted equation, respectively.

4.2.2 Effects of temperature and chemical residues

Next, FT-NIR operating temperature and amount of chemical residues presented in the sample were examined whether they would affect the predicted EEW values.

Effect of operating temperature

Epoxy resin samples from the calibration set were analyzed by FT-NIR at 40.0 °C because epoxy resins are still liquid and can be easily transferred. Epoxy resin of known average EEW values from titration (185.76 g/eq) was used to study the effect of operating temperature. The operating temperature was varied in the range of 39.0–41.0 °C. The samples were individually analyzed five times by FT-NIR. Although the spectra obtained from different temperature were similar to naked eye, the predicted EEW values were quite varied. Their EEW values and errors are shown in Table 4.2.

Table 4.2 EEW values (g/eq) obtained from FT-NIR at various temperatures. (The average EEW value of epoxy resin sample determined from titration was 185.76 g/eq).

temperature (°C)	EEW from FT-NIR	error
39.0	185.46	1.56×10^{-3}
	185.56	1.02×10^{-3}
	185.60	8.08×10^{-4}
	185.42	1.78×10^{-3}
	185.48	1.45×10^{-3}
39.5	185.66	4.84×10^{-4}
	185.71	2.15×10^{-4}
	185.68	3.77×10^{-4}
	185.65	5.38×10^{-4}
	185.61	7.54×10^{-4}
40.0	185.76	5.38×10^{-5}
	185.76	5.38×10^{-5}
	185.76	5.38×10^{-5}
	185.77	1.07×10^{-5}
	185.73	1.07×10^{-5}
40.5	187.86	1.14×10^{-2}
	187.82	1.11×10^{-2}
	187.73	1.07×10^{-2}
	187.89	1.15×10^{-2}
	187.95	1.18×10^{-2}
41.0	188.26	1.35×10^{-2}
	188.12	1.28×10^{-2}
	188.13	1.28×10^{-2}
	188.39	1.42×10^{-2}
	188.15	1.09×10^{-2}

As seen from Table 4.2, the predicted EEW values obtained from FT-NIR at 40.0 °C (the same operating temperature that used to analyze epoxy resins from the calibration set) agreed well with the EEW values obtained from titration. At lower temperature (39.0 and 39.5 °C), the predicted EEW values were slightly lower than the reference EEW values obtained from titration with high error (greater than acceptable value of 0.0004). At higher temperature (40.5 and 41.0 °C), the predicted EEW values were significantly higher than the reference EEW values with very high error of ~ 0.01. Therefore, the unknown epoxy resins must be analyzed under the same experimental conditions as those from the calibration set.

Effect of solvent

Different chemical composition of the sample can cause a change in NIR spectrum. Chemical residues in epoxy resin samples are the reagents used in the preparation process mainly toluene (solvent) and, sometimes, epichlorohydrin (reagent). Figure 4.8 showed the spectrum of epoxy resin with solvent. It was clear that the spectrum in 9000-8000 cm^{-1} range was different from Figure 4.5. Table 4.3 illustrated the effect of solvent presented in epoxy resins to the predicted EEW values.

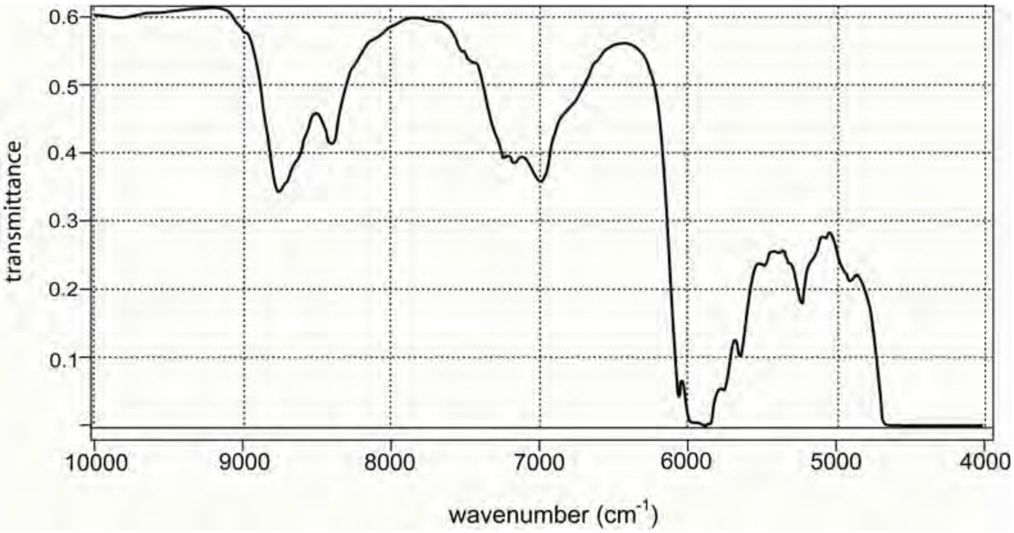


Figure 4.8 FT-NIR spectrum of epoxy resin containing solvent

Table 4.3 EEW values (g/eq) obtained from FT-NIR of different epoxy resins

epoxy resin	EEW from FT-NIR	error
without solvent	185.76	5.38×10^{-5}
	185.76	5.38×10^{-5}
	185.76	5.38×10^{-5}
	185.77	1.07×10^{-5}
	185.73	1.07×10^{-5}
with 50% solvent	207.29	3.72×10^{-3}
	207.66	3.75×10^{-3}
	207.43	3.75×10^{-3}
	207.41	3.74×10^{-3}
	207.58	3.73×10^{-3}

