สีย้อมทำเครื่องหมายจากสารสกัดเปลือกเมล็ดมะม่วงหิมพานต์และไนโตรอะนิลีน

หอสมุดกลาง สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

นายสุภาพ ศิลปคัมภีรภาพ

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

MARKER DYES FROM CASHEW NUT SHELL EXTRACT AND NITROANILINES

Mr. Supap Silapakampeerapab

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer
Graduate School Chulalongkorn University
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สุภาพ ศิลปคัมภีรภาพ : สีย้อมทำเครื่องหมายจากสารสกัดเปลือกเมล็ดมะม่วงหิมพานต์ และไนโตรอะนิลีน (MARKER DYES FROM CASHEW NUT SHELL EXTRACT AND NITRO-ANILINES) อ.ที่ปรึกษา : รศ. ดร. อมร เพชรสม, อ. ที่ปรึกษาร่วม : นางรัตนาวลี อินโอชานนท์, 102 หน้า. ISBN 974-333-012-7.

งานวิจัยนี้เกี่ยวข้องกับการสังเคราะห์สารเคมีในกลุ่มเอโซดาย ที่มีคุณสมบัติเป็นทั้งสีย้อมและสารทำเครื่องหมายในน้ำมันเชื้อเพลิง โดยให้สีเหลืองเมื่อเติมในน้ำมันและเปลี่ยนสีของส่วนสกัดเมื่อเขย่ากับสารสกัด วัตถุดิบเริ่มจากสารสกัดเปลือกเมล็ดมะม่วงหิมพานต์ ซึ่งมีแอนาคาร์ดิก แอซิด เป็นองค์ประกอบหลัก เปลี่ยนให้เป็นอนุพันธ์เอสเทอร์โดยใช้ 1-เฮกซานอล เพื่อลดความเป็นกรดของหมู่คาร์บอกซิลิกในสารตั้งต้นและเพิ่มความสามารถในการละลายในสารไฮโดรคาร์บอน อนุพันธ์เอสเทอร์ที่ได้เตรียมเป็นสารประกอบเอโซดาย โดยทำปฏิกิริยากับ เมทา, ออร์โท และ พารา ไนโตรอะนิลีน สารประกอบเอโซดายที่ได้จะให้สีเหลืองเมื่อเติมในน้ำมันเชื้อเพลิง และแสดงคุณสมบัติเป็นสารทำเครื่องหมายโดยเปลี่ยนสีของสารสกัดเอททิลีนไกลคอลที่เป็นด่างให้เป็นสีเหลืองเมื่อใช้เอโซดายที่เตรียมจากเมทาไนโตรอะนิลีน เป็นสีส้มเมื่อใช้เอโซดายที่เตรียมจากออร์โทไนโตรอะนิลีน หรือสีแดงเมื่อใช้เอโซดายที่เตรียมจากพาราไนโตรอะนิลีน ทำการศึกษาคุณสมบัติของเอโซดายที่เตรียมได้ ผลกระทบของเอโซดายต่อคุณภาพของน้ำมันที่เติม ศึกษาการตรวจหาปริมาณทั้งในภาคสนามและในห้องปฏิบัติการ และความคงตัวของเอโซดายเมื่อเติมในน้ำมันเชื้อเพลิง

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ภาควิชา –
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา 2542

ลายมือชื่อนิสิต
ลายมือชื่ออาจารย์ที่ปรึกษา
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

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KEY WORD: CASHEW NUT SHELL EXTRACT / AZO DYE / DYE / MARKER

SUPAP SILAPAKAMPEERAPAB : MARKER DYES FROM CASHEW NUT SHELL EXTRACT AND NITRO ANILINES. THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D. THESIS CO-ADVISOR : Mrs. RATANAVALEE IN-OCHANON. 102 pp. ISBN 974-333-012-7.

This research involved synthesizing of azo compounds which have marker and dye properties in petroleum oils. They give yellow color when mixed with oil and change the color of extract phase when shaken with extract solvent. Raw material was cashew nut shell extract which contained anacardic acid as a main composition. The cashew nut shell extract was esterified with 1-hexanol to block remaining carboxylic acid moiety. The resulting ester was then coupling with meta, ortho and para nitroaniline to give corresponding azo dyes. The azo dyes thus obtained were added into petroleum oils to give yellow color. The azo dyes were also used as marker in oils. They developed color when extracted with glycolic potassium hydroxide solution gave yellow color in extract solvent when used azo dye prepared from meta nitroaniline, orange color when used azo dye prepared from ortho nitroaniline or red color when used azo dye prepared from para nitroaniline. Properties of azo dyes, quality of dyed oils, qualitative and quantitative determination as well as storage stability of these azo dyes were investigated.

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ABBREVIATIONS

ASTM = American Society for Testing and Materials

CFR = Cooperative Fuels Research

CNSL = Cashew Nut Shell Liquid

CNSO = Cashew Nut Shell Oil

COC = Cleveland Open Cup

IBP = Initial Boiling Point

IP = The Institute of Petroleum

PM = Pensky-Martens closed cup

RON = Research Octane Number

RVP = Reid Vapor Pressure

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CHAPTER 1

INTRODUCTION

1.1. Statement of problems

The smuggle of petroleum oils (gasoline or diesel oils) becomes a big problems because of tax rate for those oil are high. Therefore, adulteration of higher priced products with a lower priced products such as addition of premium gasoline with regular gasoline or addition of hydrocarbon solvents to gasoline, evading taxation by addition of low-taxed marine diesel oil to vehicle high speed diesel oil become an illegal regular practice of certain gas stations. Those problems are difficult to prove or affirm because there is little or no different between tax and untaxed fuels. Moreover petroleum products are the mixture of hydrocarbons so the property of products is widely varied. For example, if some of diesel or aromatics solvent is add into gasoline, it is difficult to detect especially in the physical properties tests.

To prevent those problems, dyes (coloring agent) are procured for coloring of petroleum oils. Dyes are added to give visible color, thus make it simple to identify both type and quality of products. Normally, dark color dyes are the prefered color to add in lower cost products and the light color dyes are the color that added in high cost products, for example regular gasoline is dark red color while premium gasoline is yellow and aviation gasoline is very pale blue color. Therefore, if little of red color is added in yellow or pale blue color, it will change to orange or pale red color, that easy to detect disguised liquid containg in normal fuel.

However the use of dyes is a primary measure system does not always adequate to confirm or to classify suspected products. For example, in some case vehicle high speed diesel is an undyed fuel, therefore if it is adulterated with aromatic solvent or gasoline it cannot be examined because there is no change in color of fuels can be observed.

To encourage the function of dyes, foreign chemical, namely, a marker is introduced in petroleum products which can be detected by simple chemical or physical specific test after mixing into petroleum products.

Markers were widely used more than 40 years ago. In France, furfural and diphenylamine were used as marker in heating oil since 1956, while Germany used furfural in 1976. England implemented quinizarin and coumarin as marker for heating oil and white kerosene in 1962 and 1984, respectively. Other country, such as Japan tagged kerosene by coumarin in 1991 etc. Conventional markers have the disadvantage in many cases. Furfural is unstable for long time (30-40 % furfural decomposed when stored for four days in some fuels) and sometimes furfural was used in refining process so it might be contaminated with fuel to give positive test in an unmarked fuel. Furthermore, the detection system (by 10% aniline in acetic acid, giving red extract phase as positive test) had some drawbacks. For example, the impurity from fuel can be extracted from fuel and then giving positive test. Moreover an extraction reagent can be dissolved in light hydrocarbon, red extract phase as positive test was stabilized for a few second and decomposed in long time. Stability and poison of test reagent (aniline and acetic acid) is also another problem (1)(2).

Quinizarin, diphenylamine or coumarin were among the compounds that can be used, but they still had an disadvantage due to their poor solubility in oils, leading to inconvenient for handle, dosage, storage or transport because the large volume of marker solution must be used.

Currently, modern markers are improved to overcome a drawback of conventional markers. Many types of chemicals have been developed for tagging petroleum products such as anthraquinone derivatives, azo dyes, fluorescent chemicals, polymer etc. Those markers can be used in small concentration level even in ppb level and are efficiency to used for tagging petroleum oils.

1.2 Objectives and scope of the research

This research was aimed at the synthesis of marker dyes and also developing their test method. In addition, the stability of marker dyes was also studies by monitoring the marker dyes in marked fuels. The comparative studied of fuels properties between marked and unmarked fuels were also performed by using standard methods.

The group of azo dyes which were the compounds selected for this study as both marker and dyes. After addition into fuel, they gave yellow color which matching to the color of premium gasoline and diesel oil. However, that can be detected by specific chemical test method. Moreover, starting material for this research should be available and will not cause any significant change in fuel price.

The Cashew Nut Shell Liquid (CNSL), obtained by n-hexane extraction of the cashew nut shell was chosen as starting material. The CNSL was a mixture of phenolic compound, mostly anacardic acid. It is foreign to fuel oil.

CHAPTER 2

THEORETICAL

2.1 Color and chemical structure

The majority of organic compounds are colorless. Coloration of organic compounds related to its structure. For example, benzophenone $(C_6H_5)_2C=O$, is colorless but if oxygen is replaced by sulfur resulting thiobenzophenone, $(C_6H_5)_2C=S$, it becomes blue compound and absorption around 620 nm. For stilbene $(C_6H_5)CH=CH(C_6H_5)$ maximum absorp at 310 nm, if one of =CH is replace by =N it gives benzaniline, $C_6H_5\text{-}CH=N\text{-}C_6H_5$, the maximum absorption will shift toward 330 nm but still colorless. A compound is orange color by replacing both CH = CH with N = N, azobenzene, $(C_6H_5)\text{-}N=N\text{-}(C_6H_5)$, and maximum absorp at 450 nm. However if the azo group -N=N- is added with hydrogen and becomes hydrazobenzene, $C_6H_5\text{-}NH\text{-}NH\text{-}C_6H_5$, it will be conversed to colorless compound again (3).

Color of the compounds is a result of the ability of light absorption especially in the visible range (380-780 nm). Table 2.1 presents a simplified picture of color observed when certain wavelengths are absorbed (4).

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Table 2.1 Relationship between absorption and visual color

Wavelengths absorbed (nm)	Color absorbed	Visual color
400 - 435	violet	yellow-green
435 - 480	blue	yellow
480 - 490	green-blue	orange
490 - 500	blue-green	red
500 - 560	green	purple
560 - 580	yellow-green	violet
580 - 595	yellow	blue
595 - 605	orange	green-blue
605 - 750	red	blue-green

In 1876 Witt applied the name chromophore (chroma mean color, phoros from pherein mean bearer). The chromophore groups are C = C, C = N, C = S, C = O, N = N, N = O, NO_2 etc. Compounds, which containing those group will be present in highly colored. Absorption of some compounds were shown below (4)(5).

Chromophore	λ max	ε max
$>C=C<$	190	8000
-C = N-	190	5000
$>C=S$	205	strong
$>C=O$	195	1000
-N = N-	285 - 400	3-25
-N = O	302	100

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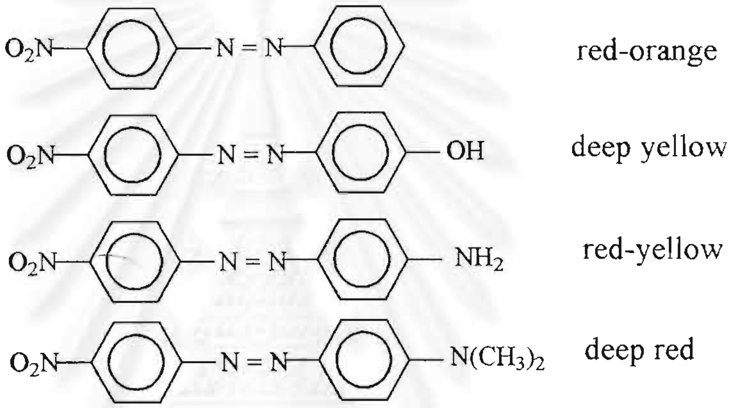
Furthermore, Witt described some groups as auxochromes (auxein mean to increase), the groups which its little or not absorp visible light but effect to absorption spectrum of chromophore group resulted in shifting of wavelength or intensity of absorption. Common auxochrome groups are -NH_2, -NHR, -NR_2, -OH, -OR, -CH_3 or halogen.

Effect of auxochrome group may be exhibited with the following series of compounds.



Position of those groups will have an effect to the color of compound. In general, auxochromes do not affect to the color when it is positioned in the meta position to the chromophore group. Morerover, pH of solution has an effect to color. Therefore, many dyes are colorless or having color and become color or change their color by treatment with an acid or alkaline to form a salts. For example, the salt of the phenolic compounds give more strongly color than the free phenol.

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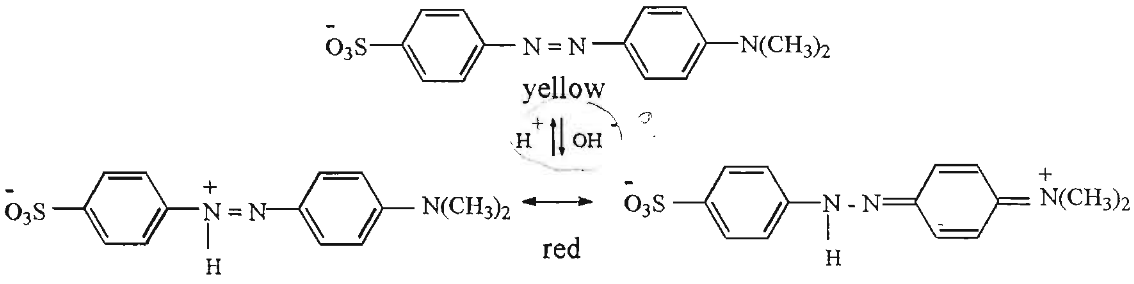


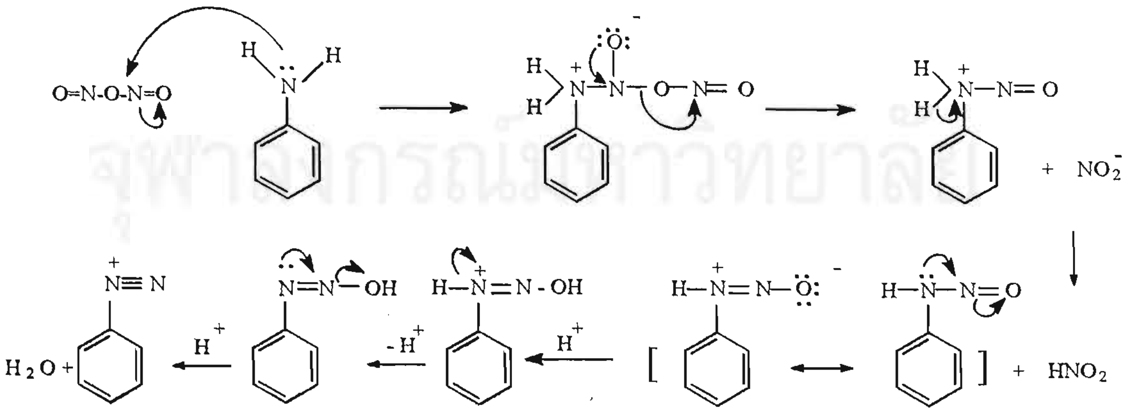
2.2 Azo dyes and coupling reaction

At least half of the synthetic dyes made of the azo type. Azo dyes are prepared by the reaction of diazonium salt of aromatic amine (primary component) and either phenol or aromatic amine (secondary component) known as coupling reaction.

An important substance for coupling reaction is a diazonium salts, which prepared by reaction of primary aromatic amine and sodium nitrite in acidic condition. The experimental conditions for diazotization were given as the following. By dissolving amine with suitable volume of water contained 2.5 - 3 equivalents of hydrochloric or sulfuric acid providing of heat, if necessary and then the solution is cooled to 0 - 5 °C. Sodium nitrite in equivalent mole of amine is dissolved in water, added portion of aqueous sodium nitrite solution to acidic amine solution. The diazonium salt form complete, if the solution give an immediate positive test for excess of nitrous acid with potassium iodide - starch paper. The reaction mixture must be kept very cold during the process (6).

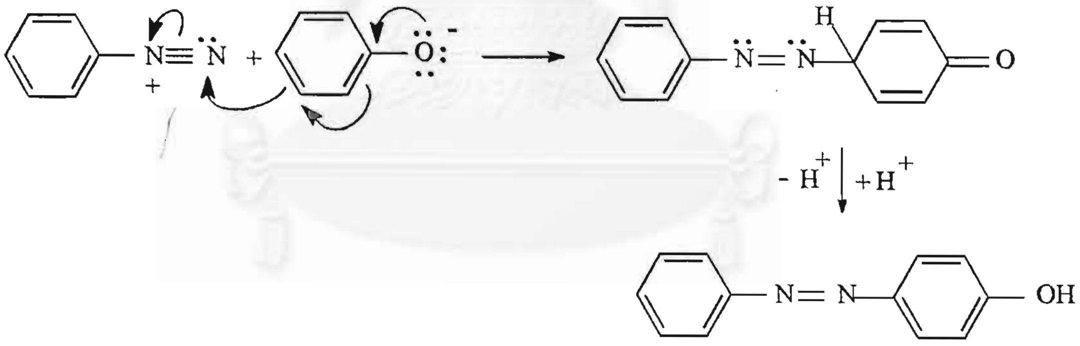
$$\mathrm{NaNO_2 + HCl \longrightarrow HON{=}O + NaCl}$$

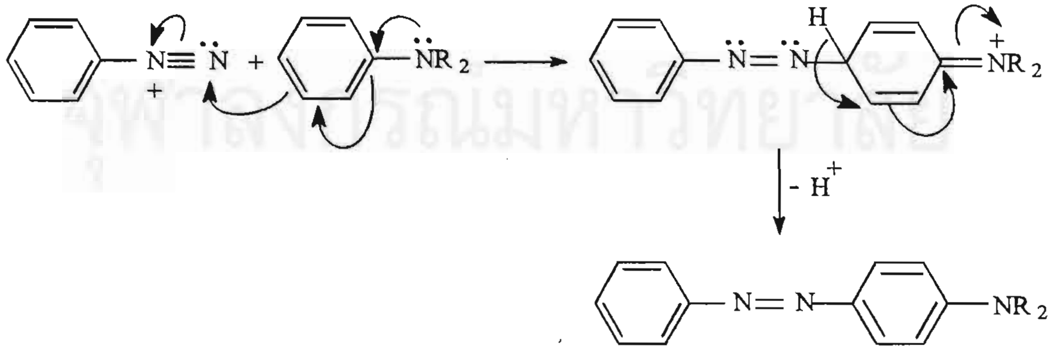
$$\mathrm{2HON{=}O \longrightarrow O{=}N\text{-}O\text{-}N{=}O + H_2O}$$



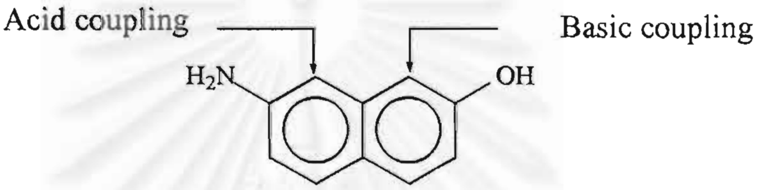
The mole ratio of acid and amine is 2.5 - 3 to 1. The first mole of acid is need to generate nitrous acid from aqueous sodium nitrite, second mole is needed to convert the diazonium hydroxide to diazonium cation and last 0.5 - 1 mole is used to maintain acidic condition to stabilise the diazonium salt and minimise reaction of diazonium salt with unchanged amine to form diazoamino compound which occurs readily in neutral solution (7).

Diazonium salts react with phenols in alkaline solution or aromatic amine in acidic solution to form azo dye. The azo group enters the para-position with respect to -OH or -NH_2 group. If the para-position is occupied, coupling occurs in the ortho-position. Coupling reacation is never reacted at meta position thus if para and ortho-position are occupied, coupling reaction will not occur (8).





With couplers containing both an aromatic amino group and a phenolic hydroxyl group, the amino group determines the position taken by the azo residue when coupling is carried out in acid solution, and the hydroxyl group is determinative in alkaline media. If coupling is carried out first in acid solution (directed by the amino group), a subsequent coupling reaction in alkaline solution can be used to introduce a second azo group (directed by the hydroxy group) (4)(9).

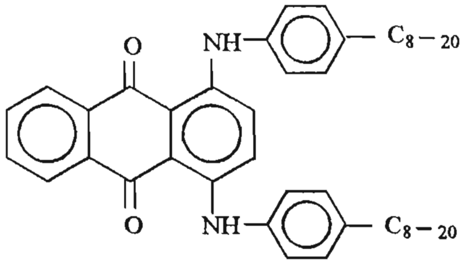


2.3 Petroleum dyes and markers

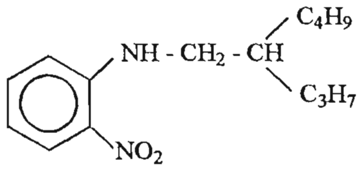
Since petroleum products are mixture of hydrocarbon and are light color, so that dyes are added to differentiate different products. Moreover, dyes are added for distinguish quality of product. For example, gasoline has three quality classes, regular gasoline, premium gasoline and aviation gasoline. Those gasolines are clear color but they can be distinguished by adding colors which are red, yellow and blue dyes, respectively.

Type of chemicals, employed as dyes in petroleum products such as anthraquinone, nitro compounds, monoazo-dyes, disazo-dyes etc.

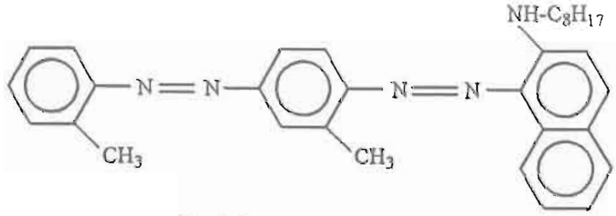
Typical example of dyes formula is expressed below (10)(11).



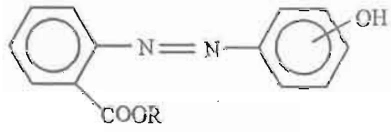
Blue green dyes



Yellow dyes



Red dye



Orange dye

Dyes must satisfy various requirements as the following (10).

1. Possess a high dyeing power.

2. Have sufficient solubility in the solvents and in the fuel, despite why ? antiknock agents have been added.

3. Have a high diffusion index.

4. Contain little or no insoluble by-product in fuels.

5. Leave only a minimum deposit of sludge in the engine.

6. Have a proper fastness to environment during storage.

7. Be compatible with additives and not cause difficulties during combustion.

8. Be brittle but not powderous in the solid form.

9. Be sufficiently fluid to be solubilized in organic solvents, if it is used in the form of concentrated solution.

Dyes used in the form of a concentrated solution have more advantages than in the powder form because it is easy to be used, rapidly of dosage, high diffusion coefficient and absence of powders.

Markers are foreign chemicals which are added in petroleum products for security purposes since they impart no color to the fuel but are detected either by chemical reaction or by special instruments.

Marker for petroleum products must have this characteristics (12)(13).

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1.Specific of properties and characteristics which were different from petroleum products.

2.Add in low level and having no effect on quality of marked oils.

3.Easy to detect by specific chemical or physical test especially in field test.

4.Difficult to identify structure or remove from petroleum products.

5.Conveniency for handle, supply by concentrated solution in suitable solvent, completely soluble in oil.

6. Stable over stroage period , fastness to environment.

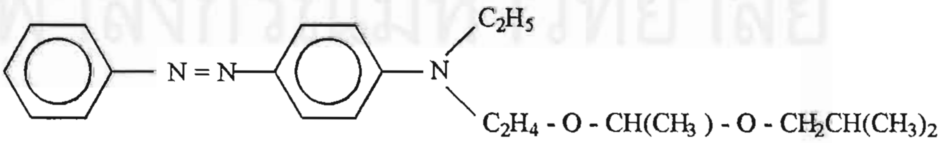
7. Have laboratory methods for confirmation of quantity of marker.

2.4 Literature review

Example of modern marker or marker dye are described in literature survey below.

US Patent 4904765 "***Dye Mixture Containing an Oil-soluble Dye and an Acid-extractable Dye*** " (11)

Acid-extractable dye are yellow dye and function as marker, giving pink to red color in aqueous or aqueous alcoholic phase when shaken with 5-10% aqueous or aqueous alcoholic mineral acids.



Oil-soluble dyes is non or little color change in aqueous or aqueous alcoholic phase. Typical example of oil-soluble dyes are the following.

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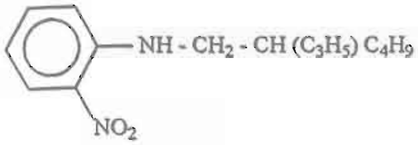
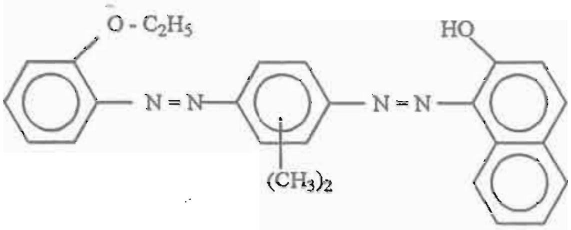
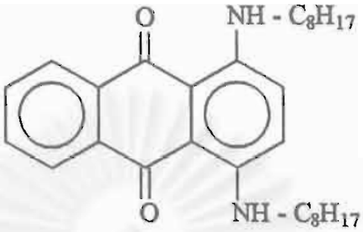


Yellow dye



Red dye

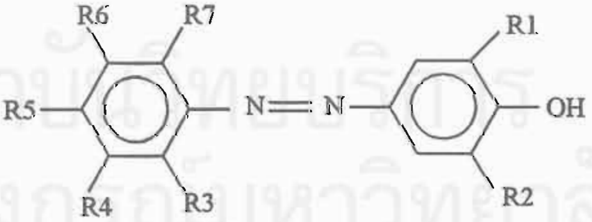


Blue dye

Acid-extractable dye and oil-soluble dye used in a weight ratio from 1:3 to 3:1. They are not only used for tagging petroleum products but also give various color in oils. For example, green dye is prepared by mixing yellow acid-extractable dye and blue oil-soluble dye.

European Patent EU 0 509 818 A1 "***Silent Markers for Petroleum, Method of Tagging, and Method of Detection***" (12)

The marker of this invention is phenylazophenols derivative have general formula.



R1, R2 are same or different of alkyls group (C1-C7) and R3, R4, R5, R6, R7 are same or different select from hydrogen, methyl, NO_2, Br, CN or Cl

The markers may be detected in liquid petroleum products by extraction with a reagent comprising water, water-soluble amine and water-miscible cosolvent such as mixture of water, methoxy ethoxy

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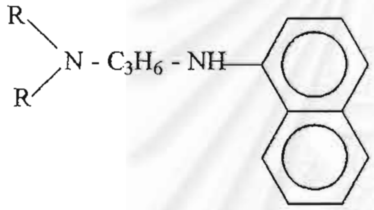
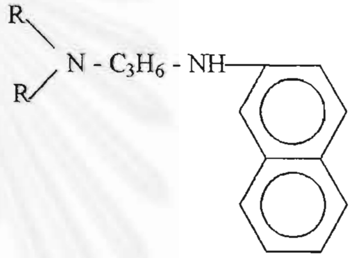
propylamine and diethylene glycol. A color develops in aqueous phase confirming the presence of marker. Color in aqueous phase is variety from red to blue color depend on character of each marker. Measurement of absorbance at λ maximum compared to standard curve report as amount of marker in fuel.

US Patent 4209302 ***"Marker for Petroleum Fuels"*** (13)

1-(alkylamino)-3-(alpha or beta naphthylamino)-propanes





where R group may be hydrogen, alkyl having 1 - 20 carbon atoms or morpholino group added in fuels as marker.

Naphthyl amino-propane compounds added in fuels which no color change of fuels. The aqueous acidic solution which is used to extract the marker from marked fuels may be a solution of methane sulfonic or hydrochloric acid. Adding diazonium salt of 2-chloro-4-nitroaniline solution, to give red color of diazo compound as positive test. Confirmation of marked compound by adding n-amyl alcohol and ammonium hydroxide to red diazo compound. If color of floating alcohol layer becomes reddish purple, it indicated the presence of marked compound.

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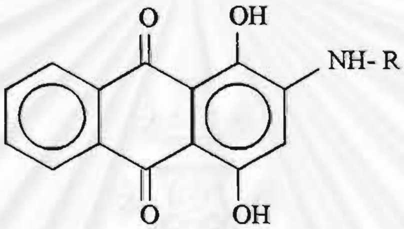
European Patent EU 0 149 125 A2 “***Tagging Compounds and Method for Detecting such Compounds***” (1) and

European Patent EU 0 147 704 A2 “***A Water Immiscible Liquid Comprising a Tagging Compound and Method for Detecting such Tagging Compound***” (14)

These two patents disclosed 1,4-Hydroxyanthraquinones derivative having the general formula below as marker.

