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SOLVENT EXTRACTION AT HIGH TEMPERATURE FOR DETERMINATION OF PHTHALATE ESTERS IN CELLULOSE LACQUERS

Miss Choltira Mahayossanun

A Thesis Submitted in Partial Fulfillment of the Requirements
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By	Miss Choltira Mahayossanun
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Thesis Advisor	Luxsana Dubas, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

S. Hannongbua
....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat)

THESIS COMMITTEE

....Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

....Thesis Advisor
(Luxsana Dubas, Ph.D.)

....Examiner
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)

....External Examiner
(Apinya Navakhun, D.Sc.)

ชลธิรา มหายศนันท์: การสกัดด้วยตัวทำละลายที่อุณหภูมิสูงสำหรับการตรวจวัดแทเลตเอสเทอร์ในเซลลูโลสแลกเกอร์ (SOLVENT EXTRACTION AT HIGH TEMPERATURE FOR DETERMINATION OF PHTHALATE ESTERS IN CELLULOSE LACQUERS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : อ.ดร. ลักษณา ดูบาส, 47หน้า.

เซลลูโลสแลกเกอร์เป็นสีชนิดหนึ่งที่นิยมใช้ในงานเคลือบผิวเฟอร์นิเจอร์และอุตสาหกรรมรถยนต์ แทเลตเอสเทอร์ใช้เป็นสารเสริมสภาพพลาสติกในสีชนิดนี้เพื่อปรับปรุงสมบัติด้านความเปราะของฟิล์ม อย่างไรก็ตามสารชนิดนี้ถูกจัดเป็นสารก่อมะเร็ง วิธีการรีฟลักซ์เป็นวิธีการเตรียมตัวอย่างที่นิยมใช้ในการตรวจวัดแทเลตเอสเทอร์ในชิ้นงานพลาสติก ซึ่งเทคนิคนี้ต้องใช้ปริมาณของตัวอย่างและตัวทำละลายในปริมาณมาก ในการศึกษาครั้งนี้ต้องการศึกษาวิธีการเตรียมตัวอย่างที่ใช้เวลาและตัวทำละลายในปริมาณที่น้อย การสกัดด้วยตัวทำละลายที่อุณหภูมิสูงได้ถูกนำมาใช้ในการสกัดแทเลตเอสเทอร์ในเซลลูโลสแลกเกอร์แล้วทำการตรวจวัดโดยแก๊สโครมาโทกราฟี แทเลตเอสเทอร์ที่ใช้ในการศึกษานี้ได้แก่ ไดบิวทิลแทเลต, ไดทูเอทิลเฮกซิลแทเลต และ ไดไอโซเดกซิลแทเลต ตัวทำละลายที่มีขั้วต่ำได้แก่ นอร์มอลเฮกเซน, โทลูอีน และ ไดคลอโรมีเทน ได้ถูกนำมาศึกษาถึงผลที่มีต่อประสิทธิภาพการสกัด นอกจากนี้อัตราส่วนระหว่างตัวอย่างต่อตัวทำละลายที่ใช้สกัด, อัตราการกวน เวลาและอุณหภูมิที่ใช้ในการสกัดก็ได้ถูกนำมาศึกษาเช่นเดียวกัน ตัวทำละลาย นอร์มอลเฮกเซน, อัตราส่วนระหว่างตัวอย่างต่อตัวทำละลายที่ใช้ในการสกัดเป็น 1:1, เวลาที่ใช้ในการสกัดเป็น 20 นาที, อุณหภูมิที่ใช้ในการสกัดเป็น 40 องศาเซลเซียส, อัตราการกวนเป็น 45 รอบต่อนาที คือสภาวะที่เหมาะสมสำหรับการศึกษานี้ เปอร์เซ็นต์การได้กลับคืนของไดนอร์มัลบิวทิลแทเลต, ไดทูเอทิลเฮกซิลแทเลต และ ไดไอโซเดกซิลแทเลตที่อุณหภูมิ 40 องศาเซลเซียส จะให้อยู่ในช่วง 68.68-90.34 เปอร์เซ็นต์ซึ่งสูงกว่าเมื่อเทียบกับอุณหภูมิของการสกัดที่ 25 องศาเซลเซียส ขีดความต่ำสุดของการวิเคราะห์เชิงปริมาณของ ไดนอร์มัลบิวทิลแทเลต, ไดทูเอทิลเฮกซิลแทเลต และ ไดไอโซเดกซิลแทเลต เป็น 4.30, 1.1 และ 0.70 กรัมต่อลิตร และส่วนเบี่ยงเบนมาตรฐานสัมพัทธ์เป็น 12.65, 15.08 และ 13.97 เปอร์เซ็นต์ ตามลำดับ วิธีที่ได้ศึกษานี้สามารถนำไปประยุกต์ใช้หาปริมาณของแทเลตเอสเทอร์ในเซลลูโลสแลกเกอร์ที่มีจำหน่ายตามท้องตลาดได้

สาขาวิชา ...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.... ลายมือชื่อนิสิต Choltira
ปีการศึกษา...2553................ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์.......

#5073405023: MAJOR PETROCHEMISRTRY AND POLYMER SCIENCE
KEYWORDS : SOLVENT EXTRACTION AT HIGH TEMPERATURE / PHTHALATE ESTERS / CELLULOSE LACQUERS

CHOLTIRA MAHAYOSSANUN: SOLVENT EXTRACTION AT HIGH TEMPERATURE FOR DETERMINATION OF PHTHALATE ESTERS IN CELLULOSE LACQUERS. ADVISOR : LUXSANA DUBAS, Ph.D., 47pp.

Cellulose lacquers is one of the paint used in surface coating furniture and automobile. Phthalate esters are used as the plasticizer in this paint for improve brittle property of film. However, they were suspected to have carcinogenic and estrogenic properties. Reflux is the most commonly used as sample preparation technique for phthalate esters determination in plastic samples. It usually required high amount of sample and solvent. In this study, we aimed to study a sample preparation technique, which required less solvent and extraction time. The solvent extraction at high temperature was investigated for the extraction of phthalate esters from cellulose lacquers paints and determined by gas chromatography. Three phthalate esters: dibutyl phthalate (DBP), di(2-ethylhexyl phthalate) (DEHP) and diisodecyl phthalate (DIDP) were used as solute probes. The effects of n-hexane, toluene and dichloromethane, which are low polarity solvent, on the extraction performance were studied. Moreover, the ratio between sample and extracting solvent, speed of mechanical stirrer, extraction time and temperature on the extraction performance were studied. n-Hexane as extracting solvent, the ratio of 1:1 between sample to n-hexane with the extraction time of 20 min at 40°C of extraction temperature at stirring rate 45 rpm were found to be the suitable condition. The recoveries of DBP, DEHP and DIDP at 40°C were in range of 68.68-90.34% which are higher comparing to the extraction temperature of 25°C. The method of quantification of DBP, DEHP and DIDP were 4.30, 1.10 and 0.70 g/L and relative standard deviations were 12.64, 15.08 and 13.97 %, respectively. This studied method was also applied to analyze phthalate esters content in commercialized cellulose lacquer.

Field of Study : Petrochemistry and Polymer Science Student's Signature ....
Academic Year : 2010 Advisor's Signature ....

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LIST OF ABBREVIATIONS AND SYMBOLS

PEs	Phthalate esters
DMP	Dimethyl Phthalate
DEP	Diethyl Phthalate
DBP	Dibutyl Phthalate
DnOP	Di-n-octyl Phthalate
DEHP	Di(2-ethylhexyl) Phthalate
DNP	Dinonyl Phtthalate
DAP	Diamyl Phthalate
DDP	Didecyl Phthalate
DIDP	Diisodecyl Phthalate
DPP	Dipropyl Phthalate
DIBP	Diisobutyl Phthalate
DCHP	Dicyclohexyl Phthalate
BBP	Benzyl Butyl Phthalate
DMA	Dimethyl Adipate
DEA	Diethyl Adipate
DBA	Dibutyl Adipate
DIBA	Diisobutyl Adipate
DEHA	Di(2-ethylhexyl) Adipate
DIDA	Diisodecyl Adipate
GC	Gas chromatography
RPM	Round per minute
RSD	Relative standard deviation
IS	Internal standard

CHAPTER I

INTRODUCTION

1.1 Statement of the problems

Phthalate esters (PEs) are widely used as plasticizers and additives in many daily used products such as plastics, pesticides, paints and cosmetics etc [1]. Leaching and migration of plasticizer molecules from polymers is a critical issue that determines a material’s usable lifetime. Plasticized polymers are often in contact with stationary or flowing fluids. In course of time, plasticizers tend to diffuse out. The leaching out rate is usually a function of temperature and initial plasticizer concentration while the rate of migration is a product of solubility and diffusion coefficients. In addition, the plasticizers coming out of the polymers often pose health and environmental risk [2]. Certain PEs as well as their metabolites and degradation products can cause effects on human health in particular on liver, kidney and testicles [3]. Due to their potential risks for human health and the environmental, several of them have been included in the priority list of pollutants of different national and supranational organizations [3].

Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP) and dioctyl phthalate (DOP) are listed by US Environmental Protection Agency (USEPA) as toxic substances [4].

Cellulose lacquers is one of the paint used in painting furniture and automobile composing of acrylic or alkyd resin, nitrocellulose, plasticizer, pigment and solvent. Phthalate esters are used as the plasticizer in cellulose lacquers. Therefore the determination of PEs in cellulose lacquers is needed. There are several methods were proposed for the determination of PEs by gas chromatography (GC) and high performance liquid chromatography (HPLC) [5]. The separation of PEs from cellulose lacquer is usually performed by liquid-liquid extraction (LLE), especially soxhlet [6]. However these methods require more time and large amount of toxic solvent. Other techniques are ultrasonic extraction, microwave-assisted extraction, supercritical fluid extraction, pyrolysis [7-10]. However these techniques require special equipment. Solid-phase extraction (SPE) is considered expensive and time consuming [11].

Generally, the solvent extraction is used as extracting solvent to extract the interested compound from sample to extracting solvent. To perform the solvent extraction on the cellulose lacquers, which is in organic solvent as well, the choice of organic extracting solvent was crucial. Moreover, cellulose lacquers are viscous liquid. The complete contact between the paint and solvent must be therefore concerned in order to achieve successful extraction of the plasticizer.

In this study, the effects of high temperature and agitation rate on the solvent extraction were investigated to enhance the extracting performance in both solvent consumption and extraction speed aspects. The increases in extraction temperature and applying the agitation can enhance solubility, diffusion rates and mass transfer [12].

1.2 Objective of this work

The objective of this study is to develop a simple, convenient, inexpensive and environmental friendly method for determination of PEs in cellulose lacquer using high temperature and agitation in the solvent extraction process.

1.3 Scope of this work

The scope of this work is to investigate the effect of high temperature and agitation on the solvent extraction in order to determine the phthalate esters in cellulose lacquers. Furthermore, a conventional reflux method was also carried out for comparison purpose.

1.4 The benefit of this work

To study an extraction method for the determination of phthalate esters in cellulose lacquer that was easy, quick and energy save by using high temperature solvent extraction and agitation by stirring.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Background of Plasticizer [2]

The primary role of plasticizers is to improve the flexibility and processability of polymers by lowering the second order transition temperature. Plasticizers can be either internal or external, where external plasticizer molecules are not attached to polymer chains by primary bonds and can therefore lost by evaporation, migration or extraction. On the other hand, internal plasticizers are inherently part of the plastic and remain part of the product.

2.2 Classification of plasticizer [13]

Plasticizers can be classified based on the chemical formula:

- Phthalates such as dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP)
- Aliphatic/aromatic monocarboxylic acid esters such as triethylene glycol di(2-ethylbutyrate), dithylelenglycol benzotaes
- Aliphatic dicarboxylic acid esters such as dibutyl adipate, bis (2-ethylhexyl) azelate
- Phosphates such as triphenyl phosphate, tris (2-ethylhexyl) phosphate
- Polyester of polymeric plasticizers such as poly(ethylene glycol), poly (1,3 butylene glycol adipate)
- Special plasticizers such as dicyclohexyl phthalate, diphenyl phthalate
- Extenders (hydrocarbons, chlorinated hydrocarbon) such as 1-hexadecene, polychlorinated biphenyls

Phthalates are the most common, especially di(2-ethylhexyl) and diisooctyl phthalate and, recently diisononyl and diisodecyl phthalate. Aliphatic dicarboxylic acid esters (adipates, sebacates and azelainates) are used to impart good low-temperature flexibility. Physical property of phthalate esters is shown in Table 2.1.