As seen from Table 4.3, the predicted EEW values obtained from FT-NIR of epoxy resins that contained 50% solvent (average of 207.47 g/eq) considerably differed from EEW values of epoxy resins that contained no solvent (average of 185.76 g/eq). In addition, the errors of the predicted EEW values of epoxy resins that contained 50% solvent is about 100 times higher than those of epoxy resins without solvent. Therefore, the solvent used in the preparation process must be removed to ppm level (confirmed by gas chromatography).

4.2.3 Validation of the method

Another independent set of samples was used as the validation sample set. Their EEW values must be within the range of those from the calibration set. The samples from the validation set were analyzed by FT-NIR to obtain the predicted EEW values and compared with EEW values obtained from titration. If the predicted values agreed with values from reference method and statistical data were good, the predicted equation is acceptable for use.

Forty samples with varied EEW values (182–189 g/eq) were used to validate the method. Each sample was individually analyzed three times using the prediction model (FT-NIR with PLS) and three times by titration. The EEW values were compared in Table 4.4. As the results shown, predicted EEW values obtained from the model were in good agreement with EEW values obtained from titration.

Table 4.4 Comparison of EEW values (g/eq) obtained from prediction model and autotitration of epoxy resin samples from the validation set

sample #	EEW from prediction model				EEW from titration			
	1	2	3	average	1	2	3	average
1	182.62	182.62	182.63	182.62	182.61	182.62	182.62	182.62
2	183.53	183.53	183.53	183.53	183.53	183.53	183.52	183.53
3	183.56	183.57	183.57	183.57	183.57	183.56	183.57	183.57
4	184.18	184.17	184.17	184.17	184.15	184.17	184.16	184.16
5	184.26	184.26	184.27	184.26	184.25	184.27	184.26	184.26
6	184.54	184.55	184.57	184.55	184.55	184.55	184.56	184.55
7	184.83	184.81	184.82	184.82	184.81	184.82	184.81	184.82
8	184.21	184.20	184.20	184.21	184.20	184.22	184.20	184.21
9	184.65	184.65	184.65	184.65	184.65	184.65	184.64	184.65
10	185.45	185.45	185.45	185.45	185.44	185.45	185.44	185.44
11	185.66	184.65	185.65	185.32	185.65	185.65	185.64	185.65
12	185.74	185.73	185.73	185.73	185.74	185.75	185.73	185.74
13	185.56	185.56	185.55	185.56	185.55	185.55	185.57	185.56
14	185.70	185.68	185.68	185.68	185.68	185.69	185.69	185.69
15	185.73	185.71	185.72	185.72	185.71	185.72	185.72	185.72
16	185.14	185.14	185.14	185.14	185.13	185.14	185.14	185.14
17	185.60	185.60	185.60	185.60	185.60	185.60	185.61	185.60
18	185.64	185.63	185.62	185.63	185.63	185.63	185.62	185.63
19	185.39	185.39	185.39	185.39	185.39	185.37	185.39	185.38
20	185.87	185.89	185.86	185.87	185.88	185.87	185.87	185.87
21	186.13	186.13	186.13	186.13	186.13	186.12	186.13	186.13
22	186.39	186.39	186.40	186.40	186.40	186.42	186.41	186.41
23	186.58	186.55	186.57	186.57	186.57	186.56	186.57	186.57
24	186.64	186.64	186.63	186.63	186.63	186.63	186.63	186.63

sample #	EEW from prediction model				EEW from titration			
	1	2	3	average	1	2	3	average
25	186.74	186.75	186.75	186.75	186.74	186.73	186.74	186.74
26	186.50	186.51	186.51	186.50	186.50	186.51	186.51	186.51
27	187.33	187.34	187.33	187.34	187.33	187.34	187.34	187.34
28	187.45	187.45	187.45	187.45	187.45	187.45	187.43	187.44
29	187.50	187.51	187.52	187.51	187.50	187.51	187.50	187.50
30	187.97	187.96	187.99	187.97	188.96	188.96	188.95	188.96
31	187.71	187.72	187.71	187.71	187.71	187.71	187.71	187.71
32	187.01	187.07	186.09	186.72	187.00	187.00	187.00	187.00
33	187.73	187.74	187.75	187.74	187.74	187.73	187.74	187.74
34	188.39	188.39	188.40	188.39	188.38	188.39	188.38	188.38
35	188.43	188.43	188.43	188.43	188.43	188.43	188.42	188.43
36	188.32	188.35	188.33	188.33	188.33	188.33	188.34	188.33
37	188.16	188.16	188.16	188.16	188.15	188.15	188.17	188.16
38	188.22	188.22	188.21	188.22	188.21	188.22	188.21	188.21
39	188.43	188.43	188.43	188.43	188.43	188.43	188.42	188.43
40	189.26	189.25	189.24	189.25	189.25	189.26	189.25	189.25

The performance of the prediction model was evaluated by RMSEC and RMSEP as shown in Table 4.5. Both RMSEC and RMSEP values were low and agreed well. The correlation coefficient, R, for the prediction model was good with the value of 0.9580.

