

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 The characterization of octylsalicylate (ester B)

Octylsalicylate (ester B) was prepared by direct esterification of salicylic acid with 1-octanol in the presence of sulfuric acid. It was yellowish-brown oily liquid, soluble in methanol, petroleum ether, chloroform, toluene and had Total Acid Number (TAN) 6.02 mg. KOH/g.

The IR spectrum of octylsalicylate (Fig. B-1) showed the phenolic -OH group at  $3400\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (stretching) at  $2924$ ,  $2852\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (ester) at  $1654\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (bending) at  $1454$ ,  $1346\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching) at  $1250\text{ cm}^{-1}$ .

The  $^{13}\text{C}$ -NMR spectrum (Fig. B-3) revealed the presence of  $\text{C}-\text{OH}$  (phenolic group) at 162.21 ppm,  $\text{CH}_2$ ,  $\text{CH}_3$  at 12-36 ppm,  $-\text{CH}=\text{CH}-$  (aromatic groups) at 112-136 ppm and  $\text{C}=\text{O}$  (ester) at 170.04 ppm.

#### 4.2 The characterization of CNSL and the esterified CNSL (ester C)

Cashew Nut Shell Liquid (CNSL) extracted by n-hexane was viscous dark brown liquid, sparingly soluble in water, freely soluble in alcohols, petroleum ether and had TOTAL Acid Number (TAN) 20.23 mg. KOH/g.

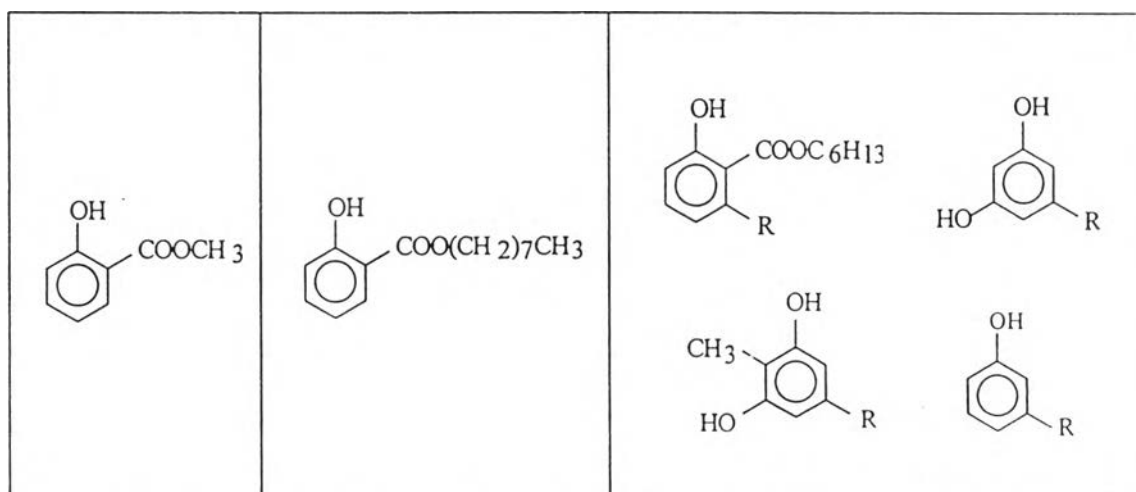
The esterified CNSL (ester C) was prepared by direct esterification of CNSL with 1-hexanol in the presence of sulfuric acid. It was viscous dark

brown liquid, immiscible with methanol, soluble in toluene, chloroform, petroleum ether and had Total Acid Number (TAN) as 5.14 mg. KOH/ g.

The IR spectrum of CNSL (Fig.C-1) showed the phenolic -OH group at  $3358\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (stretching) at  $2926$ ,  $2854\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (carboxylic acid) at  $1589\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (bending) at  $1467$ ,  $1395\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching) at  $1266\text{ cm}^{-1}$ . In consideration of the esterified CNSL (Fig. C-4), it showed the phenolic -OH group at  $3400\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (ester) at  $1659\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching, at  $1249\text{ cm}^{-1}$ .

The  $^{13}\text{C}$ -NMR spectrum (Fig.C-3) revealed the presence of  $\text{C}-\text{OH}$  (phenolic group) at  $162.54\text{ ppm}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  at  $12$ - $36\text{ ppm}$ ,  $-\text{CH}=\text{CH}-$  (aromatic groups) at  $112$ - $136\text{ ppm}$  and  $\text{C}=\text{O}$  (carboxylic acid) at  $175.32\text{ ppm}$ . In case of the esterified CNSL (Fig. C-6),  $\text{C}=\text{O}$  (ester) exhibited at  $170.52\text{ ppm}$ .

The starting phenol esters used in this research were listed in three groups following below ;



Where  $\text{R} = \text{C}_{15}\text{H}_{25-31}$

Methylsalicylate

Octylsalicylate

The esterified CNSL

(phenol ester A)

(Phenol ester B)

(Phenol ester C)

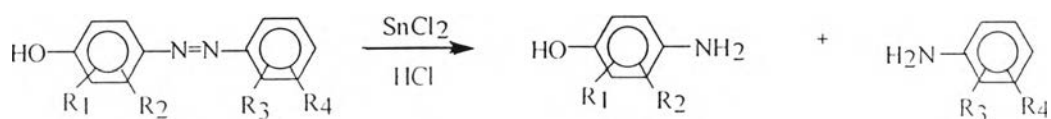
The phenol esters A, B and C were increasingly soluble in organic solvents, respectively. In case of the acidity of the starting CNSL and the esterified CNSL, the TAN values of the esterified CNSL could be descended compared with the starting CNSL. Therefore, the purposes of the esterification should be decreasing the acidity and increasing the solubility in organic solvents of phenol esters.

#### 4.3 The characterization of the marker dyes from the esters A to C and chloronitroaniline derivatives

The marker dyes were obtained from the coupling reactions between the phenolate ion of phenol esters A-C and the diazonium salt of chloronitroaniline derivatives. They were characterized by FT-IR and NMR spectroscopic techniques.

The marker dyes A<sub>1</sub>-A<sub>4</sub> were reddish-orange solid compounds. Their solubility in organic solvents was poor so they could not be used for a marker in petroleum fuels. Due to their simple structures, they could be used for comparing with marker dyes set B and C.

The formation of azo dyes groups (N=N) was confirmed by the reaction with acid. All of the marker dyes set A-C were reduced with acidic stannous chloride. They would be cleaved to amino phenol and amine compounds. So the testing solution would be colorless.[12]

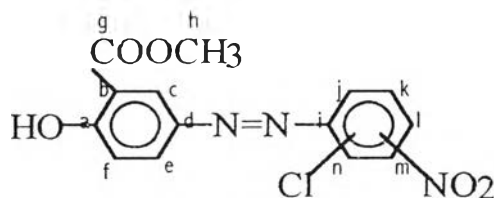


#### 4.3.1 The characterization of marker dyes set A

From the IR spectra of marker dyes set A (Figs. A-1, A-4, A-7, A-10), they displayed the phenolic -OH group at  $3390\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (stretching) at  $2924$ ,  $2847\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (ester) at  $1659\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (bending) at  $1454$ ,  $1345\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching) at  $1250\text{ cm}^{-1}$ .

The  $^{13}\text{C}$ -NMR spectra (Figs. A-3, A-6, A-9, A-12) revealed the presence of the functional groups in Table 4-1

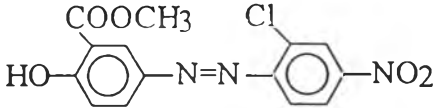
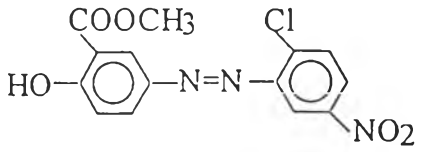
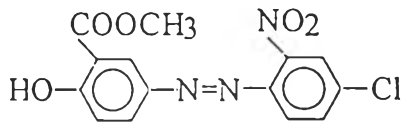
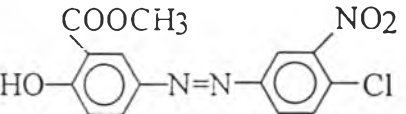
Table 4-1 : The  $^{13}\text{C}$ -NMR chemical shifts of marker dyes  $\text{A}_1$ - $\text{A}_4$ .