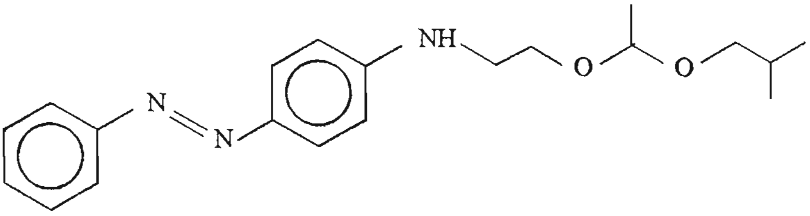


R = $CH_2CH_2CH_2$-O-CH_3 or $CH_2CH_2CH_2$- OCH_2CH_2-O-CH_3

1,4-Hydroxyanthraquinone derivatives together with ortho-sec-butyl phenol or p-nonyl phenol gave red color when added into fuel. After shaking with extract solvent (mixture of water, glycerine and organic amine), it give red color in solvent bottom layer. Unmarked fuel gives colorless or very slightly yellowish color in solvent layer. Marked fuel percolates through activated alumina column. Other component except tagging compound remove from column by elute with isooctane, acetone and ethanol, respectively. The tagging compound remained in the column as a purple zone at column head and elute with mixture of glycerine, water and cyclohexylamine. Total eluants was make up volume and measured absorbance at 556 - 557 nm to determine concentration of tagging compound.

Solvent Yellow 124 : (15)

N-Ethyl-N-[-(1-isobutoxyethoxy)ethyl](4-phenylazophenyl)amine



Solvent Yellow 124 (BASF AG, Ludwigshafen, Germany) or Dyeguard Yellow 124 (John Hogg Tech Ltd. , England) was one of the most widely used marker systems around the world. It is added in fuel to formed yellow color and detect by shaking with extraction acid aqueous solution. Bottom aqueous layer was colored red if marker was present. Quantitative analysis in laboratory by visible spectroscopy or HPLC.

US Patent 5498808 " ***Fluorescent Petroleum Markers*** " (16)

Compositions of this patent invention contain organic furanone esters derivatives.

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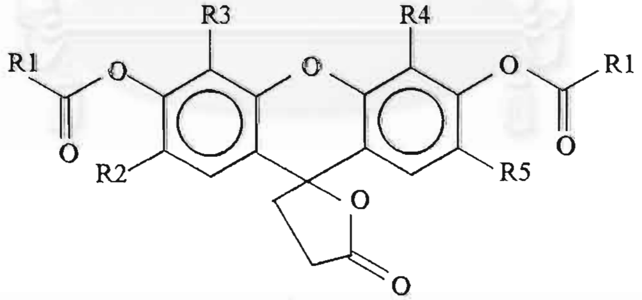

Where R1 is C_1-C_{18} alkyl or aryl group and R2, R3, R4, R5 are hydrogen, chloride, bromine, or C1-C12 alkyl.

Tagging fuels shaken with extraction medium (mixtures of water, aliphatic alcohols, glycols, glycol ethers or quaternary ammonium hydroxide compound), upper oil phase retains its light red appearance but

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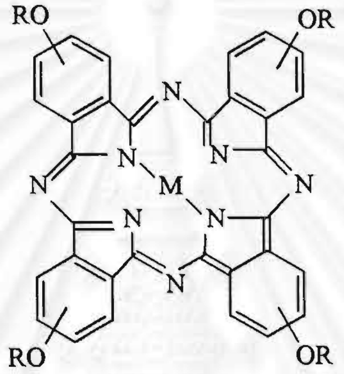
the lower aqueous phase change to strong green fluorescence. This phase may be separated and quantified by spectrofluorometer.

US Patent 5525516 " ***Method for Tagging Petroleum Products*** " (17) and WO Patent 94/02570 " ***Use of Compounds which Absorb and/or Fluoresce in I/R Range as Markers for Liquid*** " (18)

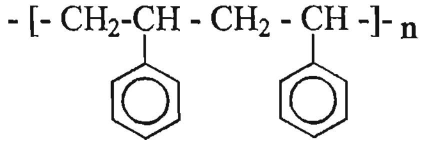
This patent provides near infrared fluorophoric compound such as phthalocyanine derivatives.



M = Li , Mg, Zn, Cu, Ni, V, Ti, Al or Si
R = alkyl, aryl, halogen or hydrogen

The invisible near infrared fluorophores markers are added to hydrocarbons fuels at extremely low levels. Detection was carried out by exposing the marked fuel to near infrared radiation having a wavelength in 670 - 850 nm and detecting the emitted fluorescent light via near infrared light detector. This tagging material can not detect by chemical reaction.

US Patent 5512066 " ***Tagging Materials for Gasoline*** " (19)



$$-[-CH_2-CH-CH_2-CH-]-_n$$

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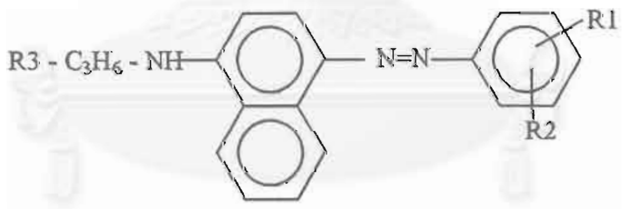
Exploration tagging system in gasoline by using polymer such as polystyrene which have number average molecular weight more than 15000 was described. Polymer was added to gasoline in amount of less than 1 ppm. The tagging gasoline can be analyse by evaporate light hydrocarbon in gasoline at 122 °C 2 mmHg. Residue was collected and make up to volume. Gel permeation chromatography with light scattering detector was used for analysis amount of present polymer in gasoline. This marker was inert to chemical reaction so field test with chemical testing could not showed any different between marked and unmarked fuel. Moreover, test method may be interfered by additive in fuel which have polymer chain in nature.

US Patent 5490872 "***Acid Extractable Petroleum Fuel Markers***" (20) Petroleum fuels are tagging with markers having formula.



Where R1 and R2 are selected from hydrogen, C1 - C2 alkyl, methoxy, halogen, cyano or nitro group, and R3 are selected from methyl, methoxy, methoxyethoxy or morpholino group.

The marker in liquid petroleum fuels may be detected by extraction with an acidic aqueous solution such as hydrochloric acid, formic acid or phosphoric acid. This acidic aqueous solution not only extracts the marker from petroleum fuels, but causes the marker to react, producing magenta, red or blue color depend on type of marker which identifies the

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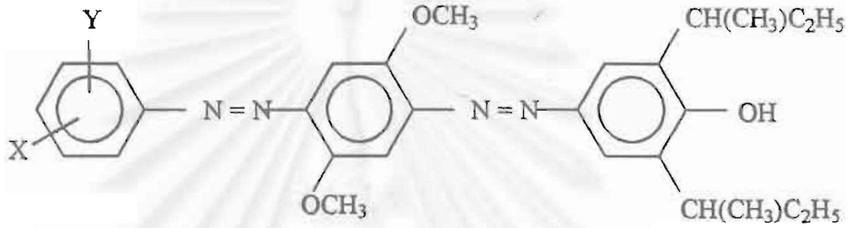
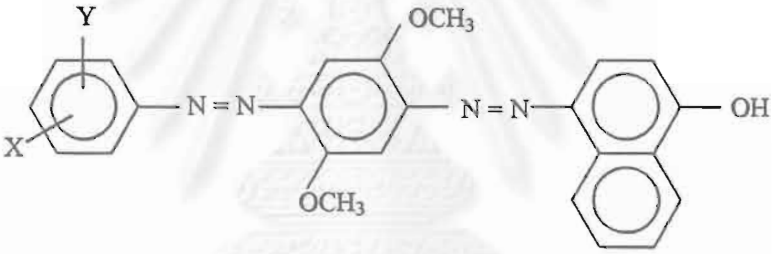
petroleum fuels as to source, permeation of use, etc. The color that is produced in aqueous layer relatively quantitative of marker. Therefore, colorimetric equipment may be used to quantify the amount of marker in fuels.

US Patent 5252106 "***Base Extractable Petroleum Markers***" (21)
Liquid petroleum products are tagging with marker having the formula.





X and Y are same or different selected from hydrogen, methyl, methoxy, halogen, nitro or cyano.

Compounds of this formula are generally pale red color at end use level, less than 100 ppm, in petroleum product and are not readily observable to the naked eyes. On the other hand, a deep color of blue shade will appear in aqueous layer when shaken with alkaline aqueous solution. Colorimetric equipment may be used to quantify the amount of marker in the aqueous phase.

9

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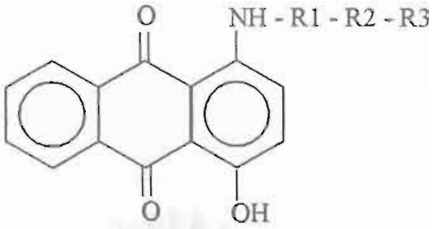
US Patent 5205840 "***Marker for Petroleum, Method of Tagging and Method of Detection***" (22)

Liquid petroleum products are tagging with a marker which is a compound or mixture of compounds having the formula.



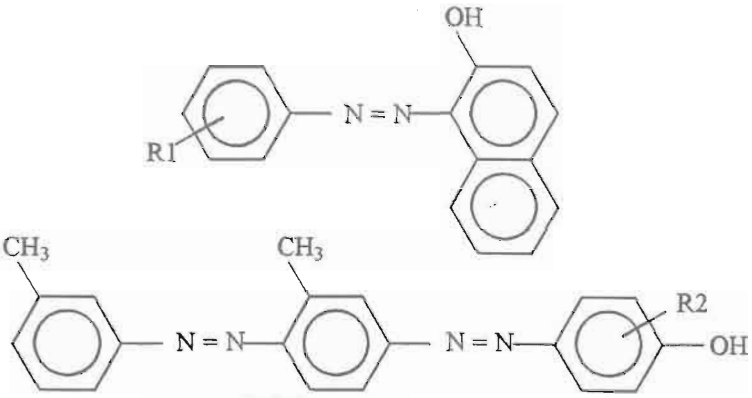
R1 is C1 - C6 alkyl and R2, R3 are nothing or C1 - C3 alkoxy.

This compounds are solids at room temperature but preferable provided as a concentrated solution in petroleum-miscible solvent and have purple color when add into petroleum products. However, at the level used to mark petroleum products, not more than 100 ppm, the marker imparts little visible color. Marker may be extracted in an alkaline aqueous solution containing an oxygenated-cosolvent such as glycerine, propylene glycol or methoxy ethoxy propylamine. If marker is present in petroleum products, it will be extracted and the color in aqueous phase is enhanced to purple color. Impurity or any dyes will not be extract by extraction mixture and color in aqueous phase is quantitative so the amount of marker in petroleum products may be analyse by colorimetric equipment.

US Patent 5487770 "***Detection of Marked Mineral Oils and Novel Azo Dyes***" (23)

import

This patent is develop the azo dyes and extraction solvents series for marked and detecting tagging oils.



R1 is hydrogen, C1 - C4 alkyl, C1 - C8 alkoxy, C1 - C9 alkyl carbonyl.
R2 is hydrogen, methoxy or alkyl amino.

This azo dyes when add as marker in mineral oils appear strongly yellow or orange color. Extraction solvent is the mixture of water and alkaline or alkaline earth metal hydroxide or carbonate such as calcium hydroxide, sodium hydroxide, lithium carbonate and water-miscible organic solvent such as dimethyl sulfoxide (DMSO), 3-methoxy-propylamine. Shaking marked oils with extraction solvent, the azo dye transfers into aqueous phase, which takes on distinctly visible color. The color of extract phase vary from strong violet, blue, green, yellow to red depends on type of azo dyes and extraction solvent system while the oil phase is colorless or weakly yellow.

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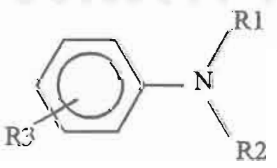
US Patent 5627077 "***Anilines as Markers for Mineral Oils***" (24)

Aniline derivatives are used for marking mineral oils.



R1 and R2 independently of one another are each hydrogen, C1 - C18 alkoxy, phenol, amino etc. or R1, R2 together with nitrogen atom which

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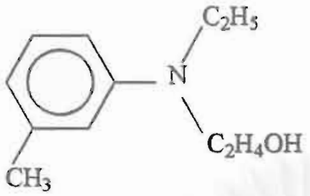
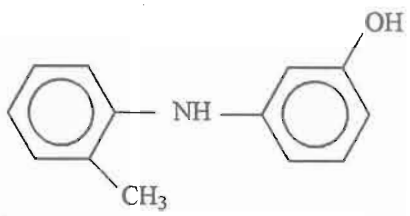
links by 5,6 member heterocyclic. R3 is hydrogen, C1 - C18 alkyl, cyano, nitro, hydroxy, alkoxy, amino etc. Example of those compounds are the following.





Tagging oils is monitored by shaking with diazonium salt of 1-amino anthraquinone or 2-(3-phenyl-1,2,4-oxadiazol-5-yl) aniline or 2-chloro-4-nitroaniline. The mixture was shaken again with 9% aqueous hydrochloric acid. After the phase is separate the lower aqueous phase found to be color. Color of aqueous phase is difference by changing of aniline derivative and diazonium salt. Moreover, intensity of the aqueous color depends on pH of aqueous phase. Aniline derivatives can be quantified by measuring absorbance of aqueous phase and then compares with the absorbance of known standard.

2.5 Raw material of this research

Cashew nut shell liquid (CNSL) or cashew nut shell oil (CNSO) was selected as the raw material for this work to develop the marker dyes. The CNSL is the oil obtained from the spongy layer between the inner and outer shells of cashew nuts tree, *Anacardium occidentale* Linn (25). Cashew nuts tree have originated in the rainforest around the Amazon river basin in South America and propagated to the Southern region of North America by Western colonizers, and to many part of Africa, India and Far East. Cashew nuts tree spread in Thailand in 1901 by Governor General of Phuket who brought seeds of cashew nut from Malaya to

Southern Province. Now, there are widely spread in many areas particular in South and North East of the country.

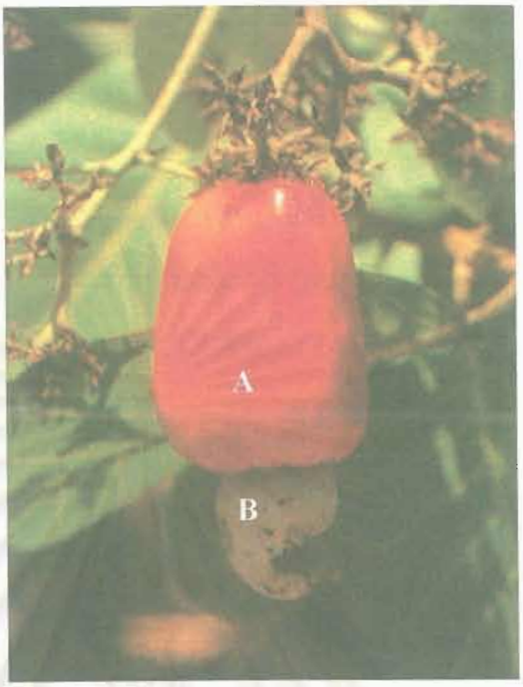


Figure 2-1 Cashew apple (A) and cashew nut (B).

2.5.1 Process for obtaining CNSL

There are two ways to obtain CNSL from cashew nut shell, heating and solvent-extraction methods (26). Heating method was done by heating unshelled cashew nuts to separate shells from nuts, there, heating the shells together with hot CNSL render oil seep from the shells and separating the oil from the solid matters to give crude CNSL.

In the solvent-extraction method, nuts are separated from the shells without heating. Then the shells are ground and extracted with a solvent and separate the CNSL by distillation and recycle the solvent.

Examples of the solvent usable in this method include organic solvents e.g., hydrocarbon such as n-pentane, n-hexane, n-heptane, n-octane, cyclohexane, cyclooctane, benzene, toluene and xylene, ketones such as acetone and methyl ethyl ketone, alcohol such as methanol and

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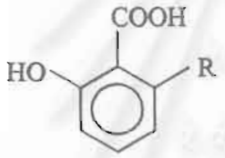
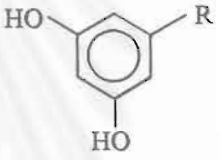
ethanol, esters such as methyl acetate and ethyl acetate. Among these solvents n-hexane is frequently employed since it is less expensive and can be easily obtained.

2.5.2 Compositions of CNSL

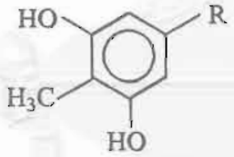
The principal components of the CNSL are phenolic compounds consisting of mixture of anacardic acid (β-pentadecylsalicylic acid) 82%, cardol (5-pentadecylresorcinol) 13.8%, 2-methylcardol (2-methyl-5-pentadecylresorcinol) 2.6% and cardanol (3-pentadecylphenol) 1.6%, which differ in their C_{15} chains as saturated, monoene, diene or triene (27)(28)(29).



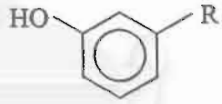
Anacardic acid



Cardol



2-Methylcardol



Cardanol

R is $(CH_2)_{14}CH_3$

or $(CH_2)_7CH = CH\ (CH_2)_5\ CH_3$

or $(CH_2)_7CH = CH\ CH_2\ CH = CH\ \text{-}(CH_2)_2\ CH_3$

or $(CH_2)_7CH = CH\ CH_2\ CH = CH\ CH_2\ CH = CH_2$

Among these components, anacardic acid is the major component with most preferable contains approximately 90% of the CNSL (25). CNSL obtained by the heating method may loose carboxylic group of anacardic acids to give cardanol (26).

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2.5.3 Utilities of CNSL

CNSL is a very useful substance. It can be used to protect the hulls against insect attack and on fishing nets for rot proofing. CNSL has been used on timber work in house as protection against termites. Moreover, it can be used as fuel by burning cashew nut shell with remain CNSL in the shell.

Futhermore CNSL is raw material for manufacture of many products such as lacquer, varnishes, plastic material, phenolic resin, dyes, paints, inks, lubricating compound, electrical insulation, rubber-like compositions, insecticide compositions, chemical derivative of CNSL composition, brake material, filter material, adhesive, coating compositions, laminated products, medicine compositions, mineral oil compositions, friction materials, photosensitive compositions, gasket etc. Throughout this work, CNSL will be used for developing the marker dyes used in petroleum oils.

2.6 Reaction in this research

2.6.1 CNSL hexyl ester

Due to strong acidity of anacardic acid, a main component of CNSL, the reduction of its acidity is necessary. Esterification reaction was used to change carboxylic group to be an ester group. The product of reaction had better solubility in hydrocarbon solvent than an anacardic acid. This was due to the number of carbon atoms in ester was increased upto 6 atoms which came from alcohol employed in this reaction.

Esterification reaction is quite simple. It was consisted of the reaction of carboxylic acid and primary alcohol in the presence of sulfuric acid, acting as a catalyst. The by-product of esterification reaction is water, which can be eliminated by adding toluene to form an azeotropic

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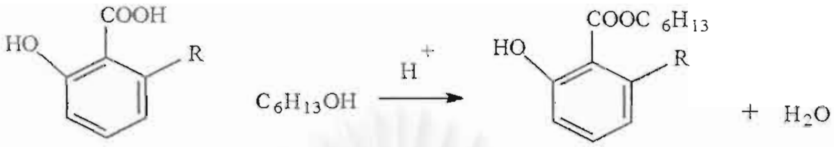
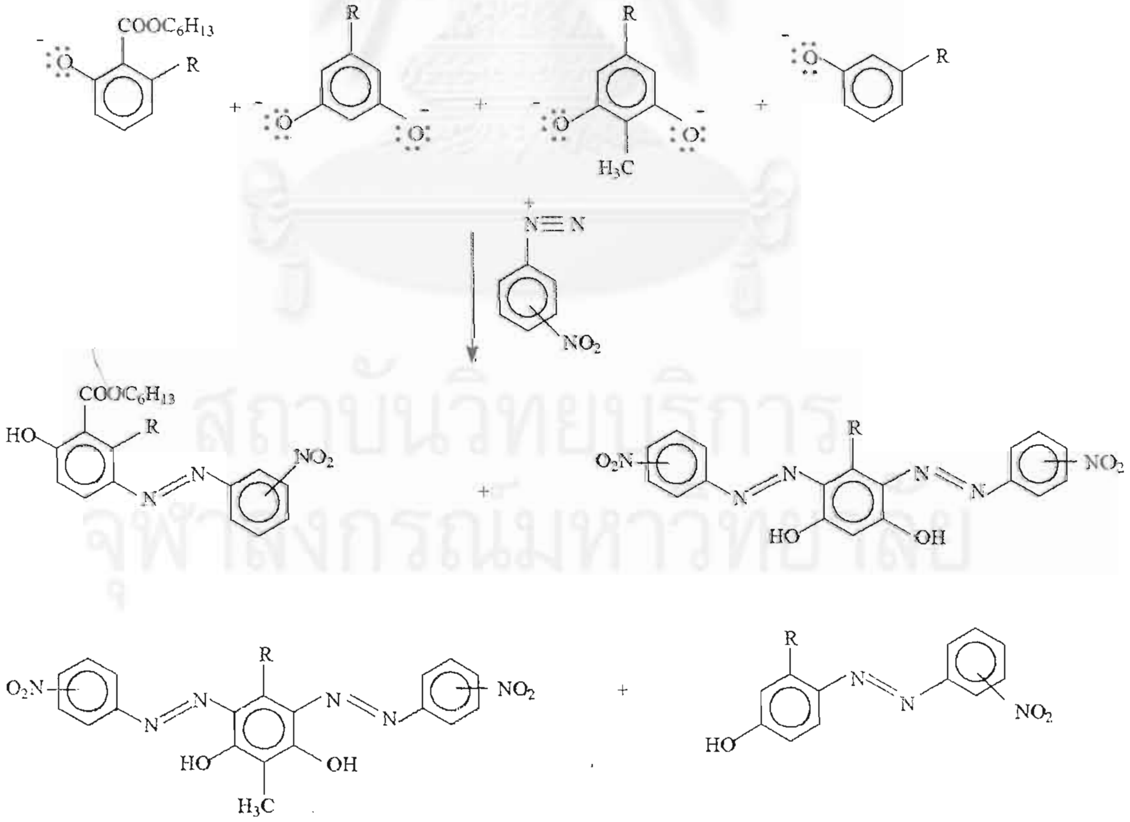
and eliminated water with water trap receiver. Esterification of carboxylic acid gave good yield by using an excess of primary alcohol together with an elimination reaction of water, causing the equilibrium of the reaction to shift to the aimed product.



2.6.2 Coupling reaction of CNSL hexyl ester and nitro-aniline derivatives

CNSL hexyl ester herein means the mixture of hexyl anacardate, cardol, 2-methyl cardol and cardanol. All of those compounds are dissolved in alkaline solution and coupling with diazonium salt of nitroaniline derivative leading to the azo compounds as the product.



The synthesize azo dyes will be used for developing the marker dyes used in petroleum oils.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Materials used in this research were obtained from various sources and tabulated in Table 3-1.

Table 3-1 Materials and sources.

Materials	Sources
Cashew nut shell	Phuket province
n-Hexane	J.T. Baker
1-Hexanol	Fluka
Toluene	Mallinckrodt
Sulfuric acid	J.T. Baker
Hydrochloric acid	BDH
Sodium nitrite	BDH
Aniline	Merck
m-Nitroaniline	Fluka
o-Nitroaniline	Fluka
p-Nitroaniline	Eastman Organic Chemical
Phenol	Merck
Resorcinol	Fluka
Stannous chloride	May & Baker
Potassium hydroxide	BDH
Ethylene glycol	Carlo Erba
Chloroform-d	Fluka
Potassium iodide	Merck

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3.2 Apparatus

Apparatus and test methods used in this research were shown in Table 3-2.

Table 3-2 Apparatus and test methods.

Test Items	Methods	Apparatus
FT-IR	FT-IR spectroscopy	PE System 2000
^{13}C -NMR	NMR	Bruker ACF 200
Maximum Absorption	UV-Vis spectroscopy	PE Lamda 2
Distillation	ASTM D86	ISL AD86 5G
Flash Point (COC)	ASTM D92	ISL CFP 92
Flash point (PM)	ASTM D93	ISL PMFP 93
Pour point	ASTM D97	Manual
Copper strip corrosion , 3 hr @50°C	ASTM D130	Manual
Existent gum	ASTM D381	Manual
Kinematic viscosity @ 40 °C	ASTM D445	Cannon Auto Vis
Total acid number	ASTM D974	Metrohm 665
API gravity @ 60 °F	ASTM D1298	Manual
Color	ASTM D1500	Manual
Crystalline temperature	ASTM D2386	Manual
Research octane number (RON)	ASTM D2699	CFR engine
Sulfur content	ASTM D4294	Outokumpu X-MET820
Oxygenated compounds	ASTM D4815	HP5890 SeriesII
Reid vapor pressure (RVP)	ASTM D4953	Grabner Ins
Benzene	ASTM D5443	HP5890 PONA
Total aromatics	ASTM D5443	HP5890 PONA
Water content	ASTM D4928	Metrohm 652 KF
Flash point (Abel)	IP 170	ISL AFP 170

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3.3 Experimental procedure

3.3.1 Properties of CNSL and CNSL hexyl ester

CNSL was obtained by pressing cashew nut shells and the oil in shell was extracted with n-hexane. The n-hexane was evaporated on water bath to obtain CNSL. CNSL was then esterified with 1-hexanol using sulfuric acid as catalyst and toluene as solvent.

Procedure

To a 500 mL 2-neck round bottom flask was added 51.75 g of CNSL, 46 g of 1-hexanol, 4 mL of concentrated sulfuric acid and 200 mL of toluene. Then 2-3 pieces of small boiling chips was charged, attached water receiver with condenser in one neck and thermometer in other neck. The mixture was refluxed for 10 hours. After completion, the reaction flask was cooled to room temperature and the product was poured into separation funnel. Cold distillate water was added with gradual stirring. The two layers were separated and discarded the lower aqueous phase. The upper layer was washed with cold water until the discarded water was not strong acid. The crude ester was collected in round bottom flask and toluene solvent and unreact alcohol were distillated off until the temperature of the crude ester reached to 160 °C, then cooled down to room temperature to obtain CNSL hexyl ester.

Structure of CNSL and CNSL hexyl ester were studied by FT-IR and ^{13}C-NMR using $CDCl_3$ as solvent. Physical properties of obtained CNSL and CNSL hexyl ester were tested according the ASTM methods.

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Methods of physical properties testing were applied from ASTM standard method. Test items and test methods were listed in Table 3-3.

Table 3-3 Test items and test methods for physical properties testing of CNSL and CNSL hexyl ester.

Test Items	Test Methods ASTM D
API gravity @ 60 °F	1298
Kinematic viscosity @ 40 °C	445
Copper strip corrosion, 3 hr @ 50°C	130
Flash Point (COC)	92
Total acid number	974
Water content	4928

3.3.2 Synthesis of azo dyes from CNSL hexyl ester and related coupling reaction with diazonium salts of aniline and nitroaniline derivatives.

Procedures

3.3.2.1 Preparation of diazonium salts

a). Aniline

Dissolved 0.93 g of aniline in a mixture of 2.5 mL concentrated hydrochloric acid and 2.5 mL of water with vigorous stirring. The solution was cooled to 0 - 5 °C. Dissolved 0.69 g of sodium nitrite in 10 mL of water and cooled to 0 - 5 °C. When both solution were cooled, nitrite solution was added dropwise to aniline hydrochloride solution with continuous stirring. The temperature of solution was kept constant and should not rised more than 5 °C. The solution should be clear. A drop of the solution was diluted with 3-4 drops of water and potassium iodine-starch paper was added (30)[†]. If there was no immediate blue color obtained at the point of contact with the paper, further dropwise of nitrite solution was added. After 3 - 4 minutes, the solution was tested again. This test was continued until a slight excess of nitrous acid was present as shown by weak blue color on iodine-starch paper. Aniline diazonium salt was stored in cool water at about 0 - 5 °C until used.

b). p-Nitroaniline and o-nitroaniline

Dissolved 1.7 mL of concentrated sulfuric acid in 1 mL of water, and a small portion of 1.38 g para or ortho nitroaniline was added with stirring with glass rod. A drop of concentrated acid was added when solid particles remained undissolve. Nitroaniline in acid solution was cooled to 0 - 5 °C. A cooled solution of 0.69 g sodium nitrite in 10 mL of water was introduced drop by drop into nitroaniline in acid solution with continuous stirring. The temperature was kept below 5 °C. The formation of nitrous acid was monitored by potassium iodine-starch paper as mentioned above.

c). m-Nitroaniline

Divided 1.38 g of m-nitroaniline into small portions and added into a mixture of 1.7 mL concentrated sulfuric acid and 1 mL of water with stirring with glass rod. The mixture was cooled down to 0 - 5 °C. Dissolved 0.69 g of sodium nitrite in 10 mL of water and cooled down to

---

[†] Pure starch (1 g) was rubbed with a small amount of water, and 100 mL of boiling water was added with thorough stirring . After the solution was cooled, 0.2 g of potassium iodide was added and sheets of clean filter paper were soaked in it and allowed to dry in a clean place.