Table 4.5 PLS regression model for EEW value

performance parameter	value
RMSEC	0.4265 g/eq
RMSEP	0.4131 g/eq
R	0.9580
acceptable BIAS	≤ 0.06
acceptable error	≤ 0.0004

EEW values of epoxy resins (in Table 4.4) obtained from FT-NIR with calibration model and from titration were compared using paired t-test at 95 % confidence. The critical t-value at 95 % confidence for 39 degree of freedom was 2.02. The experimental t-value at the same confidence level was 0.16, which was lower than the critical t-value. Therefore, the EEW values obtained from both methods were insignificantly different.

As seen from Table 4.6, the EEW values obtained from the prediction model (FT-NIR) were compared to those obtained from the reference method (titration). The same epoxy resin sample was individually analyzed by FT-NIR ten times and then model was used to predict the EEW values. The same epoxy resin samples were also autotitrated with standard perchloric acid according to the reference method. Both methods showed excellent and comparable repeatability as the SD and % RSD were low. Therefore, the developed method using FT-NIR spectroscopy can be used routinely to determine the EEW value of epoxy resins.

Table 4.6 Repeatability of EEW values (g/eq) obtained from FT-NIR and autotitration of epoxy resin sample from the validation set

entry #	EEW from FT-NIR	EEW from titration
1	185.70	185.69
2	185.75	185.80
3	185.80	185.79
4	185.68	185.69
5	185.82	185.81
6	185.81	185.81
7	185.69	185.70
8	185.77	185.78
9	185.80	185.79
10	185.71	185.73
average	185.75	185.76
SD	0.05	0.05
% RSD	0.03	0.03

CHAPTER IV

CONCLUSION

A new method was developed for the determination of EEW values of epoxy resins. At least 150 samples of epoxy resin were used as a calibration sample set. The epoxy resin samples were analyzed for their EEW values by a reference method (ASTM D 1652-04), to obtain the EEW values in the range of from 181–194 g/eq, and then analyzed by FT-NIR in a transmittance mode from 10000 to 4000 cm^{-1}. The results from both methods were used to construct a prediction model using PLS regression. The model was validated with another set of epoxy resin samples of 40 samples, called a validation sample set. The EEW values of both methods agreed well as shown by performance parameters RMSEC, RMSEP, and R values of 0.4265 g/eq, 0.4131 g/eq, and 0.9580, respectively. The newly developed method could be applied for routine analysis of EEW values of epoxy resin as it is simple, fast, non-destructive and environmental friendly. However, the unknown epoxy resins must be analyzed under the same experimental conditions as those from the calibration set because the predicted values were sensitive to temperature and chemical residues.

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APPENDIX

Table A.1 Comparison of EEW values (g/eq) obtained from prediction model and autotitration of epoxy resin samples from the calibration set

sample #	EEW from FT-NIR	EEW from titration	error
1	181.91	182.91	0.0003227
	181.91	182.92	0.0003555
	181.91	182.91	0.0003642
	181.91		0.0003447
	181.91		0.0003435
2	182.62	182.61	0.0003227
	182.62	182.62	0.0003555
	182.63	182.62	0.0003642
	182.62		0.0003447
	182.62		0.0003435
3	182.41	182.40	0.0003713
	182.40	182.40	0.0003063
	182.40	182.41	0.0003133
	182.41		0.0003424
	182.41		0.0003287
4	182.41	182.40	0.0003713
	182.40	182.40	0.0003063
	182.40	182.41	0.0003133
	182.41		0.0003424
	182.41		0.0003287
5	183.43	183.43	0.0004531
	183.43	183.43	0.0004462
	183.43	183.43	0.0004301
	183.43		0.0004205
	183.42		0.0003881
6	183.53	183.53	0.0004531
	183.53	183.53	0.0004462
	183.53	183.52	0.0004301
	183.55		0.0004205
	183.54		0.0003881
7	183.66	183.66	0.0004449
	183.66	183.65	0.0004466
	183.66	183.66	0.0004511
	183.66		0.0004558
	183.65		0.0004438