Carbon at	Chemical shifts (ppm)			
	$\text{A}_1$	$\text{A}_2$	$\text{A}_3$	$\text{A}_4$
a	162.2	162.3	161.8	162.3
b	118.3	118.2	118.3	118.3
c	126.3	126.5	126.3	126.5
d	145.1	145.2	145.2	145.2
e	128.9	128.8	128.4	128.5
f	112.5	112.5	112.4	112.5
g	170.2	170.0	170.1	170.2
h	52.5	52.5	52.4	52.5
i	152.4	152.6	152.5	151.8
j	119.0(Cl)	119.1(Cl)	136.0( $\text{NO}_2$ )	127.5
k	129.0	130.1	129.7	132.5( $\text{NO}_2$ )
l	136.2( $\text{NO}_2$ )	129.2	119.3(Cl)	119.0(Cl)
m	130.0	136.3( $\text{NO}_2$ )	129.8	128.7
n	122.6	122.6	121.4	122.6

From Table 4-1, it was confirmed that the marker dyes set A were azo dye compounds and their structures were following Table 4-2.

Table 4-2 : The marker dyes set A in the series of chloronitroaniline derivatives.

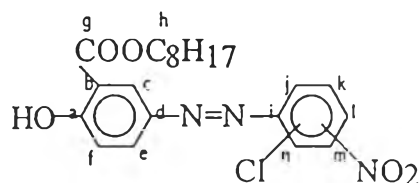
Marker dye	Structure
Marker dye A <sub>1</sub>	 <p>methylsalicylate- 2-chloro-4-nitrophenyl azo</p>
Marker dye A <sub>2</sub>	 <p>methylsalicylate- 2-chloro-5-nitrophenyl azo</p>
Marker dye A <sub>3</sub>	 <p>methylsalicylate-4-chloro-2- nitrophenyl azo</p>
Marker dye A <sub>4</sub>	 <p>methylsalicylate-4-chloro-3- nitrophenyl azo</p>

### 4.3.2 The characterization of marker dyes set B

From the IR spectra of marker dyes set B (Figs. B-4, B-7, B-10, B-13), they displayed the phenolic -OH group at  $3400\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (stretching) at  $2924$ ,  $2852\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (ester) at  $1654\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (bending) at  $1454$ ,  $1346\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching) at  $1250\text{ cm}^{-1}$

The  $^{13}\text{C}$ -NMR spectra (Figs. B-6, B-9, B-12, B-15) revealed the presence of the functional groups in Table 4-3

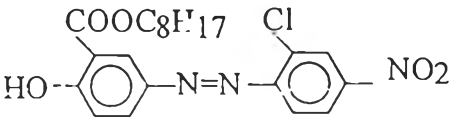
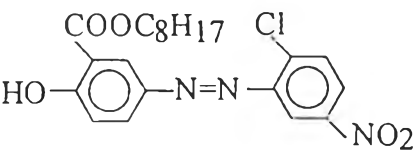
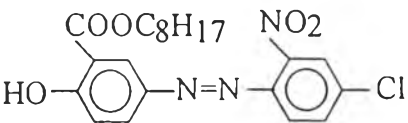
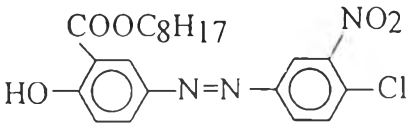
Table 4-3 : The  $^{13}\text{C}$ -NMR chemical shifts of marker dyes B<sub>1</sub>-B<sub>4</sub>.



Carbon at	Chemical shifts (ppm)			
	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>
a	162.2	162.3	162.2	162.3
b	118.3	118.4	118.2	118.3
c	126.4	126.2	126.3	126.5
d	145.2	145.2	145.2	145.2
e	128.5	128.2	128.4	128.5
f	112.5	112.6	112.4	112.5
g	170.1	170.0	170.1	170.2
h	12-35	12-35	11-35	52.5
i	152.2	152.4	152.5	151.8
j	119.2(Cl)	119.1(Cl)	136.2(NO <sub>2</sub> )	127.6
k	129.5	130.0	129.9	132.5(NO <sub>2</sub> )
l	136.3(NO <sub>2</sub> )	129.3	119.7(Cl)	119.0(Cl)
m	130.1	136.4(NO <sub>2</sub> )	129.9	128.7
n	122.4	122.2	121.4	122.6

From Table 4-3, it was confirmed that the marker dyes set B were azo dye compounds and their structures were following Table 4-4.

Table. 4-4 : The marker dyes set B in the series of chloronitroaniline derivatives.

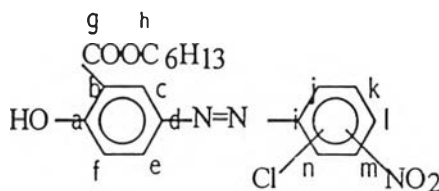
Marker dye	Structure
Marker dye B <sub>1</sub>	 <p style="text-align: center;">octylsalicylate -2-chloro-4- nitrophenyl azo</p>
Marker dye B <sub>2</sub>	 <p style="text-align: center;">octylsalicylate- 2-chloro-5- nitrophenyl azo</p>
Marker dye B <sub>3</sub>	 <p style="text-align: center;">octylsalicylate -4-chloro-2- nitrophenyl azo</p>
Marker dye B <sub>4</sub>	 <p style="text-align: center;">octylsalicylate- 4-chloro-3- nitrophenyl azo</p>

### 4.3.3 The characterization of marker dyes set C

From the IR spectra of marker dyes set C (Figs. C-4, C-7, C-10, C-13), they displayed the phenolic -OH group at  $3400\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (stretching) at  $2924$ ,  $2852\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  (ester) at  $1654\text{ cm}^{-1}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (bending) at  $1454$ ,  $1346\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  (stretching) at  $1250\text{ cm}^{-1}$

The  $^{13}\text{C}$ -NMR spectra (Figs. C-6, C-9, C-12, C-15) revealed the presence of the functional groups in Table 4-5.

Table 4-5 : The  $^{13}\text{C}$ -NMR chemical shifts of marker dyes  $\text{C}_1$ - $\text{C}_4$ .

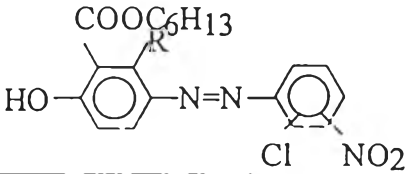
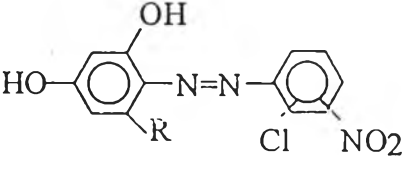
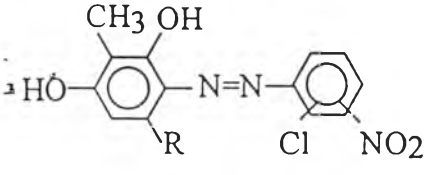
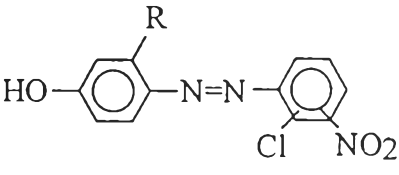


Carbon at	Chemical shifts (ppm)			
	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$
a	162.5	162.5	162.1	162.3
b	118.0	118.2	118.2	118.3
c	125.5	125.6	124.8	126.4
d	145.6	145.3	145.5	145.5
e	128.1	128.2	128.3	128.3
f	112.2	112.5	112.5	112.3
g	171.5	171.4	171.3	171.4
h	12-37	12-37	12-37	12-37
i	152.2	152.3	152.5	151.9
j	119.9(Cl)	120.1(Cl)	135.2( $\text{NO}_2$ )	127.5
k	129.3	130.0	129.7	133.8( $\text{NO}_2$ )
l	134.2( $\text{NO}_2$ )	129.5	119.8(Cl)	119.6(Cl)
m	130.1	134.1( $\text{NO}_2$ )	129.8	128.4
n	122.2	122.2	122.3	122.5



From Table 4-5, it was confirmed that the marker dyes set C were azo dye compounds and their structures were following Table 4-6.

Table 4-6: The marker dyes set C in the series of chloronitroaniline derivatives.