0 - 5 °C. The nitrite solution was then added dropwise to a solution of nitroaniline in acid in which any precipitated material will redissolve. Potassium iodine-starch paper was used to monitor the formation of nitrous acid as mentioned above. The temperature of all solutions were maintained below 5 °C.

3.3.2.2 Preparation of phenolate ions

a). Phenol

Potassium hydroxide (1.4 g) was dissolved in 5 mL of water and 0.94 g of phenol was added with continuous stirring and then cooled to 0 - 5 °C.

b). Resorcinol

Potassium hydroxide (1.4 g) was dissolved in 5 mL of water and small portion of 0.55 g of resorcinol was added with continuous stirring and then cooled to 0 - 5 °C.

c). Hexyl salicylate

Potassium hydroxide (1.4 g) was dissolved in 10 mL of methanol and small portion of 2.22 g of hexyl salicylate was added with continuous stirring and then cooled to 0 - 5 °C.

d). CNSL hexyl ester

Potassium hydroxide (1.4 g) was dissolved in 10 mL of methanol and 4.3 g of CNSL hexyl ester was added with continuous stirring and then cooled to 0 - 5 °C.

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3.3.2.3 Preparation of azo dyes

Azo dyes were prepared by coupling reaction of diazonium salts in Section 3.3.2.1 and phenolate ions in Section 3.3.2.2. Series of azo dyes were listed below.

1) phenol + aniline
2) phenol + m-nitroaniline
3) phenol + o-nitroaniline
4) phenol + p-nitroaniline
5) resorcinol + aniline
6) resorcinol + m-nitroaniline
7) resorcinol + o-nitroaniline
8) resorcinol + p-nitroaniline
9) hexyl salicylate + aniline
10) hexyl salicylate + m-nitroaniline
11) hexyl salicylate + o-nitroaniline
12) hexyl salicylate + p-nitroaniline
13) CNSL hexyl ester + aniline
14) CNSL hexyl ester + m-nitroaniline
15) CNSL hexyl ester + o-nitroaniline
16) CNSL hexyl ester + p-nitroaniline

The Azo dyes were prepared by adding the cold diazonium salt solution slowly into rigorously stirring of the cooled phenolate solution. A color solution was developed immediately, and the addition of the diazonium salt continued. When all diazonium salt solutions had been added the dyes will separate from aqueous phase and the mixture was allowed to cool for 30 minutes with continuous stirring. After that period,

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5 mL of undye gasoline was added into the dyes mixture, and collected the azo dyes oil solution in a screw cap vial.

3.3.2.4 Coloration of synthesized azo dyes

A small drops of azo dyes oil solution in Section 3.3.2.3 was added in a screw cap vial containing 25 mL of undye gasoline. The mixture was shaken and the color of the oil was compared to all other azo dyes prepared by the same method.

3.3.2.5 Reduction of Azo Dyes

Dissolved about 0.5 g of stannous chloride in 1 mL of concentrated hydrochloric acid and a small quantity of azo dyes in Section 3.3.2.3 was added and heated on water bath. A colorless solution should confirm the presence of azo group.

3.3.3 Extraction system for detection of azo dyes in fuels

Since azo dyes in this study were phenyl azo compounds which weak acid character. Therefore, in alkaline organic immiscible solvent, the azo dyes were formed ionizable salts and were removed into extraction phase. Thus gave color to this phase.

In this studied, extraction system was potassium hydroxide in ethylene glycol which immiscible with petroleum oils.

Procedure

3.3.3.1 Comparison of color in extracted phase present from synthesize azo dyes and oil soluble dyes

Synthesized azo dye was dissolved in undye gasoline and shaken with solvent system. Color in extracted phase was observed. Commercial premium gasoline and high speed diesel were extracted in the same way and the color of extracted phases were compared.

A few drops of azo dye oil in Section 3.3.2.3 were added in a screw cap vial containing 10 mL of undye gasoline with vigorous stirring. A solution of 2 mL of diluted potassium hydroxide in ethylene glycol was added. The vial was capped and shaken for 30 seconds. After the liquid had been shaken, the 2 phases were allowed to separated and observed the color in extracted lower phase. By the same procedure 10 mL of premium gasoline (yellow color) and high speed diesel were shaken with 2 mL of extract solvent and the color in extracted phases were compared.

3.3.3.2 Suitable concentration of potassium hydroxide for extraction system

Few drops of azo dye oil which synthesized from CNSL hexyl ester and p-nitroaniline in Section 3.3.2.3 were added into 250 mL of undye gasoline. Pipetted 20 mL of dyed gasoline into a 30 mL screw cap vial. Added 4 mL of 1% potassium hydroxide in ethylene glycol into the vial, capped and shaken for 30 seconds and then allowed the phase to be separated. The lower phase of extraction solvent was exhibited color. This phase was taken into 1 cm UV cuvettes cell and the maximum absorption from 340 to 750 nm was determined. The operation was repeated using 2%, 3% and 4% potassium hydroxide in ethylene glycol instead of 1% potassium hydroxide and the maximum absorption was scanned in the same waverange. The concentration of potassium hydroxide which gave the highest absorption at λ maximum was chosen for future experiments.

3.3.4 Preparation of stock 20% CNSL hexyl ester and nitroaniline derived azo dyes

Procedure

3.3.4.1 CNSL hexyl ester-p-nitrophenyl azo dye

Dissolved 7.54 g of CNSL hexyl ester obtained in Section 3.3.1 and 2.5 g of potassium hydroxide in 10 mL methanol. The phenolate ions were prepared as mentioned in Section 3.3.2.2 (d).

A p-nitroaniline diazonium salt was prepared as mentioned in Section 3.3.2.1 (b) by using 2.48 g of p-nitroaniline, 1.24 g of sodium nitrite and 3 mL of concentrated sulfuric acid.

Coupling of both components to form an azo dye was carried out as mentioned in Section 3.3.2.3.The reaction was carried out in separatory funnel. Once the coupling reaction was complete, the organic phase of dye was separated from the aqueous phase. The azo dye solution in separatory funnel was washed with water many times and allowed to stand. The water phase at the bottom was removed. The azo dye was transferred to a 25 mL volumetric flask. The remaining dye in funnel was washed with toluene and made up to volume. The obtained CNSL hexyl ester-p-nitrophenyl azo dye was calculated to be 20% weight by volume base on CNSL.

3.3.4.2 CNSL hexyl ester-o-nitrophenyl azo dye

The same procedure in Section 3.3.4.1 was carried out except p-nitroaniline was substituted with o-nitroaniline.

3.3.4.3 CNSL hexyl ester-m-nitrophenyl azo dye

The same procedure in Section 3.3.4.1 was carried out except p-nitroaniline was substituted with m-nitroaniline.

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3.3.5 Quantitative analysis of CNSL hexyl ester - nitroaniline derivative azo dye

Three products of CNSL hexyl ester-nitroaniline derivative azo dyes in Section 3.3.4.1 to 3.3.4.3 were added into undye gasoline and high speed diesel with suitable concentration. Quantitative analysis by measuring the absorption of extracted phase at λ maximum compared with the standard curve.

Procedure

3.3.5.1 Standard curve for CNSL hexyl ester-p-nitrophenyl azo dye in gasoline

a). Preparation of CNSL hexyl ester-p-nitrophenyl azo dye concentration equivalent to 2000 ppm (mg/L) of CNSL in undyed gasoline

Pipetted 1 mL of CNSL hexyl ester-p-nitrophenyl azo dye (contained 20% CNSL) to 100 mL volumetric flask and made up volume with undyed gasoline, this gasoline was developed dark yellow color and contained calculated 2000 ppm CNSL.

b). Preparation of working standard 0, 5, 15, 25 and 35 ppm CNSL hexyl ester-p-nitrophenyl azo dye

Pipetted stock standard 2000 ppm (Section 3.3.5.1 a) to a 100 mL volumetric flask and made up volume with undyed gasoline.

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Working Standard (ppm)	Volume of 2000 ppm CNSL hexyl ester-p-nitrophenyl azo dye / 100 mL
0	0
5	0.25
15	0.75
25	1.25
35	1.75

The 20 mL of each concentration was put into 30 mL screw cap vial and 2% potassium hydroxide in ethylene glycol was added 4 mL. The vial was capped and shaken for 30 seconds, when two phases were clearly separated, drew the lower glycol phase into 1 cm UV cuvettes cell. Measured absorption at λ maximum. The standard curve between absorption and concentration (0, 5, 15, 25 and 35 ppm) was made.

3.3.5.2 Standard curve for CNSL hexyl ester-p-nitrophenyl azo dye in high speed diesel

The procedure in Section 3.3.5.1 was followed but replacing undyed gasoline with high speed diesel.

3.3.5.3 Standard curve for CNSL hexyl ester-o-nitrophenyl azo dye in gasoline and high speed diesel

The procedure in Section 3.3.5.1 was followed but replacing 20% CNSL hexyl ester-p-nitrophenyl azo dye with 20% CNSL hexyl ester-o-nitrophenyl azo dye.

3.3.5.4 Standard curve for CNSL hexyl ester-m-nitrophenyl azo dye in gasoline and high speed diesel

The procedure in Section 3.3.5.1 was followed but replacing 20% CNSL hexyl ester-p-nitrophenyl azo dye with 20% CNSL hexyl ester-m-nitrophenyl azo dye.

3.3.6 Physical properties of stock 20% CNSL hexyl ester-p-nitrophenyl azo dye

Procedure

Stock 20 % CNSL hexyl ester-p-nitrophenyl azo dye in Section 3.3.4.1 was tested for the physical properties according to specification listed in Table 3-4.

Table 3-4 Test items and test methods for stock 20 % CNSL hexyl ester-p-nitrophenyl azo dye.

Test Items	Test Methods
Appearance	Visual
Density @ 15 °C	ASTM D 1298
Flash point (Abel)	IP 170
Crystalline temperature	Apply from ASTM D 2386
Water content	ASTM D 4928
Kinematic viscosity @ 40 °C	ASTM D 445
λ maximum	UV - vis spectroscopy
Solids content	Visual

3.3.7 Stability test for CNSL hexyl ester-p-nitrophenyl azo dye in gasoline and high speed diesel

CNSL hexyl ester-p-nitrophenyl azo dye was added into gasoline and high speed diesel. The concentration of azo dye in dyeing fuels was monitored every week for 3 months.

Procedure

3.3.7.1 Stability of CNSL hexyl ester-p-nitrophenyl azo dye in gasoline

To a 1 L volumetric flask, 12.5 mL of 2000 ppm CNSL hexyl ester-p-nitrophenyl azo dye in Section 3.3.5.1(a) was added and made up to volume with undyed gasoline. This gasoline contained 25 ppm of CNSL. Dyed gasoline was stored in metal container. The concentration of azo dye in container was measured by pipetted 20 mL of dyed gasoline and mixed with 4 mL of 2% potassium hydroxide in ethylene glycol and shaking for 30 seconds. Absorption of clear glycolic phase at its λ maximum was compared with calibration curve in Section 3.3.5.1 to determine amount of azo dye in gasoline. Concentration of azo dye was determined from 3 samples and average results was reported in ppm of azo dye. Stability of azo dye was monitoring for 12 weeks.

3.3.7.2 Stability of CNSL hexyl ester-p-nitrophenyl azo dye in high speed diesel

To a 1 L volumetric flask, 7.5 mL of 2000 ppm CNSL hexyl ester-p-nitrophenyl azo dye in Section 3.3.5.2 was added and made up to volume with high speed diesel. The dyed diesel was contained 15 ppm of CNSL. The concentration of azo dye in diesel oil was determined from 3 samples as practice in Section 3.3.7.1 and compared with calibration curve in Section 3.3.5.2. The stability of azo dye in diesel oil was monitoring for 12 weeks.

3.3.8 Stability test for stock 20% CNSL hexyl ester-p-nitrophenyl azo dye

The stock 20% CNSL hexyl ester-p-nitrophenyl azo dye was stored and monitored dyeing power for 3 months by measured absorption of extracted phase. The structure of azo dye was determined by FT-IR.

Procedure

Stock 20% CNSL hexyl ester-p-nitrophenyl azo dye was filled in IR sample cell with 0.05 mm spacers. The transmission at 4000 to 370 cm^{-1} was measured. The 25 ppm azo dye was added into undyed gasoline and the concentration of azo dye was determined follow the method in Section 3.3.7.1. Stability test for azo dye was monitored every month for 3 months storage.

3.3.9 Effect of CNSL hexyl ester-p-nitrophenyl azo dye to physical properties of dyed fuels

Gasoline and high speed diesel were dyed with CNSL hexyl ester-p-nitrophenyl azo dye. The physical properties of dyed and undyed fuels were tested according to ASTM method. (Note that dyed and undyed fuels were from the same base fuels).

Procedure

3.3.9.1 Physical properties of dyed and undyed gasoline

Gasoline was dyed with 25 ppm CNSL hexyl ester-p-nitrophenyl azo dye. Preparation was made by pipetted 25 mL of stock 2000 ppm

CNSL hexyl ester-p-nitrophenyl azo dye (Section 3.3.5.1a) into 2 L volumetric flask and made up to volume with undyed gasoline.

The resulting fuel was tested according to the items listed in Table 3.5.

Table 3-5 Test items and test methods for dyed and undyed gasoline.

Test Items	Test Methods ASTM D
API gravity @ 60 °F	1298
RON	2699
RVP @ 37.8 °C	4953
Existent gum	381
Copper strip corrosion, 3 hr. 50 °C	130
Distillation	86
Oxygenated compounds	4815
Water content	4928
Benzene	5443
Total aromatics	5443
Color	1500

The remainder of dyed gasoline and 1 L of undyed gasoline were stored in separate metal container for 3 months. After this period, physical properties were tested again in the same manner.

3.3.9.2 Physical properties of dyed and undyed high speed diesel

High speed diesel was dyed with 15 ppm CNSL hexyl ester-p-nitrophenyl azo dye. Preparation was made by pipetted 15 mL of stock 2000 ppm CNSL hexyl ester-p-nitrophenyl azo dye in Section 3.3.5.2 into 2 L volumetric flask and made up to volume with high speed diesel.

The physical properties of dyed and undyed diesel oil were tested according to ASTM method. Test items and test methods were listed in Table 3-6.

Table 3-6 Test items and test methods for dyed and undyed diesel.

Test Items	Test Methods ASTM D
API gravity @ 60 °F	1298
Kinematic viscosity @ 40 °C	445
Pour point	97
Sulfur content	4294
Copper strip corrosion, 3 hr @50 °C	130
Flash point (PM)	93
Distillation	86
Color	1500

Dyed and undyed diesel were stored in separate metal container and the physical properties were tested again in the same manner after 3 months of storage.

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3.3.10 Characterization of CNSL hexyl ester nitrophenyl azo dyes

CNSL hexyl ester nitrophenyl azo dyes were characterized using FT-IR and ^{13}C-NMR methods.

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CHAPTER 4
RESULTS AND DISCUSSION

4.1 Properties of CNSL and CNSL hexyl ester

CNSL is extracted from cashew nut shell by n-hexane. The CNSL thus obtained is a viscous dark brown liquid. It is sparingly soluble in water, freely soluble in alcohol, ether, petroleum ether and organic solvent.

CNSL hexyl ester prepared from the reaction of CNSL with alcohol is a red brown and viscous liquid. It is insoluble in water, freely soluble in alcohol and organic solvent. Starting with 51.75 g of CNSL, 78.05 g of CNSL hexyl ester is obtained (after evaporation of toluene and unreacted alcohol). The ester product yield is calculated as (51.75 / 78.05) × 100 = 66.3 % by weight. This percentage will be used for reference to the amount of dyes added in fuels.

Properties of CNSL and CNSL hexyl ester are tested by ASTM standard methods. Results are shown in Table 4-1.

Table 4-1 Properties of CNSL and CNSL hexyl ester.

Test Items	Results	
	CNSL	CNSL hexyl ester
API gravity @ 60 °F	15.2	19.8
Kinematic viscosity @ 40°C , cSt	64.73	185.8
Copper strip corrosion , 3hr. @ 50 °C	No 1a	No 1a
Flash point (COC) , °C	218	85
Total acid number , mg KOH / g	18.52	4.45
Water content , % wt.	0.54	0.87

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Structure of CNSL and CNSL hexyl ester are characterized by FT-IR and ^{13}C-NMR whose spectrum have been shown in Figure 4-1, 4-2, 4-3 and 4-4 respectively.

FT-IR spectrum in Figure 4-1 showed absorption of OH- group at 3348 cm^{-1}, CH- stretching of aromatic at 3025 cm^{-1}, CH- stretching of aliphatic at 2944 and 2863 cm^{-1}, C = O carbonyl group stretching at 1644 cm^{-1} combine with C = C aromatics peak at 1602 cm^{-1}, CH_2 group bending at 1448, CH_3 group bending at 1307 cm^{-1} and C-O group stretching at 1244 cm^{-1}.

Figure 4-2 showed ^{13}C - NMR peak, using $CDCl_3$ as solvent. ^{13}C - NMR spectrum indicated CH_2, CH_3 in alkane group at 13 - 36 ppm, CH = CH in alkene and aromatic group at 112 - 160 ppm. The carbon in carbonyl group at 173 ppm.

Figure 4-3 showed FT-IR spectrum of CNSL hexyl ester. The major peak was OH- group at 3348 cm^{-1}, CH- stretching of aromatic at 3025 cm^{-1}, CH- stretching of aliphatic at 2944 and 2863 cm^{-1}, C = O carbonyl group stretching of ester at 1658 cm^{-1}, CH_2 group at 1448 cm^{-1}, CH_3 group at 1311 cm^{-1} and C-O group at 1238 cm^{-1}.

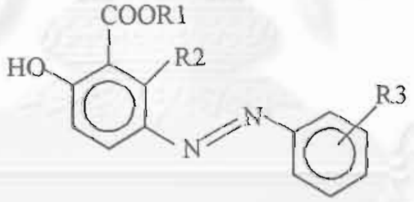
FT-IR spectrum of starting CNSL and CNSL hexyl ester product were somewhat similar except the appearance of OH group and the position of C = O group. The ^{13}C- NMR could differentiate between CNSL and ester product . ^{13}C- NMR spectrum in Figure 4-4 showed peak of CH_2, CH_3 alkane at 13 - 36 ppm, C - OH from unreacted alcohol at 62 ppm, -O-C-R from ester product at 71 ppm, C = C alkene and aromatic at 100 - 162 ppm and carbonyl group at 174 ppm.

4.2 Characteristic of azo dyes from CNSL hexyl ester and relate coupling product with aniline and nitroaniline derivatives

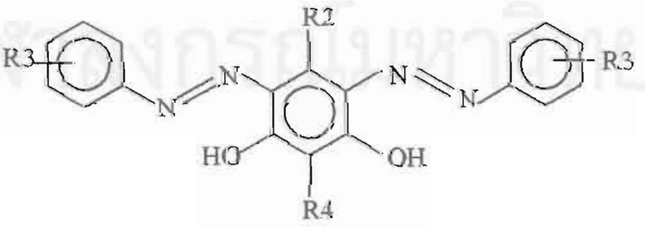
Azo dyes were synthesized from CNSL hexyl ester, hexyl salicylate, resorcinol and phenol coupling with aniline, m-nitroaniline, o-nitroaniline and p-nitroaniline.Those azo dyes were dissolved in gasoline. The color of each dyed gasoline was shown in Table 4-2.

Table 4-2 also showed the color of extracted phase when shaken dyed gasoline with extracted solvent. The dyed gasoline was reducted with stannous chloride and the color of solution was also showed in Table 4-2.

Since CNSL hexyl ester are mixture of phenolic compounds, consisted of hexyl anacardate, cardol, 2-methyl cardol and cardanol. Thorefore, when those coupling with aniline and nitroaniline derivatives gave typical formulas of azo dyes as follow.



R1 = C_6H_{13} and R2 = $C_{15}H_{25-31}$; hexyl anacardate
or R1 = C_6H_{13} and R2 = H ; hexyl salicylate
and R3 = H or NO_2



R2 = $C_{15}H_{25-31}$ and R4 = H ; cardol
or R2 = $C_{15}H_{25-31}$ and R4 = CH_3 ; 2-methyl cardol
or R2 = H and R4 = H ; resorcinol
and R3 = H or NO_2

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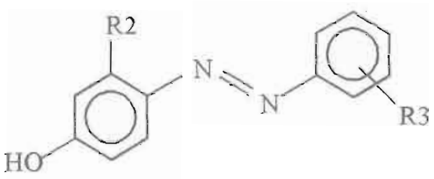

$R2 = C_{15}H_{25\text{-}31}$; cardanol
or R2 = H ; phenol
and R3 = H or NO_2

All azo dyes developed amber yellow color in fuel or organic solvent. It is noteworthy that phenolic compounds such as hexyl salicylate, resorcinol or phenol gave the same yellow color when coupling with aniline or nitroaniline derivatives. Therefore, CNSL hexyl ester consists with those compounds will develop yellow color in the same solvent system too.

Consideration of the color of potassium hydroxide ethylene glycol extracted phase, those phenolic compounds generated different color when coupling with different aniline derivatives. Figure 4-5 to Figure 4-8 were demonstrated the color of extracted phase for all azo dyes system.

Azo dyes obtained from those phenolic compounds and aniline generated yellow color in extracted phase similar to the azo dyes that obtained with m-nitroaniline, while the extracted phase of azo dyes from o-nitroaniline and p-nitroaniline generated orange-yellow color and red color in extracted phase respectively.

When phenyl azo compounds are dissolved in alkaline solution, phenol compounds will form ionized salts, which may be different color from the original azo compounds as illustrated below.

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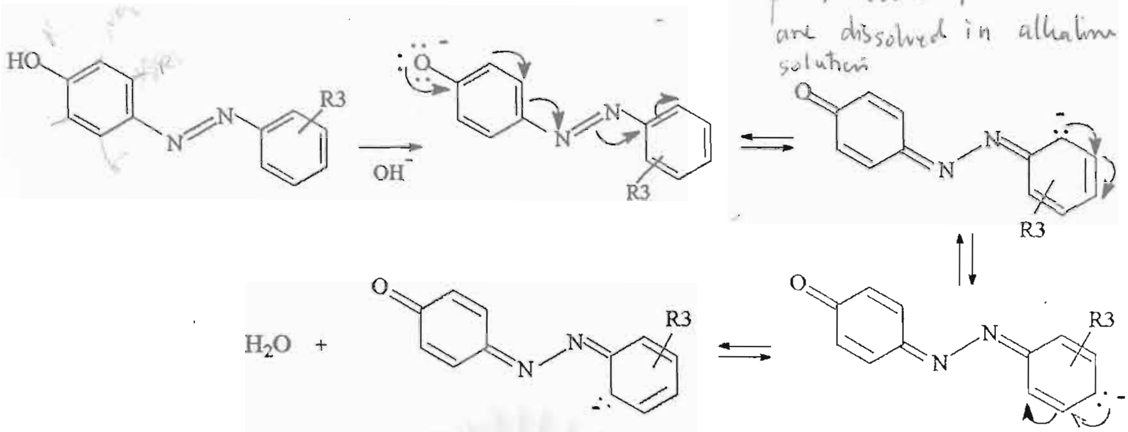
phenyl azo compounds.
are dissolved in alkaline
solution



From ionization structure, it has been shown that the negative charge is occurred at ortho and para position of aniline aromatic ring. Note that meta position can not accommodate the negative charge from ionize salts, so if ortho and or para position are occupy with electron withdrawing group such as nitro group, ionized structure will be more stable because its could distribute negative charge more effectively, especially nitro group which could distribute the negative charge with resonance effect, $-\underset{\underset{O^-}{|}}{N}-O^-$.

On the other hand, if meta position is occupied with electron withdrawing group, it will not give any effect to the ionized structure. It can be noticed that, ionized salt which is more stable will shift the color of extracted phase to red shade. Table 4-2 clearly demonstrated that phenolic compounds coupling with aniline and m-nitroaniline gave similar color in extracted phase while those coupling with o-nitroaniline and p-nitroaniline gave difference color of the extracted phase.

Table 4-2 Characteristic of azo dyes from CNSL hexyl ester and related structure.

	Phenol			Resorcinol			Hexyl salicylate			CNSL hexyl ester		
	Color in oil	Color in extracted phase	Color in $SnCl_2$/ HCl	Color in oil	Color in extracted phase	Color in $SnCl_2$/ HCl	Color in oil	Color in extracted phase	Color in $SnCl_2$/ HCl	Color in oil	Color in extracted phase	Color in $SnCl_2$/ HCl
Aniline	Yellow	Yellow	Colorless	Yellow	Yellow	Colorless	Yellow	Yellow	Colorless	Yellow	Yellow	Colorless
m-Nitroaniline	Yellow	Yellow	Colorless	Yellow	Yellow-orange	Colorless	Yellow	Yellow	Colorless	Yellow	Yellow	Colorless
o-Nitroaniline	Yellow	Orange-yellow	Colorless	Yellow	Orange-yellow	Colorless	Yellow	Orange-yellow	Colorless	Yellow	Orange-yellow	Colorless
p-Nitroaniline	Yellow	Red	Colorless	Yellow	Red-brown	Colorless	Yellow	Red	Colorless	Yellow	Red	Colorless

Note: The commercial premium gasoline and diesel oil gave clear extracted phase under the same condition.

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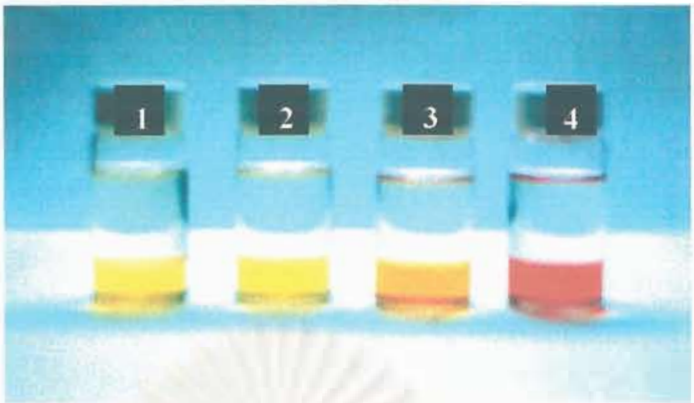

Figure 4-5 Color of extract phase (lower phase) of azo dyes from phenol coupling with

1. aniline
2. m-nitroaniline
3. o-nitroaniline
4. p-nitroaniline

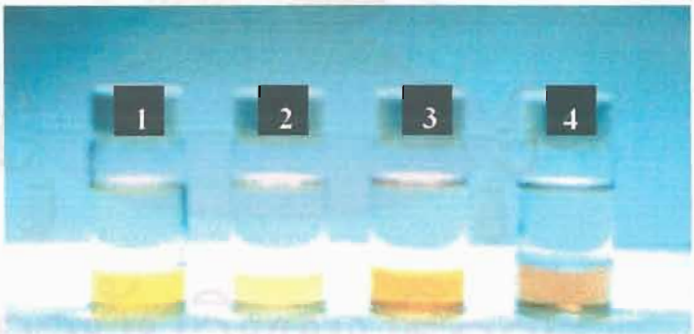

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Figure 4-6 Color of extract phase (lower phase) of azo dyes from resorcinol coupling with

1. aniline
2. m-nitroaniline
3. o-nitroaniline
4. p-nitroaniline

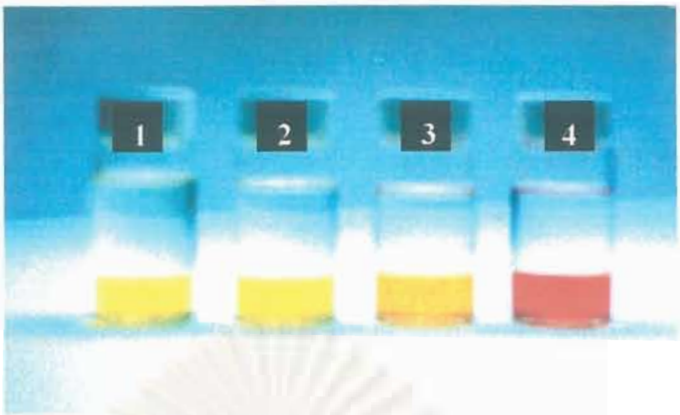

Figure 4-7 Color of extract phase (lower phase) of azo dyes from hexyl salicylate coupling with

1. aniline
2. m-nitroaniline
3. o-nitroaniline
4. p-nitroaniline

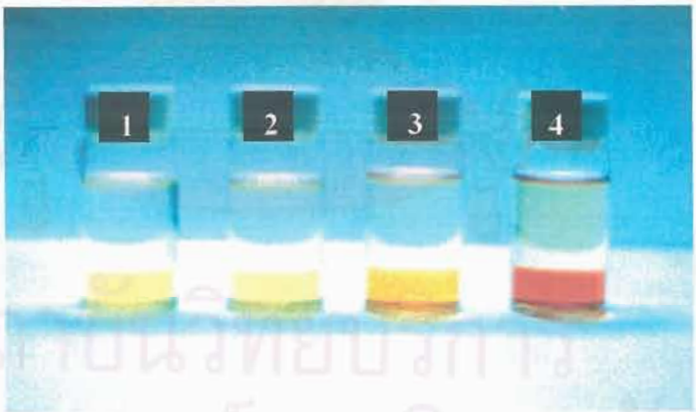

Figure 4-8 Color of extract phase (lower phase) of azo dyes from CNSL hexyl ester coupling with

1. aniline
2. m-nitroaniline
3. o-nitroaniline
4. p-nitroaniline

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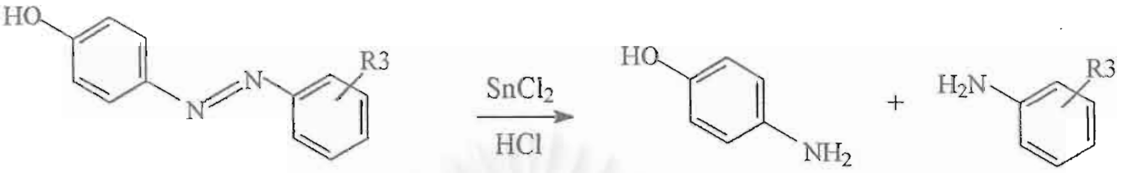
Reaction of azo dyes and acidic stannous chloride showed that the azo compounds were reduced and cleavaged to amino phenol and amine compound which are colorless (31).



