

CHAPTER IV RESULTS AND DISCUSSION

4.1 Characteristics of 2-Ethyl-1-hexyl salicylate

2-Ethyl-1-hexyl salicylate was prepared by direct esterification of salicylic acid with a 2-ethyl-1-hexanol in the presence of sulfuric acid. An ester was obtained as a viscous pale yellow liquid and was freely soluble in organic solvent such as toluene or xylene. This compound did not absorb UV-VIS light in 370-400 nm range.

The IR spectrum of 2-ethyl-1-hexyl salicylate (Fig.1-1), which was assigned in Table 4.1, indicated that this compound contained an ester functional group (at 1680 cm^{-1}). Other important bands were observed at 3200 and 1090 cm^{-1} which were the characteristics of O-H stretching vibration and C-O stretching vibration, respectively.

Table 4.1: The FT-IR absorption band assignments of 2-Ethyl-1-hexyl salicylate

Frequency (cm^{-1})	Band type	Tentative assignments
3200	w	O-H stretching vibration of phenolic
2900, 2850	s	C-H stretching vibration of - CH_2 -
1680	s	C=O stretching vibration of ester
1470	m	C-H bending vibration of CH_3
1090	m	C-O stretching vibration of ester

The $^1\text{H-NMR}$ spectrum (Fig.1-2) exhibited two signals belonged to protons of ester could be assigned. One which appeared at δ 4.27 ppm, should be the chemical shift of α -proton in alcoholic portion of the molecule and the other was also a quartet signal at 7.8 ppm which could be assigned for the chemical shift of α -proton in the acidic part.

The $^{13}\text{C-NMR}$ spectrum (Fig.1-3) displayed the important signal at 170.3 ppm, which corresponded to a carbonyl signal of carbonyl group of ester. The signal at 67.7 ppm could be assigned for a α -carbon that was attached to oxygen atom. Other signals around 38.3 to 14.0 ppm ought to be the signals of other sp^3 carbons belong to 2-ethyl-1-hexyl moiety.

The results of ^{13}C -NMR and ^1H -NMR spectrum of 2-ethyl-1-hexyl salicylate were summarized in Table 4.7 and 4.8, respectively. Therefore, this compound was 2-ethyl-1-hexyl salicylate.

4.2 Properties of CNSL and Esterified-CNSL

Cashew nut shell liquid, which was a viscous dark brown liquid and a strong acidity, was extracted from cashew nut shell by n-hexane followed by heat-treatment. It was sparingly soluble in water and freely soluble in alcohol, ether or organic solvent. For esterified-CNSL, it was prepared by esterification of CNSL with a hexanol and was a viscous red brown liquid. It was insoluble in water but still freely soluble in alcohol and organic solvent.

CNSL and esterified-CNSL did not show any absorption peaks in Ultraviolet region, this information implied the absence of functional groups capable of acting as chromophores in these substances.

The physical properties of CNSL and esterified-CNSL were tested by ASTM standard methods and tabulated in Table 4.2. The properties of esterified-CNSL were almost identical to CNSL except for viscosity which was smaller in the latter.

Table 4.2: The physical properties of CNSL and esterified-CNSL.

Test item	ASTM	Result	
		CNSL	esterified-CNSL
Specific Gravity @15.6/15.6°C	D 1298	0.9665	0.9648
Kinematic Viscosity @40°C,cSt	D 445	Too Viscous	15.14
	D 445	40.42	11.14
	D 445	7.52	3.58
Pour Point, °C	D 97	1	1
Flash Point, (P.M.), °C	D 93	115-120	100-112

The IR spectrum (Fig.3-1) of esterified-CNSL, which was assigned as shown in Table 4.3, revealed the strong absorption peaks at 1730 and 1265 cm^{-1} due to the C=O and C-O stretching vibration of ester, respectively.