	
 <p>Where R = C<sub>15</sub>H<sub>25-31</sub></p>	

Marker dye C<sub>1</sub>: the esterified CNSL-2-chloro-4-nitrophenyl azo

Marker dye C<sub>2</sub>: the esterified CNSL-2-chloro-5-nitrophenyl azo

Marker dye C<sub>3</sub>: the esterified CNSL-4-chloro-2-nitrophenyl azo

Marker dye C<sub>4</sub>: the esterified CNSL-4-chloro-3-nitrophenyl azo

The esterified CNSL was the mixtures of phenolic compounds consisting of hexylanacardate, cardol, 2-methylcardanol and cardanol. Therefore, the obtained marker dyes C<sub>1</sub>-C<sub>4</sub> would be the mixtures of phenol ester-chloronitrophenyl azo, as well.

#### 4.4 The appropriate solvent extraction systems for the marker dyes

The 10 ppm marker dyes set A-C in diesel oil were prepared to study the appropriate solvent extraction systems. The marker dyes set A had a limited solubility and a low rate of dissolution in diesel oil because they were solid compounds. It was shown that the concentrations of marker dyes set A could not be precisely prepared in diesel oil. For the mentioned reasons, the liquid marker dyes set B and C should be only used for marking diesel oil.

The solvent extraction systems in Table 3-1 should be investigated. The appropriate solvent extraction systems should be chosen by the observation of hue of aqueous phase, the efficiency of each solvent, emulsion performances in oil and aqueous phase and the stability of the solvents were studied.

The terms of efficiency of solvent in Table 4-7:

- means The marker dye could not be extracted into the aqueous phase.
- poor means The marker dyes could be extracted into the aqueous phase and shown the weak specific visual color.
- good means All of marker dye could be extracted into the aqueous phase and moderately shown the specific visual color.
- excellent means All of marker dye could be extracted into the aqueous phase and obviously shown the specific visual color.

Table 4-7 : The results of solvent extraction systems for marker dyes A-C in diesel oil

The solvent extraction systems	Efficiency
1. 5% wt KOH in Methanol 2. 10% wt KOH in Methanol 3. 5% wt KOH in Ethylene glycol 4. 10% wt KOH in Ethylene glycol 5. 5% wt KOH in 10% vol. Methanol + 90% vol. Ethylene glycol	poor poor poor poor poor
6. 30% wt Ethylene glycol + 40% vol. Methanol + 30% vol. Methylamine 7. 30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Diisopropylamine 8. 30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Ethylenediamine 9. 30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Morpholine	good good excellent good

Table 4-7: The results of solvent extraction systems for marker dyes A-C in diesel oil. (continued)

The solvent extraction systems	Efficiency
10. 2.5% Ferric chloride in methanol	-
11. 2.5% Ferric chloride in ethylene glycol	-
12. 90% vol. Ethylene glycol + 10% vol. Ethylenediamine	poor
13. 80% vol. Ethylene glycol + 20% vol. Ethylenediamine	poor
14. 70% vol. Ethylene glycol + 30% vol. Ethylenediamine	good
15. 60% vol. Ethylene glycol + 40% vol. Ethylenediamine	excellent
16. 60% vol. Ethylene glycol + 40% vol. Ammonium hydroxide	-
17. 60% vol. Ethylene glycol + 40% vol. Ethylenediamine	excellent
18. 60% vol. Ethylene glycol + 40% vol. Diethylenetriamine	good
19. 60% vol. Ethylene glycol + 40% vol. Triethylenetetramine	poor
20. 60% vol. Ethylene glycol + 40% vol. Morpholine	poor

From Table 4-7, it could be concluded following below :

The solvent extraction systems comprising methanol as a cosolvent were not the appropriate solvent extraction systems. Because it could be miscible in both oil and aqueous phases. Although it was a solvent which had very low costs. Oily drops which might be in the aqueous phase could be an error in the quantitative determinations. The calibration curves could not be linear because of their error absorbances.

The solvent extraction systems using strong aqueous alkali solution were not the preferred extraction and detection method. Because the color developed from the markers with strong alkaline was not as intense as might be desired. Furthermore, it was unstable which was reducing the ability to obtain the quantitative determinations. [3]

From the solvent extraction systems 6-9, it was found that alkyl amines were generally less preferred because of their less extractive power and odors. Ethylenediamine was preferred because of the most extractive power. [3]

From the solvent extraction systems 10-11, ferric chloride usually reacts with phenol and obtains the intense color complexes. But the marker dyes were added into diesel oil in parts-per-million quantity so they could not be extracted by these solvent extraction systems and developed the intense specific visual color.

It was referred that cosolvents which were miscible with water and immiscible with the petroleum products had significantly advantageous effects with respect to shade, intensity of the developed color and degree of interference from fuel components. Importantly, the developed color was stable,

the quantitative determinations of marker levels would be facilitated. [3] When methanol was compared with ethylene glycol, using ethylene glycol was preferred.

From the solvent extraction systems 12-15, when the percent volume of base (ethylenediamine) in ethylene glycol was increasingly added, the efficiency of the solvent extraction systems would be more extractive power. If percent volume of base was added more than 40%, the cost of the extractant was not suitable. From Figure 4-1 and Table 4-8, they were shown that the specific maximum absorption wavelength of each solvent extraction phase and their specific visual color differed following below :

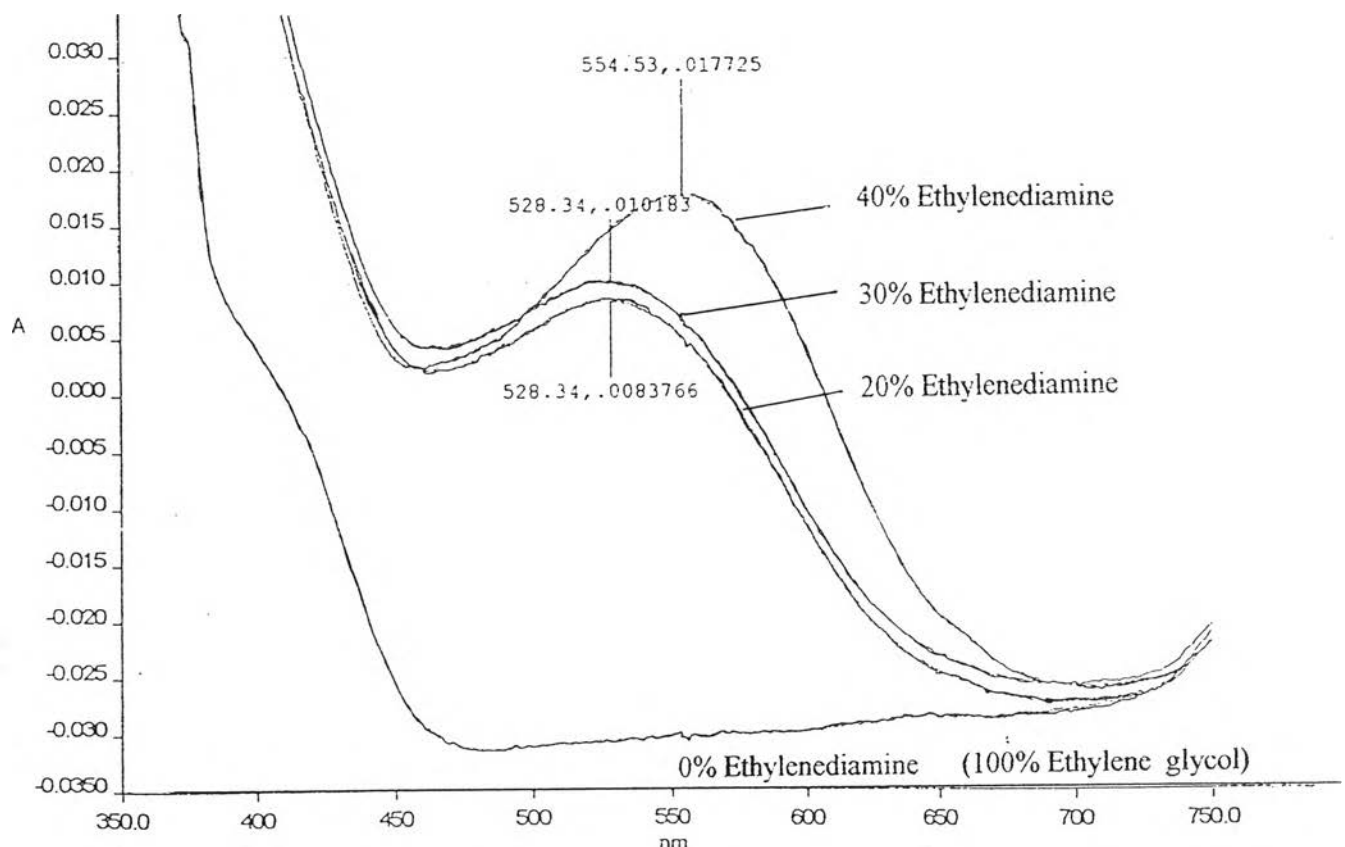


Fig. 4-1 : The variation of base quantity in ethylene glycol for the 5 ppm of marker dye  $C_1$  in diesel oil. (ratio 9:1)

Table 4-8 : The maximum absorption wavelengths and their specific visual colors of 5 ppm marker dye B<sub>1</sub> in diesel oil.