sample #	EEW from FT-NIR	EEW from titration	error
8	183.77	183.77	0.0002071
	183.77	183.78	0.0002105
	183.76	183.77	0.0002062
	183.78		0.0002163
	183.77		0.0002542
9	183.56	183.57	0.0004449
	183.57	183.56	0.0004466
	183.57	183.57	0.0004511
	183.57		0.0004558
	183.57		0.0004438
10	183.43	183.43	0.0004531
	183.43	183.43	0.0004462
	183.43	183.43	0.0004301
	183.43		0.0004205
	183.42		0.0003881
11	183.53	183.53	0.0004531
	183.53	183.53	0.0004462
	183.53	183.52	0.0004301
	183.55		0.0004205
	183.54		0.0003881
12	183.66	183.66	0.0004449
	183.66	183.65	0.0004466
	183.66	183.66	0.0004511
	183.66		0.0004558
	183.65		0.0004438
13	183.77	183.77	0.0002071
	183.77	183.78	0.0002105
	183.76	183.77	0.0002062
	183.78		0.0002163
	183.77		0.0002542
14	183.56	183.57	0.0004449
	183.57	183.56	0.0004466
	183.57	183.57	0.0004511
	183.57		0.0004558
	183.57		0.0004438
15	184.02	184.02	0.0001812
	184.10	184.10	0.0001575
	184.11	184.10	0.0001609
	184.10		0.0001505
	184.10		0.0001296

sample #	EEW from FT-NIR	EEW from titration	error
16	184.56	184.56	0.0003355
	184.56	184.56	0.0003247
	184.57	184.55	0.0003038
	184.56		0.0003641
	184.56		0.0003499
17	184.18	184.15	0.0003353
	184.17	184.17	0.0003481
	184.17	184.16	0.0003901
	184.17		0.0003359
	184.16		0.0003367
18	184.61	184.61	0.0003444
	184.61	184.61	0.0003718
	184.60	184.61	0.0003791
	184.60		0.0003546
	184.61		0.0003778
19	184.35	184.35	0.0003353
	184.36	184.35	0.0003481
	184.35	184.35	0.0003901
	184.35		0.0003359
	184.36		0.0003367
20	184.26	184.25	0.0003444
	184.26	184.27	0.0003718
	184.27	184.26	0.0003791
	184.23		0.0003546
	184.26		0.0003778
21	184.54	184.55	0.0003355
	184.55	184.55	0.0003247
	184.57	184.56	0.0003038
	184.55		0.0003641
	184.55		0.0003499
22	184.83	184.81	0.0004046
	184.81	184.82	0.0003580
	184.82	184.81	0.0003503
	184.82		0.0003419
	184.83		0.0003647
23	184.21	184.20	0.0003250
	184.20	184.22	0.0003248
	184.20	184.20	0.0003396
	184.20		0.0003469
	184.23		0.0003202

sample #	EEW from FT-NIR	EEW from titration	error
24	184.02	184.02	0.0001812
	184.10	184.10	0.0001575
	184.11	184.10	0.0001609
	184.10		0.0001505
	184.10		0.0001296
25	184.56	184.56	0.0003355
	184.56	184.56	0.0003247
	184.57	184.55	0.0003038
	184.56		0.0003641
	184.56		0.0003499
26	184.18	184.15	0.0003353
	184.17	184.17	0.0003481
	184.17	184.16	0.0003901
	184.17		0.0003359
	184.16		0.0003367
27	184.61	184.61	0.0003444
	184.61	184.61	0.0003718
	184.60	184.61	0.0003791
	184.60		0.0003546
	184.61		0.0003778
28	184.35	184.35	0.0003353
	184.36	184.35	0.0003481
	184.35	184.35	0.0003901
	184.35		0.0003359
	184.36		0.0003367
29	184.26	184.25	0.0003444
	184.26	184.27	0.0003718
	184.27	184.26	0.0003791
	184.23		0.0003546
	184.26		0.0003778
30	184.54	184.55	0.0003355
	184.55	184.55	0.0003247
	184.57	184.56	0.0003038
	184.55		0.0003641
	184.55		0.0003499
31	184.83	184.81	0.0004046
	184.81	184.82	0.0003580
	184.82	184.81	0.0003503
	184.82		0.0003419
	184.83		0.0003647

sample #	EEW from FT-NIR	EEW from titration	error
32	184.21	184.20	0.0003250
	184.20	184.22	0.0003248
	184.20	184.20	0.0003396
	184.20		0.0003469
	184.23		0.0003202
33	184.65	184.65	0.0004109
	184.65	184.65	0.0003994
	184.65	184.64	0.0004192
	184.66		0.0004247
	184.63		0.0004397
34	185.45	185.44	0.0004250
	185.45	185.45	0.0004322
	185.44	185.44	0.0004033
	185.44		0.0004020
	185.45		0.0004285
35	184.65	184.65	0.0004109
	184.65	184.65	0.0003994
	184.65	184.64	0.0004192
	184.66		0.0004247
	184.63		0.0004397
36	185.45	185.44	0.0004250
	185.45	185.45	0.0004322
	185.45	185.44	0.0004033
	185.44		0.0004020
	185.45		0.0004285
37	185.50	185.50	0.0003860
	184.51	185.50	0.0003918
	185.50	185.50	0.0003833
	185.51		0.0003940
	185.50		0.0003494
38	185.57	185.57	0.0003671
	185.57	185.57	0.0003309
	185.57	185.57	0.0003506
	185.57		0.0003421
	185.57		0.0003349
39	185.66	185.65	0.0003860
	184.65	185.65	0.0003918
	185.65	185.64	0.0003833
	185.65		0.0003940
	185.67		0.0003494