Table 4.3: The FT-IR absorption band assignments of CNSL

Frequency (cm^{-1})	Band type	Tentative assignments
3400-3200	Very b.	O-H stretching vibration
3050-2850	s	C-H stretching vibration of CH_3 ,- CH_2 -
1480-1430	s	C-H bending vibration of CH_3 ,- CH_2 -

Table 4.4: The FT-IR absorption band assignments of esterified-CNSL

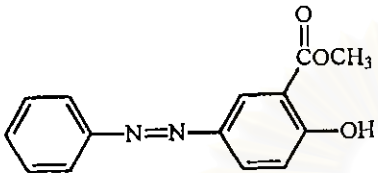
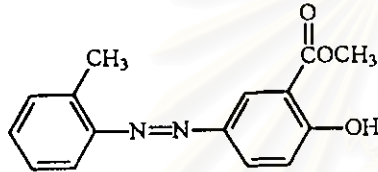
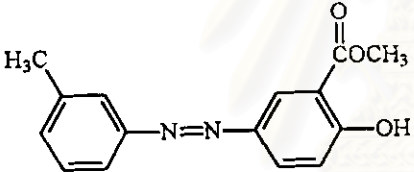
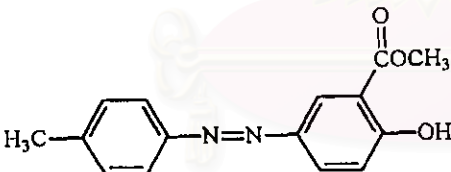
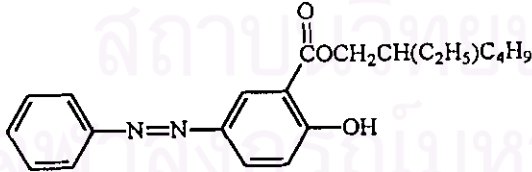
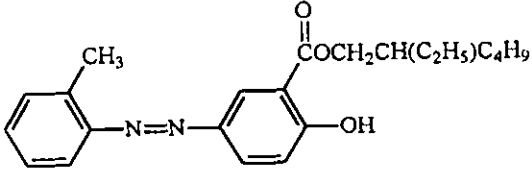
Frequency (cm^{-1})	Band type	Tentative assignments
2950	s	C-H stretching vibration of CH_3
2900, 2850	s	C-H stretching vibration of - CH_2 -
1650	s	C=O stretching vibration of ester

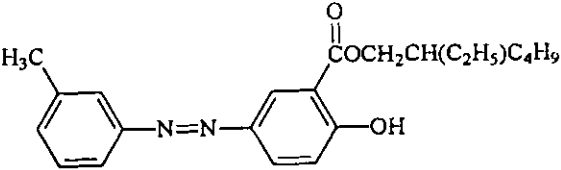
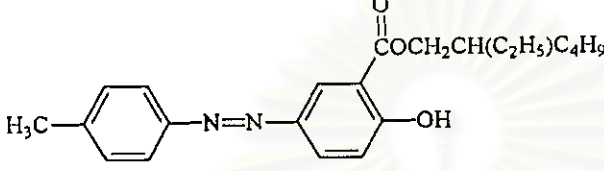
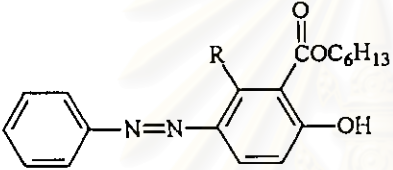
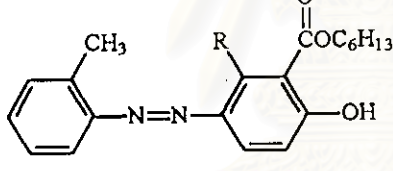
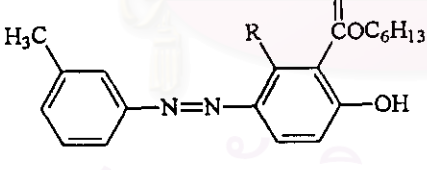
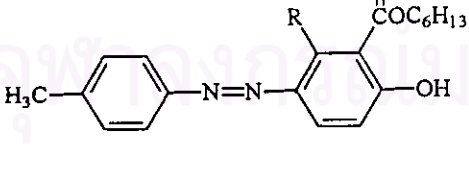
The ^1H -NMR spectrum (Fig.3-2) displayed a significant signal at 4.35 ppm, which attributed to α -hydrogen in the alcoholic portion of ester molecule. In addition, the ^{13}C -NMR spectrum (Fig.3-3) exhibited the signal at 171.8 ppm, which was a carbon signal of ester, and the signal at 71 ppm was a signal of C-O peak. The signal at 62 ppm. showed the excess unreacted alcohol.