Solvent extraction systems	$\lambda_{\max}$ (nm)	Absorbances
80% vol. Ethylene glycol + 20% vol. Ethylenediamine	528.34	0.0084
70% vol. Ethylene glycol + 30% vol. Ethylenediamine	528.34	0.0102
60%vol. Ethylene glycol + 40% vol. Ethylenediamine	554.53	0.0177

From Table 4-8, the using of 60% vol. ethylene glycol + 40% vol. ethylenediamine solvent extraction system was shown the most extractive power and intense specific visual color. The maximum absorption wavelength shifted to longer wavelength as well as increasing its intensity. It was the attractive polarization force between the solvent and marker dye that resulted to the energy levels of both the unexcited and excited states tended to lower. When the energy difference was decreased, the bathochromic shift was occurred. [25]

From the solvent extraction systems 16-20, they were the variation of 40% vol. bases in 60% vol. ethylene glycol. The results of variation of 40% vol. bases in 60% vol. ethylene glycol were in Table 4-9.

Table 4-9 : The variation of bases in ethylene glycol extracting the 5 ppm marker dye C<sub>1</sub> in diesel oil.

Solvent extraction system	$\lambda_{\max}$ (nm.)	Absorbance	Hue of aq. phase
5% wt KOH in Ethylene glycol	522.29	0.1643	pink
30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Ethylenediamine	580.73	0.3022	bluish violet
60% vol. Ethylene glycol +40% vol. Ethylenediamine	567.63	0.1014	violet
60% vol. Ethylene glycol + 40% vol. Diethylenetriamine	568.64	0.0875	violet
60% vol. Ethylene glycol + 40% vol. Morpholine	545.47	0.0822	weakly violet

The using of ethylenediamine in the extraction system showed the most extractive power comparing with diethylenetriamine, triethylenetetramine and morpholine. Although they were more basic than ethylenediamine but their extractive power, stability and cost were not suitable for the extraction systems.

The consideration of the solvent 8 and 17; 40% ethylenediamine in 60% ethylene glycol compared with the mixture of ethylene glycol, methanol and ethylenediamine at the ratio of 3:4:3 by volume as the solvent extraction systems, it was shown that the solution of methanol and ethylene glycol as



cosolvents had more extractive power than only ethylene glycol. The solvent 8 extracting the marker dye  $C_1$  showed the bluish violet shading (the maximum absorption wavelength at 580.73 nm.) but the solvent 17 showed the violet shading (the maximum absorption wavelength at 567.63 nm.) following Table 4-9.

The appropriate solvent extraction systems used for the detection procedures and the quantitative determinations were these solvents :

Solvent 1 : 60% vol. Ethylene glycol + 40% vol. Ethylenediamine

Solvent 2 : 60% vol. Ethylene glycol + 40% vol. Diethylenetriamine

Solvent 3 : 30% vol. Ethylene glycol + 30% vol. Methanol

+ 40% vol. Ethylenediamine

#### 4.5 The detection procedures for the marker dyes in the series of chloronitroaniline derivatives in diesel

The purposes of the detection procedures were to investigate the ranges of maximum absorption wavelengths, the concentration of marker dyes to which added in diesel oil and the appropriate ratio of oil to extraction phase. The ranges of the maximum absorption wavelengths depended on the specific visual color of the extraction phases. These conditions should be used for the quantitative determinations to obtain the linear calibration curves and measure the marker levels.

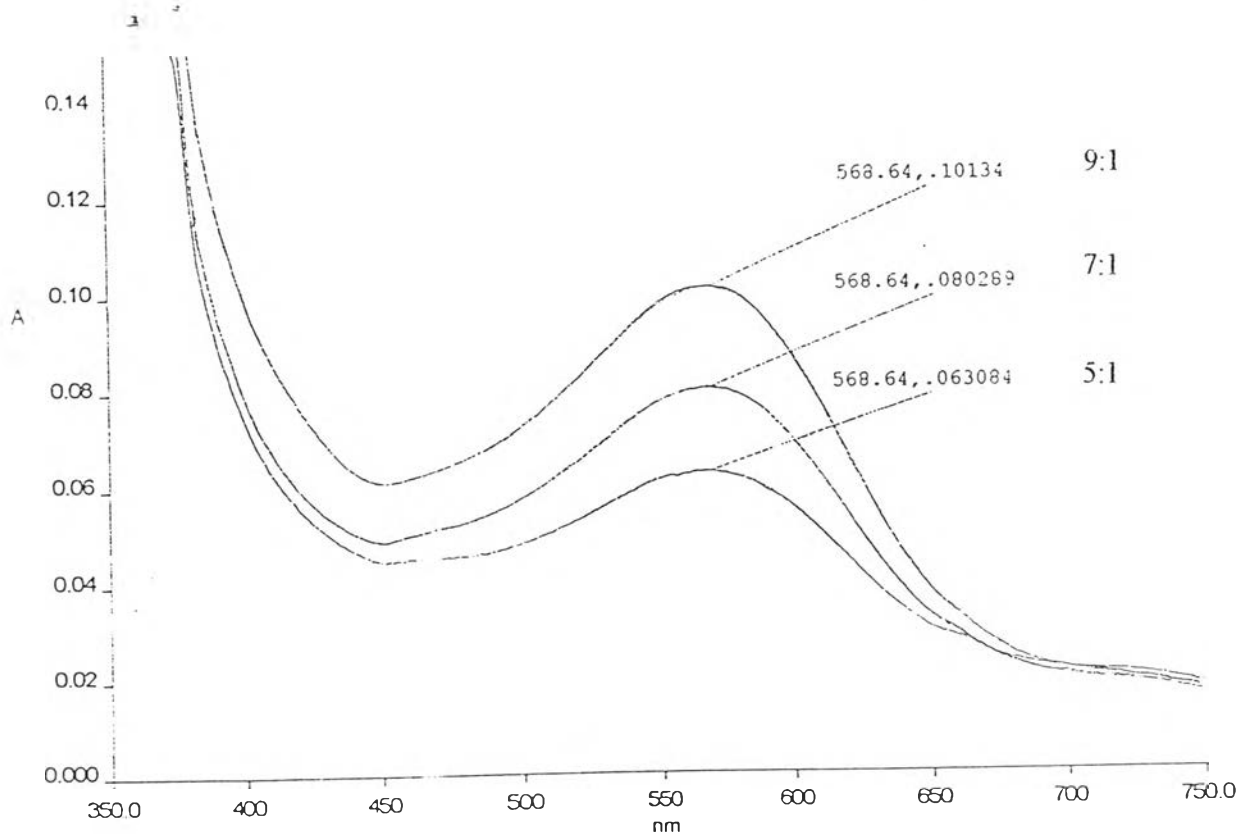


Figure 4-2 : The absorption curves of 5 ppm marker dye  $C_1$  in diesel oil extracting with solvent 1 for the ratios of 5:1, 7:1 and 9:1.