The characteristic of the obtained CNSL hexyl ester azo dyes indicated that it could be used as dyes and marker. They gave yellow color in fuel and generated unique color in extracted phase when shaking with alkaline ethylene glycol solution. The commercial premium gasoline gave no color change when extracted with the same solvent system. The same results were obtained in commercial high speed diesel.

4.3 Suitable concentration of potassium hydroxide for extraction system

Gasoline is dyed with CNSL hexyl ester-p-nitrophenyl azo dye and extract with potassium hydroxide in ethylene glycol. The concentration of alkaline are varying from 1% to 4%. Lower extracted phase is scanned for the absorption maximum in visible range. Absorption spectrum is shown in Figure 4-9.

The spectrum shows maximum absorption at 463.93 nm and indicates that 2 and 3% of potassium hydroxide in ethylene glycol gives maximum absorption of extracted phase. Therefore, 2% of potassium hydroxide in ethylene glycol will be used for future test.

4.4 20% Stock azo dyes of CNSL hexyl ester-nitroaniline derivative azo dyes

The CNSL hexyl ester-p-nitrophenyl azo dye, CNSL hexyl ester-o-nitrophenyl azo dye and CNSL hexyl ester-m-nitrophenyl azo dye are prepared in concentrate form base on calculated 20% CNSL. Since, synthesized CNSL hexyl ester contains 66.3 %wt CNSL, therefore, CNSL hexyl ester 7.54 g contains 7.54 × (66.3/100) = 5 g of CNSL. The final volume of concentrated azo dye is 25 mL thus the stock azo dyes contains (5/25) × 100 = 20 % wt/vol of CNSL.

All synthesized azo dyes are red brown liquid, aromatic odour, give yellow film in side the flask when stirring, insoluble in water, slightly soluble in alcohol, freely soluble in hydrocarbon solvents and give yellow color.

4.5 Quantitative analysis of CNSL hexyl ester-nitroaniline derivative azo dye

CNSL hexyl ester-nitroaniline azo dyes were added in to undyed gasoline and high speed diesel in concentration range from 0 - 35 ppm (wt/vol.) base on CNSL. The extracted phase was examined by measuring the absorption at wavelength of the maximum absorption.

Calibration curve of CNSL hexyl ester-p-nitrophenyl azo dye in gasoline is presented in Figure 4-10 and absorption spectrum of azo dye in gasoline at various concentration is presented in Figure 4-11. The calibration curve and absorption spectrum of this azo dye in high speed diesel are shown in Figure 4-12 and 4-13 respectively.

Figure 4-14 and Figure 4-15 presented calibration curve and absorption spectrum of CNSL hexyl ester-o-nitrophenyl azo dye in gasoline. Figure 4-16 and 4-17 presented the same information in high speed diesel.

The calibration curves of CNSL hexyl ester-m-nitrophenyl azo dye in gasoline and high speed diesel are presented in Figure 4-18 and 4-20 and the absorption spectra are presented in Figure 4-19 and 4-21 respectivety.

measuring the absorption at wavelength of the maximum absorption

The calibration curves at the same concentration level of dyed gasoline presented in Figure 4-10, 4-14 and 4-18 indicated that CNSL hexyl ester-p-nitrophenyl azo dye give the highest absorption. For example, at 25 ppm p-nitrophenyl azo dye develop red color of extracted phase and absorption is 0.3345 at 463.9 nm., while at the same concentration o-nitrophenyl azo dye develop orange-yellow color in extracted phase with 0.2246 absorption at 449.5 nm and m-nitrophenyl azo dye develop yellow color in extracted phase with 0.2235 absorption at 425.0 nm.

Dyed diesel oils give similar result as gasoline, that is the CNSL hexyl ester-p-nitrophenyl azo dye give the highest absorption in the same concentratation range. For example, p-nitrophenyl azo dys develops red color of extracted phase with 0.4532 absorption at 463.9 nm, while o-nitrophenyl azo dye give orange-yellow color of extracted phase with 0.2010 absorption at 449.5 nm, and m-nitrophenyl azo dye give yellow color of extracted phase with 0.3211 absorption at 425.0 nm . All absorption are determine at 15 ppm concentratation.

It is noteworthy that all azo dyes show higher the absorption of extracted phase in diesel than in gasoline, even though color of extracted phase in gasoline and diesel are the same for the same azo dyes. For example, gasoline dyed with 25 ppm p-nitrophenyl azo dye give 0.3345

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absorption while the absorption is 0.6384 in diesel at the same concentration and wavelength of 463.9 nm.

Moreover, when extract with 2% potassium hydroxide in ethylene glycol, diesel oil give longer setting time than gasoline. Measurement for UV/vis absorption of cloud extracted phase give unreliable results.

For all results discussed above the CNSL hexyl ester-p-nitrophenyl azo dye is more advantage in performance over the other since;

1) Extracted phase develops red color, which is easier to observe with naked eyes than orange-yellow of CNSL hexyl ester-o-nitrophenyl azo dye or yellow color of CNSL hexyl ester-m-nitrophenyl azo dye.

2) In same concentration level CNSL hexyl ester-p-nitrophenyl azo dye give higher absorption of extracted phase than the other two azo dyes.

3) The p-nitroaniline is easy to dissolve in acid solution thus it convenient to prepare its diazonium salt solution.

4) Cost of p-nitroaniline is reasonable because 98% purity p-nitroaniline is 16.65 US dollar/250 g while o-nitroaniline is 20.45 US dollar/250 g and m-nitroaniline is 40.60 US dollar/250 g (Fluka and RdH Laboratory Chemicals and Analytical Reagents Catolog 1999/2000).

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4.6 Physical properties of stock 20% CNSL hexyl ester-p-nitrophenyl azo dye

Stock 20% CNSL hexyl ester-p-nitrophenyl azo dye is test for the physical properties and the tested results are presented in Table 4-3.

Table 4-3 Physical properties of 20% stock CNSL hexyl ester-p-nitrophenyl azo dye.

Test Items	Test Methods	Results
Appearance	Visual	free-flowing brown liquid, aromatic odour
Density @ 15 °C	ASTM D 1298	0.9359
Flash point (Abel),°C	IP 170	< 10
Crystalline temp., °C	apply from ASTM D 2386	< - 25
Water content , % wt.	ASTM D 4928	0.34
Viscosity @ 40°C, cSt	ASTM D 445	< 2.0
λ maximum, nm.	UV-vis spectroscopy	403
Solids content	Visual	none

4.7 Stability test for CNSL hexyl ester-p-nitrophenyl azo dye in gasoline and high speed diesel

Concentration monitoring of CNSL hexyl ester-p-nitrophenyl azo dye at 25 ppm in gasoline and 15 ppm in high speed diesel are disclosed in Table 4-4 and 4-5 respectively. Measurement of azo dye concentration is carried out by scanning of absorption in visible range and then calculated azo dye concentration from absorption at λ maximum. The example of scanning spectrum of gasoline and diesel oil are shown in Figure 4-22 and Figure 4-23 resepctively.

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Table 4-4 Concentration monitoring of CNSL hexyl ester-p-nitrophenyl azo dye at 25 ppm in gasoline.

Weeks	Concentration (ppm)			Concentration Average (ppm)	Error (ppm)
	Repeat 1	Repeat 2	Repeat 3		
1	24.77	24.84	24.15	24.59	-0.41
2	25.10	25.58	25.04	25.24	0.24
3	24.79	24.82	25.59	25.07	0.07
4	25.56	25.25	24.69	25.17	0.17
5	25.64	25.49	25.56	25.56	0.56
6	25.41	25.73	25.50	25.55	0.55
7	24.82	24.80	24.57	24.73	-0.27
8	24.57	24.76	25.09	24.81	-0.19
9	24.83	25.18	25.17	25.39	0.39
10	25.05	25.09	25.23	25.12	0.12
11	25.21	24.82	24.99	25.01	0.01
12	25.33	24.95	24.81	25.03	0.03

From Table 4-4, plot of stability curve between average concentration and times.

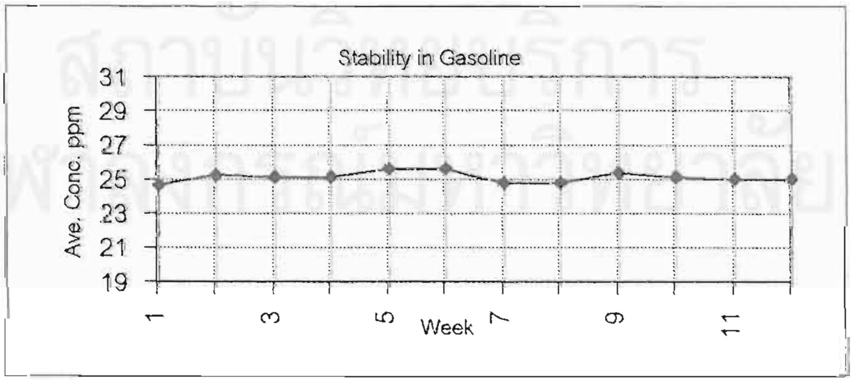

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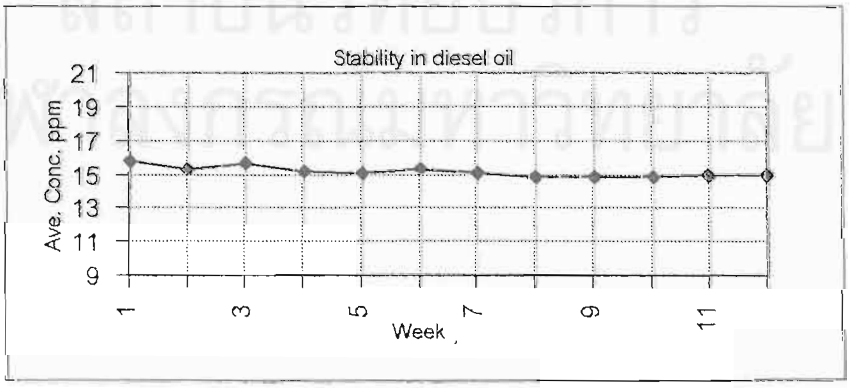
Table 4-5 Concentration monitoring of CNSL hexyl ester-p-nitrophenyl azo dye at 15 ppm in high speed diesel.

Weeks	Concentration (ppm)			Concentration Average (ppm)	Error (ppm)
	Repeat 1	Repeat 2	Repeat 3		
1	15.82	15.68	15.75	15.75	0.75
2	14.80	15.91	15.23	15.31	0.31
3	15.93	15.75	15.22	15.63	0.63
4	15.32	15.04	15.19	15.18	0.18
5	15.46	14.87	15.01	15.11	0.11
6	14.86	15.79	15.29	15.31	0.31
7	15.24	14.92	14.94	15.03	0.03
8	14.69	14.81	14.93	14.81	-0.19
9	14.89	14.74	14.96	14.86	-0.14
10	14.75	14.75	15.10	14.87	-0.13
11	15.01	14.76	14.91	14.89	-0.11
12	15.01	15.01	14.89	14.97	-0.03

From Table 4-5, plot of stability curve between average concentration and times.



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Concentration monitoring of CNSL hexyl ester azo dye in gasoline and diesel oil points out that CNSL hexyl ester-p-nitrophenyl azo dye is stable during 3 months period. In common acceptable range of measurement is +/- 10 % error, so in gasoline at 25 ppm, the acceptable concentration of measuring are 25 +/- 2.5 = 23.5 to 27.5 ppm and at 15 ppm in diesel oil acceptable range are 15 +/- 1.5 = 13.5 to 16.5 ppm. The results in Table 4-4 and 4-5 were clarified that concentration of measuring were in acceptable range. Moreover, by repeating the measurement, the results were shown to have good repeatability.

4.8 Stability test for stock 20 % CNSL hexyl ester-p-nitrophenyl azo dye

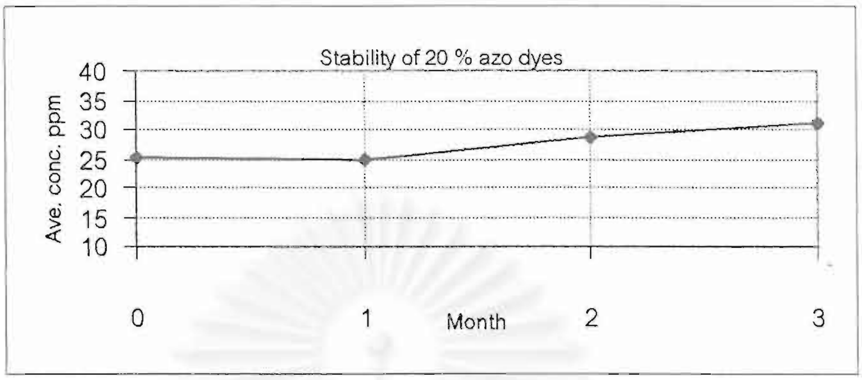
The CNSL hexyl ester-p-nitrophenyl azo dye is stored for 1 month, 2 months and 3 months in order to check dyeing power and structure of azo dye.

Dyeing powder of 20% azo dye is determined by adding 25 ppm azo dye in to undyegasoline and scanning absorption of red extracted phase in visible range. Calculation of azo dye was obtained from absorbance at λ maximum. Results of the test are shown in Table 4-6.

Table 4-6 Concentration monitoring of stock 20 % CNSL hexyl ester-p-nitrophenyl azo dye.

Months	Concentration (ppm)			Concentration	Error
	Repeat 1	Repeat 2	Repeat 3	Average (ppm)	(ppm)
Start	25.48	24.95	24.77	25.07	0.07
1	25.16	24.75	24.84	24.92	-0.08
2	28.96	28.98	28.38	28.77	3.77
3	31.30	30.77	30.72	30.93	5.93

Plot between time (month) and measuring concentration average from data in Table 4-6 is shown below.



From the curve, concentration of azo dyes in second and third months are tended to be higher may be from the evaporation of toluene solvent in stock azo dyes.

Stability of azo dyes is perform by FT-IR at the begining, 1 month, 2 months and 3 months. Figure 4-24 , 4-25, 4-26 and 4-27 are represented of dyes storage for the begining, 1 month, 2 months and 3 months respectively. Figure 4-28 showed FT-IR spectrum of azo dyes at the begining, 1, 2 and 3 months storage in the same scale.

Figure 4-28 exhibits similar peak pattern and transmittance for each spectrum at same wave number. It indicates that the stock 20% CNSL hexyl ester-p-nitrophenyl azo dye is rather stable within 3 months.

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4.9 Effect of CNSL hexyl ester-p-nitrophenyl azo dye to physical properties of dyed and undyed fuels

4.9.1 Physical properties of dyed and undyed fuels

Physical properties of 25 and 15 ppm of CNSL hexyl ester-p-nitrophenyl azo dye in gasoline and high speed diesel, respectively, are compared with undyed fuel. Results of the test in gasoline present in Table 4-7 and high speed diesel in Table 4-8.

Table 4-7 Physical properties of dyed and undyed gasoline.

Test Items	Results	
	Dyed	Undyed
API gravity @ 60 °F	53.5	53.4
RON	97.0	96.8
RVP @ 37.8 °C, kPa	32.5	31.0
Existent gum, g /100 ml	0.0012	0.0010
Copper strip corrosion, 3 hr. @ 50 °C	No. 1a	No. 1a
Distillation, correct temp.		
IBP	36.9	36.8
10% vol. evaporated, °C	67.0	66.2
50% vol. evaporated, °C	111.2	111.3
90% vol. evaporate, °C	146.4	146.3
end point, °C	175.6	176.3
recovery, % vol.	98.4	98.7
residue, % vol.	1.0	1.0
Water content, % wt.	0.013	0.014
Oxygenated compounds , % vol	3.122	3.138
Benzene, % vol	2.63	2.66
Total aromatics % vol	55.30	56.65
Color	L 1.0	L 0.5

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Table 4-8 Physical properties of dyed and undyed high speed diesel.

Test Items	Results	
	Dyed	Undyed
API gravity @ 60 °F	40.5	40.4
Kinematic viscosity @ 40 °C	3.148	3.145
Pour point , °C	-6	-6
Sulfur content, %wt	0.047	0.048
Copper strip corrosion, 3 hr. @ 50°C	No. 1a	No. 1a
Flash point (PM), °C	67	66
Distillation , Correct temp.		
IBP	171.1	170.7
10% rec, °C	201.7	199.7
50% rec, °C	282.1	282.6
90% rec, °C	353.4	354.4
Color	L 1.0	L 0.5

Physical properties of gasoline (Table 4-7) and high speed diesel (Table 4-8) were tested in order to determine the effect of azo dyes to the quality of oils. Test results in both tables show that CNSL hexyl ester p-nitrophenyl azo dye do not give any effect on the quality of dyed oil. The physical properties differences of dyed and undyed fuels are not significant, and they are within the repeatability range. However, color of dyed fuels are deeper than undyed fuels but they are well within the commercial specifications. (The commercial specification indicates that the color of premium gasoline is yellow with 0.5 - 1.0 ASTM color scale test by ASTM D1500 and not over 2.0 ASTM color scale in high speed diesel by the same test method).

4.9.2 Physical properties of dyed and undyed fuels after storage for 3 months

After 3 months of storage, the physical properties of dyed gasoline and high speed diesel were tested and then compared with undyed fuels keep in the same conditions. Results of the tests of gasoline and high speed diesel are presented in Table 4-9 and 4-10, respectively.

Table 4-9 Physical properties of dyed and undyed gasoline after storage for 3 months.

Test Items	Results	
	Dyed	Undyed
API gravity @ 60 °F	48.0	47.0
RON	97.0	97.1
RVP @ 37.8 °C, kPa	26.0	26.5
Existent gum, g /100 ml	0.0015	0.0013
Copper strip corrosion, 3 hr. @ 50 °C	No. 1a	No. 1a
Distillation, correct temp.		
IBP	47.3	44.8
10% vol. evaporated , °C	76.9	76.1
50% vol. evaporated, °C	114.3	114.3
90% vol. evaporate , °C	147.4	147.1
end point, °C	175.5	177.9
recovery, % vol.	97.9	97.9
residue, % vol.	1.0	1.0
Water content, % wt.	0.013	0.014
Oxygenated compounds, % vol	2.995	2.980
Benzene, % vol	2.60	2.65

Table 4-9 Physical properties of dyed and undyed gasoline after storage for 3 months (cont.).

Test Items	Results	
	Dyed	Undyed
Benzene, % vol	2.60	2.65
Total aromatics % vol	57.35	58.38
Color	L 1.0	L 0.5

Table 4-10 Physical properties of dyed and undyed high speed diesel after storage for 3 months.

Test Items	Results	
	Dyed	Undyed
API gravity @ 60 °F	39.8	40.0
Kinematic viscosity @ 40 °C	3.230	3.147
Pour point, °C	-6	-6
Sulfur content, %wt	0.048	0.046
Copper strip corrosion, 3 hr. @ 50°C	No. 1a	No. 1a
Flash point (PM), °C	68	68
Distillation , Correct temp.		
IBP	177.1	168.1
10% rec, °C	212.3	208.6
50% rec, °C	283.3	283.6
90% rec, °C	353.1	355.2
Color	L 1.0	L 0.5

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After 3 months of storage, the properties of dyed and undyed fuels were tested again.The results are shown in Table 4-9 and 4-10. They were found that these properties were not significantly change, compared with the fresh fuels, as in Table 4-7 and 4-8. Therefore, the synthesized azo dyes do not give any effect on the qualities of fuels even after 3 months of storage.

4.10 Characterization of CNSL hexyl ester nitrophenyl azo dyes

FT-IR spectrum of CNSL hexyl ester-p-nitrophenyl azo dye, CNSL hexyl ester-o-nitrophenyl azo dye and CNSL hexyl ester-m-nitrophenyl azo dye were shown in Figure 4-29, 4-30 and 4-31, respectively. Those spectra of azo dyes were similar to FT-IR spectrum of CNSL hexyl ester in Figure 4-3 but the azo dyes had 2 little peaks of -NO_2 group at about 1530 and 1392 cm^{-1}.

^{13}C-NMR spectra of CNSL hexyl ester-p-nitrophenyl azo dye, CNSL hexyl ester-o-nitrophenyl azo dye and CNSL hexyl ester-m-nitrophenyl azo dye were shown in Figure 4-32, 4-33 and 4-34, respectively. The ^{13}C-NMR spectrum of azo dyes were similar to that of CNSL hexyl ester in Figure 4-4 but the azo dyes had difference peaks in aromatic region at 100-160 ppm.

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CHAPTER 5

CONCLUSION AND SUGGESTION

Esterification of CNSL with 1-hexanol to CNSL hexyl ester reduces the acidity of raw material, for example, TAN 18.52 mgKOH/g in CNSL is reduced to 4.45 mgKOH/g in CNSL hexyl ester. The azo dyes obtained from coupling reaction between phenol, resorcinol, hexyl salicylate and CNSL hexyl ester with aniline and nitroaniline derivatives give the same yellow color in petroleum oils. However, the color in glycolic extracted phase is different and depended on aniline derivatives. Azo dyes obtained from coupling of aniline or m-nitroaniline give yellow color while o-nitroaniline gives orange color and p-nitroaniline gives red color in the extracted phase. Comparing the performance of azo dyes above, CNSL hexyl ester coupling with p-nitroaniline is more appropriate to be used as marker dyes. It gives red color in extracted phase which is easy to detect and give high absorption value even at low level of dosing (25 ppm in gasoline and 15 ppm in diesel). Stability test of azo dyes from CNSL hexyl ester and p-nitroaniline shows that it is stable in oils for at least 3 months of storage. Moreover, the storage period has no effect on quality of dyed oils even after 3 months of storage. Quantity of marker dye in this research is conveniently done by UV-visible spectrophotometry. This method gives good precision and repeatability less than 10% error.

From this research, the azo dye from CNSL hexyl ester and p-nitroaniline is most suitable and conformed with marker and dye requirements to be used as marker dye in petroleum oils.

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SUGGESTION

According to this research, there are some properties of marker dyes needed to be improve.

1. Flash point of marker dyes is low (< 10 °C by IP 170 method) and concentration of stock marker dye is increased during storage because of evaporation toluene being used as solvent. Therefore high boiling point aromatic solvents should be used to replace toluene.

2. In high speed diesel, the time needed for separation of glycolic extraction phase in an extracting solvent system is too long. Therefore new compositions and methods of extraction systems for marker dyes should be developed.

3. The electron withdrawing group at ortho and para positions of aniline shift the color of extracted phase to red shade, therefore, effect of the other electron withdrawing groups in those positions should be studied in order to have more markers of choice.

4. In this study, marker dyes are synthesized in laboratory scale, therefore large scale synthesis should be explored.

Moreover, it is also important to consider the cost of production, convenience in operation and conformation of marker dyes requirements.

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APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

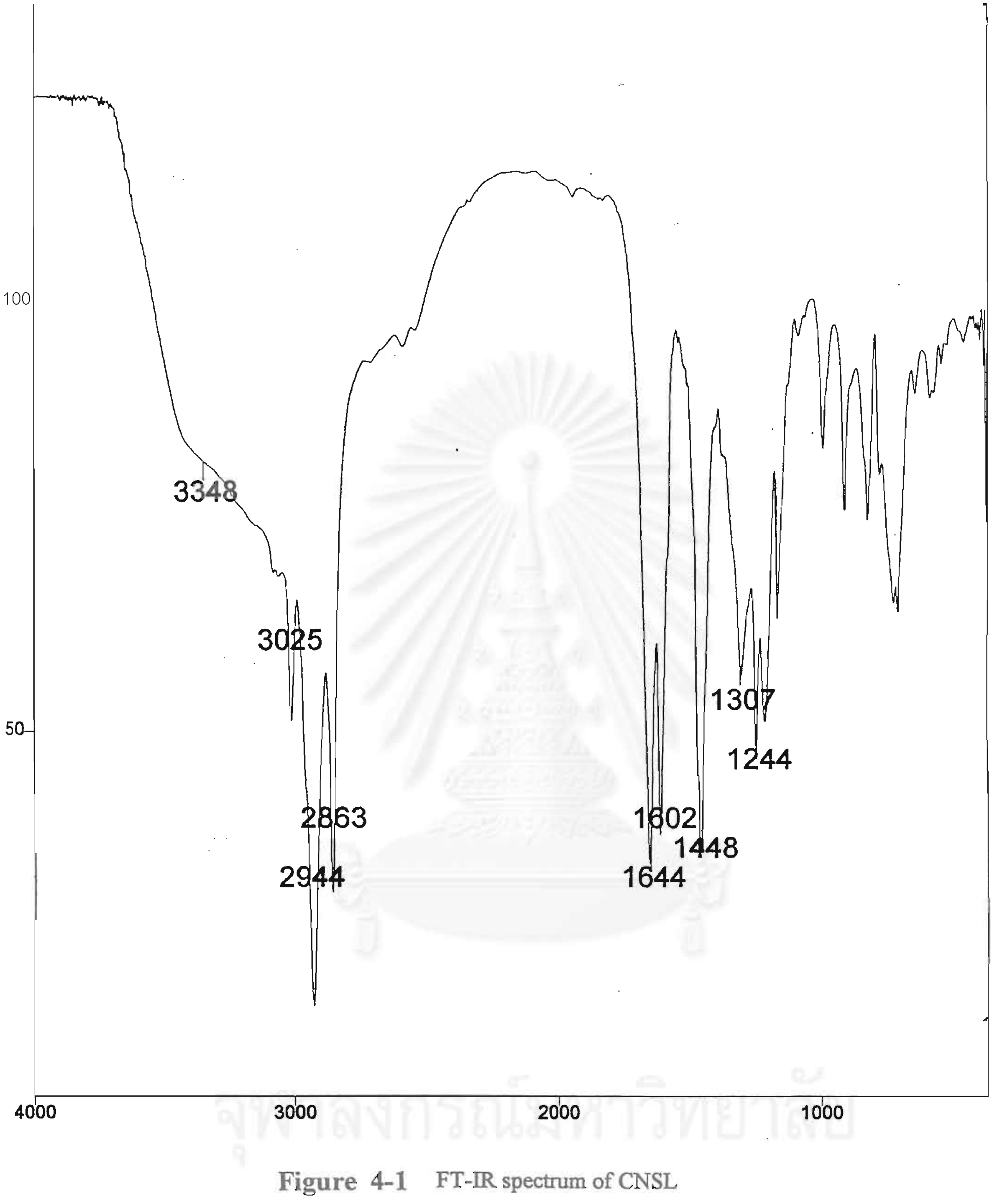

Figure 4-1 FT-IR spectrum of CNSL

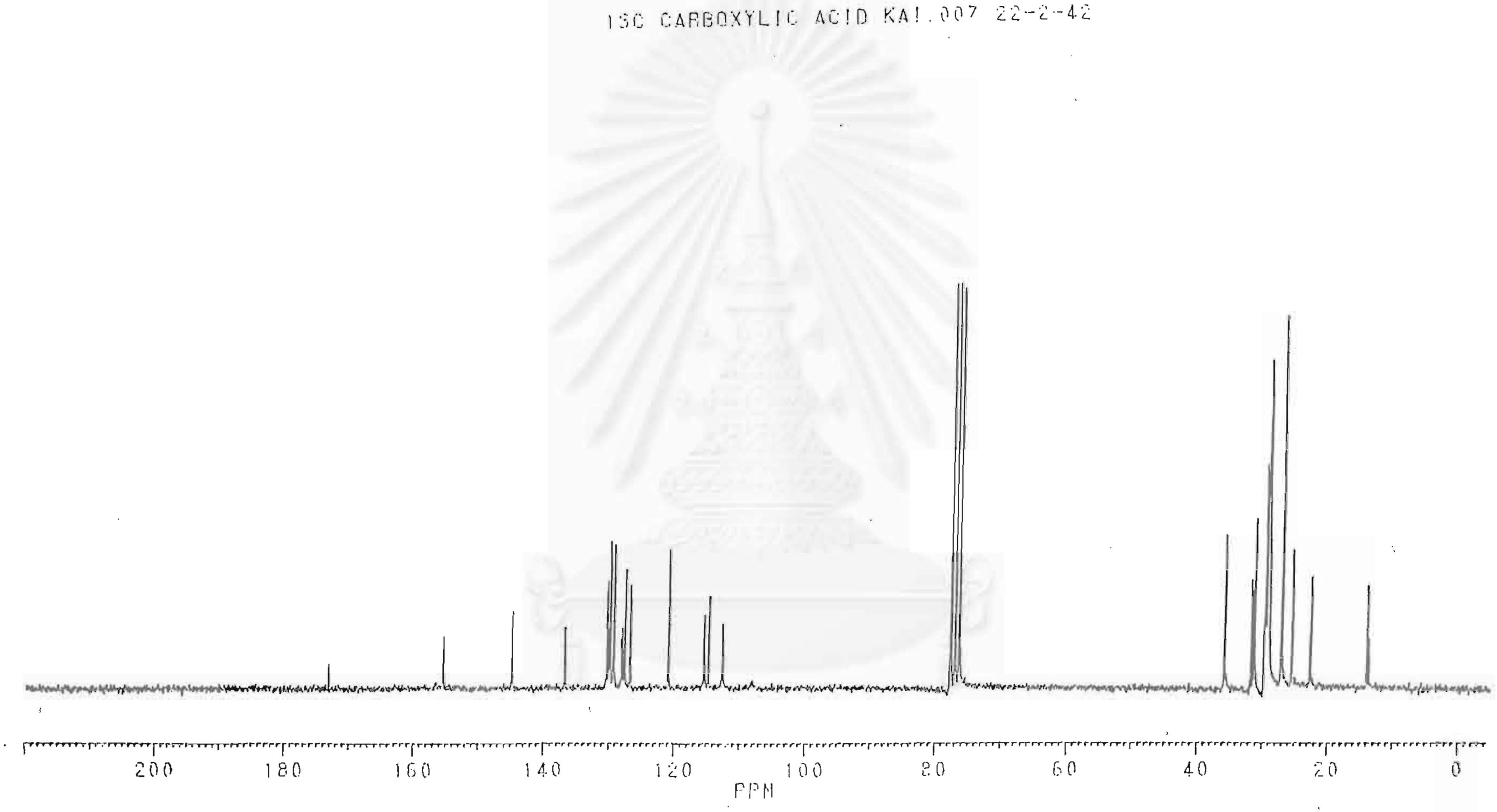

Figure 4-2 ^{13}C NMR spectrum of CNSL.