Table 2.1 Physical property of some phthalate esters [14-15].

PEs	Molecular weight	Boiling point (°C)	$(K_{ow})^a$	Water solubility (mg/L at 20°C)
DBP	278.34	340	4.57	10
DEHP	391.0	370	7.54	0.0026
DOTP	390.56	400	9.98	Insoluble
DIDP	446.67	>400	8.8	0.0002

^{a}Octanol/water partition constant.

2.3 Plasticizers for the Nitrocellulose lacquer [16]

Nitrocellulose is the commercial name for the product resulting from the reaction of cellulose with nitric acid. Cellulose can be considered as a trihydric alcohol, the structural formula for which is shown in Figure 2.1. Cellulose is thus composed of a large number of anhydroglucose units in the molecule is several thousand for most naïve celluloses; it ranges from 500 to 2500 for chemically purified celluloses. High nitrogen (11.8-12.2 per cent) nitrocellulose is used chiefly in the manufacture of wood and metal finishes. The medium nitrogen (11.3-11.7 per cent) and low nitrogen (10.9-11.2 per cent) types, because of their thermoplasticity at lower temperature, are often chosen for special coatings such as heat-sealing lacquers for paper and cellophane. The low nitrogen type requires less complex solvent combinations and is useful particularly where solvent containing a substantial amount of low molecular weight alcohol is helpful controlling odor of al lacquer or in assuring compatibility of lacquer ingredients.

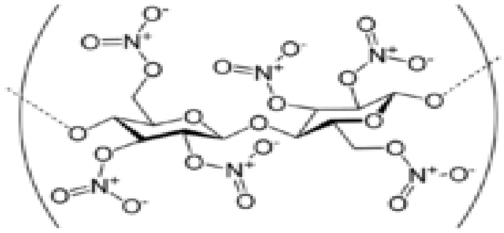


Figure 2.1 Structure of Nitrocellulose [17]

Most of the common plasticizer types are compatible with nitrocellulose to some extent depending on whether they are solvents or nonsolvents for nitrocellulose. Nitrocellulose can dissolve in ester, ketone, alcohol and glycolether.

2.4 Acrylic resin for the Nitrocellulose lacquer [18]

Acrylic resin is synthesis polymer or copolymer that synthesized by addition polymerization of acrylic acid, derivative of acrylic acid or ester of acrylic acid. It is added to nitrocellulose lacquer for increase film properties are surface tension, hardness, gloss, water resistance and chemical resistance. It is usually dissolve in organic solvent such as aromatic hydrocarbon, ester and ketone and alcohol.

2.5 Theory of solvent extraction [19]

Solvent extraction is a method of separation based on the transfer of a solute from one solvent into another, essentially immiscible solvent when two solvents are brought into contact. The advantage of this technique is quick, easy, convenience and no problem about coprecipitation. The extraction process occurs in three parts, first is distribution of the extractable species second is chemical interaction in aqueous phase and the last is chemical interaction in organic phase. There are three parameters that determine the extraction efficiency. The first is distribution ratio, this parameter is generally used as a measure of the extent of extraction that equal to the ratio of concentration of solute in organic phase divide by its concentration in aqueous phase. The second parameter is separation factor, it is measure the ability of the system to separate two solutes it defines as one distribution ratio divide by another and the last is fraction extracted, this parameter demonstrate the possibility to increase the extent of extraction.

2.6 High temperature solvent extraction [12]

Temperature raises increase solubility, diffusion rates and mass transfer, whereas viscosity and surface tension of the solvents are less than at room temperature. Furthermore at elevate temperature, the activation energy of desorption is more readily overcome, and the kinetics of desorption and solubilization are also more favorable.

2.7 Gas chromatography-flame ionization detector (GC-FID) [20-21]

Chromatography is a physical method for separating components in a mixture. The basis of the method lies within the separation column, which normally is a small-diameter tubing packed with a stationary bed of large surface area. A mobile phase percolates through the stationary bed. The name “gas chromatography” denotes that the moving phase is a gas. The basic processes responsible for separations by gas-solid and gas-liquid chromatography are adsorption and partition, respectively. In the elution method of gas chromatography, a stream of carrier gas flows through the column. Separation of components that comprise the sample results from a difference in the multiple forces by which the column materials tend to retain each of the components. Whether the nature of retention is adsorption, solubility, chemical bonding, polarity, or molecular filtration, the column retains some components longer than others. When in the gas phase the components are moved toward the column outlet, but they are selectively retarded by the stationary phase. Consequently, all components pass through the column at varying speeds and emerge in the inverse order of their retention by the column materials. A detector senses the effluents from the column and provides a record of the chromatography in the form of a chromatogram. The detector signals are proportionate to the quantity of each solute (analyte) making possible quantitative analysis.

The FID is the most widely used GC detector, and is an example of the ionization detectors invented specifically for GC. The column effluent is burned in a small oxy-hydrogen flame producing some ions in the process. These ions are collected and form a small current that becomes the signal. When no sample is being burned, there should be little ionization, the small current (10^{-14} a) arising from impurities in the hydrogen and air supplies. Thus, the FID is a specific property-type detector with characteristic high sensitivity.

The column effluent is mixed with hydrogen and led to small burner tip that is surrounded by a high flow of air to support combustion. An igniter is provided for remote lighting of the flame. The collector electrode is biased about +300V relative to the flame tip and the collected current is amplified by a high impedance circuit. Since water is produced in the combustion process, the detector must be heated to at least 125^0C to prevent condensation of water and high boiling samples. Most FIDs are run at 250^0C or hotter.

The FID responds to all organic compounds that burn in the oxy-hydrogen flame. The signal is approximately proportional to the carbon content, giving rise to the so-called equal per carbon rule.

2.8 Parameters in Gas chromatography [21]

Retention time

This parameter is expressed as the interval of time between the instant of injection and the detection of component. It vary with the identity of the component such as boiling point, polarity so it is utilized for qualitative and quantitative analysis.

Resolution

This parameter is described the separation of two solutes depends on their retention behavior. The degree to which two chromatographic peaks are separated can be characterized as a function of the column. It can be expressed according to equation 2.1.

$$R_{AB} = 2[(d_R(B)-d_R(A)/w(B)+w\ (A)] \qquad 2.1$$

Where R_{AB} is the resolution, $d_R(A)$ and $d_R(B)$ are the retention distances (time) of each eluted component A and B, w(A) and w(B) are the respective widths of each peak at its base.

2.9 Literature reviews

Many determination methods of phthalate esters in water samples by using liquid-phase microextraction (LPME) were developed. This technique provides analyte extraction in a few microliters of organic solvent. It is inexpensive and there is considerable freedom in selecting appropriate solvents for extraction of different analyte. Since very little solvent is used, there is minimal exposure to toxic organic solvent for the operator [22]. LPME can be preformed by several modes such as single drop microextraction (SDME), where the extractant phase is a microdrop of a water-immisible solvent suspended on the tip of a conventional syringe and immersed in sample solution [22]. Dymanic LPME is one mode that used microsyringe is employed as a microseparatory funnel for extraction, which allow the mass transfer of analyte between the solvent microfilm formed on the inner surface of the microsyringe and the sample solution by the repeated movement of the plunger [22]. Hollow fibre LPME this mode using porous hollow-fibre that connect at one of its end of the needle tip of a microsyringe while the other end is left suspended in the sample solution [23]. From three modes that had been mentioned, LPME not suitable for extraction of PEs from nitrocellulose lacquer because it is paint and other component such as resin, pigment can diffuse from sample solution into extractant phase. Solid-phase extraction (SPE) was also used to determine the phthalate esters in water samples [24-25]. SPE uses the affinity of solutes dissolved or suspended in a liquid (known as the mobile phase) for a solid through which the sample is passed (known as the stationary phase) to separate a mixture into desired and undesired components. This technique is considered expensive and time-consuming [11].

Ultrasonic extraction has been developed by Xiujuan Li et al. for determination of phthalate esters (DMP, DEP, DBP, DAP, DnOP, DEHP, DNP and DDP) in plastic such as blood bags, transfusion tubing, food packaging and mineral water [25]. By using methanol as extraction solvent and combine with solid-phase microextraction (SPME) with calix[4]arene/hydroxyl-terminated silicone as fibre. Limit of detection (LOD) of this research was in range 0.006-0.084 µg/L, relative standard deviation was less than 10% and recoveries were in range 95.5-101.4%. In 2005, H.Y. Shen et al has been developed ultrasonic extraction combine with solid-phase extraction for determination of phthalate esters (DEP, DPP, DIBP, DBP, BBP, DCHP, DEHP and DOP) in plastic products for food [7]. These samples are sonicated in n-hexane, treatment by nitrogen and clean-up by solid phase extraction (SPE) with LC-C18 as cartridge this research show complicate of working and limit of detection (LOD) of this research was 10 µg/Kg, recoveries were 82-106% and relative standard deviation were in range 3.8-102%. This technique provides more efficient contact between the solid and solvent than shake-flask method, usually resulting in a greater recovery of analyte.

Microwave-assisted extraction is the technique that use microwave radiation for treatment of solid and liquid samples. This technique has been developed to determination of adipate plasticizers (DMA, DEA, DBA, DIBA, DEHA and DIDA) in plastics PVC [8] with methanol as extraction solvent, 10 minutes extraction and 120ºC of extraction temperature. This research provided recoveries in range 75-98% and relative standard deviation were in range 2-7%.

Supercritical fluid extraction (SFE) has become an important and useful technique to prepare samples before analysis. The use of supercritical CO_2 yields a rapid and quantitative it also has been developed for determination of phthalate esters (DBP, DOP, DIHP, DINP and DIDP) in PVC products [9] at extraction temperature was in range 90-100ºC, pressure 34 MPa, 8 minutes extraction time and cyclohexane as collection fluid. This research provided recoveries in range 90-100%.

Ultrasonic extraction, microwave-assisted extraction and supercritical fluid extraction required special equipment and expensive.

Soxhlet was also used to analysis the plasticizer mixtures in various plastic sample including vinyl chloride plastics [6] in PVC plastics such as toys [26] and food packaging [27]. However, this method consumed both time and the large amount of toxic solvents such as chloroform and carbon tetrachloride.

Due to the viscosity of the sample, many reported sample preparation methods such as SPE and LPME is not suitable. In this study, the simple solvent extraction, which do not require any special instrument, was employed as the sample preparation method for nitrocellulose lacquer. Therefore, the aim of this study is to increase the extraction efficiency of solvent extraction in aspect of both the shorter extraction time and less amount of organic solvent by using higher temperature solvent extraction and applying the agitation.

CHAPTER III

EXPERIMENTAL

3.1 Instrument and apparatus

3.1.1 Gas chromatography GC 2010 with flame ionization detector (GC-FID) system (Shimadzu, Japan)

3.1.2 Auto injector AOC-20i (Shimadzu, Japan)

3.1.3 Capillary column Rtx-5 (5% diphenyl-95% dimethyl polysiloxane) 30m×0.53 mm i.d., 0.25µm film thickness (Restek, USA)

3.1.4 Autosampler syringe 10µL (S.G.E., Japan)

3.1.5 Vial 1.5 mL with cap and septum (Shimadzu, Japan)

3.1.6 Mechanical stirrer Model: IKA RM 20 digital (Becthai, Thailand)

3.1.7 Water bath Model: WB 14 (NC Sciencetech, Thailand)

3.1.8 Electronic balance Model: AB 204 (Mettler, Switzerland)

3.1.9 Centrifuge Model: EBA 20 (Hettich, Germany)

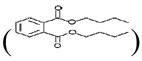
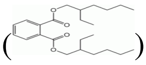
3.1.10 Stop watch (Casio, Japan)

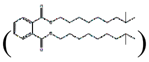
3.1.11 Round bottom flask 50 mL

3.1.12 Volumetric flask 5 ml (Witeg, Germany)

3.1.13 Transfer pipette 2 ml and measuring pipette 5 ml (HBG, Germany)

3.2 Chemical reagents

3.2.1 Dibutyl phthalate ()and di(2-ethylhexyl) phthalate ()(purity 99.9%, I.C.P. Chemical, Thailand)

3.2.2 Diisodecyl phthalate () and dioctyl terephthalate () (Purity 99.9%, Kodaflex, USA)

3.2.3 n-Hexane (ACS reagent grade, RCI Labscan, Thailand)

3.2.4 Toluene (ACS reagent grade, Merck, USA)

3.2.5 Dichloromethane (ACS reagent grade, Mallinckrodt, France)

3.2.6 Acrylic resin (Siam Chemical, Thailand)

3.2.7 Titanium Dioxide (Special Chem, Thailand)

3.2.8 Nitrocellulose (28% by W, Sangsahamit, Thailand)

3.2.9 Helium gas (purity 99.999%, TIG, Samutprakarn, Thailand)

3.2.10 Hydrogen gas (purity 99.99%, TIG, Samutprakarn, Thailand)

3.2.11 Air zero (purity 99.99%, TIG, Samutprakarn, Thailand)

3.3 Preparation of internal standard solution

The 50 g/L of dioctyl tetephthalate (DOTP) as internal standard was prepared using the studied solvents.