Table 4-10 : The absorbances of solvent 1 : 60% vol. Ethylene glycol + 40% vol. Ethylenediamine extracting the marker dyes set B<sub>1</sub>-B<sub>4</sub> and set C<sub>1</sub>-C<sub>4</sub> from diesel oil.

dye	Hue of aqueous phase	Absorbances								
		3 ppm			5 ppm			7 ppm		
		5:1	7:1	9:1	5:1	7:1	9:1	5:1	7:1	9:1
B <sub>1</sub>	purple---- strongly purple $\lambda_{\max}$ 523-526 nm.	0.1248	0.1594	0.2059	0.2052	0.2791	0.3205	0.2879	0.3770	0.4467
C <sub>1</sub>	weakly violet -----violet $\lambda_{\max}$ 570-573 nm.	0.0660	0.0721	0.0830	0.1232	0.1427	0.1679	0.1989	0.2294	0.2406
B <sub>2</sub>	weakly orange-----orange $\lambda_{\max}$ 468-470 nm.	0.0739	0.0984	0.1194	0.1052	0.1694	0.1917	0.1348	0.2383	0.2642
C <sub>2</sub>	weakly orange -----orange $\lambda_{\max}$ 494-497 nm.	0.0246	0.0387	0.0489	0.0426	0.0684	0.0841	0.0763	0.0976	0.1184

Table 4-10 : The absorbances of solvent 1 : 60% vol. Ethylene glycol + 40% vol. Ethylenediamine extracting the marker dyes set B<sub>1</sub>-B<sub>4</sub> and set C<sub>1</sub>-C<sub>4</sub> from diesel oil. (continued)

dye	Hue of aqueous phase	Absorbances								
		3 ppm			5 ppm			7 ppm		
		5:1	7:1	9:1	5:1	7:1	9:1	5:1	7:1	9:1
B <sub>3</sub>	weakly orange--- orange $\lambda_{\max}$ 466-468 nm.	0.0508	0.0692	0.0911	0.0934	0.1219	0.1573	0.1345	0.1654	0.2188
C <sub>3</sub>	weakly orange---- orange $\lambda_{\max}$ 497-499 nm.	0.0215	0.0368	0.0492	0.0563	0.0764	0.0968	0.1216	0.1333	0.1433
B <sub>4</sub>	weakly orange-----orange $\lambda_{\max}$ 454-456 nm.	0.1371	0.1935	0.2079	0.2432	0.3038	0.3339	0.3507	0.4347	0.4705
C <sub>4</sub>	weakly orange -----orange $\lambda_{\max}$ 485-487 nm.	0.0266	0.0314	0.0475	0.0545	0.0762	0.0928	0.1326	0.1515	0.1701

The detection of marker dyes set B and C was shown in Figure 4-3 and 4-4:

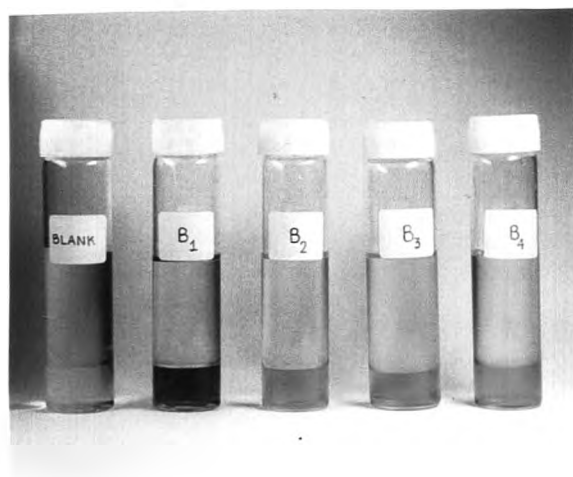


Figure 4-3 : The detection of marker dyes set B extracted with solvent 3.

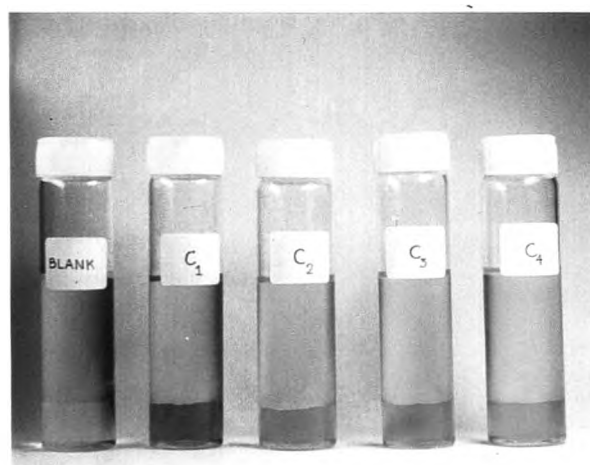
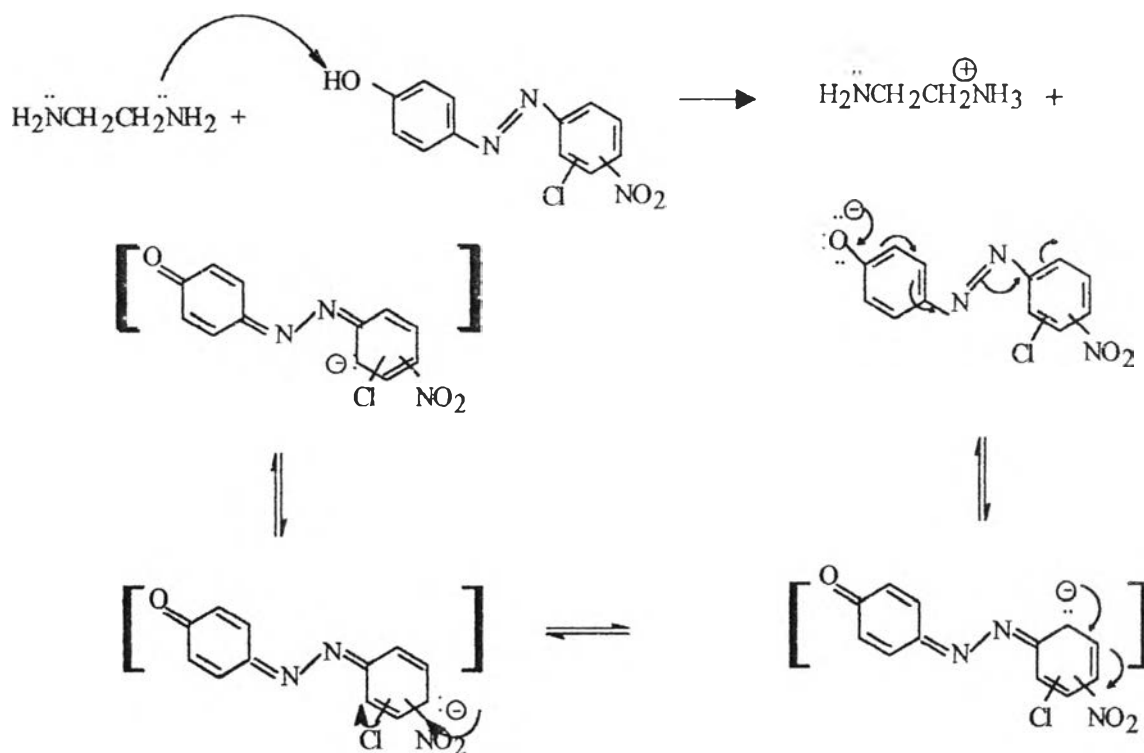


Figure 4-4 : The detection of marker dyes set C extracted with solvent 3

In this section, the appropriate ratio of oil to aqueous phase was 9:1. It was relatively chosen with the concentration of marker dyes set B and C. By the remarkably visual color of the aqueous phase (solvent phase), 5 ppm of marker dyes set B and C were added in diesel oil. The specific visual colors of the marker dyes were occurred by the complexation. These reactions or complexations resulted in the solvent-soluble marker being rendered soluble in aqueous medium and developed the specific visual color following this mechanism :



From the mechanism, it was shown that the negative charge could accommodate at the ortho- and para- positions. If the ortho- and para- positions were occupied with the electron withdrawing groups such as nitro- and chloro- groups, the ionized structures would be more stable by the inductive effect, and especially nitro- group could distribute the negative

charge with resonance effect because of  $-\text{NO}_2^-$  resonance structure. But if the meta- position was occupied with the nitro- or chloro- groups, it would not effectuate these results to the ionized structures.

From Table 4-10, the marker dyes  $B_1$  and  $C_1$  were synthesized by the coupling reactions between the phenolate ion of phenol ester B, C and the diazonium salt of 2-chloro-4-nitroaniline. The p- nitro group and m- chloro group in the marker dyes  $B_1$  and  $C_1$  caused the resonance and inductive effects. Their solvent extraction phases were purple and violet shading. On the other hands, the solvent extraction phases of marker dyes  $B_3$  and  $C_3$  were yellowish orange to reddish orange. They were obtained by the coupling reactions between the phenolate ion of ester B, C and the diazonium salt of 4-chloro-2-nitroaniline. They were considered that the ortho- position of the electron withdrawing groups resulted in the shade of the specific visual color of the solvent extraction phases less than the para- position.