4.3 Characteristics of Marker dyes

Marker dyes, which were synthesized in this study, had the following formula and physical properties. (Table 4.5)

Table 4.5: The marker dyes

Ex. No.	Marker Dye	Hue in aromatics	Solubility in oil	λ_{max} [nm] (toluene)
1		Yellow	Poor	437
2		Yellow	Poor	432
3		Yellow	Poor	430
4		Yellow	Poor	429
5		Yellow	Good	440
6		Yellow	Good	439

Ex. No.	Marker Dye	Hue in aromatics	Solubility in oil	λ_{max} (nm) (toluene)
7		Yellow	Good	435
8		Yellow	Good	439
9		Yellow	Good	425
10		Yellow	Good	423
11		Yellow	Good	427
12	 <p data-bbox="288 1704 845 1874"> R = $-(CH_2)_{14}CH_3$ $-(CH_2)_7CH=CH(CH_2)_5CH_3$ $-(CH_2)_7CH=CHCH_2CH=CH(CH_2)_2CH_3$ $-(CH_2)_7CH=CHCH_2CH=CHCH_2CH=CH_2$ </p>	Yellow	Good	426

4.3.1 Characteristics of Marker dyes 1, 2, 3 and 4

Marker dyes 1, 2, 3 and 4, which were obtained as orange solids gave a yellow color in organic solvent. Their solubility in non-polar solvent was poor, was that; they can not dissolve in the solvent immediately and can not prepare in a high concentration. The marker dyes 1 – 4 were slightly soluble in organic solvent, so they were not evaluated for using in detection procedures. Therefore, they are unsuitable to be markers in the mineral oil such as gasoline, kerosene or diesel. However, marker dyes 1, 2, 3 and 4 had the simplest structure of azo dyes which were useful as models to compare with the structure of other marker dyes.

The UV (toluene) spectral data gave the maximum absorption peaks (λ max) at about 430 nm. which indicated the presence of an azophenol functional group as their chromophores.

Stannous chloride reduction of the azo-compounds gave colorless solution. Reaction of marker dyes 1-4 in acidic stannous chloride showed that azo groups were reduced and cleaved to amino phenol and amine. Consequently, these marker dyes contained azo groups.

Their FT-IR spectra (Fig.4-1 to 8-1), which were assigned as shown in Table 4.6, revealed absorption band belonging to C=O stretching vibration at ν_{\max}^{KBr} 1680 cm^{-1} . Other important bands were observed at 3200 and 1090 cm^{-1} which were the characteristics of O-H stretching vibration and C-O stretching vibration, respectively.

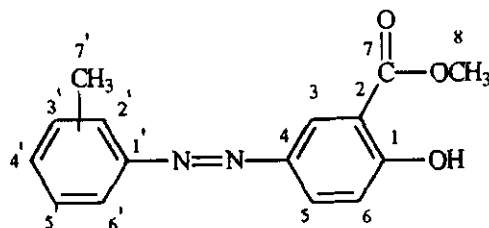
Table 4.6: The FT-IR absorption band assignments of marker dye 1 - 4

Frequency (cm^{-1})	Band type	Tentative assignments
3200	w	O-H stretching vibration of phenolic
2900, 2850	s	C-H stretching vibration of - CH ₂ -
1680	s	C=O stretching vibration of ester
1470	m	C-H bending vibration of CH ₃
1090	m	C-O stretching vibration of ester

Table 4.7: The $^1\text{H-NMR}$ chemical shift of methyl salicylate and marker dyes 1-4

Compounds	Chemical shift (ppm)		
	Phenolic proton	Aromatic proton	Aliphatic proton
Methyl salicylate	10.00 (1H,s)	7.90 (1H,d) 7.45 (1H,t) 7.00 (1H,d) 6.89 (1H,t)	3.95 (3H,s)
Marker dye <u>1</u>	11.08 (1H,s)	8.42 (1H,s) 8.05 (1H,d) 7.87 (2H,d) 7.48 (2H,t) 7.42 (1H,t) 7.06 (1H,d)	3.95 (3H,s)
Marker dye <u>2</u>	11.08 (1H,s)	8.36 (1H,s) 7.98 (1H,d) 7.57 (1H,d) 7.26 (2H,m) 7.20 (1H,t) 7.01 (1H,d)	3.90 (3H,s) 2.66 (3H,s)
Marker dye <u>3</u>	11.08 (1H,s)	8.45 (1H,s) 8.09 (1H,d) 7.70 (2H,s) 7.38 (1H,t) 7.26 (1H,t) 7.09 (1H,d)	3.95 (3H,s) 2.47 (3H,s)
Marker dye <u>4</u>	11.08 (1H,s)	8.44 (1H,s) 8.08 (1H,d) 7.78 (2H,d) 7.29 (2H,d) 7.08 (1H,d)	3.95 (3H,s) 2.44 (3H,s)