3.4 Preparation of spiked cellulose lacquer sample.

Cellulose lacquer was performed following formulation of paste (resin+pigment)/nitrocellulose/phthalate ester of 70/20/10 (% w of resin). Mixing the acrylic resin with titanium dioxide then, solvent was added for adjust the viscosity. After that mixed until it is homogeneous. The nitrocellulose was added 26.06% w. Finally, the DBP, DEHP and DIDP were added into this synthesis paint sample with 3.67%, 3.67% and 2.09% w of paint, respectively.

3.5 Gas chromatographic conditions

Analysis of DBP, DEHP and DIDP was performed by using GC-FID. The GC condition is shown in Table 3.1

Table 3.1 The gas chromatographic conditions for analysis of DBP, DEHP and DIDP

GC Parameters	GC condition
Carrier gas, linear velocity	Helium, 27.8 cm/s
Column	Rtx-5 (5% diphenyl-95% dimethyl polysiloxane) 30m×0.53 mm i.d., 0.25μm film thickness
Injector	Split mode; split ratio 1:10
Injector temperature	300^{0}C
Temperature program	150^{0}C for 5 min, ramped up to 320^{0}C at rate 10^{0}C/min and held for 5 min
Detector	FID
Detector temperature	320^{0}C
Make up gas	Helium, 3 mL/min

3.6 Extraction procedure of PEs from cellulose lacquer

The objective of this study was to study the parameters that can enhance the extraction efficiency of solvent extraction by using smaller amount of extracting solvent, higher extraction temperature and agitator for determination of phthalate esters in cellulose lacquer. The extraction procedure of PEs can be described as follow:

In this study, the experiment was performed by weighing 3.0000±0.0005g of spiked sample into the 50 mL round bottom flask. Then, the 3.00 mL of studied solvent was added. The mixture of this solution (1:1 ratio by weight/volume) was stirred by mechanical stirrer at 55 rpm for 10 minutes at 25^{o}C for all experiments in the optimization study section unless stated. The experimental set up is shown in Figure 3.1. The joint was sealed with parafilm and aluminium foil to prevent the solvent evaporation and the extraction temperatures were controlled by water bath. After the extraction, the solution was centrifuged and the liquid phase was transferred into 5 mL-volumetric flask. The 2 mL of the internal standard, DOTP (50 g/L) was added using pipette. Then GC analysis was performed by transferring solution into GC vial and 1.0 µL of solution was injected to GC.

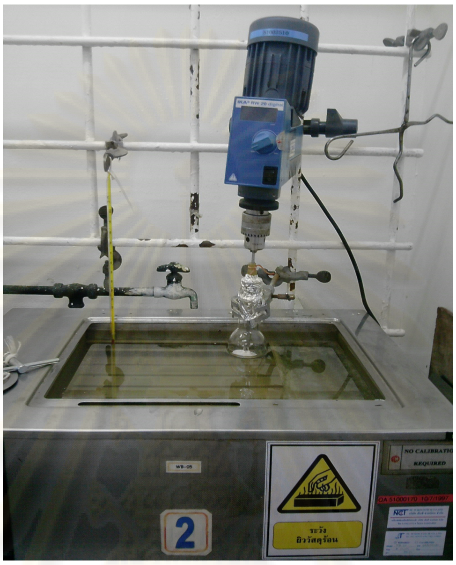


Figure 3.1 Experiment set up of solvent extraction at high temperature of phthalate esters from cellulose lacquer.

3.7 The solvent extraction optimization for PEs extraction

3.7.1 Study of the extracting solvent

For solvent extraction, the choice of extracting solvent is quite crucial. In this study, we chose the organic solvent based on several considerations. First, cellulose lacquers were dissolved in organic solvents. Second, PEs are low polarity and usually dissolve in organic solvents. Therefore, three organic solvents including n-hexane, toluene, dichloromethane were used in this study. The boiling point of three solvent was shown in Table 3.3. The extraction procedure was performed that described in Section 3.6.

Table 3.2 The ratio of mixed solvent.

Studied extracting solvent	Ratio (% v/v)
n-Hexane/toluene	0/100
	30/70
	40/60
	50/50
	60/40
	70/30
	100/0
n-Hexane/dichloromethane	50/50
	60/40
	70/30
	0/100
Toluene/dichloromethane	30/70
	40/60
	50/50

After extraction procedure, the physical appearance of cellulose lacquer sample was observed.

Table 3.3 Boiling point of studied solvent

Studied solvent	Boiling point (ºC)
n-Hexane	70
Toluene	111
Dichloromethane	40

3.7.2 Study of the effect of extraction time on the extraction efficiency

Extraction time is one of the parameters should be optimized to obtain the optimal extraction efficiency. Extracting times were studied at 5, 10, 15, 20, 40, 60 and 90 minutes and the extraction procedure was performed as described in Section 3.6 using the suitable organic solvent obtained from the section 3.7.1.

3.7.3 Study of the effect of extraction temperature on the extraction efficiency

Temperature is one parameter that important in this technique so in this parameter the studied extraction temperatures were 25ºC, 30ºC, 40ºC, 50ºC and 60ºC and extraction procedure was performed as described in Section 3.6.

3.7.4 Study of the effect of ratio of sample to extraction solvent (w/v) on the extraction efficiency

The ratio between sample to extraction solvent is one parameter that affected the extraction efficiency. The extraction was performed by varying ratios between sample to extracting solvent as followed: 1:1 (sample 1±0.0005g and extracting solvent 1 mL); 1:2 (sample 1g±0.0005g and extracting solvent 2 mL) and 2:1 (sample 2g±0.0005g and extracting solvent 1 mL). The extraction was stirred at 55 rpm for 10 minutes at 25ºC. After extraction the solution was performed that described in Section 3.6.

3.7.5 Study the effect of agitation on the extraction efficiency

The agitations were applied in the study using mechanical stirrer. All extraction were performed as described in the Section 3.6. The stirring rates were controlled at 0 (no stir), 45, 55, 65, 110 and 220 rpm.

3.7.6 Study the lost of extraction solvent from high temperature solvent extraction

Because the lost of extracting solvent during the extraction process under high temperature was concerned, the study to investigate the solvent lost was conducted. In this study, the samples prepared as described in Section 3.6 were divided into 2 groups. For the first group, the extraction was conducted as described before without applying the agitation. The other set, the round bottom flasks were connected to the condenser. The extraction process was performed at 40ºC, 50ºC and 60ºC for 10 minutes. After the extraction, the volumes of extracting solvent of both groups were measured. The lost of extracting solvent was calculated based on equation the lost volume divide initial volume and multiply with 100.

3.8 Reflux method for extraction of PEs from cellulose lacquer

The aim of this section is to compare the extraction efficiency of this study with conventional method that performed at high temperature. In this study, the 3.0000±0.0005g of spiked sample was weighed. Then, 3 mL of the suitable extracting solvent that obtained from the study in the Section 3.7.1 was added. The temperature was set at 80ºC and refluxed for 20 and 60 minutes. Then, the extract was performed as described in Section 3.6. Comparison the result that obtained from Section 3.7.2 at 20 and 60 minutes.

3.9 Method validation

From the result in Section 3.7, the optimum extraction conditions were obtained. In this section, the developed extraction and analysis method was validated.

3.9.1 Calibration curve

The calibration curves were prepared by weighing DBP, DEHP and DIDP following Table 3.2. The PEs were dissolved using the suitable extracting solvent and transferred into 5 mL-volumetric flask that contained 2.00 mL of DOTP as internal standard. The relative peak areas of standard and internal standard were plotted against the concentration of each PEs standard solution. Calibration curve was shown in the APPENDIX .

Table 3.4 Weight and working range concentration of each PEs for calibration curve.

Weight (±0.0005g)	**Working concentration range (g/L)**		
	DBP	**DEHP**	**DIDP**
0.00500	1.00±0.10	1.00±0.10	1.00±0.10
0.0100	2.00±0.10	2.00±0.10	2.00±0.10
0.0200	4.00±0.10	4.00±0.10	4.00±0.10
0.0400	8.00±0.10	8.00±0.10	8.00±0.10
0.0800	16.00±0.10	16.00±0.10	16.00±0.10
0.1600	32.00±0.10	32.00±0.10	32.00±0.10

3.9.2 Study the effect of Matrix

Matrix calibration curves were constructed to study the matrix effect. First, the extraction of a blank nitrocellulose lacquer with suitable extracting solvent obtained from the study in the Section 3.7.1 was conducted as described in Section 3.6. Then, the PEs standard solutions were prepared as detailed in the Section 3.9.1 using the extract from the blank sample. PEs were weighed following Table 3.4. The results were shown in Section 4.4.1 and comparison slope of each standard PEs from both methods. Calibration from matrix curve was shown in APPENDIX.

3.9.3 Method quantification limit (MQL)

The method of quantification limit (MQL) was defined by the concentrations of PEs in cellulose lacquer at 10SD of a blank signal [28]. The MQL was determined by injection of extracting solvent of blank nitrocellulose lacquer sample into GC. The results were shown in Section 4.4.2. If blank not show peaks of PEs, add PEs in small concentration. Performed with optimum condition after that calculate standard deviation (SD) of concentration of each PEs and MQL is equal to 10SD. In this experiment was performed of high concentration so it not necessary to determine method of detection limit (MDL).

3.9.4 Study of accuracy and precision

Accuracy is the difference between the average value determined for the analyte of interest and the known level added in the synthetic nitrocellulose lacquer at 10 times of MQL. The accuracy was accomplished by calculating the average of recovery. Precision is the repeatability of measurement. Precision is commonly reported in the value of relative standard deviation (%RSD). The accuracy and precision was performed by analyzing PEs spiked cellulose lacquer. The spiked concentration level of DBP, DEHP and DIDP were 4.30, 1.10 and 7.00 g/L, respectively. The result was shown in Section 4.4.3.

3.10 The determination of PEs in cellulose lacquer

The developed method was applied to analyze PEs in two brands of cellulose lacquer selling in the market. These paints were determined following optimum condition and repeated 3 times for each sample. The results were shown in Section 4.5.

CHAPTER IV

RESULT AND DISCUSSION

4.1 Gas chromatographic condition

The standard solution of PEs 8 g/L in n-hexane was injected according to GC condition in Table 3.1. The chromatogram and resolution of standard PEs were shown in Figure 4.1 and Table 4.1, respectively.