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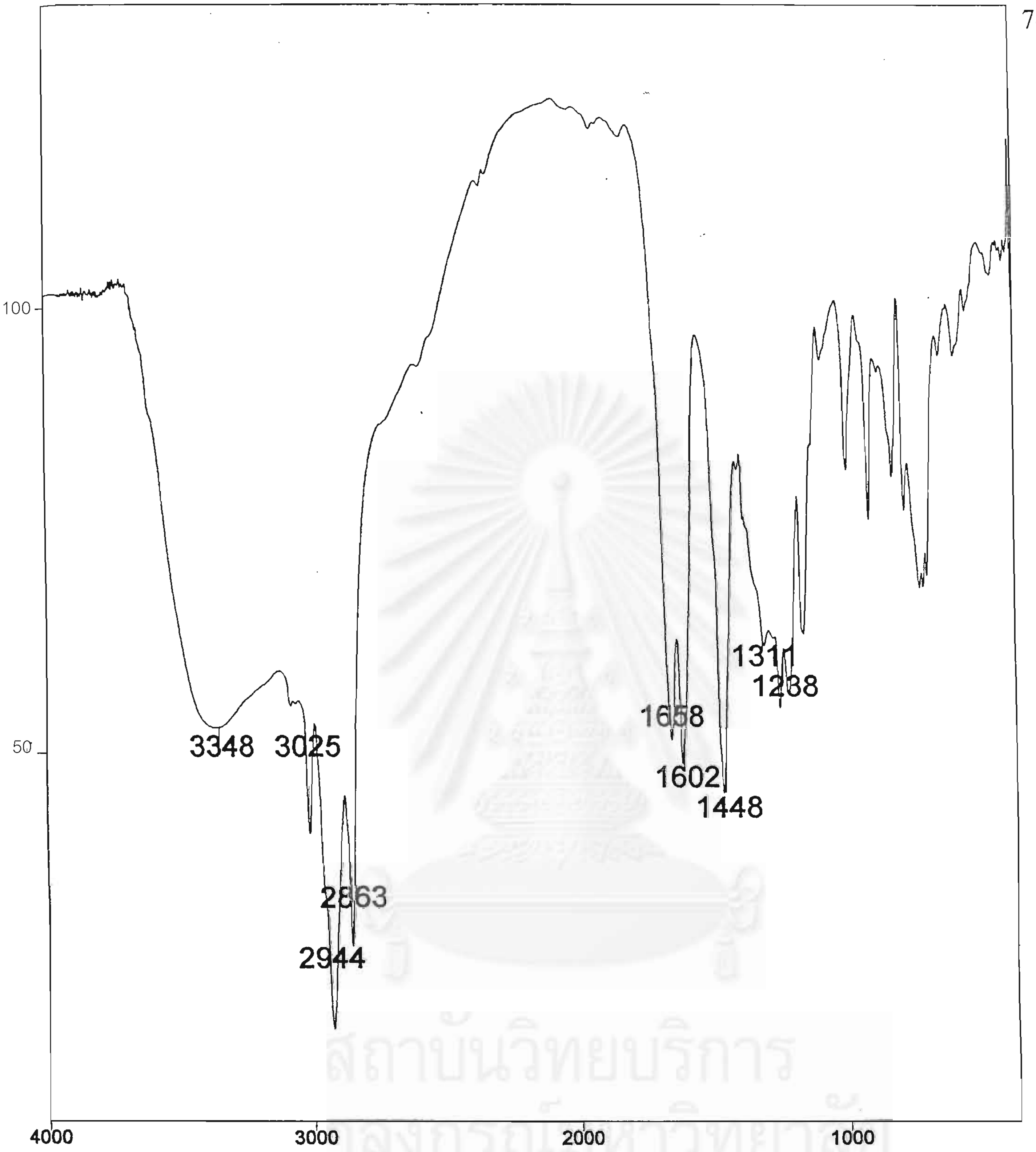

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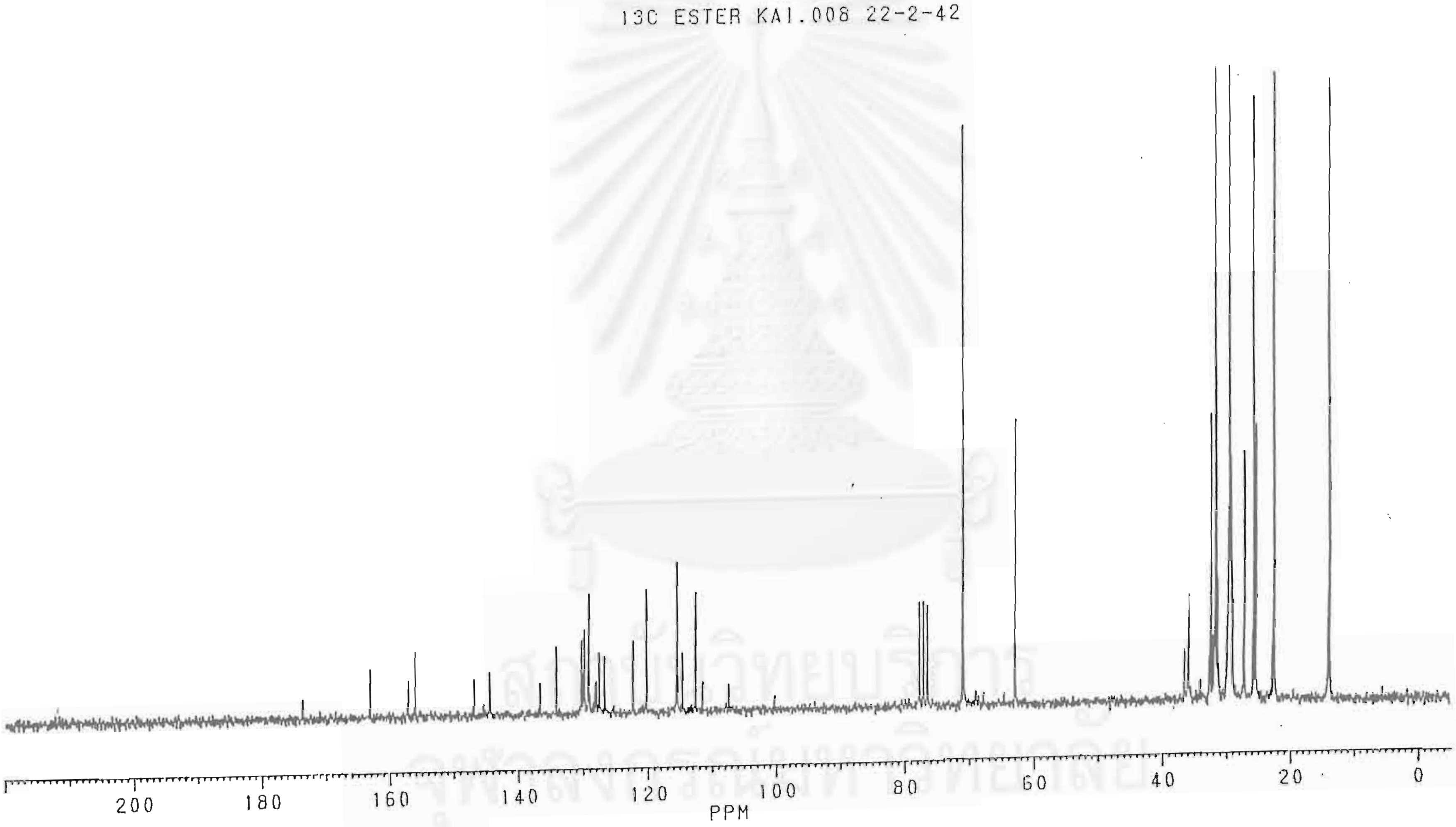

Figure 4-4 ^{13}C NMR spectrum of CNSL hexyl ester.

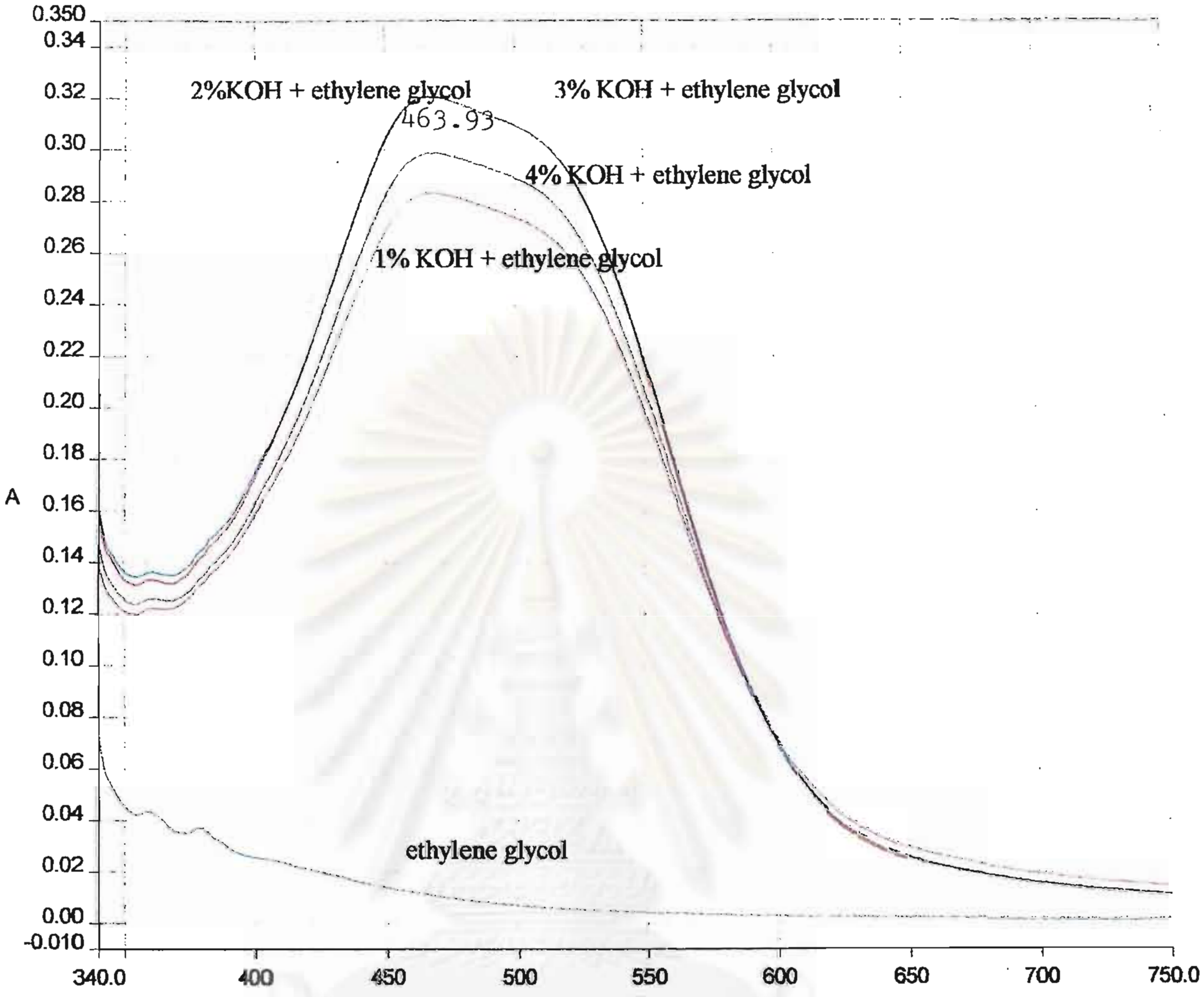

Figure 4-9 Visible absorption spectrum for the determination of suitable concentration of potassium hydroxide

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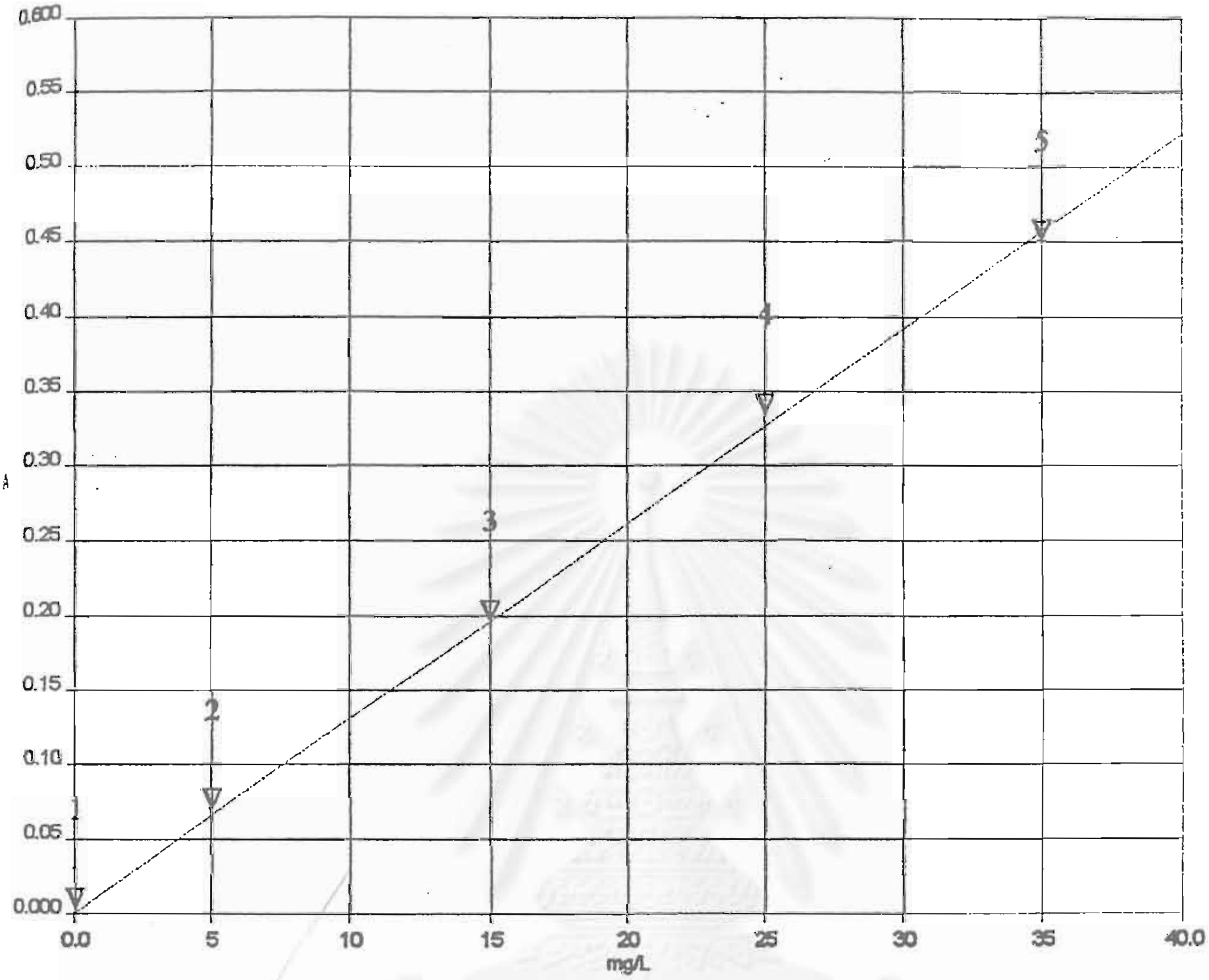

Figure 4-10 Calibration curve for CNSL hexyl ester-p-nitrophenyl azo dye in gasoline.

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : p-ulg
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
463.9	0.0	0ppm.A01	0.0000	mg/L.	0.0032	
463.9	0.0	5ppm.A02	5.0000	mg/L.	0.0695	
463.9	0.0	15ppm.A03	15.000	mg/L.	0.1964	
463.9	0.0	25ppm.A04	25.000	mg/L.	0.3345	
463.9	0.0	35ppm.A05	35.000	mg/L.	0.4501	

Equation : y = 1.305121e-02 * x
Residue error : 0.005939
Correlation coefficient : 0.999481

จุฬาลงกรณ์มหาวิทยาลัย

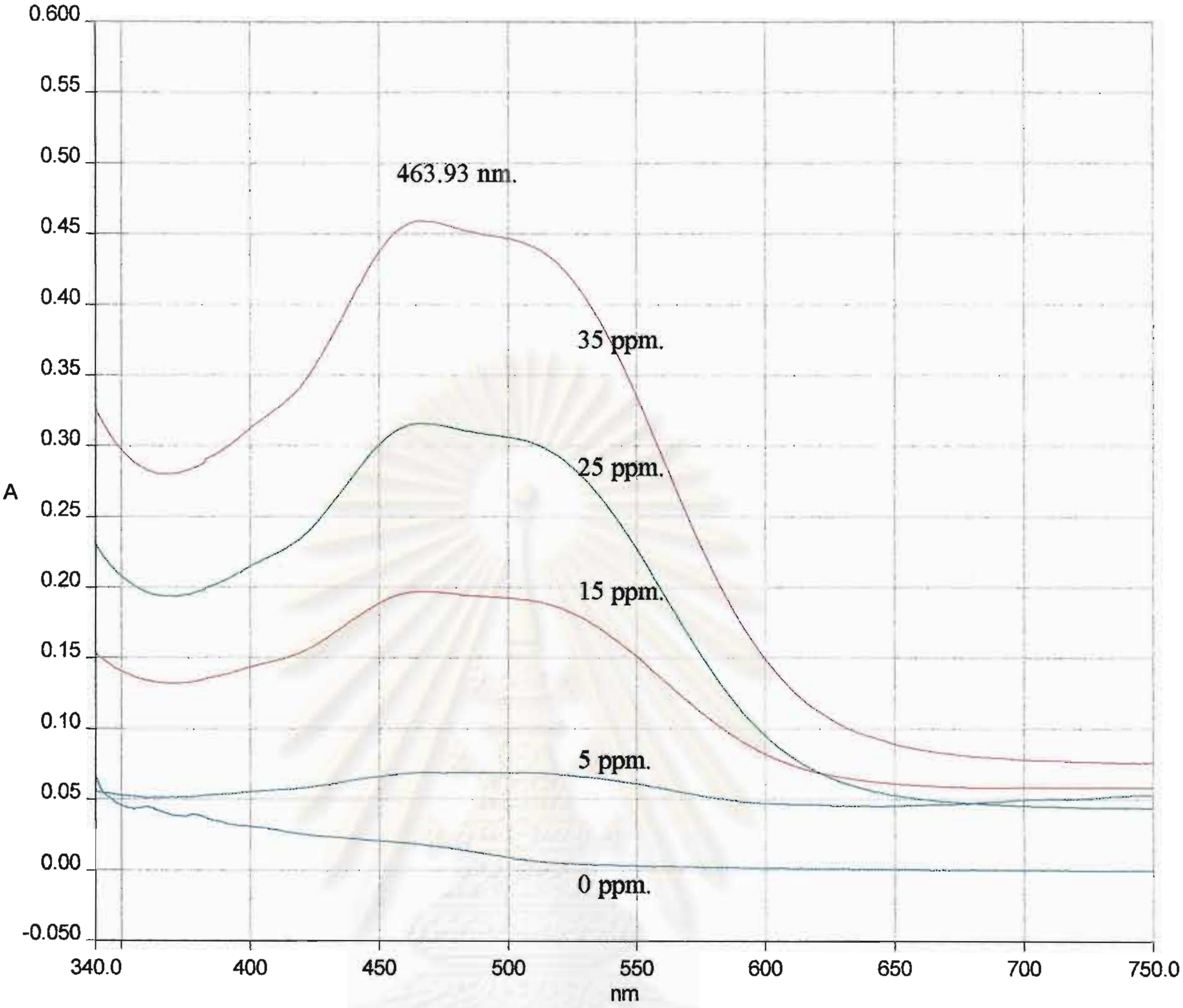

Figure 4-11 Visible absorption spectrum of CNSL hexyl ester-p-nitrophenyl azo dye in gasoline.

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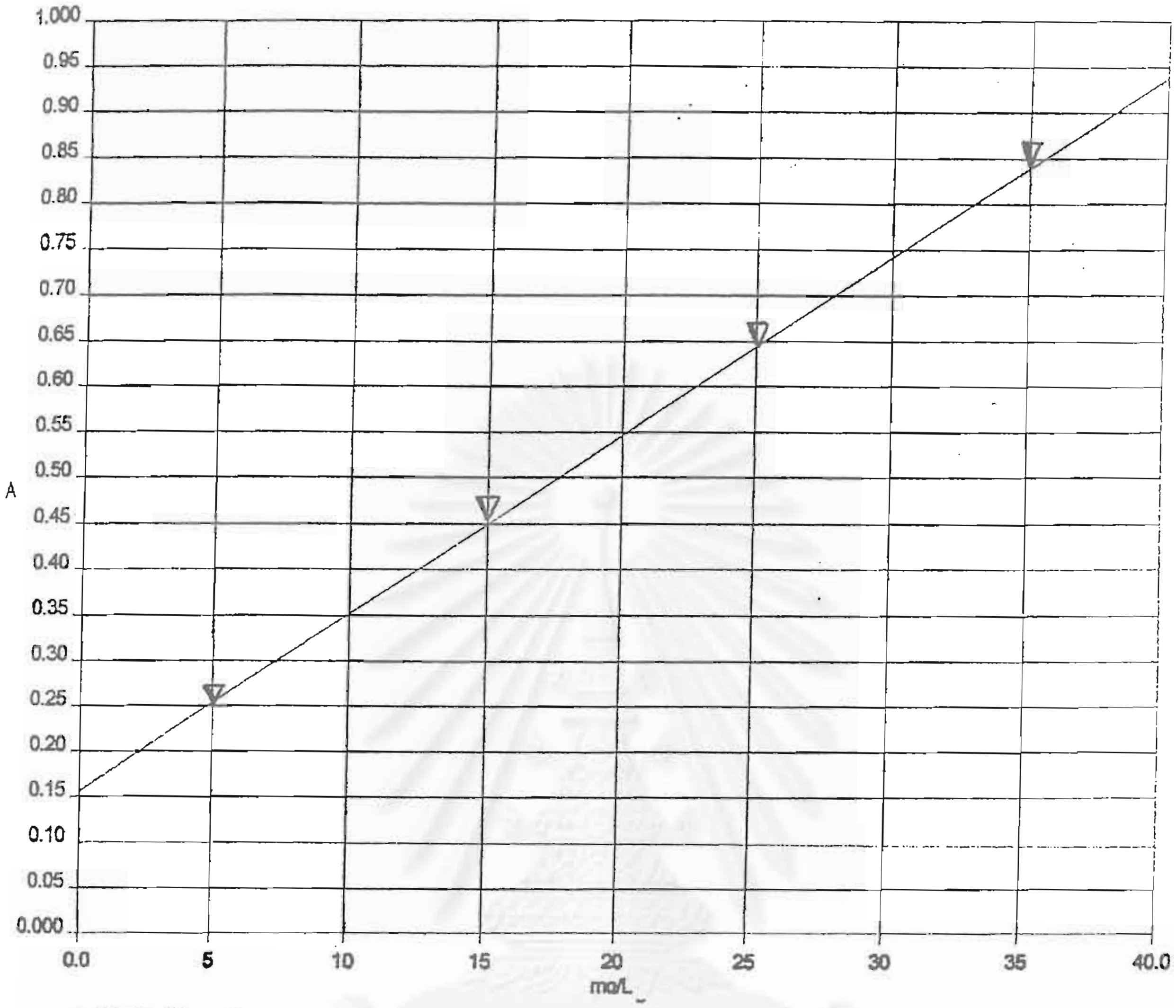

igure 4-12 Calibration curve for CNSL hexyl ester-p-nitrophenyl azo dye in high speed diesel.