Table 4.8: The ^{13}C NMR chemical shifts of marker dye 1, marker dye 2, marker dye 3, and marker dye 4



Carbon	Chemical shifts (ppm)			
	Marker dye <u>1</u>	Marker dye <u>2</u>	Marker dye <u>3</u>	Marker dye <u>4</u>
1	163.7	163.5	163.7	163.4
2	118.3	118.2	118.2	118.2
3	126.6	126.2	126.5	126.3
4	145.2	145.5	145.2	145.2
5	128.7	127.9	128.5	128.6
6	112.3	112.1	112.2	112.2
7	170.3	170.2	170.2	170.3
8	52.5	52.3	52.4	52.3
1'	152.4	150.2	152.4	150.4
2'	122.6	137.7	122.7	122.6
3'	128.9	130.5	138.7	129.6
4'	130.6	127.5	131.3	141.1
5'	128.9	118.2	128.7	129.6
6'	122.6	115.2	120.1	122.6
7'	-	17.3	21.2	21.3

The $^1\text{H-NMR}$ spectrum (Fig.4-2 to 8-2) displayed the singlet signal at 3.95 ppm. which should be the signal of the proton on the methyl group attaching to the oxygen atom. The $^1\text{H-NMR}$ chemical shifts of marker dyes 1 – 4 and methyl salicylate were presented in Table 4.7. In general, the chemical shifts of many resonance signal of marker dyes was found to be down field relative to methyl salicylate due to the effect of azo group.

The $^{13}\text{C-NMR}$ spectrum of marker dye 1 (Fig.4-3 to 8-3) exhibited 13 carbon signals that could be assigned as follow: the signal at 145.2 and 152.4 ppm. these absorption peaks when marker dye 1 was the azo dye. The procedure in determining the $^{13}\text{C-NMR}$ of marker dyes 2 – 4, which showed 14 carbon signals, was the same as these of marker dye 1. The results were summarized in Table 4.8.

All of results confirmed that the marker dyes 1 – 4 were azo dye compounds, and the structure of these compounds were shown in Table 4.5.

4.3.2 Characteristics of Marker Dyes 5, 6, 7 and 8

The results of UV (toluene) spectral data and stannous chloride reduction of marker dyes 5 – 8 were similar to marker dyes 1 – 4, therefore these compounds should be azophenol compounds.

The FT-IR data of these marker dyes presented in Table 4.6, revealed the strong absorption peak at 1680 cm^{-1} due to the C=O stretching vibration.

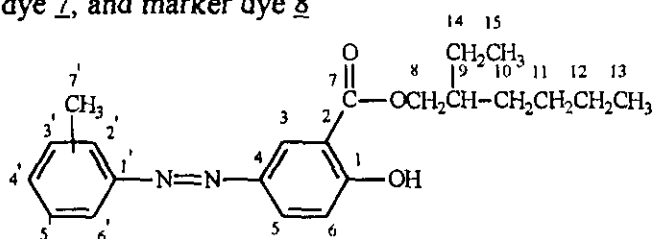
Table 4.9: The FT-IR absorption band assignments of marker dye 5 - 8

Frequency (cm^{-1})	Band type	Tentative assignments
3200	w	O-H stretching vibration of phenolic
2900, 2850	s	C-H stretching vibration of -CH ₂ -
1680	s	C=O stretching vibration of ester
1470	m	C-H bending vibration of CH ₃
1090	m	C-O stretching vibration of ester

Table 4.10: The $^1\text{H-NMR}$ chemical shift assignments of 2-ethyl-1-hexyl salicylate and marker dyes 5-8