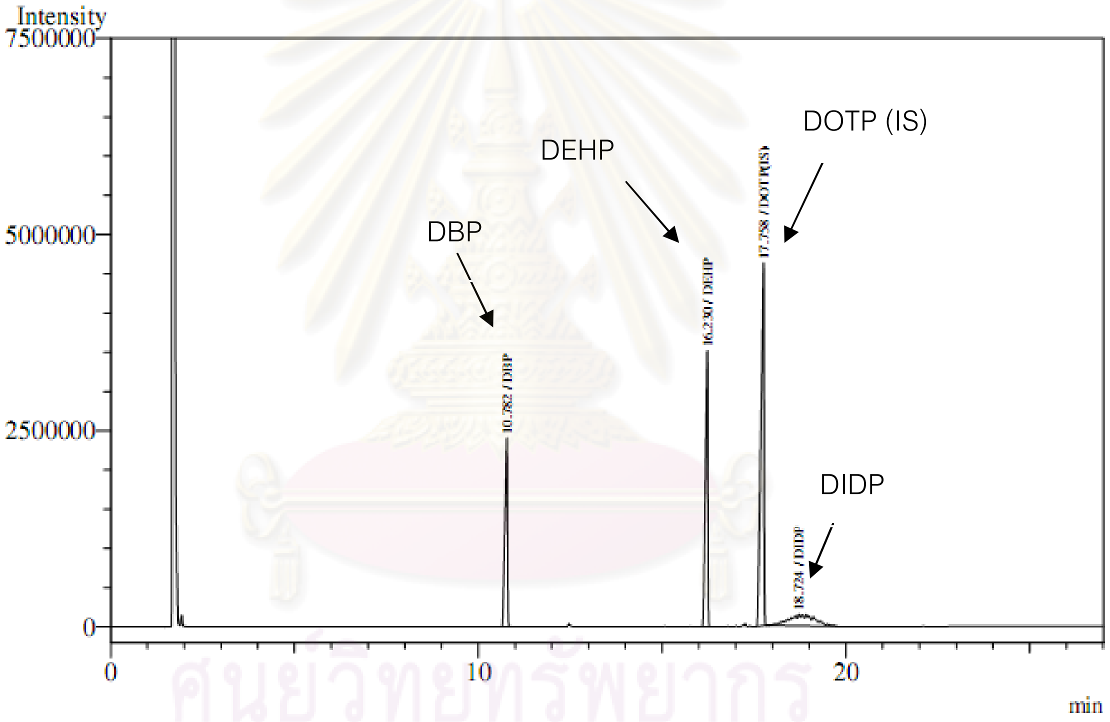


Figure 4.1 The chromatogram of standard PEs under GC condition in Table 3.1.

The low polarity stationary phase column was chosen to separate PEs because of the similarity in the polarity between stationary phase and PEs. The elution sequence was DBP, DEHP, DOTP and DIDP, respectively. This separation is based on the boiling point and the interaction between stationary phase and PEs. DBP was eluted first based on its low molecular weight and low boiling point (340ºC).

However, the boiling points of DEHP, DOTP and DIDP are quite similar. Thus, the separation of these compounds should follow the polarity of each compound.

Table 4.1 Retention time and resolution of standard PEs under GC condition in Table 3.1.

PEs	Retention time (min)[a]	Resolution[b]
DBP	10.782±0.01	19.88±0.06
DEHP	16.230±0.02	15.17±0.03
DIDP	18.724±0.01	3.10±0.03

[a,b] n=3

The GC condition in Table 3.1 can be used to separate three PEs because the resolutions of each peak in Table 4.1 are greater than 1.5. However, the DIDP showed the grouping peaks because there are the other isomers.

4.2 The solvent extraction optimization for PEs extraction

4.2.1 Study of the extracting solvent

The extracting solvent is the key in solvent extraction techniques. The challenge in this study is that the cellulose lacquer is in organic solvent. There are many desired properties of a suitable extracting solvent for extracting PEs. First, it should be able to dissolve PEs. Second, the boiling point should be high so we could work at high extraction temperature. Importantly, it should not dissolve with the other components in the nitrocellulose lacquer sample, which are resin, nitrocellulose, and pigment. In this study, n-hexane, toluene, dichloromethane were chosen due to the their low polarity that should dissolve PEs. The results were shown in Table 4.2. From Table 4.2, the physical appearance of the sample indicated that 100% n-hexane exhibited better phase separation between sample and extracting solvent, while 100% toluene could dissolve the sample. On the other hand, the sample was coagulated when 100% dichloromethane was added.

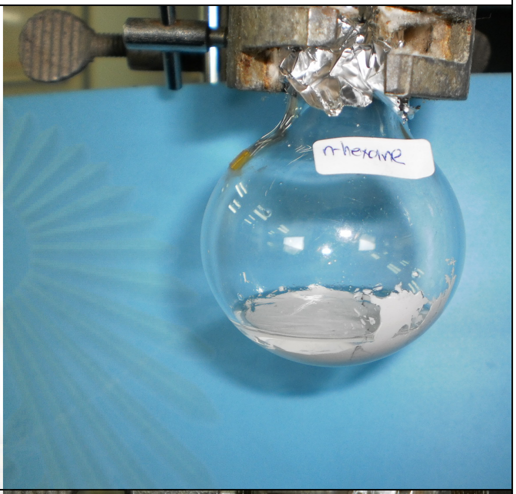
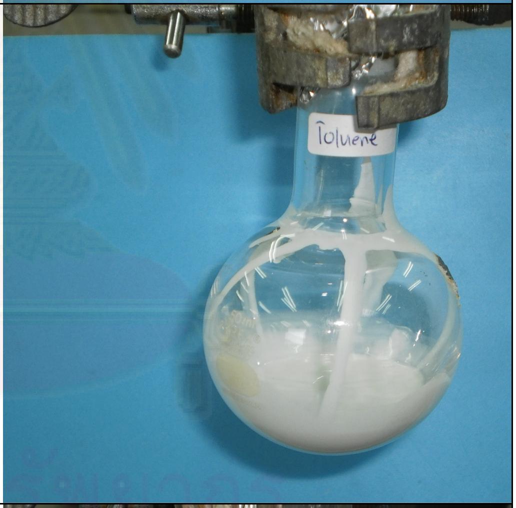
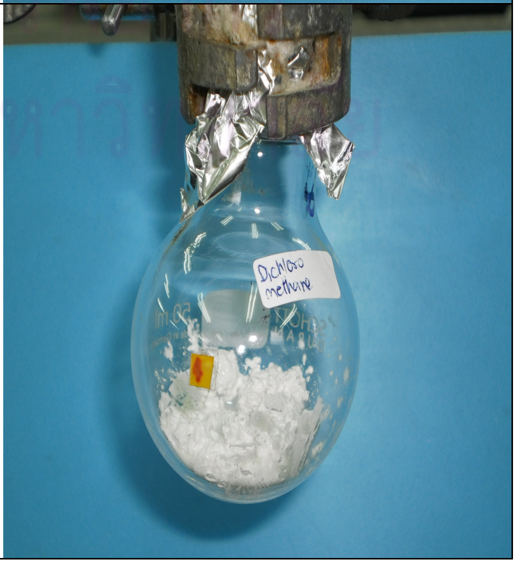
Therefore, the reaction of each component with each extracting solvent was investigated. Three solvents were added in the paste (resin+ titanium dioxide) and nitrocellulose separately. The physical appearance was observed. We could see that the hexane could not dissolve paste and nitrocellulose resulting in the 2 phase separation. This might be the result of the different polarity between hexane and these components. For example, nitrocellulose is more polar more than hexane due to the nitro groups. Therefore, it could not be dissolved with n-hexane, while the phthalate esters can be dissolved due to its low polarity.

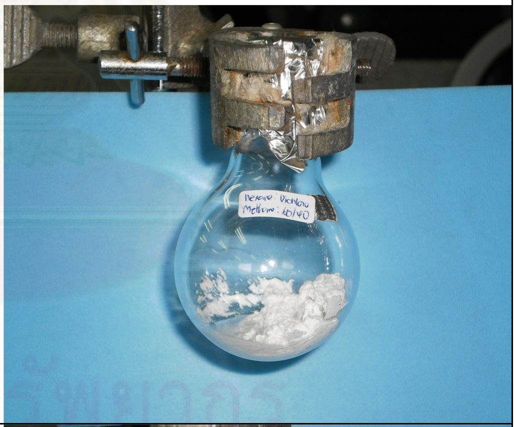
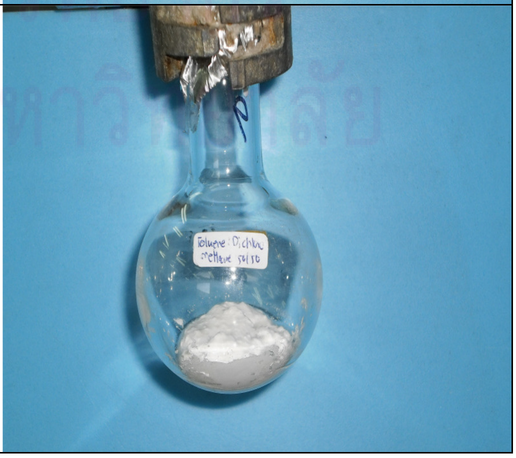
Toluene could dissolve both paste and nitrocellulose due to the aromatic rings which can interact with the aromatic rings in the sample (¶-¶ interaction). Dichloromethane could dissolve paste but coagulate with nitrocellulose.

The mixed solvent of these three solvents were also studied. For any mixing ratio of n-hexane/toluene greater than 30%, the two phase separation was still observed. However, for any mixing ratios of n-hexane/dichloromethane and toluene/dichloromethane, the coagulation was observed.

From the observation of physical appearance with different types of solvent and mixed solvents in Table 4.2, the suitable extracting solvent in this study is to create two phases after mixing with sample and can dissolve PEs. Therefore, pure n-hexane and the mixture of hexane and toluene with the volume ratios ranging from 40 to 70% of hexane were chosen to test the extraction efficiency.

Table 4.2 The physical appearance of cellulose lacquer sample mixed with organic solvents.

Solvent	Observation
n-Hexane	
Toluene	
Dichloromethane	

n-Hexane/toluene (30/70)	
n-Hexane/toluene (40/60) n-Hexane/toluene (50/50) n-Hexane/toluene (60/40) n-Hexane/toluene (70/30)	
n-Hexane/dichloromethane (50/50) n-Hexane/dichloromethane (60/40) n-Hexane/dichloromethane (70/30)	
Toluene/dichloromethane (30/70) Toluene/dichloromethane (40/60) Toluene/dichloromethane (50/50)	

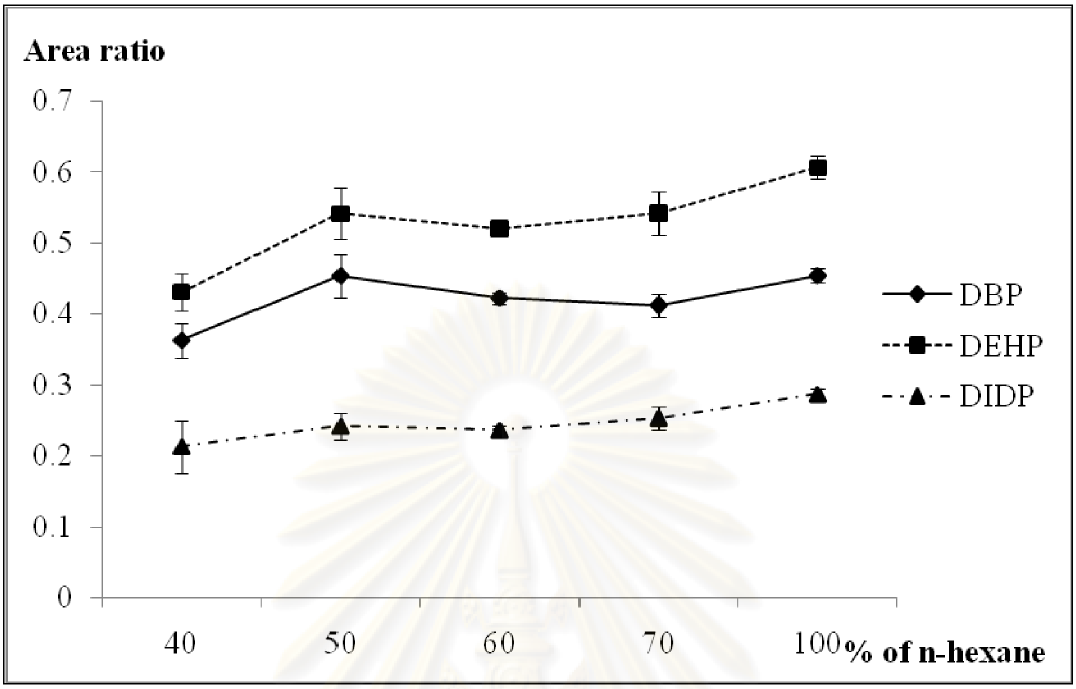


Figure 4.2 The extraction performance of PEs with different % n-hexane in toluene. (Experimental condition: 1:1 ratio of sample: extraction solvent, 10 minutes extraction time at 25°C with stirring rate 55 rpm, n=3)

From Figure 4.2, area ratio was defined as area of each standard PEs divided by area of internal standard. The extraction efficiencies were enhanced with the increasing in the percentage of n-hexane. Due to the increase in the percentage of n-hexane in the more precipitate. Then, PEs was extracted out more into the studied extracting solvents. Therefore, the suitable extraction solvent is n-hexane.