จุฬาลงกรณ์มหาวิทยาลัย

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : p-hsd
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
463.9	0.0	0ppm.A01	0.0000	mg/L.	0.0741	
463.9	0.0	5ppm.A02	5.0000	mg/L.	0.2515	
463.9	0.0	15ppm.A03	15.000	mg/L.	0.4532	
463.9	0.0	25ppm.A04	25.000	mg/L.	0.6384	
463.9	0.0	35ppm.A05	35.000	mg/L.	0.8408	

Equation : y = 1.553905e-01 + 1.953110e-02 * x
Residue error : 0.005330
Correlation coefficient : 0.999851

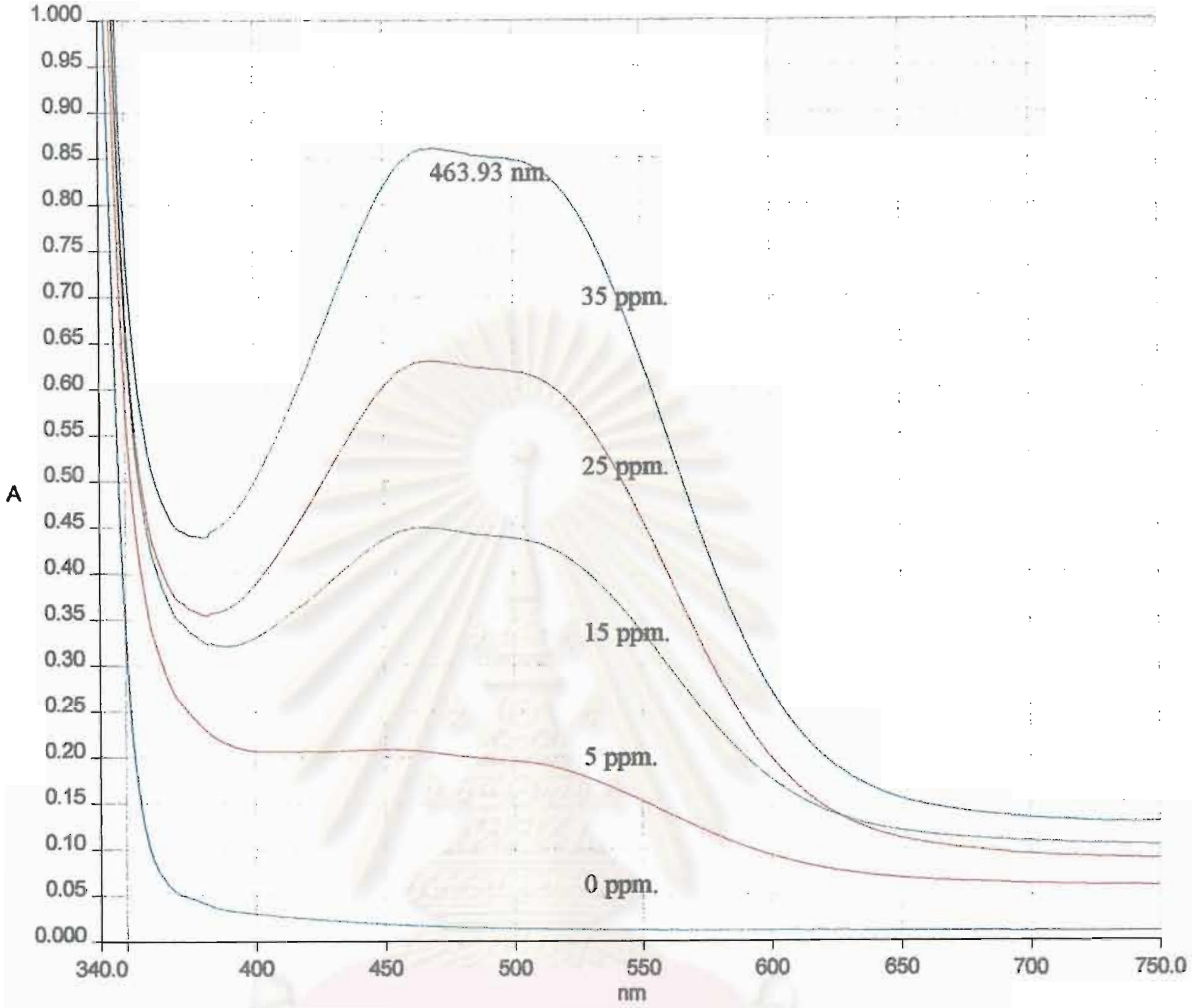

Figure 4-13 Visible absorption spectrum of CNSL hexyl ester-p-nitrophenyl azo dye in high speed diesel.

จุฬาลงกรณ์มหาวิทยาลัย

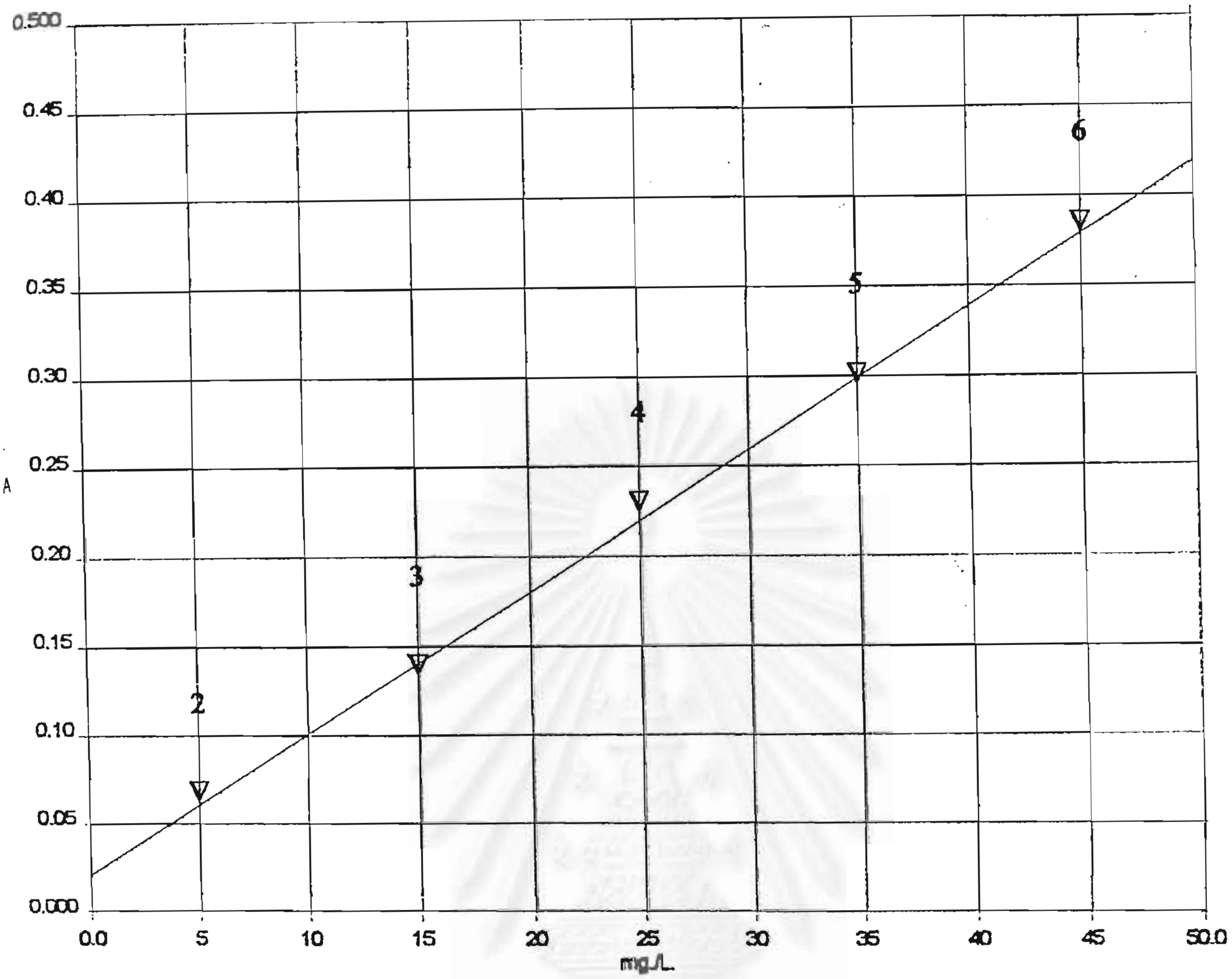

Figure 4-14 Calibration curve for CNSL hexyl ester-o-nitrophenyl azo dye in gasoline.

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : o-ulg
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
449.5	0.0	5ppm.A02	5.0000	mg/L.	0.0626	
449.5	0.0	15ppm.A03	15.000	mg/L.	0.1339	
449.5	0.0	25ppm.A04	25.000	mg/L.	0.2246	
449.5	0.0	35ppm.A05	35.000	mg/L.	0.2956	
449.5	0.0	45ppm.A06	45.000	mg/L.	0.3795	

Equation : y = 2.035600e-02 + 7.956000e-03 * x
Residue error : 0.005198
Correlation coefficient : 0.999360

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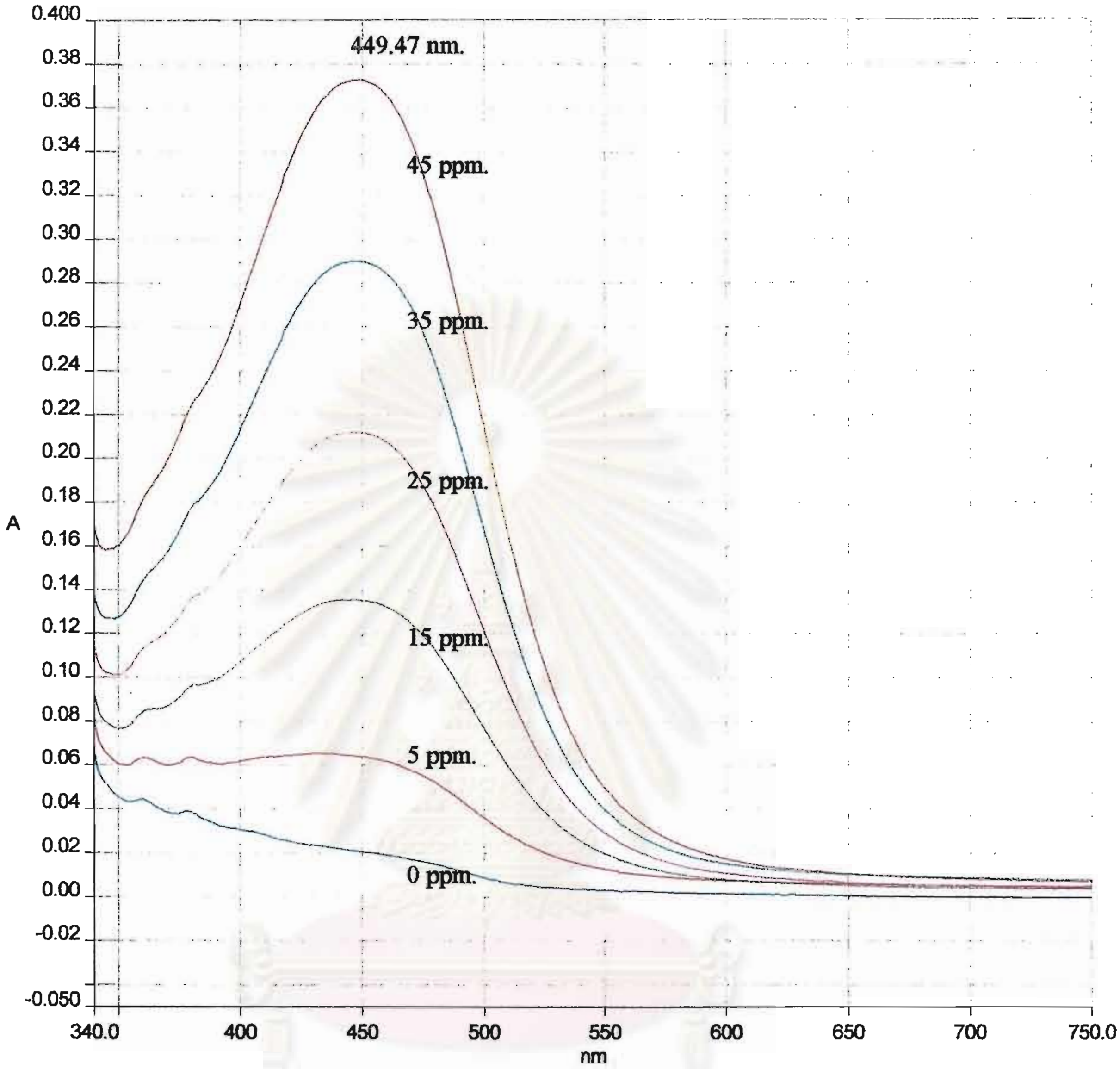

Figure 4-15 Visible absorption spectrum of CNSL hexyl ester-o-nitrophenyl azo dye in gasoline.

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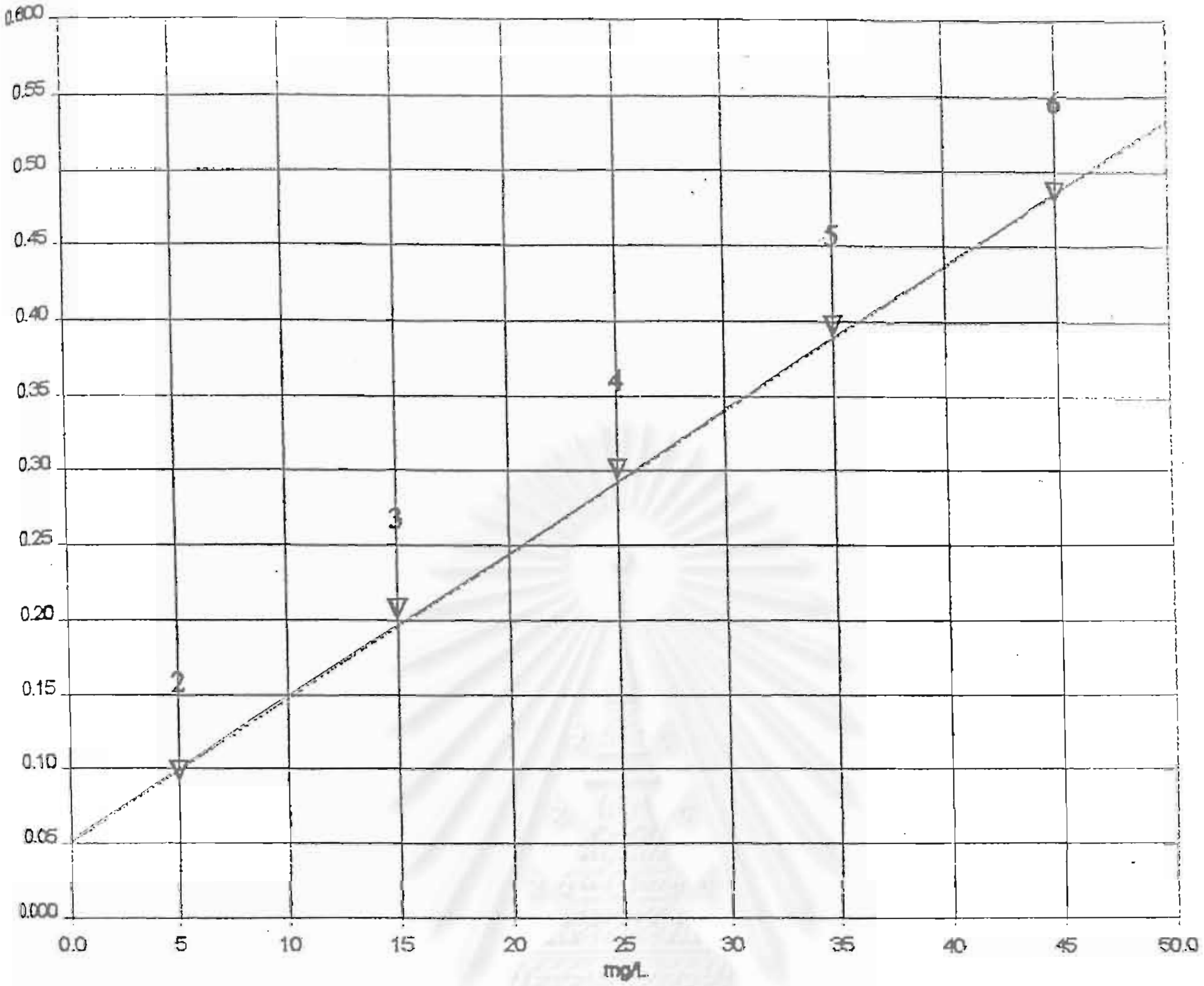

Figure 4-16 Calibration curve for CNSL hexyl ester-o-nitrophenyl azo in dye high speed diesel.

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : o-hsd
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
449.5	0.0	5ppm.A02	5.0000	mg/L.	0.0916	
449.5	0.0	15ppm.A03	15.000	mg/L.	0.2010	
449.5	0.0	25ppm.A04	25.000	mg/L.	0.2942	
449.5	0.0	35ppm.A05	35.000	mg/L.	0.3903	
449.5	0.0	45ppm.A06	45.000	mg/L.	0.4795	

Equation : y = 5.004750e-02 + 9.650500e-03 * x
Residue error : 0.006315
Correlation coefficient : 0.999358

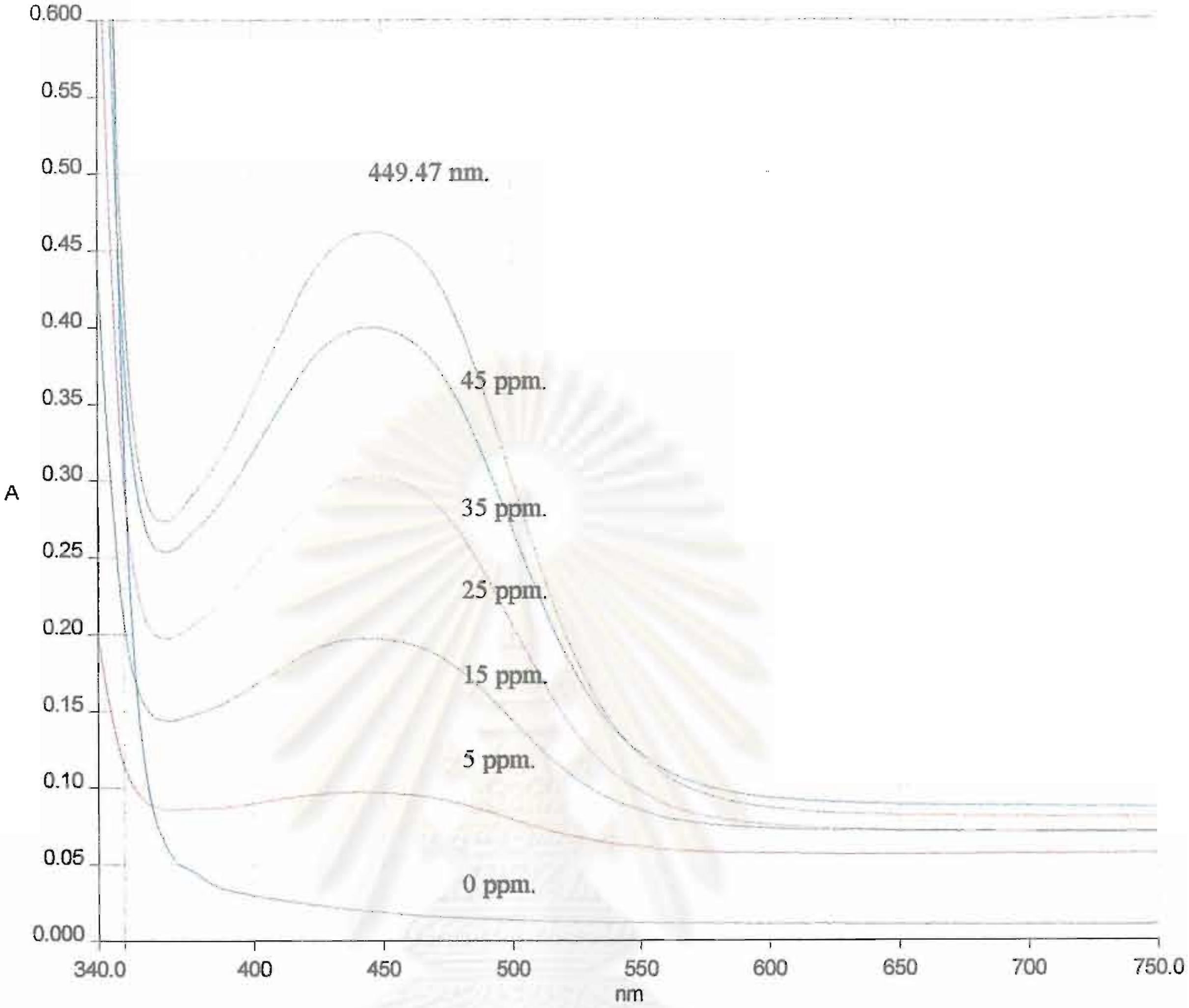

Figure 4-17 Visible absorption spectrum of CNSL hexyl ester-o-nitrophenyl azo dye in high speed diesel.

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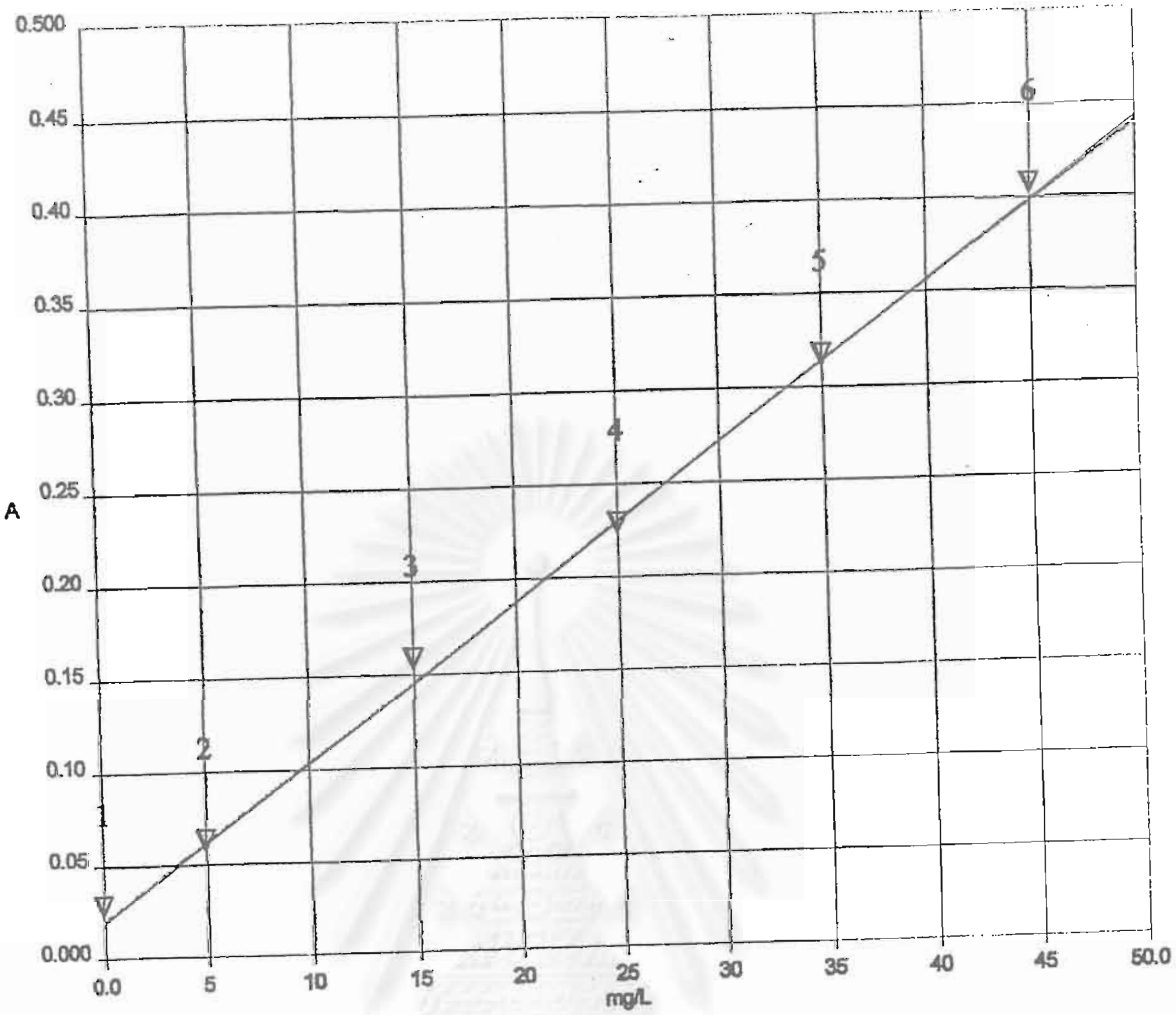

Figure 4-18 Calibration curve for CNSL hexyl ester-m-nitrophenyl azo dye in gasoline.

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : m-ulg
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
425.0	0.0	0ppm.A01	0.0000	mg/L.	0.0226	
425.0	0.0	5ppm.A02	5.0000	mg/L.	0.0576	
425.0	0.0	15ppm.A03	15.000	mg/L.	0.1532	
425.0	0.0	25ppm.A04	25.000	mg/L.	0.2235	
425.0	0.0	35ppm.A05	35.000	mg/L.	0.3116	
425.0	0.0	45ppm.A06	45.000	mg/L.	0.4019	

Equation : y = 1.996192e-02 + 8.404548e-03 * x
Residue error : 0.005948
Correlation coefficient : 0.999342

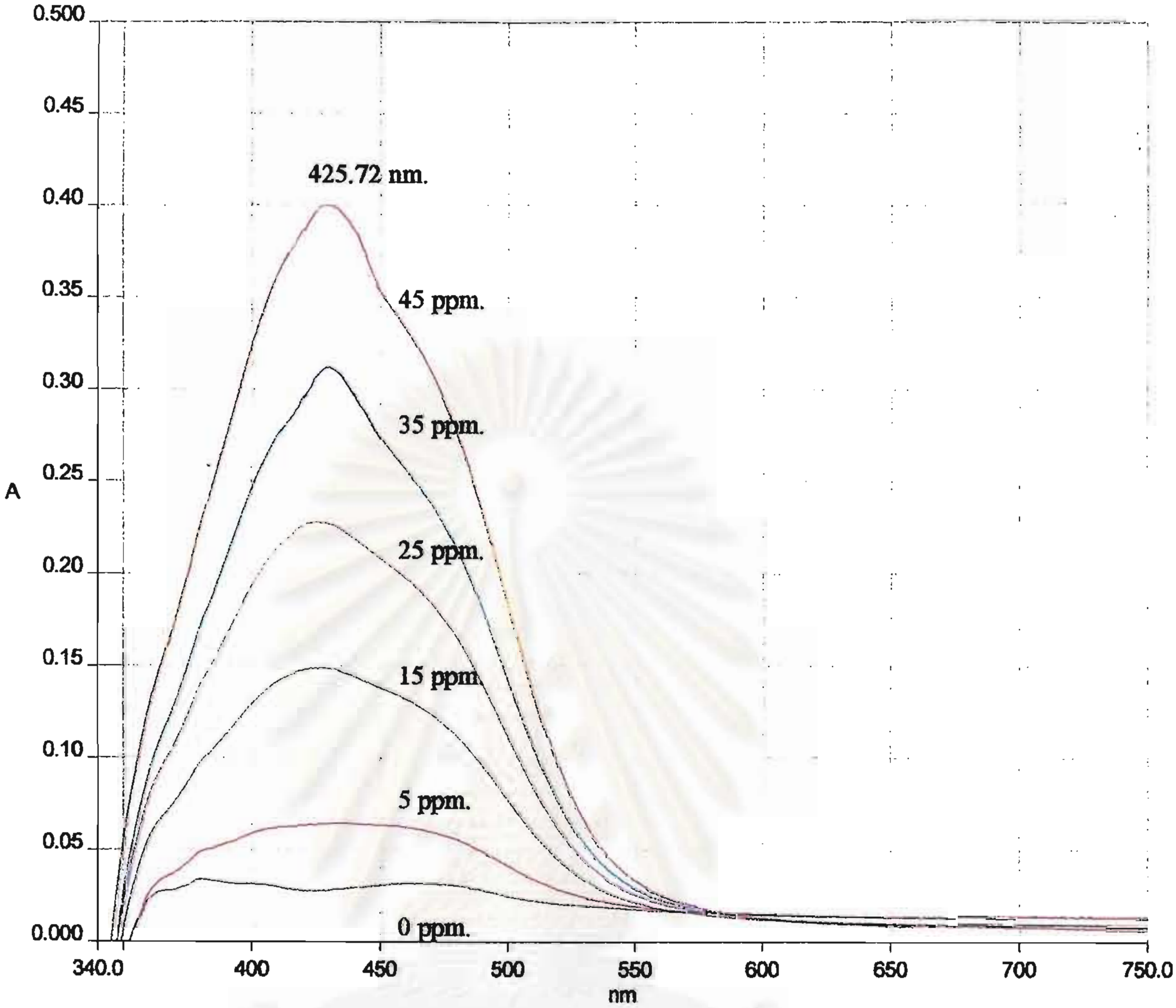

Figure 4-19 Visible absorption spectrum of CNSL hexyl ester-m-nitrophenyl azo dye in gasoline.