#### **4.6 The effect of marker dyes set B and C to the physical properties of diesel oil compared with the unmarked diesel oil**

The marked diesel oil containing 5 ppm marker dyes set B and C were provided to test the physical properties and compared with the unmarked diesel oil in Table 4-11 .

Table 4-11 : The physical properties of marked diesel oil compared with unmarked diesel oil.

Test item	marked diesel oil	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
API gravity @ 60°F	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
Specific gravity @ 15.6/15.6°C	0.8227	0.8227	0.8227	0.8227	0.8227	0.8227	0.8227	0.8227	0.8227
Calculated cetane index						56.6067	56.5629	56.7375	56.8891
Kinematic viscosity @ 40°C, cSt	2.722	2.597	2.595	2.594	2.595	2.597	2.595	2.595	2.595
Pour point, °C	-9.0	-12.0	-12.0	-12.0	-12.0	-12.0	-12.0	-12.0	-12.0
Sulfur content, % wt	0.045	0.041	0.038	0.049	0.045	0.043	0.036	0.046	0.045
Copper strip corrosion, 3hrs @ 50°C	No.1	No.1	No.1	No.1	No.1	No.1	No.1	No.1	No.1
Flash point (P.M.), °C	54	56	57	57	57	55	57	56	57
Distillation (Correct temp.)									
IBP	157.2	156.7	158.8	159.5	160.3	156.8	159.0	160.7	161.6
10% rec, °C	194.1	196.5	194.0	195.2	196.2	197.1	193.5	193.9	196.1
50% rec, °C	268.4	267.2	266.7	267.7	268.2	266.5	266.7	267.3	268.2
90% rec, °C	349.2	348.0	347.9	348.2	347.0	347.6	347.7	347.2	348.8
Color	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5





Table 4-12 : The maximum absorption wavelengths used for the quantitative determinations

Solvent	The maximum absorption wavelengths (nm.)		
	1	2	3
Marker dyes			
B <sub>1</sub>	523-526	527-530	527-530
C <sub>1</sub>	570-573	570-573	581-583
B <sub>2</sub>	468-470	469-471	465-468
C <sub>2</sub>	494-497	494-496	500-503
B <sub>3</sub>	466-468	466-468	464-467
C <sub>3</sub>	497-499	497-499	502-505
B <sub>4</sub>	454-456	466-468	460-463
C <sub>4</sub>	485-487	489-491	491-494

When each of marker dyes was detected by solvent 1-3 in the quantitative determinations, the maximum absorption wavelengths in Table 4-12 were used. The standard calibration equations of marker dyes B<sub>1</sub>-B<sub>4</sub> and C<sub>1</sub>-C<sub>4</sub> were shown in Table 4-12. The calibration curves of marker dyes in the series of chloronitroaniline derivatives extracted with solvent 1-3 were shown in appendix section. They were concluded that these marker dyes B<sub>1</sub>-B<sub>4</sub> and C<sub>1</sub>-C<sub>4</sub> could be precisely provided in diesel oil and detected by the detection procedures and the quantitative determinations.

Table 4-13 : The standard calibration equations for the quantitative determinations of marker dyes B<sub>1</sub>-B<sub>4</sub> and C<sub>1</sub>-C<sub>4</sub> .

Marker	The standard calibration equations		
	Solvent 1	Solvent 2	Solvent 3
B <sub>1</sub>	$y = 1.357250 \text{ e} - 04 + 6.019750 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 526.0 nm. )	$y = 1.110112 \text{ e} - 04 + 4.077500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 530.8 nm. )	$y = 1.382161 \text{ e} - 04 + 1.002500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 528.3 nm. )
C <sub>1</sub>	$y = 2.261500 \text{ e} - 04 + 2.520000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 570.0 nm. )	$y = 1.231821 \text{ e} - 04 + 3.286500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 570.0 nm. )	$y = 1.070950 \text{ e} - 04 + 5.537060 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 581.7 nm. )
B <sub>2</sub>	$y = 2.173823 \text{ e} - 04 + 3.770000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 470.2 nm. )	$y = 1.18263 \text{ e} - 04 + 2.692500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 471.2 nm. )	$y = 1.367182 \text{ e} - 04 + 8.510000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 465.8 nm. )
C <sub>2</sub>	$y = 1.982000 \text{ e} - 04 + 1.902500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 496.2 nm. )	$y = 2.373231 \text{ e} - 04 + 2.670000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 498.2 nm. )	$y = 1.932716 \text{ e} - 04 + 4.921281 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 500.6 nm. )

Table 4-13 : The standard calibration equations for the quantitative determinations of marker dyes B<sub>1</sub>-B<sub>4</sub> and C<sub>1</sub>-C<sub>4</sub> .(continued)

Marker	The standard calibration equations		
	Solvent 1	Solvent 2	Solvent 3
B <sub>3</sub>	$y = 2.132103 \text{ e} - 04 + 3.142500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 464.8 nm. )	$y = 1.134721 \text{ e} - 04 + 3.371300 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 467.9 nm. )	$y = 1.705162 \text{ e} - 04 + 8.055161 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 465.9 nm. )
C <sub>3</sub>	$y = 2.134000 \text{ e} - 04 + 1.8225000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 498.2 nm. )	$y = 0.091217 \text{ e} - 05 + 1.942510 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 498.9 nm. )	$y = 1.232516 \text{ e} - 04 + 4.172501 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 502.0 nm. )
B <sub>4</sub>	$y = 1.188266 \text{ e} - 04 + 9.110000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 449.9 nm. )	$y = 0.810936 \text{ e} - 05 + 3.455013 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 467.2 nm. )	$y = 1.021812 \text{ e} - 04 + 1.440000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 460.8 nm. )
C <sub>4</sub>	$y = 2.232418 \text{ e} - 04 + 2.225000 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 486.8 nm. )	$y = 1.089617 \text{ e} - 04 + 2.725162 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 490.1 nm. )	$y = 1.619800 \text{ e} - 04 + 2.572500 \text{ e} - 02 \text{ x}$ ( $\lambda_{\text{max}}$ 492.1 nm. )

#### 4.8 The stability of the marker dyes B<sub>1</sub> and C<sub>1</sub> in diesel oil

The stability of these marker dyes could be detected by the measurements of dye contents in diesel oil. The 5 ppm of marker dyes B<sub>1</sub> and C<sub>1</sub> in diesel oil were extracted with solvent 3. The maximum absorption wavelengths and the standard calibration equations in Table 4-12 were used. The concentration of marker dyes were shown in Table 4-13.

Table 4-14 : The concentration detection of marker dyes B<sub>1</sub> ( Octylsalicylate-2-chloro-4-nitrophenyl azo ) and C<sub>1</sub> (The esterified CNSL – 2-chloro-4-nitrophenyl azo ) in the period of 3 months.

Weeks	The concentration of marker dye B <sub>1</sub>				The concentration of marker dye C <sub>1</sub>			
	1	2	3	Average	1	2	3	Average
1	4.97	4.92	4.96	4.95	5.03	4.96	4.89	4.96
2	5.12	4.98	4.99	5.03	5.10	4.93	4.89	4.97
3	4.96	5.01	4.98	4.98	4.98	4.92	5.15	5.01
4	4.98	4.95	5.10	5.01	4.98	4.95	4.98	4.97
5	4.93	5.02	4.96	4.97	5.15	4.95	4.96	5.02
6	4.91	4.89	5.05	4.95	5.08	4.96	5.10	5.04
7	5.02	4.93	5.10	5.01	5.08	4.98	4.95	5.00
8	4.87	5.10	4.96	4.93	4.89	4.98	5.23	5.03
9	4.99	5.01	4.96	4.99	4.92	4.98	5.05	4.98
10	4.93	5.13	4.99	5.01	4.97	5.25	4.98	5.06
11	5.18	5.07	4.95	5.06	5.21	4.95	5.08	5.08
12	5.09	4.99	5.01	5.03	5.08	4.98	4.94	5.00

From Table 4-14, the stability curves between the average concentration (ppm) and time (weeks) were plotted in Figure 4-5.