4.2.2 Study of the effect of extraction time on the extraction efficiency

Extraction time is one parameter that can affect the extraction efficiency. The effect of extraction time on the extraction efficiency was shown in Figure 4.3

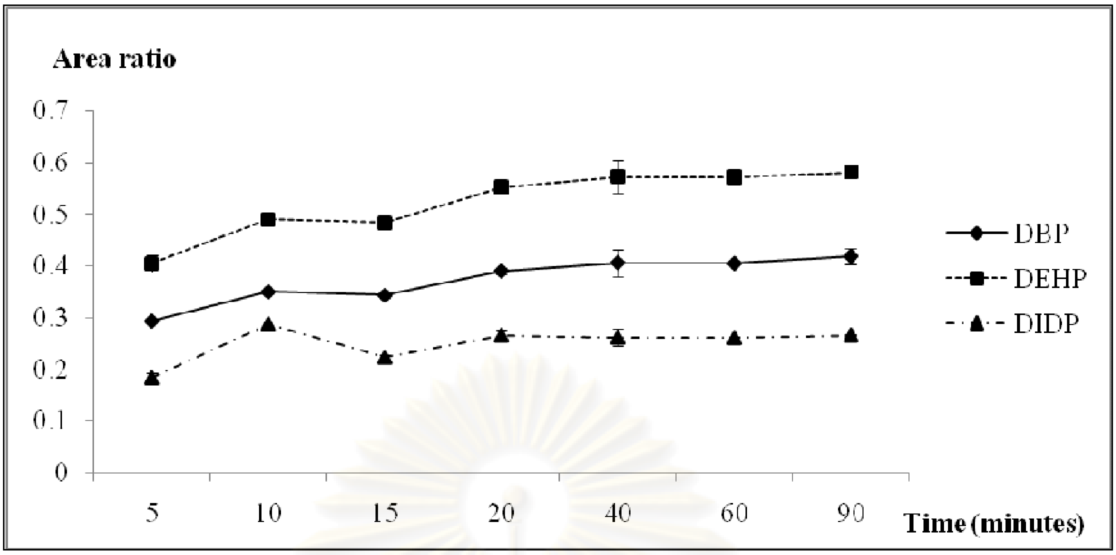


Figure 4.3 The extraction performance with different extraction times. (Experimental condition: Solvent was n-hexane, 1: 1 ratio of sample: extraction solvent at 25°C with stirring rate of 55 rpm, n=3).

From Figure 4.3, the extraction efficiency was increased with the increasing in extraction time till 20 minutes where we observed the plateau. Therefore, the extraction time of 20 minutes was chosen for further studies.

4.2.3 Study of the effect of extraction temperature on the extraction efficiency

The effect of extraction temperature on the extraction performance was examined from 25-60°C. The results were shown in Figure 4.4. From Figure 4.4, the extraction efficiency was enhanced with increasing temperatures from room temperature to 60°C. This might be due to the higher temperatures inducing better solubility and mass transfer rate and decreasing the surface tension and viscosity of solvent [12].

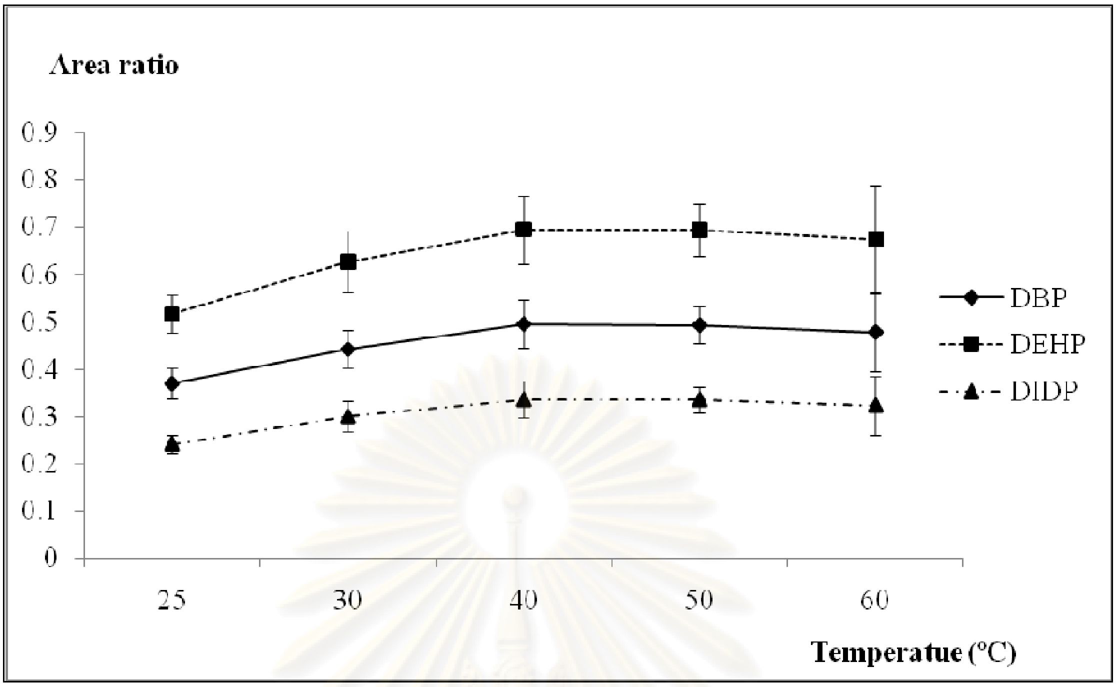


Figure 4.4 Effect of the extraction temperature on the extraction performance (Experimental condition: ratio of sample: n-hexane: 1:1, extraction time: 10 minutes , stirring rate:55 rpm, n=3).

From Figure 4.4, at 40ºC and 50ºC the extraction efficiencies were not significantly. Above 60ºC, the declining trend was observed. It is possible that at this temperature, the crosslink of cellulose lacquer occurred and trapped the PEs within the crosslinked polymer more. Furthermore, performing the extraction at 60ºC risks to the loss of extracting solvent as obtained at 60ºC showing the large standard deviation. Therefore, the lost of solvent was studied in section 3.7.6, after testing the result shown that at 40ºC, the lost of solvent was at 3.3 % and at 50ºC and 60ºC the losts of solvent were 16.7 and 20%, respectively. Therefore, to prevent the lost of extracting solvent and the occurrence of crosslinking process, the suitable temperature was 40ºC.

4.2.4 Study of the effect of ratio of sample to extraction solvent (w/v) on the extraction efficiency.

In this section, the effect of the mass over volume ratios of sample to extracting solvent (g/mL) is one of the important factors on the extraction efficiencies. As illustrated in Figure 4.5, the extraction was decreased when increasing either the sample weight or hexane volume by the factor of 2.

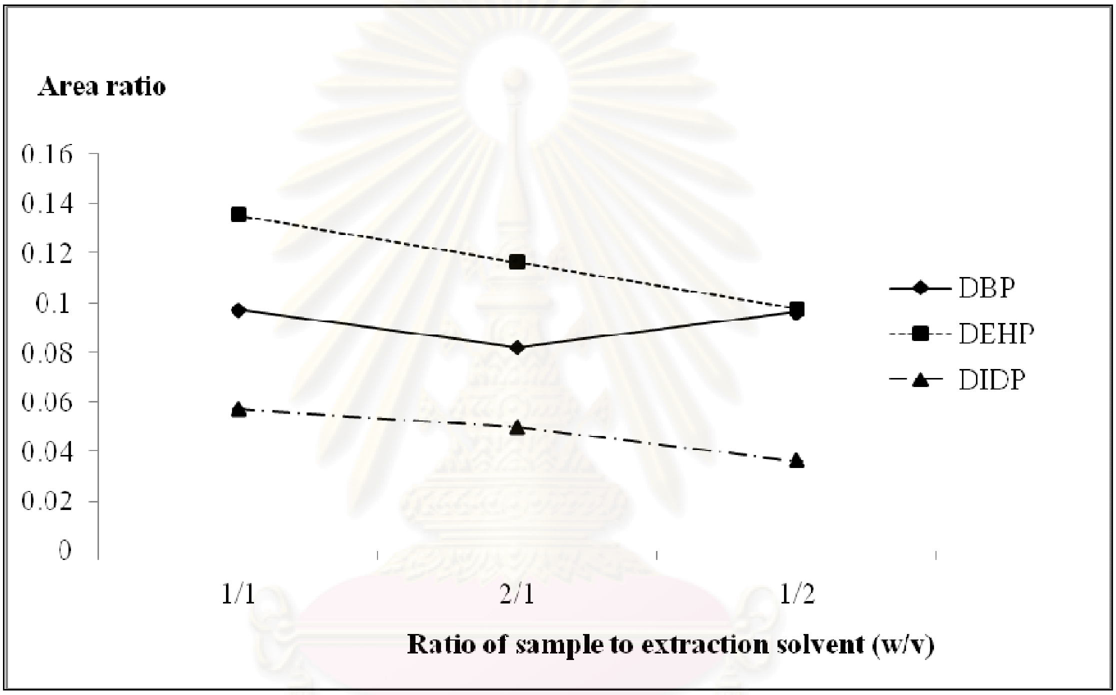


Figure 4.5 The plot of area ratio of area of standard PEs/area of internal standard against different sample mass to volume of hexane ratios. (Experimental condition: 10 minute extraction time at 25°C, with stirring rate of 55 rpm, n=3.)

From Figure 4.5, the increase in the extraction volume of hexane resulted in the decrease in the extraction efficiency of DEHP and DIDP except for DBP. In case of DBP, increasing extraction volume did not affect the extraction efficiency. This might be that the precipitation of resin and nitrocellulose with adding hexane was not affected by the increase in the extraction volume from 1 to 2 mL. Therefore, the extraction performances were similar. The decreasing in the extraction performance of DEHP and DIDP should be further investigated.

With increasing the ratio of sample weight by factor of 2, the smaller extraction performance comparing to 1:1 ratio was obtained. This should be that the increasing in sample weight with the same extraction volume might cause more precipitate to trap PEs when contact with n-hexane. The extraction performance also decrease. In this study, we chose to work with the ratio of sample mass to the volume of hexane equals to 1:1.

4.2.5 Study the effect of stirring rate on the extraction efficiency

The effect of stirring rate was shown in Figure 4.6

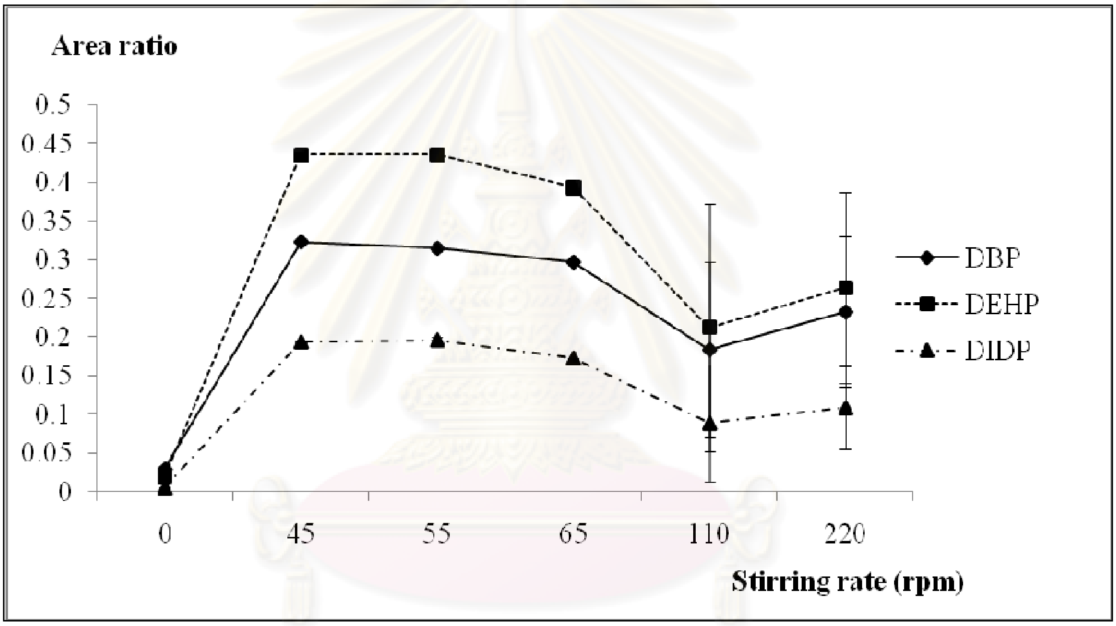


Figure 4.6 The extraction performance with different stirring rate (Experimental condition: solvent was n-hexane, ratio sample: extraction solvent 1:1, 10 minutes extraction time at 25ºC, with stirring rate of 55 rpm, n=3).