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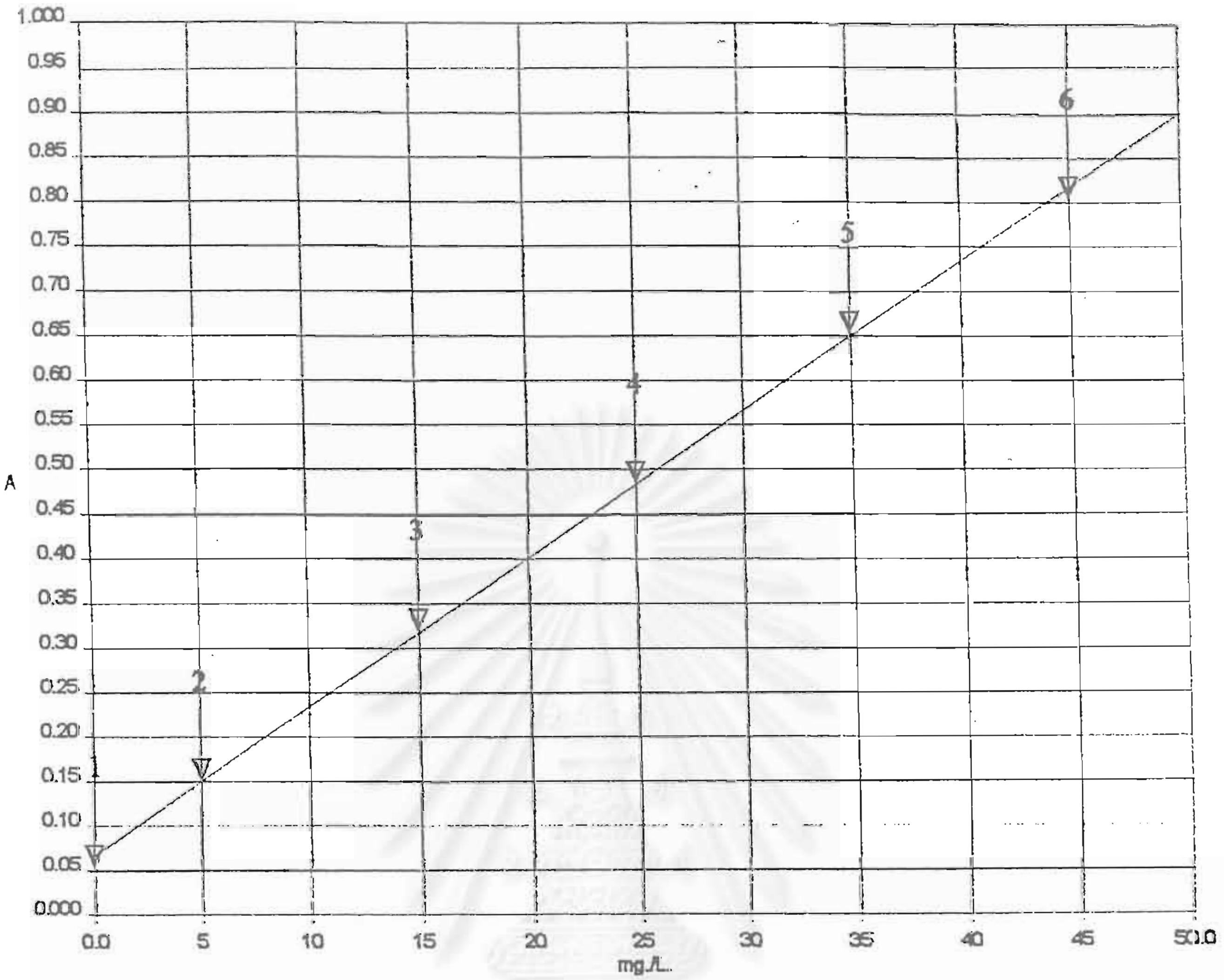

Figure 4-20 Calibration curve for CNSL hexyl ester-m-nitrophenyl azo dye in high speed diesel.

CALIBRATION

Instrument : Perkin-Elmer Lambda 2 Serial No : 5189
Method : m-hsd
Ordinate mode : Single wavelength
Baseline : No correction (0.00 0.00)
Analyst : PTT Lab.

Wavelength (s)		Sample ID	Concentration		Ord. Value	Comment
425.0	0.0	0ppm.A01	0.0000	mg/L.	0.0558	
425.0	0.0	5ppm.A02	5.0000	mg/L.	0.1517	
425.0	0.0	15ppm.A03	15.000	mg/L.	0.3211	
425.0	0.0	25ppm.A04	25.000	mg/L.	0.4858	
425.0	0.0	35ppm.A05	35.000	mg/L.	0.6555	
425.0	0.0	45ppm.A06	45.000	mg/L.	0.8068	

Equation : y = 6.524027e-02 + 1.668271e-02 * x
Residue error : 0.008184
Correlation coefficient : 0.999684

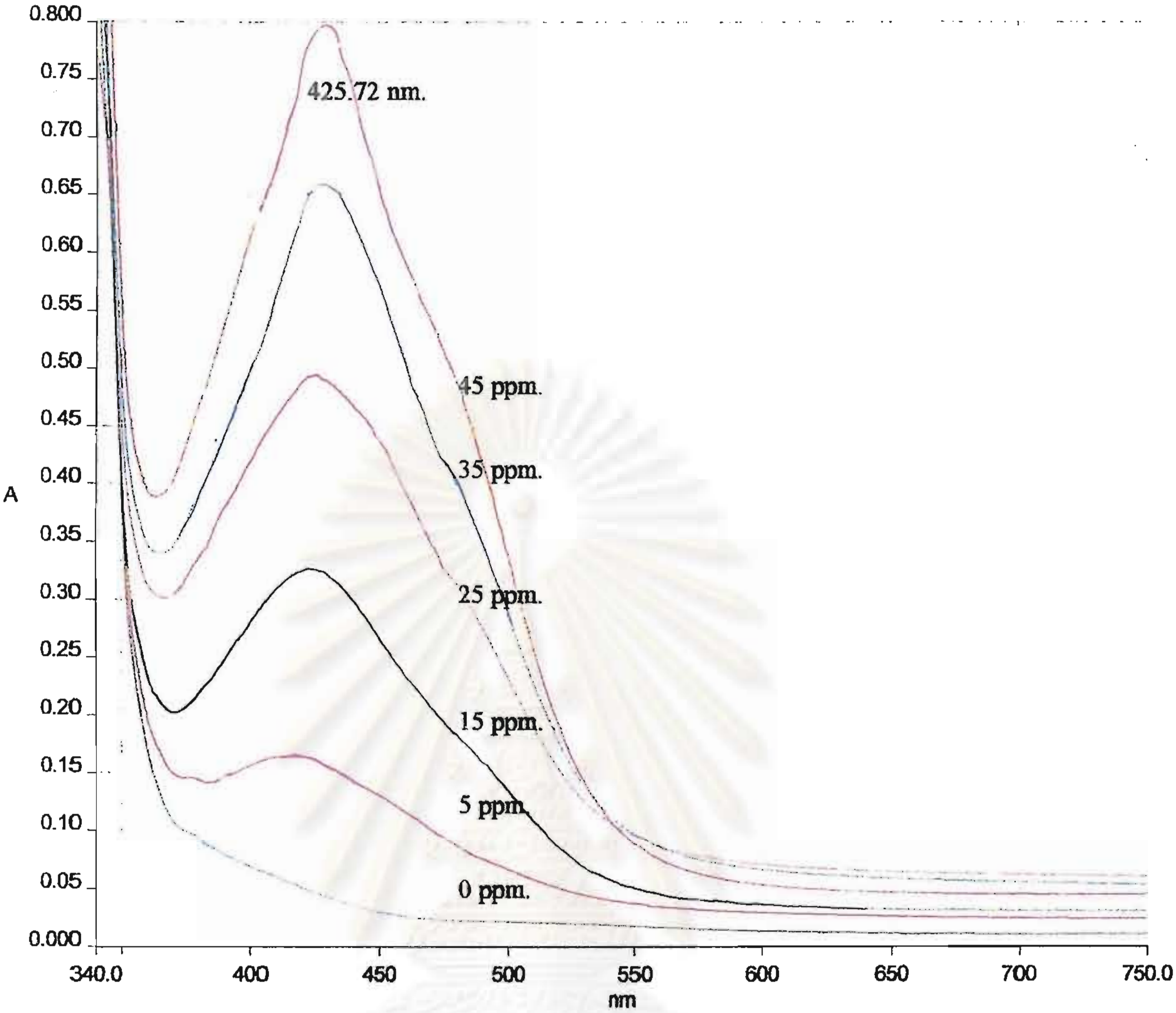

Figure 4-21 Visible absorption spectrum of CNSL hexyl ester-m-nitrophenyl azo dye in high speed diesel.

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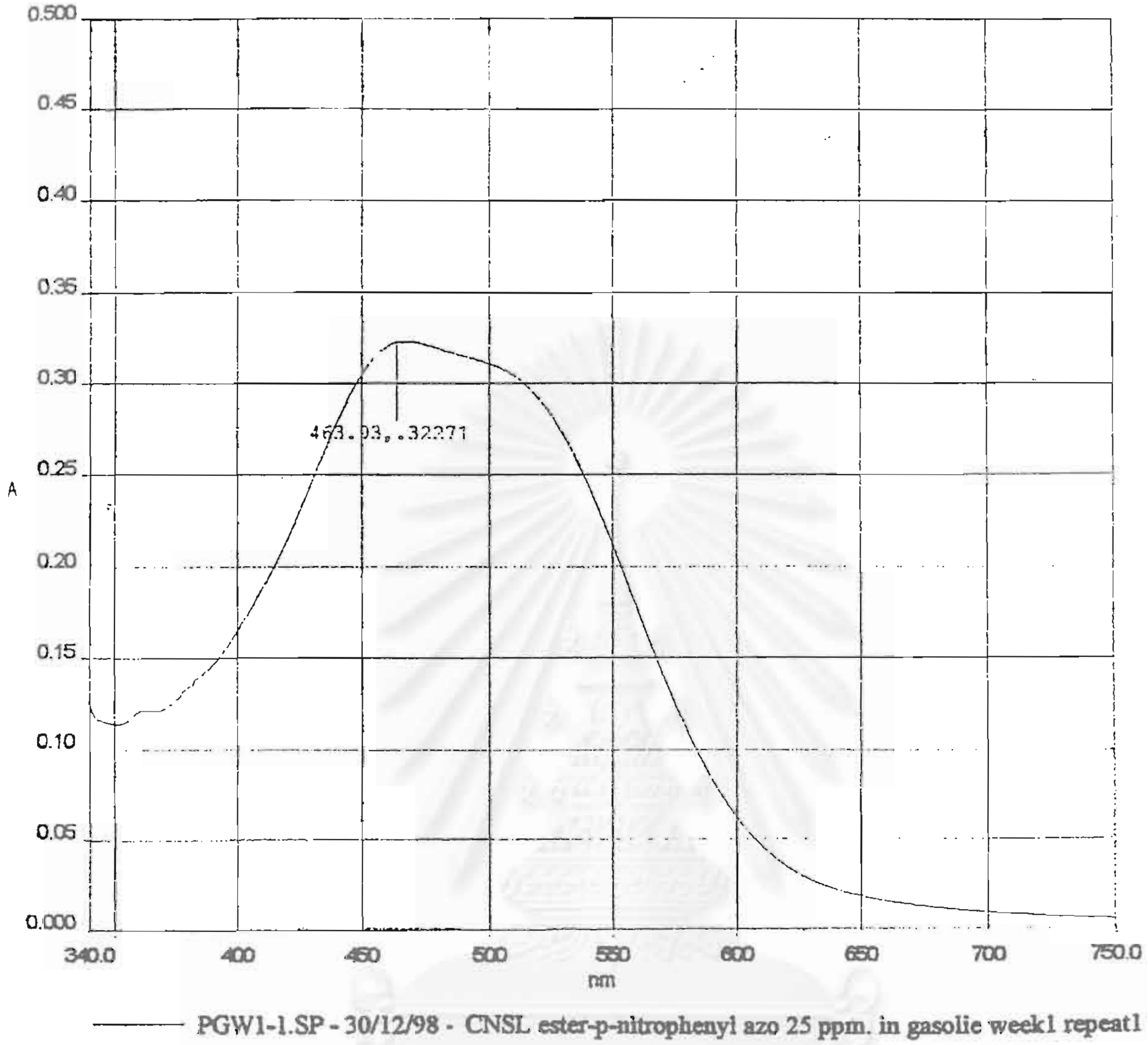

Figure 4-22 Visible absorption spectrum of 25 ppm CNSL hexyl ester-p-nitrophenyl azo dye in gasoline.

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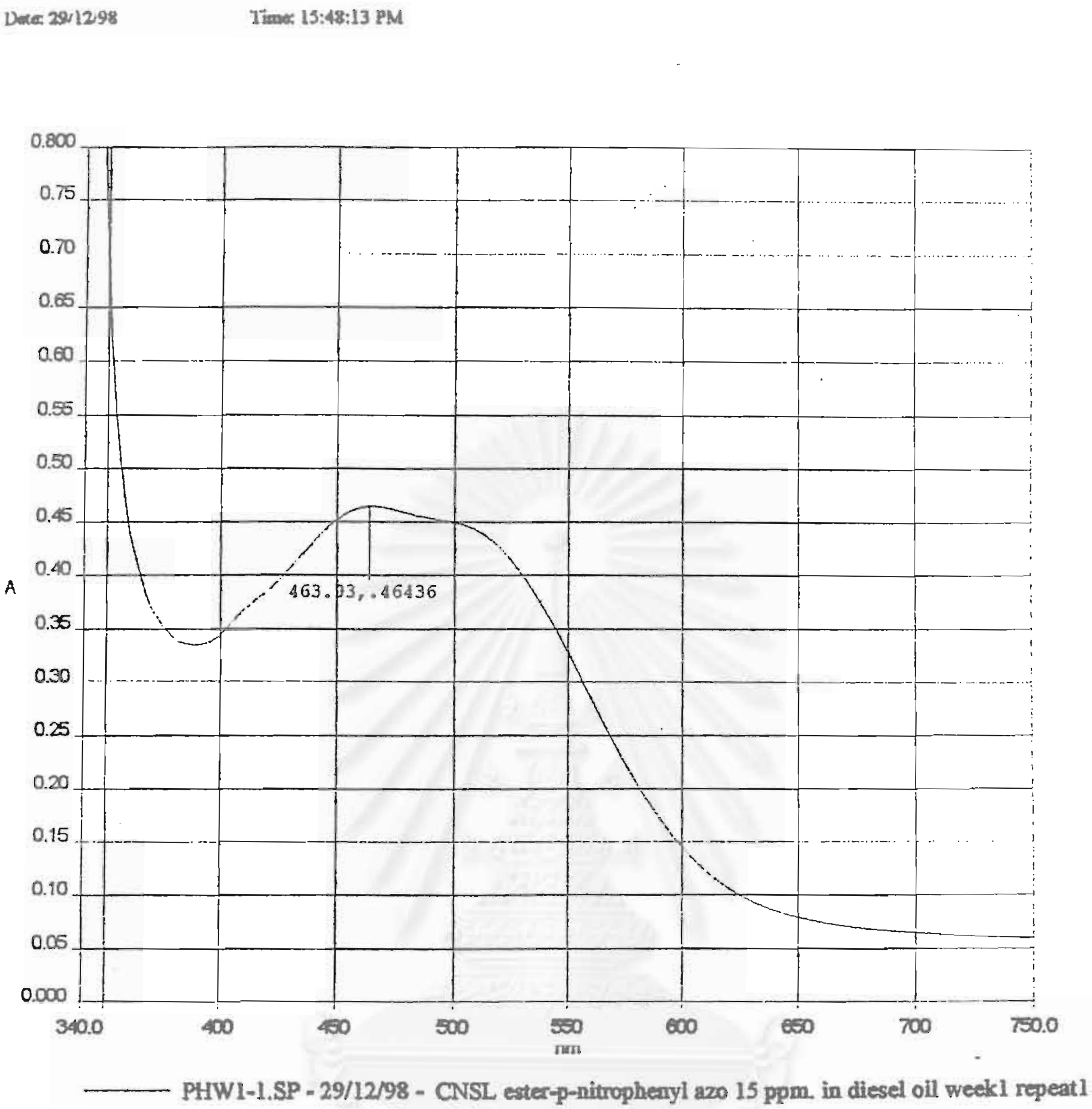

Figure 4-23 Visible absorption spectrum of 15 ppm CNSL hexyl ester-p-nitrophenyl azo dye in high speed diesel.

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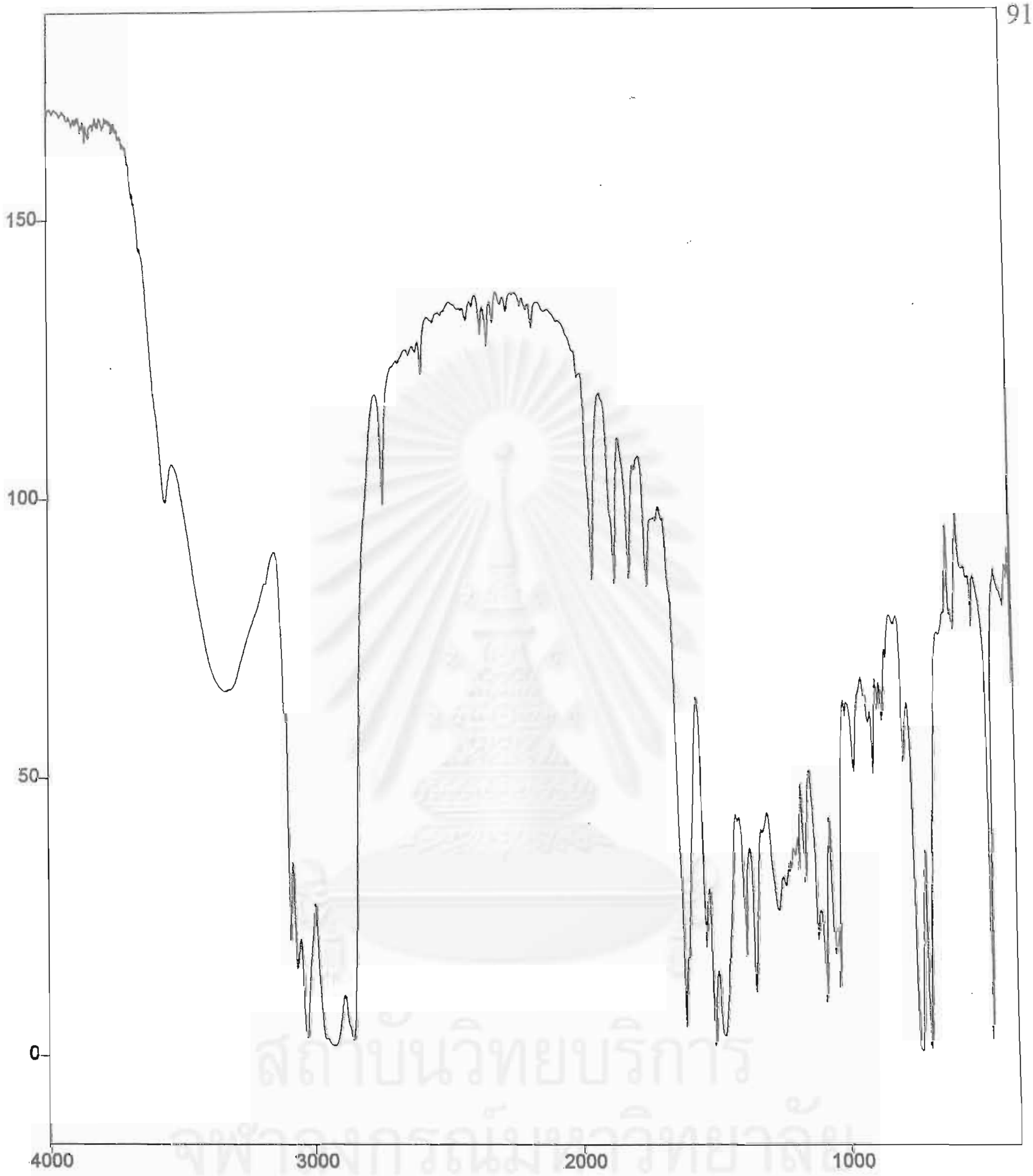

Figure 4-24 FT-IR spectrum of 20% CNSL hexyl ester-p-nitrophenyl azo dye in beginning.

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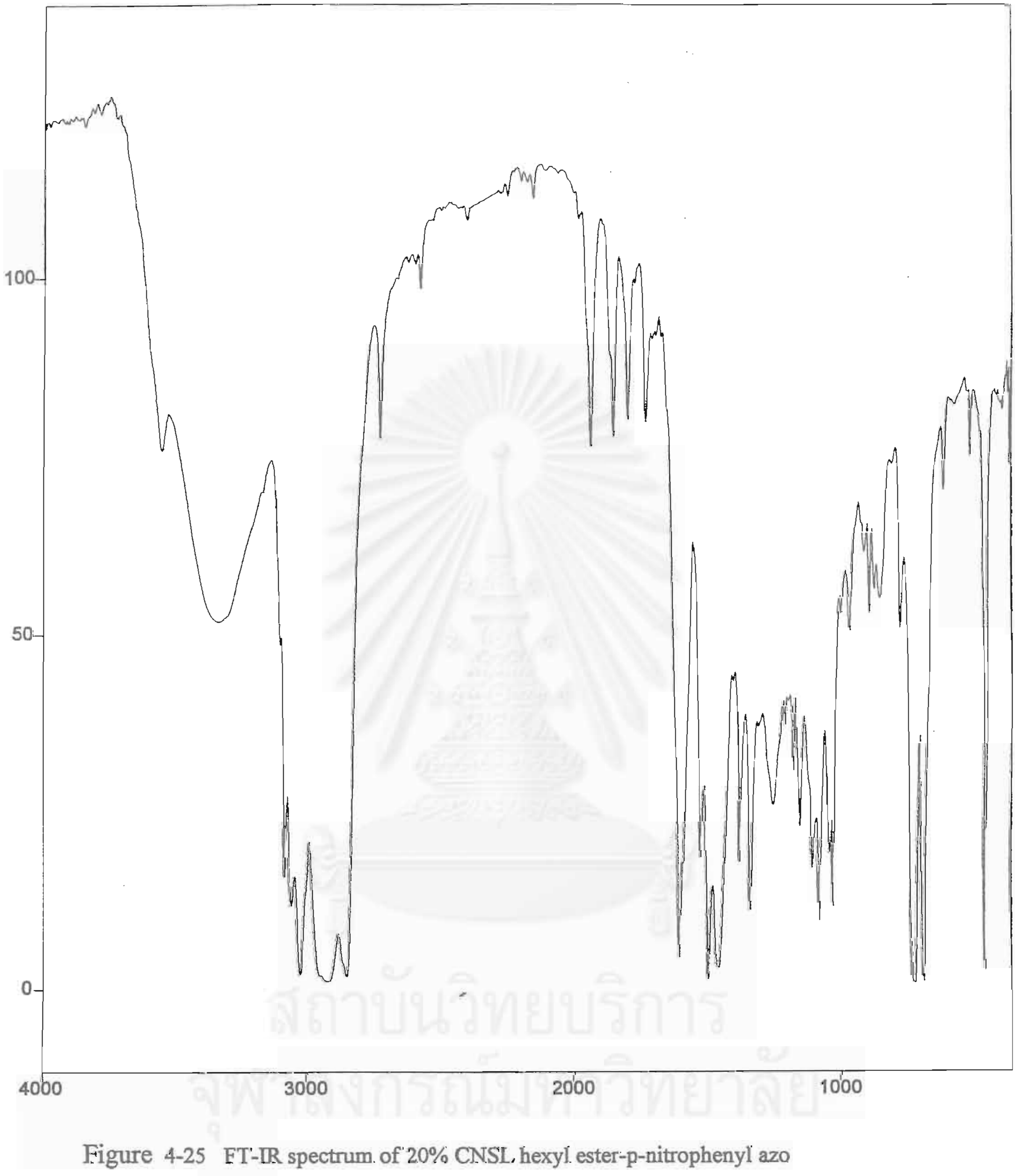

Figure 4-25 FT-IR spectrum of 20% CNSL hexyl ester-p-nitrophenyl azo dye after 1 month storage.

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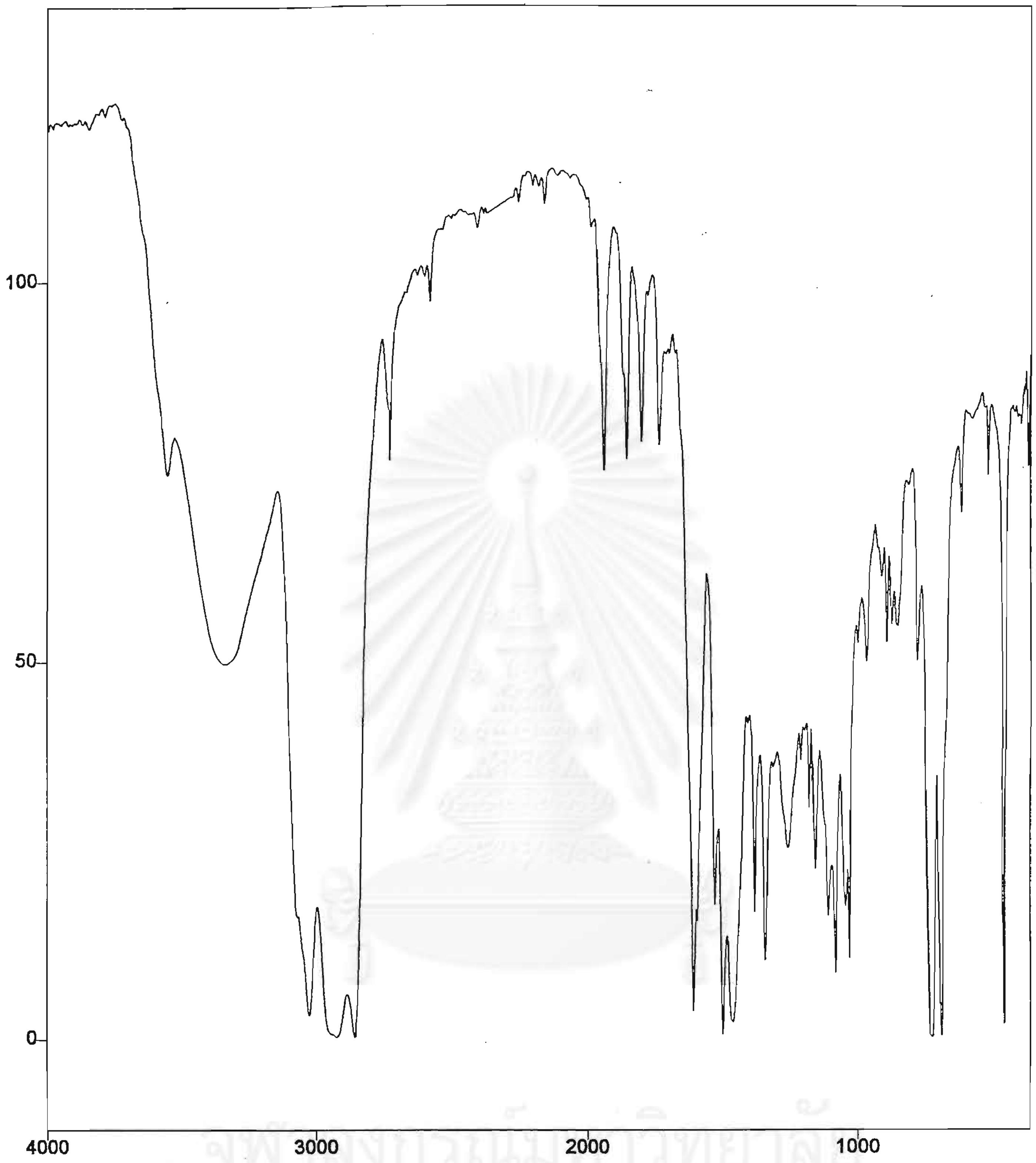

Figure 4-26 FT-IR spectrum of 20% CNSL hexyl ester-p-nitrophenyl azo dye after 2 months storage.