Compounds	Chemical shift (ppm)		
	Phenolic proton	Aromatic proton	Aliphatic proton
2-Ethyl-1-hexyl salicylate	10.86 (1H,S)	7.83 (1H,d) 7.45 (1H,t) 6.98 (1H,d) 6.89 (1H,t)	4.27 (2H,m) 1.73 (1H,m) 1.30-1.48 (8H,m) 0.90-0.96 (6H,m)
Marker dye <u>5</u>	11.25 (1H,s)	8.46 (1H,s) 8.09 (1H,d) 7.89 (2H,d) 7.52 (2H,t) 7.45 (1H,m) 7.10 (1H,d)	4.34 (2H,m) 1.79 (1H,m) 1.30-1.50 (8H,m) 0.90-1.00 (6H,m)
Marker dye <u>6</u>	11.21 (1H,s)	8.46 (1H,s) 8.08 (1H,d) 7.62 (1H,d) 7.34 (2H,m) 7.26 (1H,m) 7.10 (1H.d)	4.34 (2H,m) 2.71 (3H,s) 1.78 (1H,m) 1.30-1.50 (8H,m) 0.90-1.00 (6H,m)
Marker dye <u>7</u>	11.23(1H,s)	8.43 (1H,s) 8.06 (1H,d) 7.68 (2H,s) 7.43 (1H,t) 7.38 (1H,t) 7.08 (1H,d)	4.32 (2H,m) 2.44 (3H,s) 1.78 (1H,m) 1.30-1.50 (8H,m) 0.90-1.00 (6H,m)
Marker dye <u>8</u>	11.22 (1H,s)	8.43 (1H,s) 8.07 (1H,d) 7.79 (2H,d) 7.29 (2H,d) 7.08 (1H,d)	4.33 (2H,m) 2.42 (3H,s) 1.78 (1H,m) 1.30-1.50 (8H,m) 0.90-1.00 (6H,m)

Table 4.11: The ^{13}C NMR chemical shifts of 2-ethyl-1-hexyl salicylate, marker dye 5, marker dye 6, marker dye 7, and marker dye 8



Carbon	Chemical shifts (ppm)				
	Ester	Marker dye <u>5</u>	Marker dye <u>6</u>	Marker dye <u>7</u>	Marker dye <u>8</u>
1	161.6	164.0	163.8	163.8	163.7
2	117.5	118.5	118.4	118.5	118.3
3	129.8	127.7	126.4	127.5	127.2
4	119.1	145.4	145.8	145.4	145.3
5	135.5	130.7	128.3	128.9	127.6
6	112.7	112.7	112.7	112.6	112.6
7	170.3	170.3	170.2	170.2	170.1
8	67.6	67.6	67.6	67.6	67.5
9	38.8	38.8	38.9	38.8	38.7
10	30.5	30.5	30.5	30.5	30.4
11	28.9	28.9	28.9	28.9	28.9
12	22.9	22.9	22.9	22.9	22.9
13	11.0	11.0	11.1	11.0	11.0
14	23.9	23.9	23.9	23.9	23.9
15	14.0	14.0	14.0	14.0	14.0
1'	-	152.5	150.2	152.6	150.5
2'	-	122.6	137.8	122.7	122.6
3'	-	129.1	130.7	138.9	129.6
4'	-	130.7	127.0	139.5	141.1
5'	-	129.1	117.5	128.9	129.6
6'	-	122.6	115.2	120.3	122.6
7'	-	-	17.4	21.4	21.4

The $^1\text{H-NMR}$ chemical shifts assignments of marker dyes 5 – 8, which compared with 2-ethyl-1-hexyl salicylate, are presented in Table 4.10. This result indicated that the chemical shifts of marker dyes were higher than 2-ethyl-1-hexyl salicylate due to the effect of azo derivative.

The $^{13}\text{C-NMR}$ spectrum of marker dye 5 (Fig.8-3) exhibited 21 carbon signals which included the important signals at 145.7 and 152.5 ppm that was corresponded to the carbon signals attaching to the azo group ($-\text{C-N}=\text{N-C}-$). Other signals at 122.6, 129.1, 130.7, 129.1 and 122.6 ppm could be assigned for aromatic carbons of aniline.

For the marker dyes 6, 7 and 8, the $^{13}\text{C-NMR}$ spectrums (Fig.9-3 to 11-3) showed 22 carbon signals. The carbon signals of azo dyes, were 150.2, 152.6 and 150.5 ppm, respectively, which were the carbon signals of azophenol. The signals at 17.4, 21.4 and 21.4 ppm, which were analogous with methyl carbon of toluidine of marker dyes 6, 7 and 8, respectively.