From Figure 4.6, the extraction efficiency was enhanced with increasing the stirring rate from 0 to 55 rpm. This is because that the increase in the stirring rate resulting in the enhancement of diffusion rate between PEs from sample to hexane. However, the decrease in extraction efficiency was observed when the stirring rate larger than 55 rpm. This observation might be due to the viscosity of sample, when stirring rate was increase the sample was attached to the blade. Moreover, increasing of stirring rate it might crate the thermal energy that raised the temperature higher resulted in the crosslink of cellulose lacquer. Therefore, the suitable stirring rate was 45 rpm.

4.3 Reflux method for extraction of PEs from cellulose lacquer

The aim of this section is to compare the extraction efficiency of this studied method with the conventional method. Reflux is one of a standard method established by American Society for Testing and Materials (ASTM) to analysis PEs in vinyl chloride plastic [6]. Here, the comparison study on the extraction efficiency between reflux and studied method was also conducted. The results were shown in Figure 4.7, 4.8.

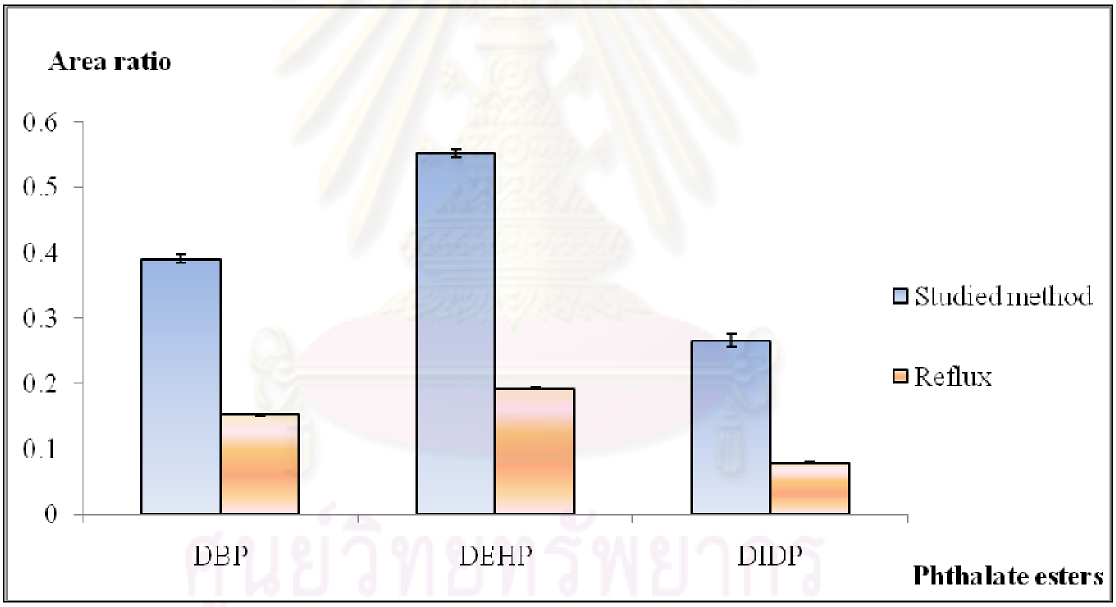


Figure 4.7 Comparison extraction performance of DBP, DEHP and DIDP between the studied method and reflux. Extraction condition: 1:1 ratio of sample: n-hexane, 20 minutes extraction time at 25ºC with stirring rate of 55 rpm, n=3. Reflux: 1:1 ratio of sample: n-hexane, temperature of reflux 80ºC for 20 minutes, no stirring, n=3.

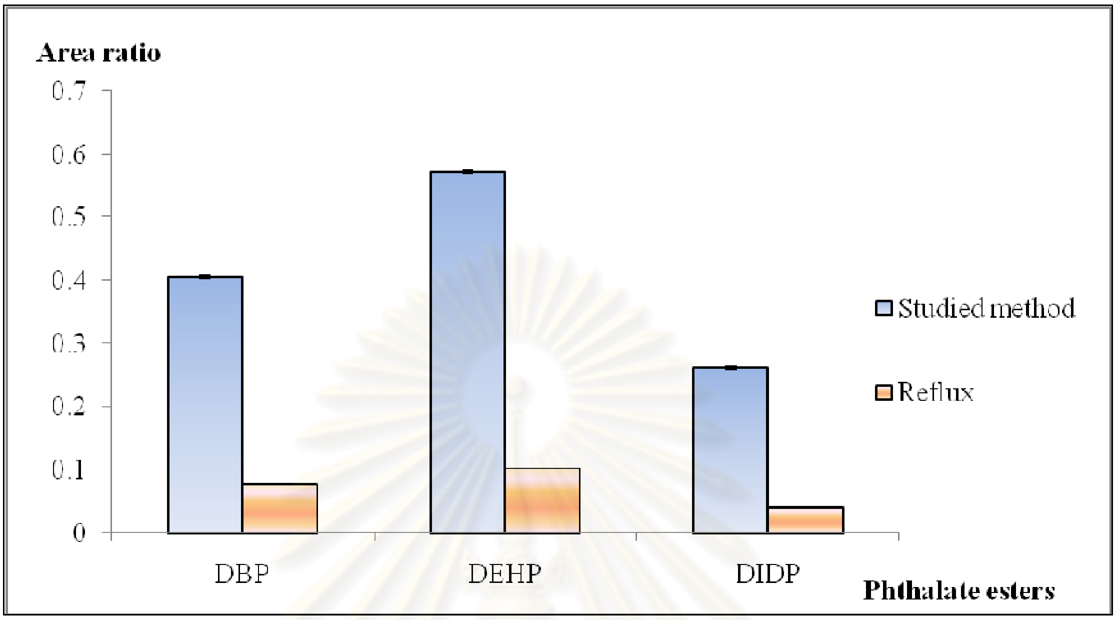


Figure 4.8 Comparison extraction performance of DBP, DEHP and DIDP between the studied method and reflux. Extraction condition: 1:1 ratio of sample: n-hexane, 60 minutes extraction time at 25℃ with stirring rate of 55 rpm, n=3. Reflux: 1:1 ratio of sample: n-hexane, temperature of reflux 80℃ for 60 minutes, no stirring, n=3.

This section was performed without any stirring because reflux method generally was performed without it. The extraction efficiencies of reflux method for all PEs at 20 and 60 minutes were 60-80% smaller than the studied method. For the reflux method, the temperature was raised more than the boiling point of hexane, 70°C. This is around the curing temperature of the cellulose lacquer which is around 60-80℃ [13]. When the curing process began, plasticizers could interact with this painttr and were trapped inside the crosslinked polymer resulting in the smaller extraction performance of reflux method comparing to the studied method. Hence, the reflux method was not the suitable sample preparation method for this paint.

4.4 Method validation

4.4.1 Calibration curve and matrix effect

The calibration curve and matrix calibration curve were established in the concentration range from 1-32 g/L. The slopes obtained from matrix calibration curve and normal calibration curve were shown in Table 4.3. Linear equation and correlation coefficient (R^2) of matrix and normal calibration was shown in Table 4.4.

Table 4.3 Slope from matrix calibration and normal calibration curve.

PEs	**Slope (L/g)**	
	Matrix	**Normal**
DBP	0.0377	0.0378
DEHP	0.0431	0.0424
DIDP	0.0358	0.0374

Table 4.4 Linear equation and correlation coefficient (R^2) from matrix and normal calibration curve.

PEs	**Linear equation**		**Correlation coefficient (R^2)**	
	Matrix	**Normal**	**Matrix**	**Normal**
DBP	y=0.0377x-0.0078	y=0.0378x-0.0104	0.9994	0.9997
DEHP	y=0.0431x+0.0008	y=0.0424x+0.0018	1.0000	1.0000
DIDP	y=0.0358x-0.0052	y=0.0374x-0.016	0.9999	0.9994

From Table 4.3, the slopes obtained from these two calibration curves were statistically tested by t-test, where the t-test$_{cal}$ was 0.3350 and t$_{crit}$ at 95% confidence is 2.9200. Therefore, the matrix of sample had a minor role on the calibration curve. The normal calibration curve with linear equation and correlation coefficient (R^2) that shown in Table 4.4 was used in this study.

4.4.2 Linearity

Linearity defined as linear range and correlation coefficient (R^2) that obtain from calibration curve and the result was shown in Table 4.5.

Table 4.5 Linear range and correlation coefficient (R^2).

PEs	Linear range (g/L)	Correlation coefficient (R^2)
DBP	1.06-32.07	0.9997
DEHP	1.07-32.03	1.0000
DIDP	1.08-32.07	0.9994

Linear range of DBP, DEHP and DIDP were observed in range 1.06-32.07, 1.07-32.03 and 1.08-32.07 (g/L), respectively. Three PEs had correlation coefficient (R^2) greater than 0.999 that shown good linearity.

4.4.2 Method quantification limit (MQL)

Method quantification limit (MQL) is the lowest concentration level at which a measurement is quantitatively meaningful. It most often defined as 10 times the signal/noise ratio. If the noise is approximated as the standard deviation of the blank, MQL is (10×SD blank) [28].

From optimum condition to be determined the performance of this technique, the method of quantification limit (MQL) of three PEs were shown in Table 4.6

Table 4.6 Method of quantification (MQL).

PEs	MQL (g/L)[a]
DBP	0.43
DEHP	0.11
DIDP	0.70

[a] n=5

MQL of DBP, DEHP and DIDP were 0.43, 0.11 and 0.70 g/L respectively. PEs contents normally are added in cellulose lacquer with concentration about 20-30 g/L so MQL of this study can be applied to determine content of PEs in this paint.

4.4.3 Study of accuracy and precision

In this work, accuracy is the deviation from the known value. It was estimated as the deviation of the mean from the known value in this work. Accuracy was reported by % recovery.

Precision is a measure of reproducibility and is affected by the error. An estimation of this error is necessary to predict within what range the true value or known value may lie and this is done by repeating a measurement several times [28]. Precision were reported by calculating the %relative standard deviation (%RSD) of recoveries from nitrocellulose lacquer sample spiked with PEs. In this study, the sample was spiked with PEs at 10 times of MQL. The spiked concentration of DBP, DEHP and DIDP were 4.30, 1.10 and 7.70 g/L, respectively. The recoveries and % RSD were shown in Table 4.6.

Table 4.7 Concentration, recoveries and % relative standard deviations of PEs spiked cellulose lacquer.

PEs	**Concentration (g/L)**		**Recoveries**	**%RSD (n=7)**
	Added	**Found**		
DBP	4.30	2.76	68.68	12.64
DEHP	1.10	0.99	90.34	15.08
DIDP	7.70	5.85	83.30	13.97

% Recoveries of this technique was in range 68.68-90.34% and % RSD was in range 12-15%. DBP provided the low % recovery because it is low molecular weight and more polar comparing to the other studied PEs . Therefore, it might form stronger bond in cellulose lacquer than DEHP and DIDP. This studied method can be applied to determine DEHP and DIDP in cellulose lacquer.

4.5 The determination of PEs in commercialized cellulose lacquer.

The studied method was applied to analyze PEs in two brands of cellulose lacquer selling in the market. The result was shown in Table 4.8.