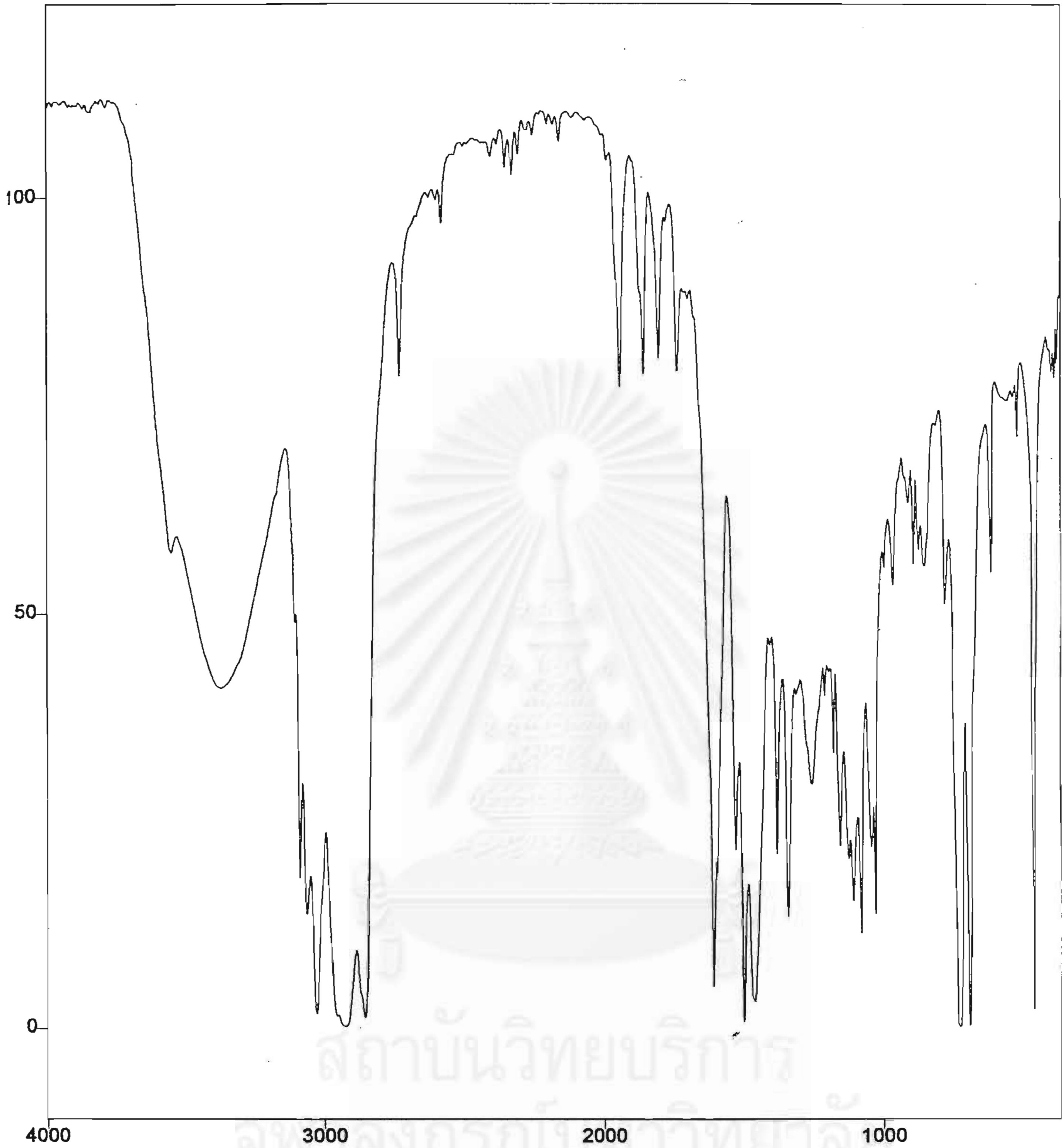

Figure 4-27 FT-IR spectrum of 20% CNSL hexyl ester-p-nitrophenyl azo dye after 3 months storage.

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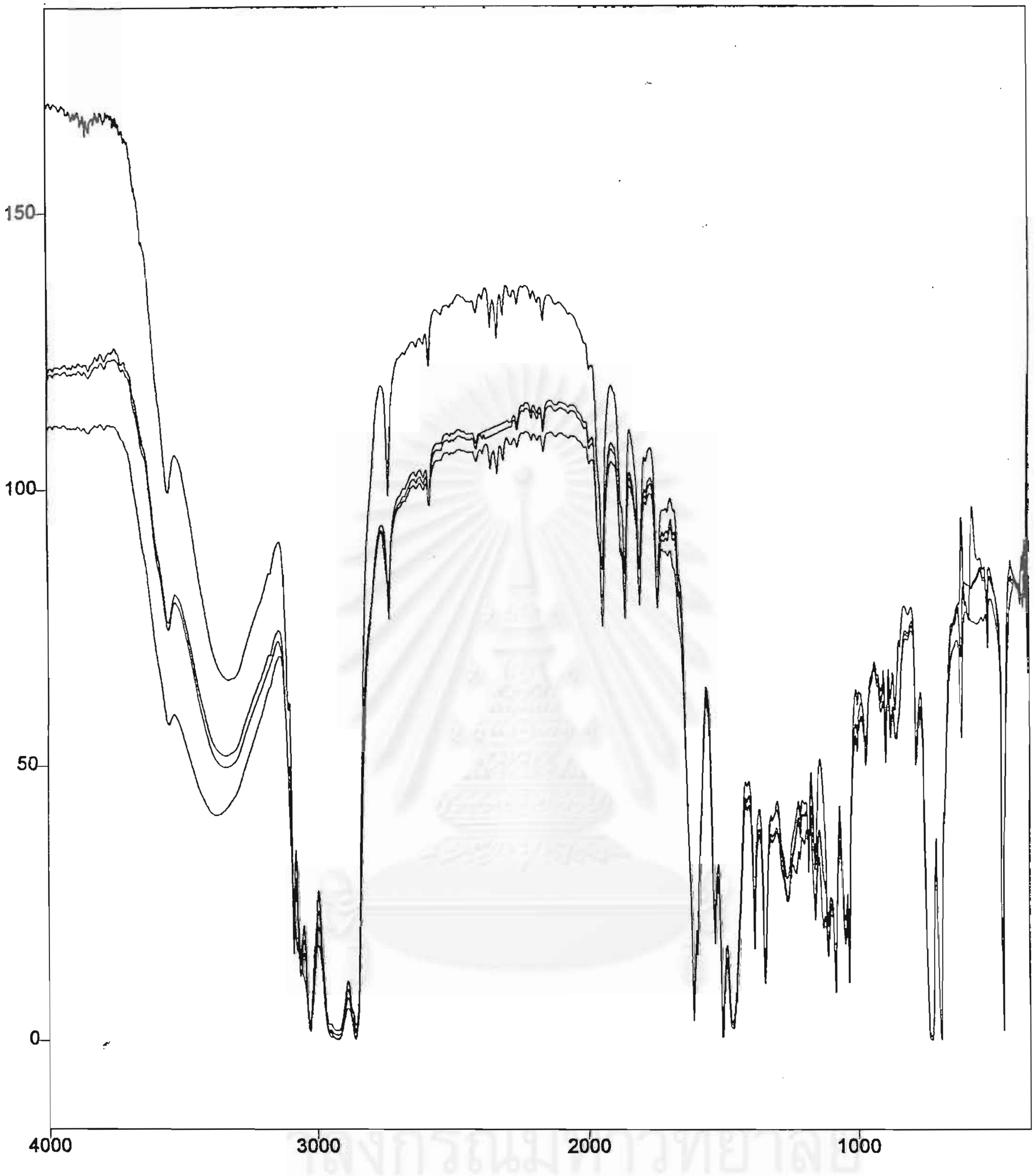

Figure 4-28 FT-IR spectrum of 20% CNSL hexyl ester-p-nitrophenyl azo dye after 0, 1, 2 and 3 months storage.

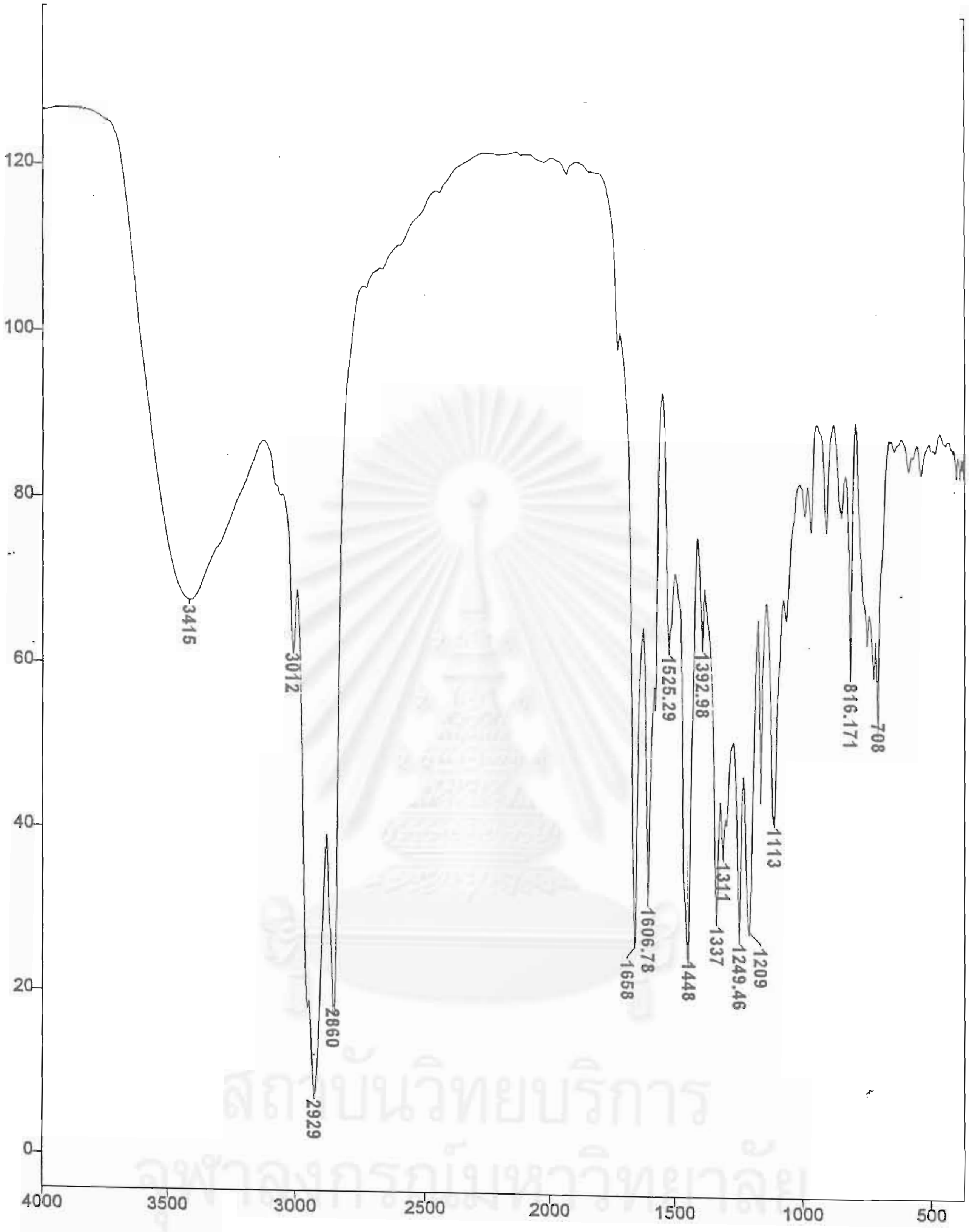

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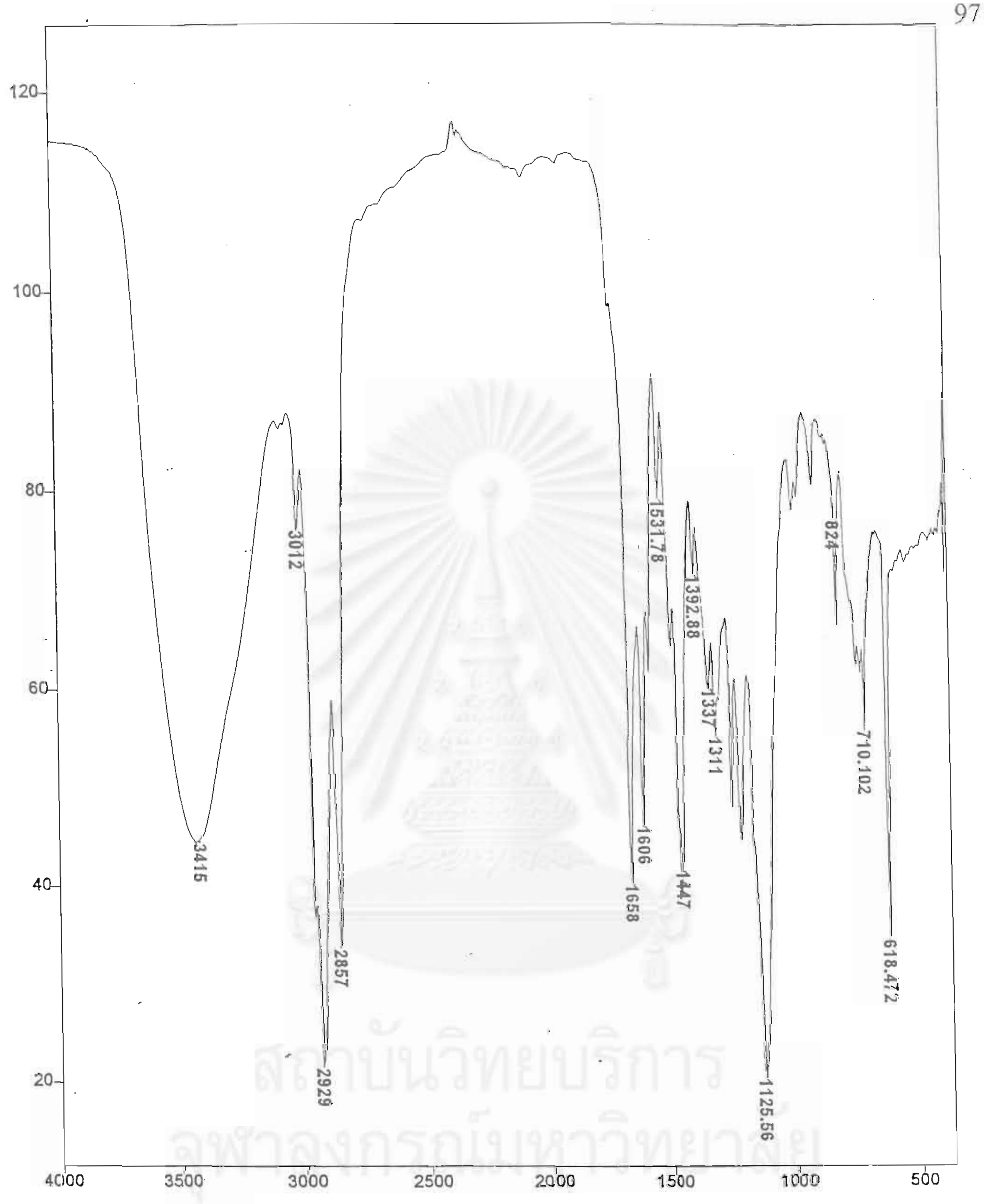
Figure 4-29 FT-IR spectrum of CNSL hexyl ester-p-nitrophenyl azo dye.



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จุฬาลงกรณ์มหาวิทยาลัย

Figure 4-30 FT-IR spectrum of CNSL hexyl ester-o-nitrophenyl azo dye.

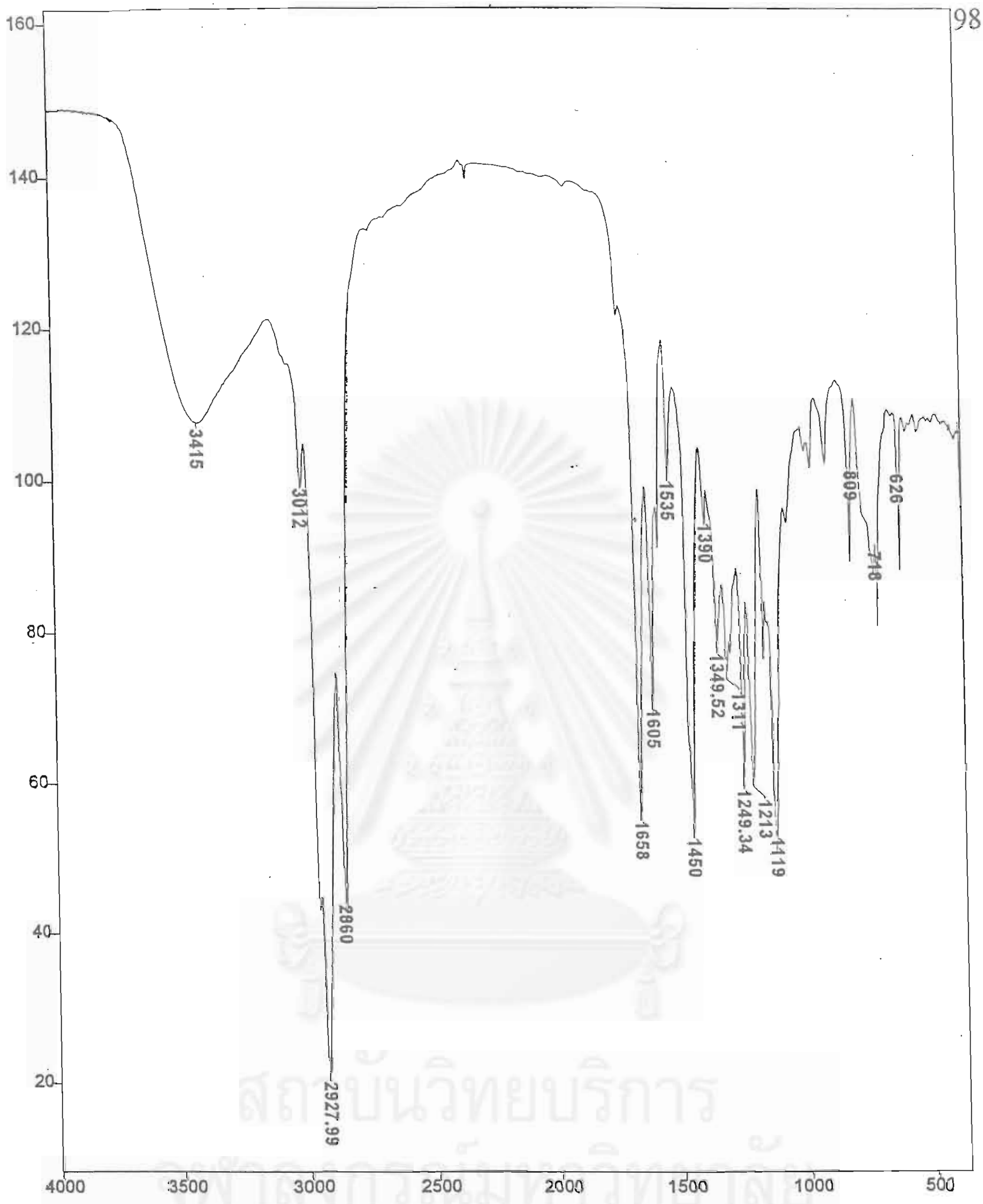

Figure 4-31 FT-IR spectrum of CNSL hexyl ester-m-nitrophenyl azo dye.

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จุฬาลงกรณ์มหาวิทยาลัย

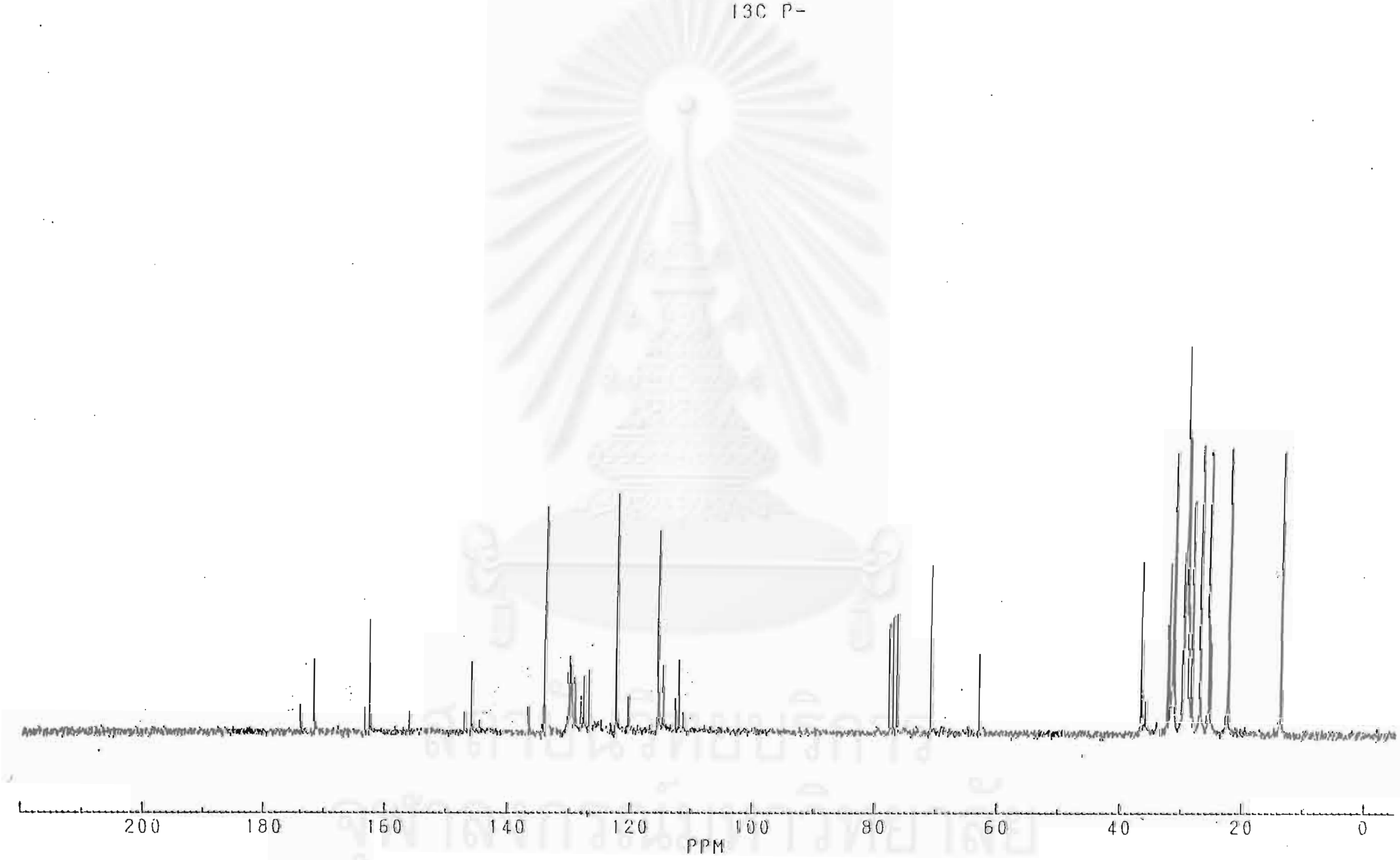

Figure 4-32 ^{13}C-NMR spectrum of CNSL hexyl ester-p-nitrophenyl azo dye.

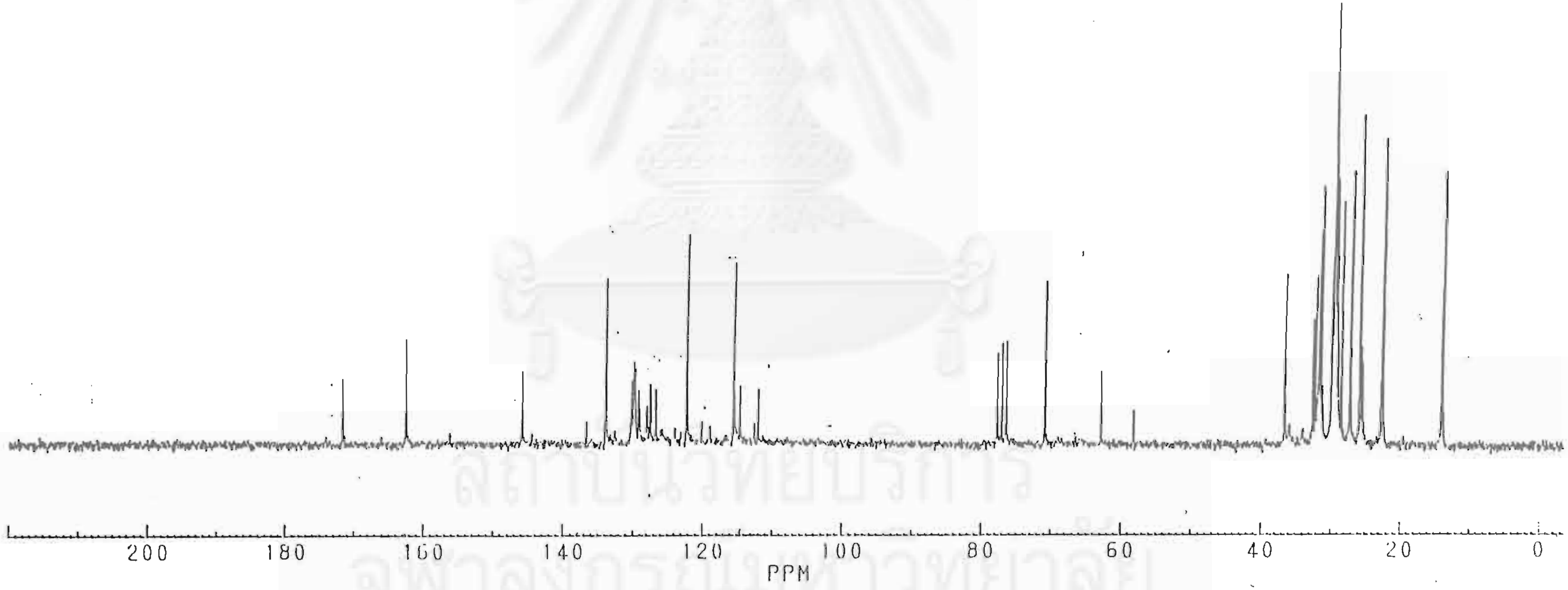

Figure 4-33 ^{13}C-NMR spectrum of CNSL hexyl ester-o-nitrophenyl azo dye.

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จุฬาลงกรณ์มหาวิทยาลัย

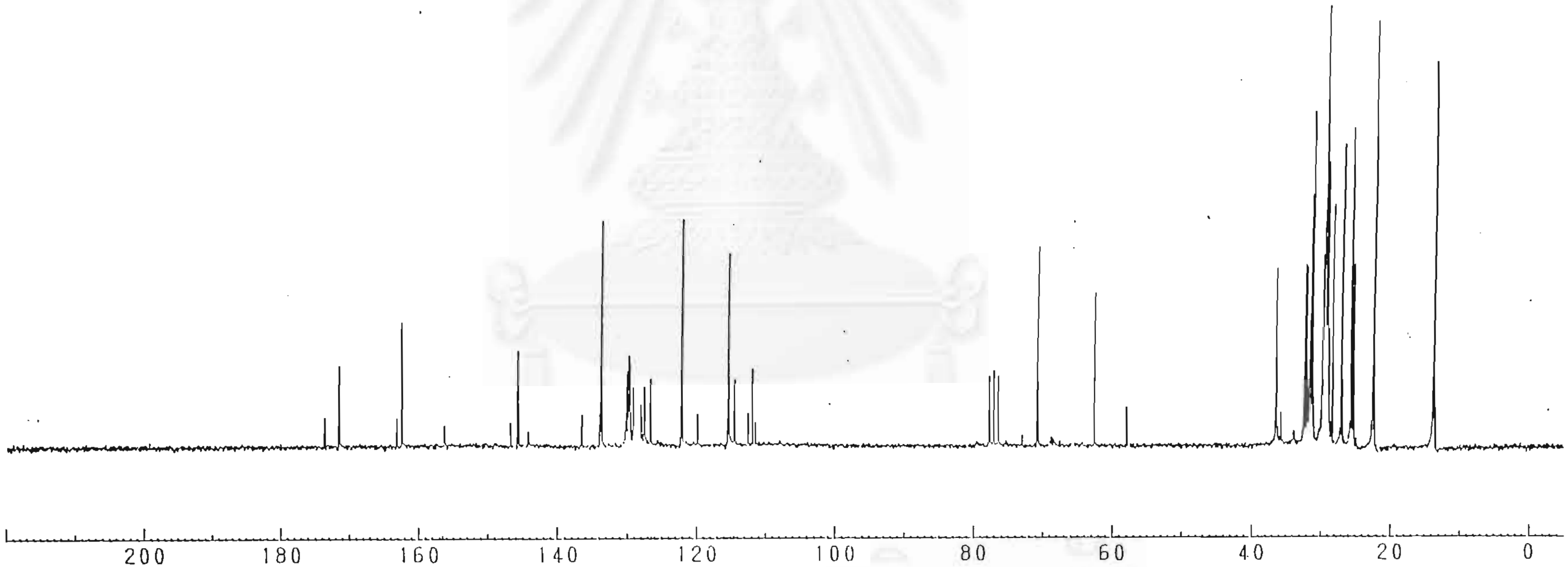

Figure 4-34 ^{13}C-NMR spectrum of CNSL hexyl ester-m-nitrophenyl azo dye

จุฬาลงกรณ์มหาวิทยาลัย

VITA

Mr. Supap Silapakampeerapab was born on September 9, 1971 in Samutsakhon, Thailand. He received his Bachelor of Science degree in Chemistry, Chulalongkorn University in 1994.He studies for the Master's degree of Science in program of Petrochemistry and Polymer, Graduate School, Chulalongkorn University, in 1997 and completed the program in 1999. Now he is working for the Petroleum Authority of Thailand.

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