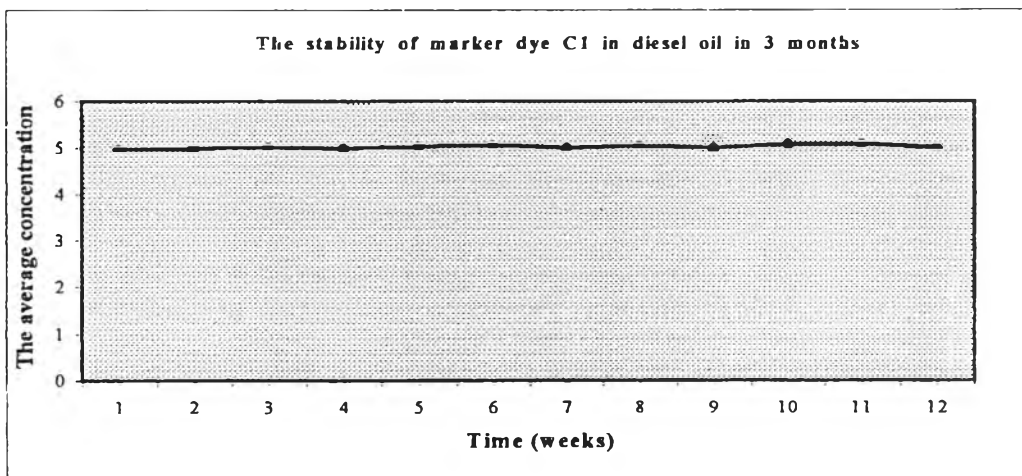
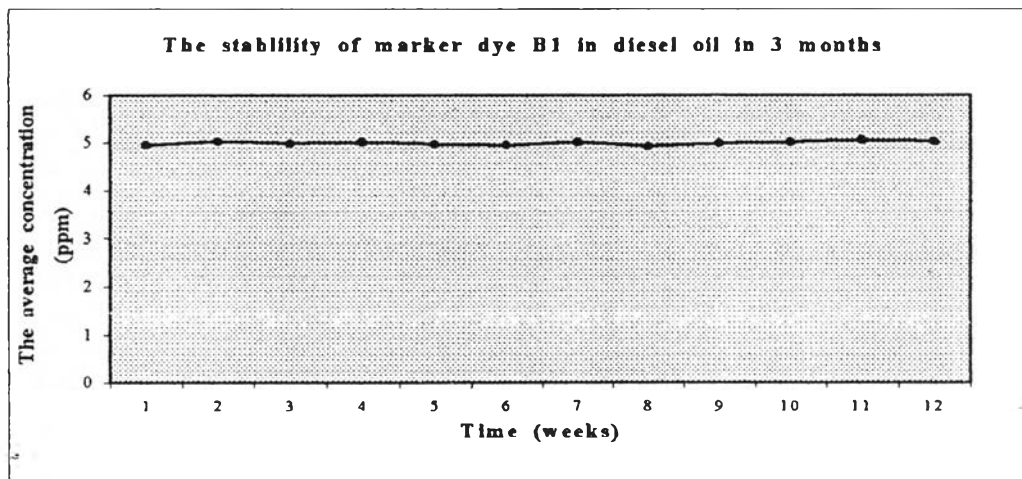


Figure 4-5 : The stability curve plotted between the average concentration of maker dye B<sub>1</sub> and C<sub>1</sub> in diesel oil and time (weeks) by solvent 3

From Figure 4-5, it was shown that the concentrations of marker dyes in the marked diesel oil was stable and this method had very good repeatability. The errors might be occurred by the personal and equipment errors which could be accepted.

#### 4.9 The method for detecting the suspected diesel oil

##### 4.9 a) The dilution or adulteration of marked diesel oil.

When the marked diesel oil was diluted by unmarked or smuggled diesel oil, the absorption of solvent extraction phase which was detected would decrease. Because the dye content in diesel oil was descended that resulted to the absorption. Although the absorption would be changed, the maximum absorption wavelength was still in the range (Table 4-11). The examples of dilutions of marked diesel oil were shown in Figure 4-4

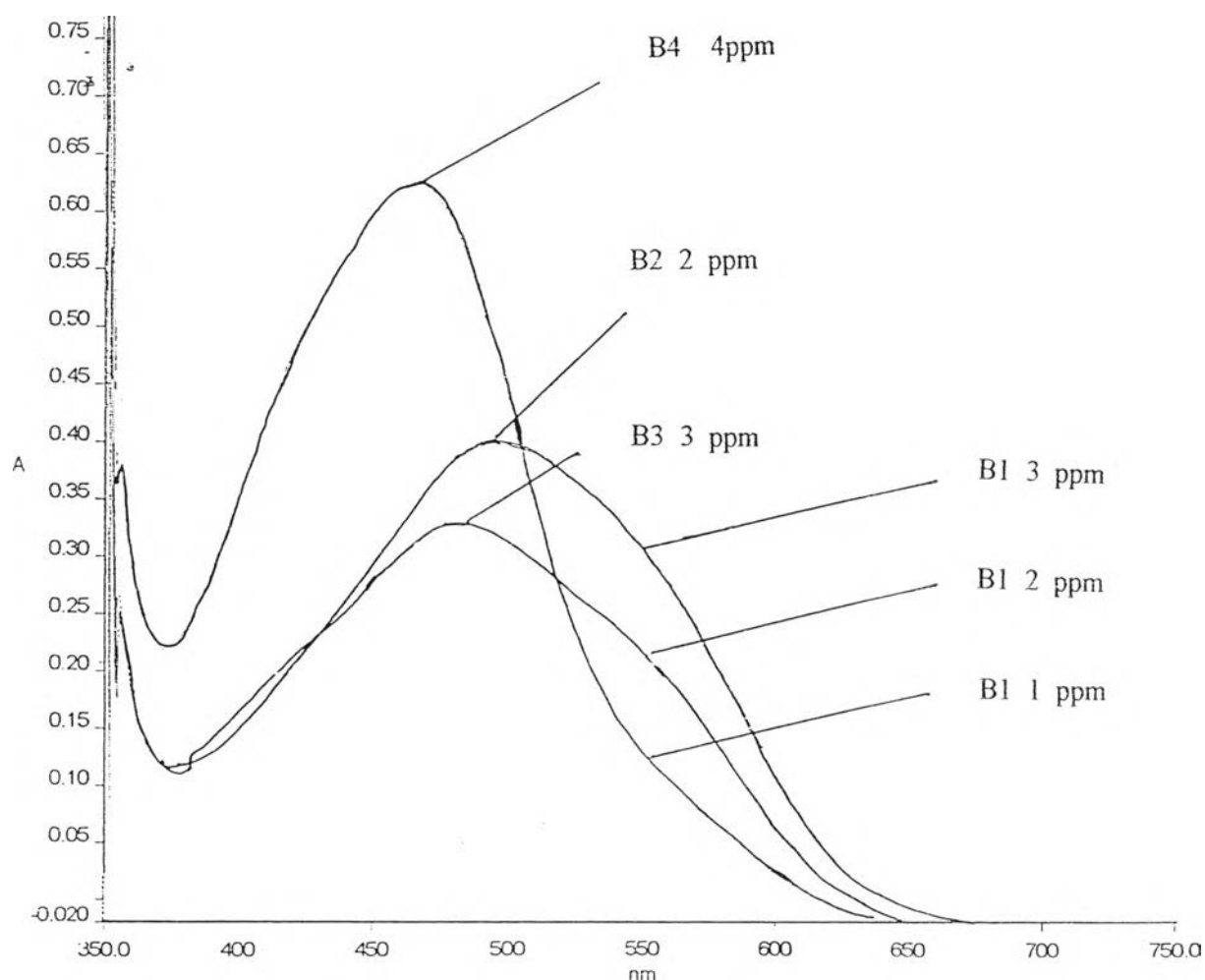


Figure 4-6 : The dilution of marked diesel oil with 2, 5 and 10 – fold dilution.

4.9 b) The mixed marker dyes in the series of chloronitroaniline derivatives  
in diesel oil

The marked diesel oil which was tagged with the marker dyes B<sub>1</sub>-B<sub>4</sub> and C<sub>1</sub>-C<sub>4</sub> were detected by the solvent 3. The marker dye B<sub>1</sub> and C<sub>1</sub> could show the most intense visual color so they should be the one part of the mixed marker dyes in diesel oil following Figure 4-7 and 4-8.