Table 4.8 Concentration of PEs in cellulose lacquer from two brands in the market.

Cellulose lacquer	**Concentration (g/L)**		
	DBP	**DEHP**	**DIDP**
Brand No. 1	ND	ND	ND
Brand No. 2	8.59	ND	ND

ND= not detected at concentration that lower than MQL.

This studied method can’t detect PEs in brand No .1 because the content of it may be lower than MQL. Content of DBP in brand No.2 is not still reliable because this studied provide low efficiency (68.68 of % recovery) for DBP with high % RSD.

CHAPTER V

CONCLUSION

High temperature solvent extraction followed by gas chromatography- flame ionization detector (GC-FID) was developed and applied for sample preparation and determination of phthalate esters (PEs) in cellulose lacquers.

The parameters that affecting to this study such as type of solvent, extraction time, extraction temperature, ratio of sample to extracting solvent and stirring rate were investigated. n-Hexane was found to be the suitable extracting solvent because it made other components such as resin, nitrocellulose precipitated out. The optimized extraction time was found to be 20 minutes whereas the suitable temperature was 40°C with the stirring rate of mechanical stirrer of 45 rpm. The optimized ratio of nitrocellulose lacquer:n-hexane was found to be 1:1. In this study not only temperature but stirring can also enhance extraction efficiency. However, this technique faced with problem of loss of extracting solvent at high temperature higher than 40ºC. Furthermore, the cellulose lacquer can be cured at temperature about 60-80°C. Therefore, the extraction temperature cannot be higher than 60ºC. Moreover, the low stirring rate was more suitable condition compared to the high stirring rate due to viscosity property of this paint. The comparison study between the reported method and reflux method was also conducted. The reflux method caused the paint to be cured and showed low extraction efficiency.

This technique was shown to have good linearity (R^2 higher than 0.999) and low MQL. The recoveries of DBP, DEHP and DIDP in spiked sample were 68.68%, 90.34% and 83.30%, respectively. % RSD of DBP, DEHP and DIDP were 12.64%, 15.08% and 13.97%, respectively.

This method can be applied to determine PEs content in commercialized cellulose lacquer in the market. The result shows that DBP, DEHP and DIDP could not be detected in some brands due to low concentration of MQL, and one brand showed some content of DBP.

It can be concluded that this technique could applied to determine PEs in cellulose lacquer with small amount of sample, extracting solvent at temperature of about 40ºC and less time for saving.

Future work

Improvement of the reproducibility by designing experiment set up and study of the leaching of PEs from furniture this paint was applied on.

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APPENDIX

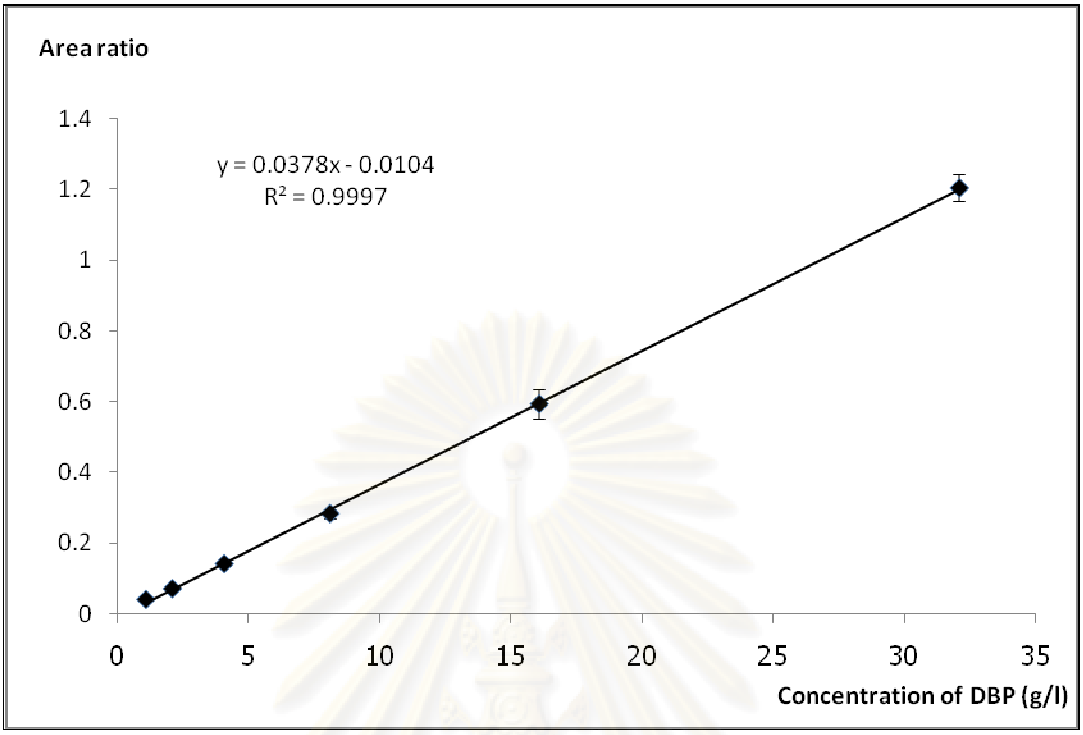

Figure 1 The calibration curve of DBP by condition in Table 3.2.

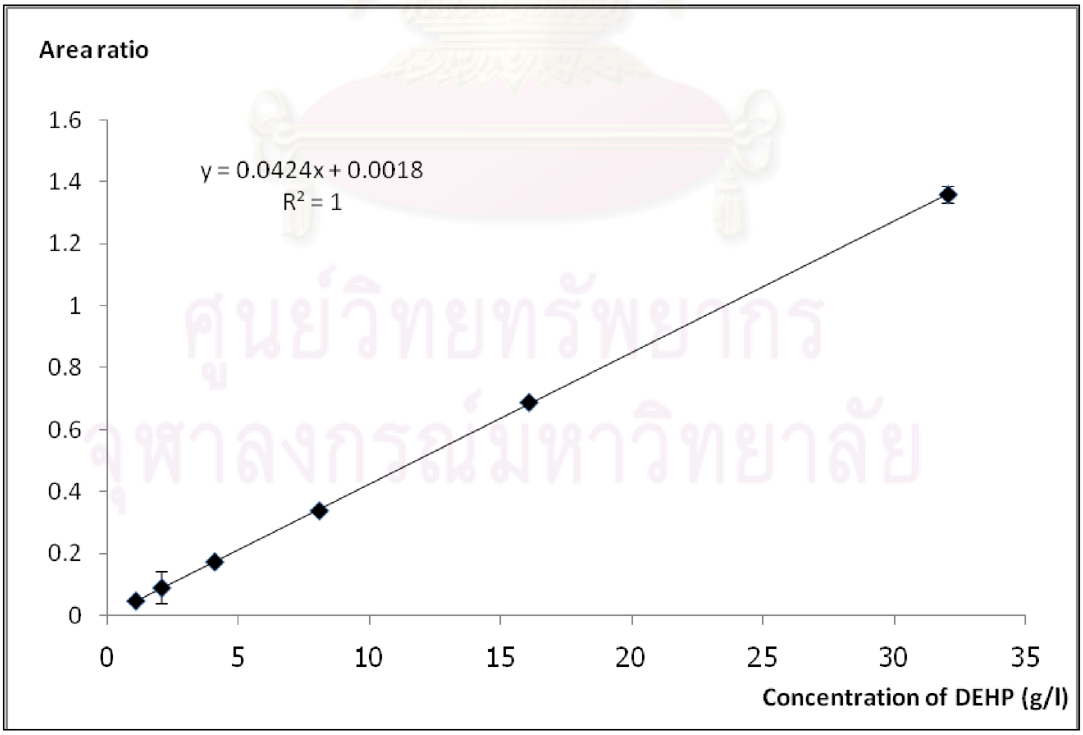

Figure 2 The calibration curve of DEHP by condition in Table 3.2.

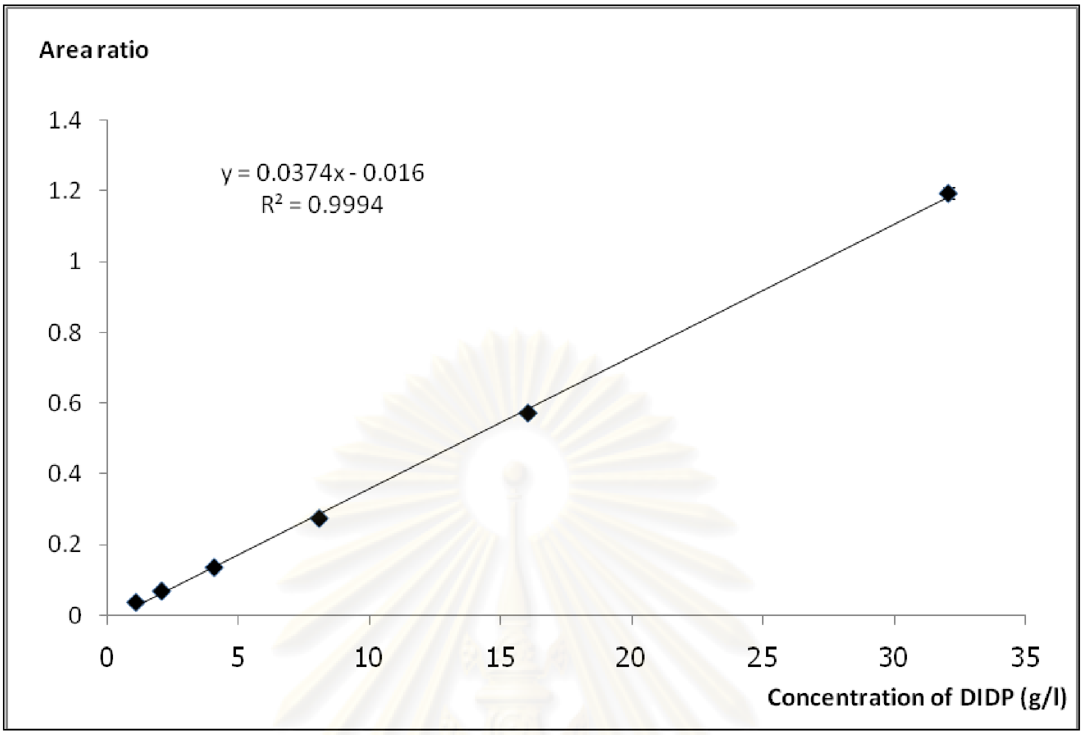

Figure 3 The calibration curve of DIDP by condition in Table 3.2.

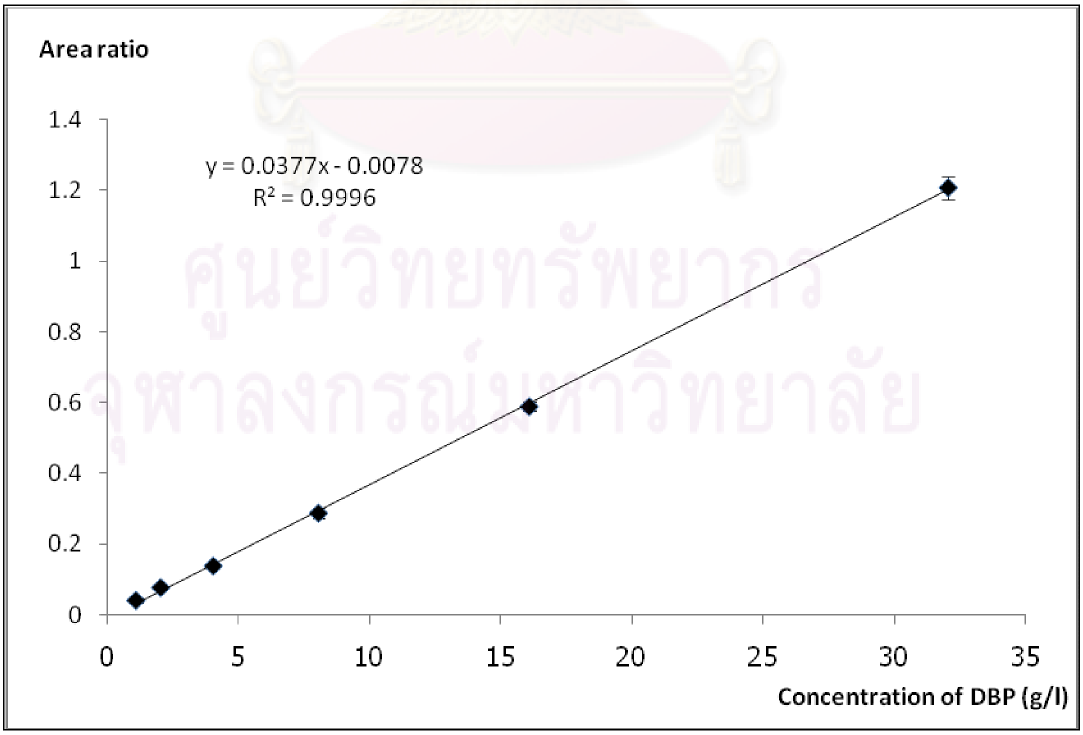

Figure 4 The matrix calibration curve of DBP by condition in Table 3.2.