sample #	EEW from FT-NIR	EEW from titration	error
40	185.74	185.74	0.0003226
	185.73	185.75	0.0003095
	185.73	185.73	0.0003246
	185.73		0.0003353
	185.73		0.0003466
41	185.56	185.55	0.0003671
	185.56	185.55	0.0003309
	185.55	185.57	0.0003506
	185.56		0.0003421
	185.56		0.0003349
42	185.70	185.68	0.0003468
	185.68	185.69	0.0003504
	185.68	185.69	0.0003339
	185.70		0.0003141
	185.70		0.0003007
43	185.73	185.71	0.0004033
	185.71	185.72	0.0003841
	185.72	185.72	0.0004030
	185.73		0.0004025
	185.72		0.0003896
44	185.14	185.13	0.0003471
	185.14	185.14	0.0002957
	185.14	185.14	0.0003492
	185.15		0.0002990
	185.14		0.0003011
45	185.60	185.60	0.0002802
	185.60	185.60	0.0003093
	185.60	185.61	0.0003284
	185.61		0.0004351
	185.59		0.0004474
46	185.64	185.63	0.0002873
	185.63	185.63	0.0002815
	185.62	185.62	0.0002879
	185.63		0.0002732
	185.63		0.0002900
47	185.39	185.39	0.0004260
	185.39	185.37	0.0003381
	185.39	185.39	0.0003934
	185.39		0.0003480
	185.38		0.0003466

sample #	EEW from FT-NIR	EEW from titration	error
48	185.87	185.88	0.0002981
	185.89	185.87	0.0002928
	185.86	185.88	0.0003224
	185.88		0.0002986
	185.87		0.0003150
49	185.61	185.61	0.0003471
	185.61	185.61	0.0002957
	185.61	185.62	0.0003492
	185.61		0.0002990
	185.61		0.0003011
50	185.50	185.50	0.0003860
	185.51	185.50	0.0003918
	185.50	185.50	0.0003833
	185.51		0.0003940
	185.50		0.0003494
51	185.57	185.57	0.0003671
	185.57	185.57	0.0003309
	185.57	185.57	0.0003506
	185.57		0.0003421
	185.57		0.0003349
52	185.66	185.65	0.0003860
	185.65	185.65	0.0003918
	185.65	185.64	0.0003833
	185.65		0.0003940
	185.67		0.0003494
53	185.74	185.74	0.0003226
	185.73	185.75	0.0003095
	185.73	185.73	0.0003246
	185.73		0.0003353
	185.73		0.0003466
54	185.56	185.55	0.0003671
	185.56	185.55	0.0003309
	185.55	185.57	0.0003506
	185.56		0.0003421
	185.56		0.0003349
55	185.70	185.68	0.0003468
	185.68	185.69	0.0003504
	185.68	185.69	0.0003339
	185.70		0.0003141
	185.70		0.0003007

sample #	EEW from FT-NIR	EEW from titration	error
56	185.73	185.71	0.0004033
	185.71	185.72	0.0003841
	185.72	185.72	0.0004030
	185.73		0.0004025
	185.72		0.0003896
57	185.14	185.13	0.0003471
	185.14	185.14	0.0002957
	185.14	185.14	0.0003492
	185.15		0.0002990
	185.14		0.0003011
58	185.60	185.60	0.0002802
	185.60	185.60	0.0003093
	185.60	185.61	0.0003284
	185.61		0.0004351
	185.59		0.0004474
59	185.64	185.63	0.0002873
	185.63	185.63	0.0002815
	185.62	185.62	0.0002879
	185.63		0.0002732
	185.63		0.0002900
60	185.39	185.39	0.0004260
	185.39	185.37	0.0003381
	185.39	185.39	0.0003934
	185.39		0.0003480
	185.38		0.0003466
61	185.87	185.88	0.0002981
	185.89	185.87	0.0002928
	185.86	185.88	0.0003224
	185.88		0.0002986
	185.87		0.0003150
62	185.61	185.61	0.0003471
	185.61	185.61	0.0002957
	185.61	185.62	0.0003492
	185.61		0.0002990
	185.61		0.0003011
63	185.69	185.69	0.0002802
	185.69	185.69	0.0003093
	185.69	185.69	0.0003284
	185.69		0.0004351
	185.69		0.0004474