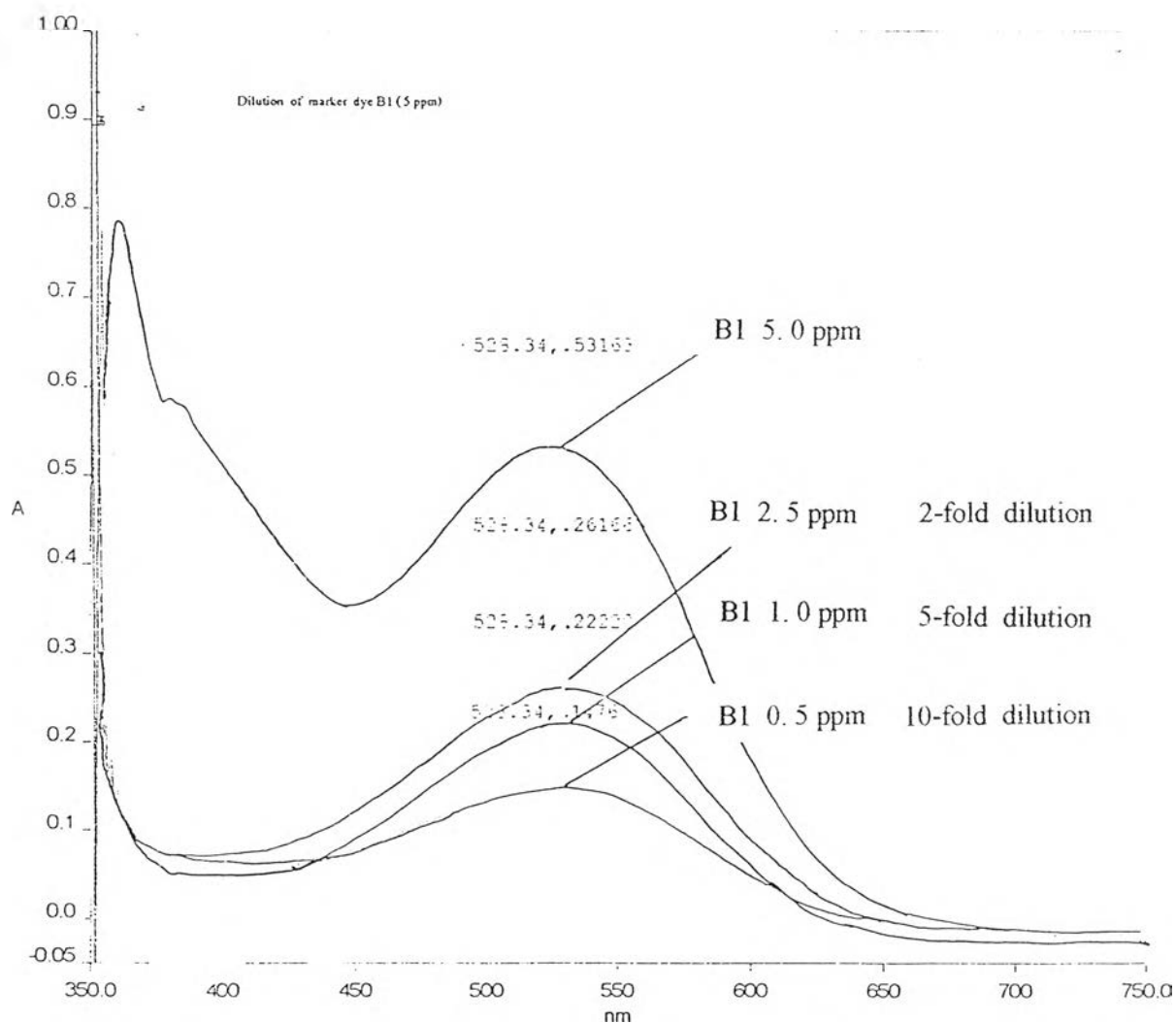


Figure 4-7: The mixed marker dyes set B in diesel oil extracted with solvent 3



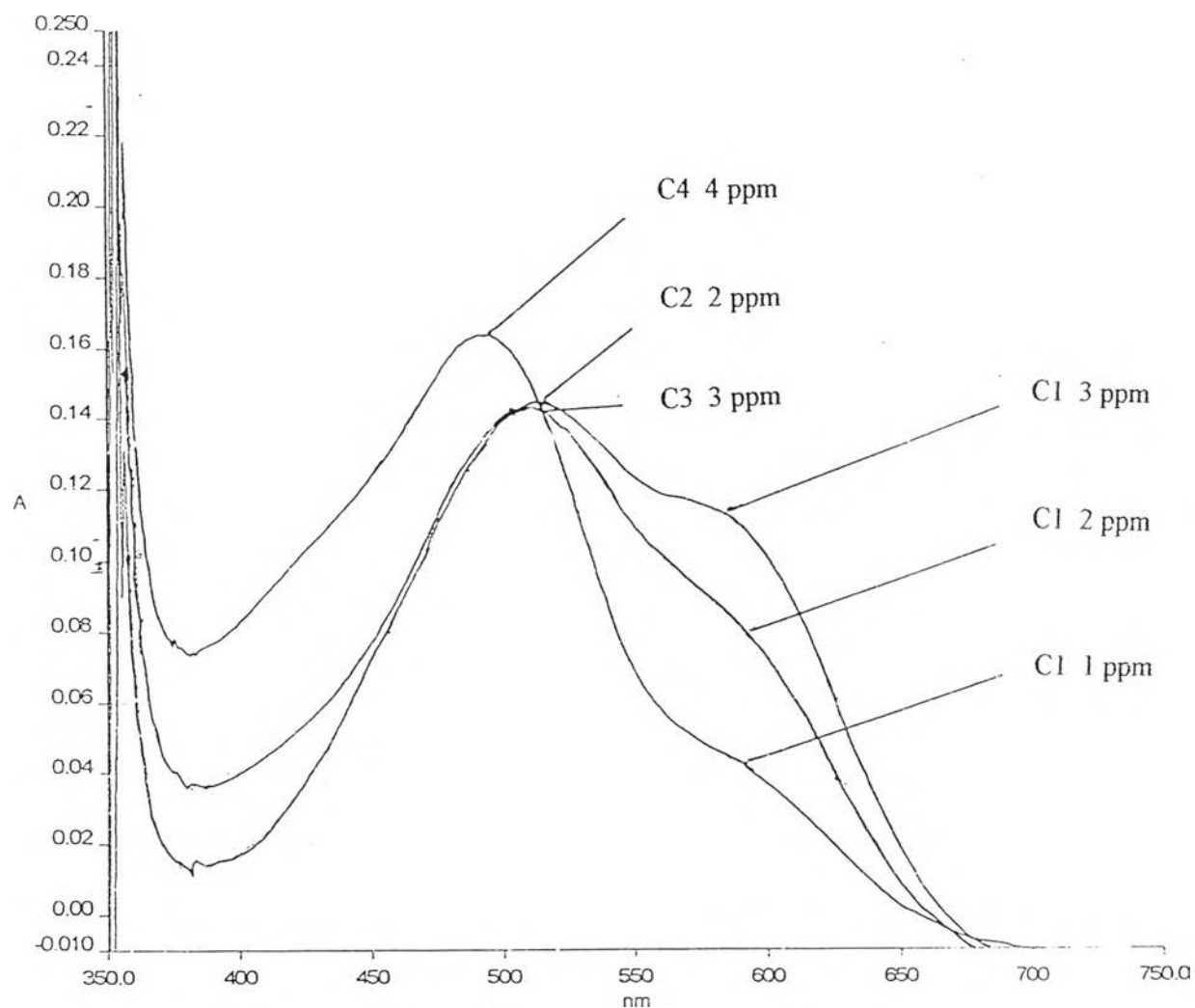


Figure 4-8 : The mixed marker dyes set C in diesel oil extracted with solvent 3

From Figure 4-7 and 4-8, they were shown that if the marked diesel oil was tagged with the mixed marker dyes, the maximum absorption wavelengths shown much more one peak following their specific maximum absorption wavelengths, the types of marker dye and concentrations which were added.