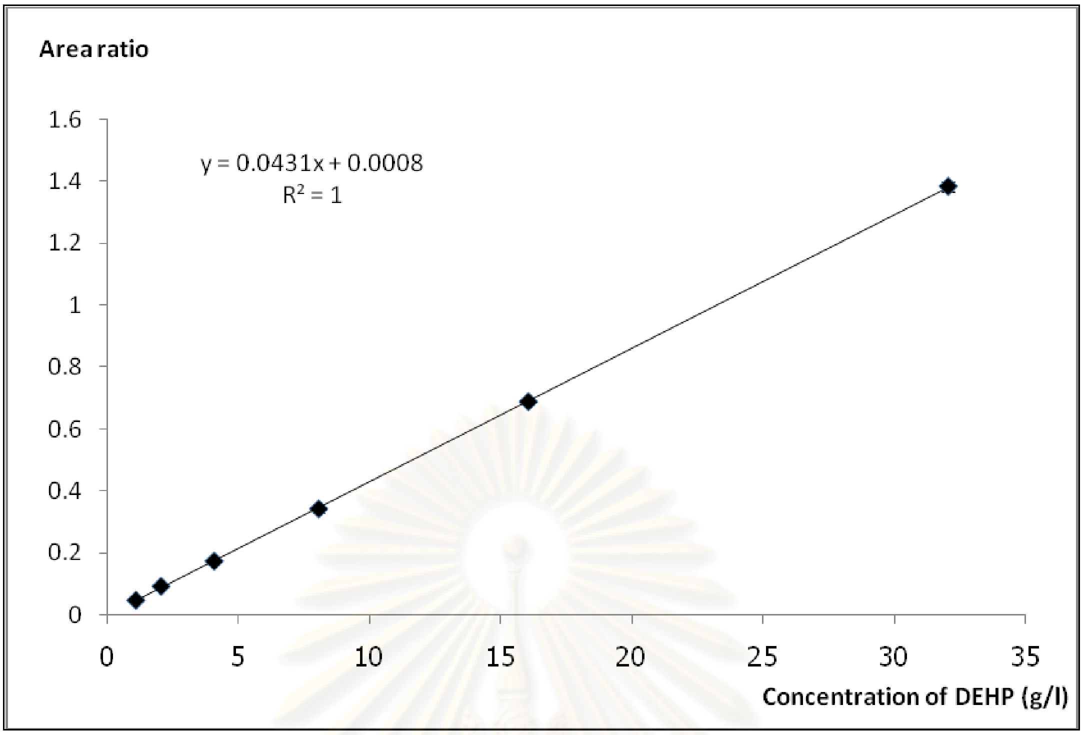

Figure 5 The matrix calibration curve of DEHP by condition in Table 3.2.

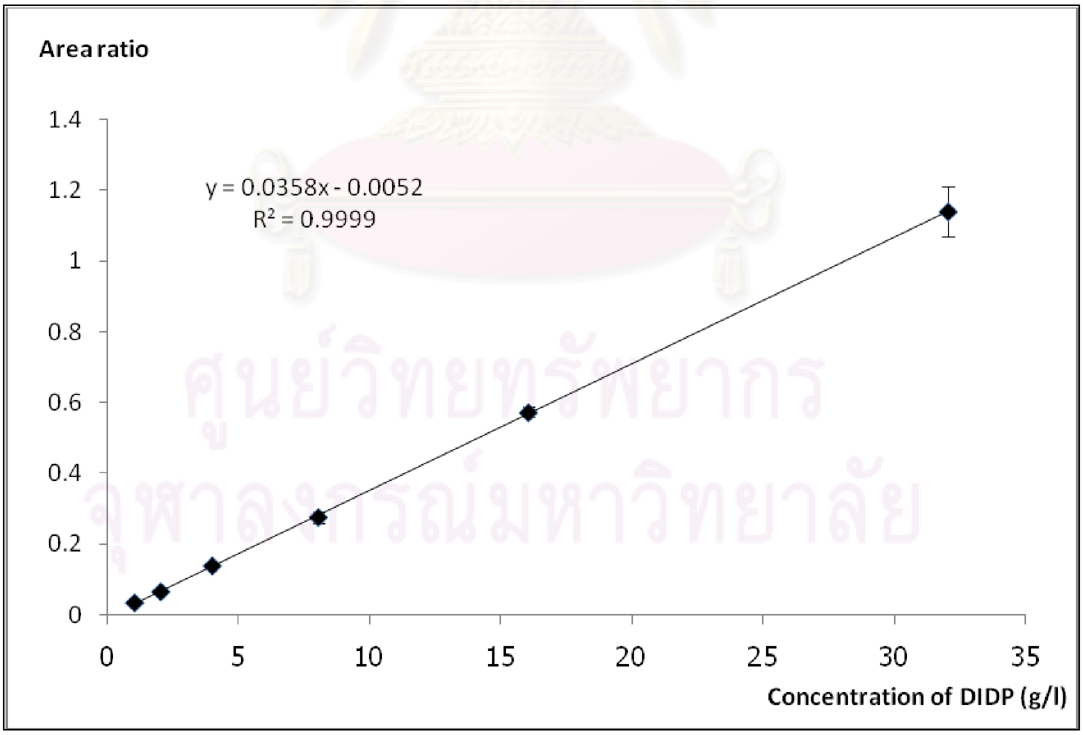

Figure 6 The matrix calibration curve of DIDP by condition in Table 3.2.

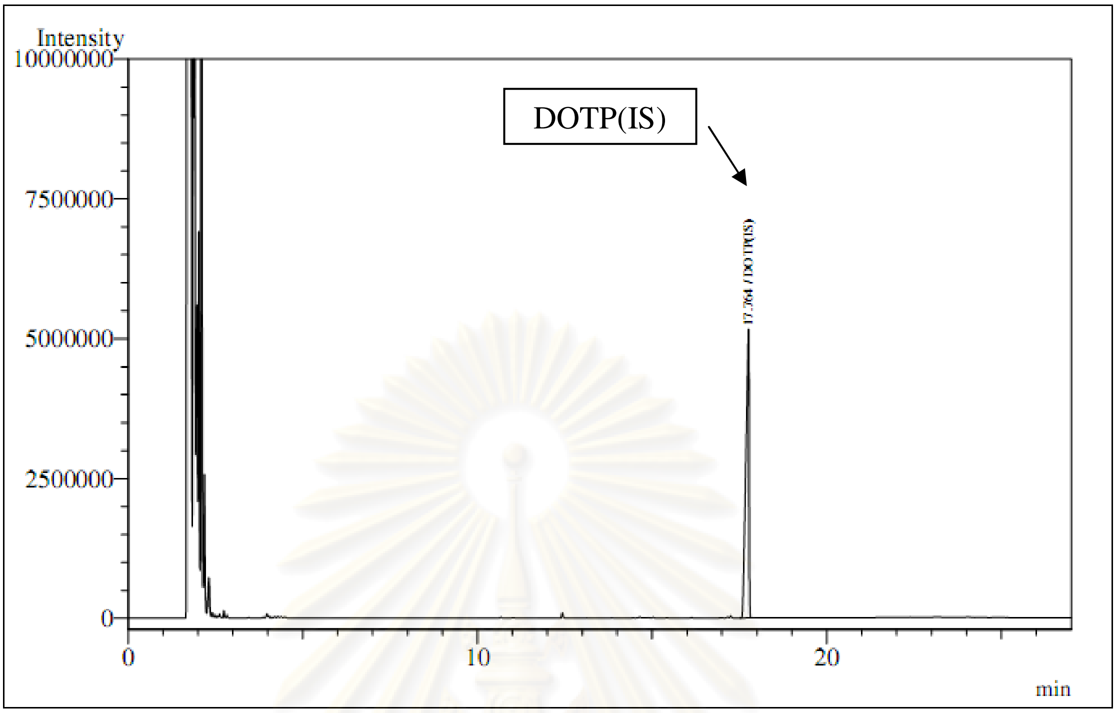

Figure 7 Chromatogram of PEs in paint brand no.1 after extracted with developed method.

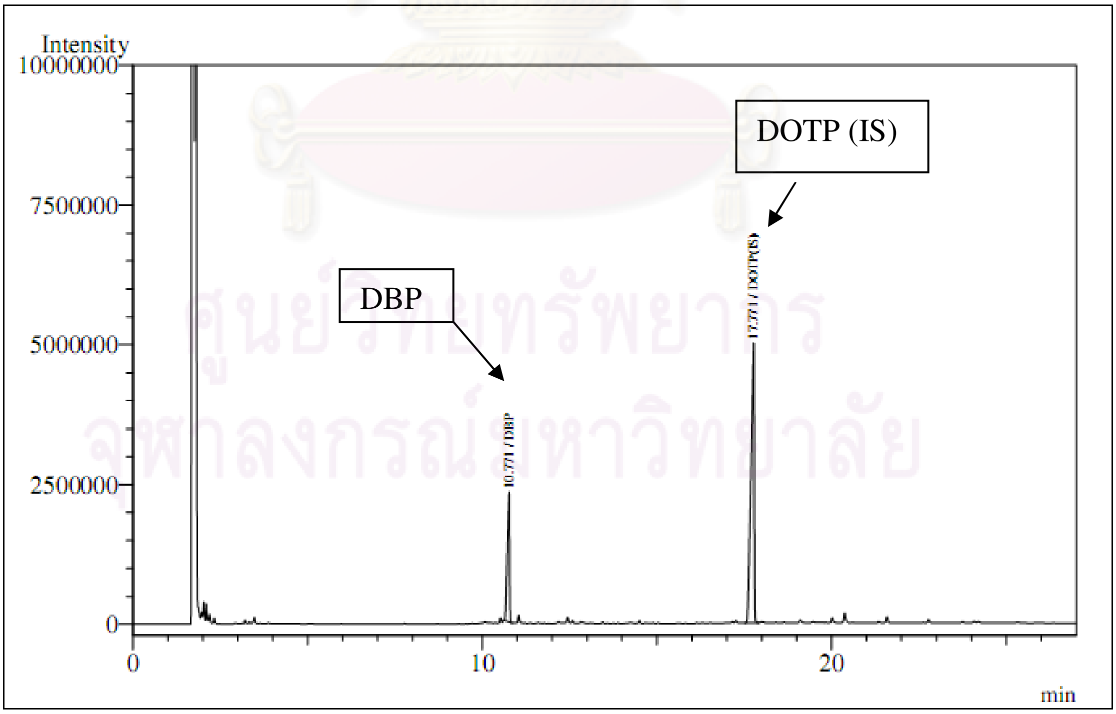

Figure 8 Chromatogram of PEs in paint brand no. 2 after extracted with developed method.

Biograghy

Name: Ms. Choltira Mahauossanun

Date of birth: 2nd July 1982

Place of birth: Nan, Thailand

Education:

2007-2010 Chulalongkorn University

Master’s Degree of Science (Petrochemistry and Polymer Science)

2002-2005 Chiangmai University

Bachleor’s Degree of Science (Chemistry)

1996-2001 Satrisrinan School

Working Place: Siam Chemical Industry Co., Ltd, Samutprakarn

Presentation:

C. Mahayossanun and L.Dubas, “Green Sample Preparation Technique for Determination of Phthalate Ester Content in Cellulose Lacquers”, Presented at Paccon 2011, 5-7 January 2011, Bangkok, Thailand.