sample #	EEW from FT-NIR	EEW from titration	error
64	185.31	185.31	0.0002873
	185.31	185.31	0.0002815
	185.30	185.30	0.0002879
	185.31		0.0002732
	185.31		0.0002900
65	185.29	185.30	0.0004260
	185.31	185.30	0.0003381
	185.30	185.30	0.0003934
	185.31		0.0003480
	185.30		0.0003466
66	185.81	185.81	0.0002981
	185.81	185.81	0.0002928
	185.81	185.80	0.0003224
	185.80		0.0002986
	185.81		0.0003150
67	185.69	185.69	0.0002802
	185.69	185.69	0.0003093
	185.69	185.69	0.0003284
	185.69		0.0004351
	185.69		0.0004474
68	185.31	185.31	0.0002873
	185.31	185.31	0.0002815
	185.30	185.30	0.0002879
	185.31		0.0002732
	185.31		0.0002900
69	185.29	185.30	0.0004260
	185.31	185.30	0.0003381
	185.30	185.30	0.0003934
	185.31		0.0003480
	185.30		0.0003466
70	185.81	185.81	0.0002981
	185.81	185.81	0.0002928
	185.81	185.80	0.0003224
	185.80		0.0002986
	185.81		0.0003150
71	186.13	186.13	0.0004121
	186.13	186.13	0.0004253
	186.13	186.13	0.0003795
	186.13		0.0003611
	186.14		0.0003710

sample #	EEW from FT-NIR	EEW from titration	error
72	186.39	186.40	0.0002076
	186.39	186.42	0.0002007
	186.40	186.41	0.0002179
	186.41		0.0002215
	186.43		0.0002233
73	186.58	186.57	0.0003474
	186.55	186.56	0.0003384
	186.57	186.57	0.0003404
	186.57		0.0003278
	186.56		0.0002919
74	186.64	186.63	0.0003115
	186.64	186.63	0.0002933
	186.63	186.63	0.0003151
	186.63		0.0002933
	186.63		0.0003379
75	186.74	186.74	0.0005063
	186.75	186.73	0.0005076
	186.75	186.74	0.0005071
	186.73		0.0004960
	186.75		0.0004939
76	186.31	186.30	0.0005296
	186.30	186.30	0.0004258
	186.30	186.30	0.0003895
	186.30		0.0003961
	186.30		0.0004182
77	186.51	186.50	0.0003474
	186.50	186.50	0.0003384
	186.50	186.50	0.0003404
	186.50		0.0003278
	186.51		0.0002919
78	186.40	186.40	0.0002076
	186.40	186.40	0.0002007
	186.40	186.40	0.0002179
	186.40		0.0002215
	186.41		0.0002233
79	186.31	186.30	0.0003115
	186.31	186.30	0.0002933
	186.31	186.30	0.0003151
	186.30		0.0002933
	186.30		0.0003379

sample #	EEW from FT-NIR	EEW from titration	error
80	186.60	186.60	0.0004763
	186.61	186.60	0.0004544
	186.61	186.60	0.0004433
	186.60		0.0003988
	186.60		0.0003780
81	186.51	186.50	0.0004673
	186.50	186.50	0.0004562
	186.50	186.50	0.0004359
	186.50		0.0004680
	186.50		0.0004375
82	185.10	186.10	0.0003604
	185.11	186.10	0.0003704
	185.10	186.10	0.0003771
	185.10		0.0003543
	185.10		0.0003576
83	186.71	186.70	0.0005063
	186.70	186.70	0.0005076
	186.70	186.70	0.0005071
	186.70		0.0004960
	186.70		0.0004939
84	186.13	186.13	0.0004121
	186.13	186.13	0.0004253
	186.13	186.13	0.0003795
	186.13		0.0003611
	186.14		0.0003710
85	186.39	186.40	0.0002076
	186.39	186.42	0.0002007
	186.40	186.41	0.0002179
	186.41		0.0002215
	186.43		0.0002233
86	186.58	186.57	0.0003474
	186.55	186.56	0.0003384
	186.57	186.57	0.0003404
	186.57		0.0003278
	186.56		0.0002919
87	186.64	186.63	0.0003115
	186.64	186.63	0.0002933
	186.63	186.63	0.0003151
	186.63		0.0002933
	186.63		0.0003379

sample #	EEW from FT-NIR	EEW from titration	error
88	186.74	186.74	0.0005063
	186.75	186.73	0.0005076
	186.75	186.74	0.0005071
	186.73		0.0004960
	186.75		0.0004939
89	186.31	186.30	0.0005296
	186.30	186.30	0.0004258
	186.30	186.30	0.0003895
	186.30		0.0003961
	186.30		0.0004182
90	186.51	186.50	0.0003474
	186.50	186.50	0.0003384
	186.50	186.50	0.0003404
	186.50		0.0003278
	186.51		0.0002919
91	186.40	186.40	0.0002076
	186.40	186.40	0.0002007
	186.40	186.40	0.0002179
	186.40		0.0002215
	186.41		0.0002233
92	186.31	186.30	0.0003115
	186.31	186.30	0.0002933
	186.31	186.30	0.0003151
	186.30		0.0002933
	186.30		0.0003379
93	186.60	186.60	0.0004763
	186.61	186.60	0.0004544
	186.61	186.60	0.0004433
	186.60		0.0003988
	186.60		0.0003780
94	186.51	186.50	0.0004673
	186.50	186.50	0.0004562
	186.50	186.50	0.0004359
	186.50		0.0004680
	186.50		0.0004375
95	185.10	186.10	0.0003604
	185.11	186.10	0.0003704
	185.10	186.10	0.0003771
	185.10		0.0003543
	185.10		0.0003576

sample #	EEW from FT-NIR	EEW from titration	error
96	186.71	186.70	0.0005063
	186.70	186.70	0.0005076
	186.70	186.70	0.0005071
	186.70		0.0004960
	186.70		0.0004939
97	186.60	186.60	0.0002937
	186.60	186.60	0.0003408
	186.60	186.60	0.0002835
	186.60		0.0003094
	186.61		0.0003539
98	186.43	186.43	0.0003104
	186.43	186.43	0.0003418
	186.43	186.43	0.0003425
	186.43		0.0003368
	186.43		0.0003766
99	186.50	186.50	0.0004673
	186.51	186.51	0.0004562
	186.51	186.51	0.0004359
	186.51		0.0004680
	186.51		0.0004375
100	186.60	186.60	0.0002937
	186.60	186.60	0.0003408
	186.60	186.60	0.0002835
	186.60		0.0003094
	186.61		0.0003539
101	186.43	186.43	0.0003104
	186.43	186.43	0.0003418
	186.43	186.43	0.0003425
	186.43		0.0003368
	186.43		0.0003766
102	186.50	186.50	0.0004673
	186.51	186.51	0.0004562
	186.51	186.51	0.0004359
	186.51		0.0004680
	186.51		0.0004375
103	187.33	187.33	0.0003200
	187.34	187.34	0.0003284
	187.33	187.34	0.0003353
	187.35		0.0003333
	187.34		0.0003231

sample #	EEW from FT-NIR	EEW from titration	error
104	187.45	187.45	0.0003151
	187.45	187.45	0.0003244
	187.45	187.43	0.0003302
	187.46		0.0003444
	187.44		0.0003323
105	187.50	187.50	0.0003381
	187.51	187.51	0.0003346
	187.52	187.50	0.0003461
	187.51		0.0003285
	187.51		0.0003272
106	187.97	188.96	0.0003538
	187.96	188.96	0.0003317
	187.99	188.95	0.0003514
	187.96		0.0003521
	187.96		0.0003621
107	187.71	187.71	0.0003015
	187.72	187.71	0.0002959
	187.71	187.71	0.0002818
	187.72		0.0002725
	187.70		0.0002594
108	187.01	187.00	0.0002764
	187.07	187.00	0.0003000
	187.09	187.00	0.0002908
	187.05		0.0002871
	187.04		0.0003080
109	187.73	187.74	0.0002962
	187.74	187.73	0.0003256
	187.75	187.74	0.0003329
	187.74		0.0003434
	187.74		0.0003170
110	187.41	187.41	0.0003322
	187.41	187.40	0.0003400
	187.41	187.41	0.0003394
	187.41		0.0003593
	187.41		0.0003280
111	187208.00	187.20	0.0003653
	187.20	187.20	0.0004026
	187.20	187.20	0.0003924
	187.20		0.0003971
	187.21		0.0004112

sample #	EEW from FT-NIR	EEW from titration	error
112	187.50	187.50	0.0003473
	187.50	187.50	0.0003829
	187.50	187.50	0.0003018
	187.50		0.0003007
	187.49		0.0003110
113	187.33	187.33	0.0003200
	187.34	187.34	0.0003284
	187.33	187.34	0.0003353
	187.35		0.0003333
	187.34		0.0003231
114	187.45	187.45	0.0003151
	187.45	187.45	0.0003244
	187.45	187.43	0.0003302
	187.46		0.0003444
	187.44		0.0003323
115	187.50	187.50	0.0003381
	187.51	187.51	0.0003346
	187.52	187.50	0.0003461
	187.51		0.0003285
	187.51		0.0003272
116	187.97	188.96	0.0003538
	187.96	188.96	0.0003317
	187.99	188.95	0.0003514
	187.96		0.0003521
	187.96		0.0003621
117	187.71	187.71	0.0003015
	187.72	187.71	0.0002959
	187.71	187.71	0.0002818
	187.72		0.0002725
	187.70		0.0002594
118	187.01	187.00	0.0002764
	187.07	187.00	0.0003000
	187.09	187.00	0.0002908
	187.05		0.0002871
	187.04		0.0003080
119	187.73	187.74	0.0002962
	187.74	187.73	0.0003256
	187.75	187.74	0.0003329
	187.74		0.0003434
	187.74		0.0003170

sample #	EEW from FT-NIR	EEW from titration	error
120	187.41	187.41	0.0003322
	187.41	187.40	0.0003400
	187.41	187.41	0.0003394
	187.41		0.0003593
	187.41		0.0003280
121	187.21	187.20	0.0003653
	187.20	187.20	0.0004026
	187.20	187.20	0.0003924
	187.20		0.0003971
	187.21		0.0004112
122	187.50	187.50	0.0003473
	187.50	187.50	0.0003829
	187.50	187.50	0.0003018
	187.50		0.0003007
	187.49		0.0003110
123	187.89	187.90	0.0003649
	187.90	187.90	0.0003677
	187.89	187.90	0.0003610
	187.90		0.0003593
	187.90		0.0003534
124	187.95	187.95	0.0002754
	187.95	187.95	0.0002847
	187.94	187.95	0.0002716
	187.95		0.0002552
	187.95		0.0002923
125	187.93	187.93	0.0004265
	187.93	187.93	0.0004096
	187.93	187.93	0.0004178
	187.93		0.0004166
	187.93		0.0003993
126	187.95	187.97	0.0003788
	187.97	187.97	0.0003762
	187.98	187.96	0.0003644
	187.97		0.0003609
	187.96		0.0003396
127	187.05	187.04	0.0003592
	187.04	187.04	0.0003541
	187.04	187.04	0.0003499
	187.04		0.0003507
	187.04		0.0003768

sample #	EEW from FT-NIR	EEW from titration	error
128	187.89	187.90	0.0003649
	187.90	187.90	0.0003677
	187.89	187.90	0.0003610
	187.90		0.0003593
	187.90		0.0003534
129	187.95	187.95	0.0002754
	187.95	187.95	0.0002847
	187.94	187.95	0.0002716
	187.95		0.0002552
	187.95		0.0002923
130	187.93	187.93	0.0004265
	187.93	187.93	0.0004096
	187.93	187.93	0.0004178
	187.93		0.0004166
	187.93		0.0003993
131	187.95	187.97	0.0003788
	187.97	187.97	0.0003762
	187.98	187.96	0.0003644
	186.97		0.0003609
	187.96		0.0003396
132	187.05	187.04	0.0003592
	187.04	187.04	0.0003541
	187.04	187.04	0.0003499
	187.04		0.0003507
	187.04		0.0003768
133	188.39	188.38	0.0003242
	188.39	188.39	0.0003498
	188.40	188.38	0.0002959
	188.39		0.0003171
	188.38		0.0002960
134	188.43	188.43	0.0002924
	188.43	188.43	0.0003220
	188.43	188.42	0.0003055
	188.43		0.0002903
	188.43		0.0002876
135	188.32	188.33	0.0003133
	188.35	188.33	0.0003130
	188.33	188.34	0.0003192
	188.33		0.0003297
	188.34		0.0003070

sample #	EEW from FT-NIR	EEW from titration	error
136	188.16	188.15	0.0003117
	188.16	188.15	0.0002793
	188.16	188.17	0.0002941
	188.14		0.0004610
	188.15		0.0004053
137	188.39	188.38	0.0003242
	188.39	188.39	0.0003498
	188.40	188.38	0.0002959
	188.39		0.0003171
	188.38		0.0002960
138	188.43	188.43	0.0002924
	188.43	188.43	0.0003220
	188.43	188.42	0.0003055
	188.43		0.0002903
	188.43		0.0002876
139	188.32	188.33	0.0003133
	188.35	188.33	0.0003130
	188.33	188.34	0.0003192
	188.33		0.0003297
	188.34		0.0003070
140	188.16	188.15	0.0003117
	188.16	188.15	0.0002793
	188.16	188.17	0.0002941
	188.14		0.0004610
	188.15		0.0004053
141	189.76	189.75	0.0003133
	189.75	189.76	0.0003003
	189.75	189.75	0.0003143
	189.76		0.0003155
	189.75		0.0003121
142	188.22	188.21	0.0003130
	188.22	188.22	0.0003120
	188.21	188.21	0.0002782
	188.22		0.0002723
	188.23		0.0003157
143	188.43	188.43	0.0002924
	188.43	188.43	0.0003220
	188.43	188.42	0.0003055
	188.42		0.0002903
	188.43		0.0002876

sample #	EEW from FT-NIR	EEW from titration	error
144	189.26	189.25	0.0003029
	189.25	189.26	0.0003056
	189.24	189.25	0.0003037
	189.26		0.0003163
	189.26		0.0003564
145	189.76	189.75	0.0003133
	189.75	189.76	0.0003003
	189.75	189.75	0.0003143
	189.76		0.0003155
	189.75		0.0003121
146	191.55	191.55	0.0002029
	191.56	191.56	0.0002056
	191.55	191.55	0.0002037
	191.56		0.0002063
	191.55		0.0002574
147	194.22	194.21	0.0003029
	194.21	194.22	0.0003056
	194.22	194.22	0.0003037
	194.22		0.0003163
	194.21		0.0003564
148	191.58	191.58	0.0002029
	191.58	191.58	0.0002056
	191.58	191.58	0.0002037
	191.58		0.0002063
	191.58		0.0002574
149	194.12	194.11	0.0003029
	194.12	194.12	0.0003056
	194.11	194.11	0.0003037
	194.11		0.0003163
	194.11		0.0003564
150	194.52	194.53	0.0003029
	194.53	194.52	0.0003056
	194.52	194.51	0.0003037
	194.52		0.0003163
	194.52		0.0003564

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