Therefore, the $^{13}\text{C-NMR}$ chemical shifts of marker dyes 5, 6, 7 and 8 (Table 4.11), when compared with 2-ethyl-1-hexyl salicylate, could be used as supporting information for ensuring that these compounds were the desired azo dyes (Formula: Table 4.5).

The marker dyes of the formula 5, 6, 7 and 8 had the advantage of very good solubility. These marker dyes gave a yellow solution in aromatic solvents. The marker dyes were used at about 5 ppm or less so that the marked commercial diesel oil had barely any or no visible color.

4.3.3 Characteristics of Marker Dyes 9, 10, 11 and 12

The marker dyes 9, 10, 11 and 12 were azo dyes synthesized from the coupling reaction of diazonium salts of aniline, *o*-toluidine, *m*-toluidine and *p*-toluidine with the esterified-CNSL. The products were obtained as viscous dark red liquids. These marker dyes had very good solubility and gave a yellow solution in aromatic solvents.

The FT-IR data of these marker dyes were presented in Table 4.12.

Table 4.12: The FT-IR absorption band assignments of marker dye 9 - 12

Frequency (cm ⁻¹)	Band type	Tentative assignments
3200	w	O-H stretching vibration of phenolic
2900, 2850	s	C-H stretching vibration of - CH ₂ -
1680	s	C=O stretching vibration of ester
1470	m	C-H bending vibration of CH ₃
1090	m	C-O stretching vibration of ester

The ¹³C-NMR spectrum of marker dye 9 - 12 (Fig.12-3 to 15-3) displayed the important signals at 146 and 152 ppm corresponded to the carbon signals of azo dye (-C-N=N-C-).

The characteristics of marker dyes 9 - 12 were similar to those of marker dyes 1 - 8 obtained by the same instruments therefore it can be concluded that marker dyes 9 - 12 were also the desired azo dyes.

4.4 Effect of Marker Dyes to Commercial High-Speed Diesel

The physical properties of commercial high speed diesel marked with 3 ppm marker dyes 5 - 8 and 5 ppm marker dyes 9 - 12 were determined according to specific ASTM methods. The results of marker dyes 5 - 8 and marker dyes 9 - 12 are presented in Table 4.13 and 4.14, respectively.

From Table 4.13, marker dyes 5, 6, 7 and 8 were mixed only 3 ppm. in the commercial high speed diesel, so the ASTM color scale of marked oils were equivalent with unmarked oil. The physical properties of marked and unmarked high-speed diesel oil had merely a little difference, not to mention the fact that these differences were within the repeatability range.

Therefore, the results in Table 4.13 and 4.14 indicated that the marker dyes could be used in diesel oils without any effect on the properties of the marked commercial diesel oil.

Table 4.13: The effect of marker dye 5, 6, 7 and 8 to commercial high-speed diesel

TEST ITEM	ASTM D	Results				
		Marked <u>5</u>	Marked <u>6</u>	Marked <u>7</u>	Marked <u>8</u>	Unmarked
1. API Gravity @ 60 °F	1298	40.5	40.5	40.5	40.4	40.6
2. Calculated Cetane Index	976	56.6	57.0	56.9	56.6	56.9
3. Kinematic Viscosity @ 40 °C, cSt	445	2.632	2.626	2.624	2.617	2.632
4. Pour Point, °C	97	-4	-4	-4	-4	-4
5. Sulphur Content, %wt	4294	0.04	0.04	0.04	0.04	0.04
6. Copper Strip Corrosion, Number (3hrs.@50 °C)	130	No. 1a	No. 1a	No. 1a	No. 1a	No. 1a
7. Flash Point, (P.M.), °C	93	60	60	60	60	61
8. Distillation: (Correct Temp.)	86					
IBP		163.3	163.3	163.6	163.3	163.3
10% rec., °C		194.2	195.3	195.1	194.5	195.3
50% rec., °C		267.2	268.6	267.5	268.2	267.2
90% rec., °C		349.3	350.5	350.1	349.7	350.3
End point		375.8	375.0	375.2	375.5	374.9
9. Color, ASTM	1500	<0.5	<0.5	<0.5	<0.5	<0.5

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Table 4.14: The effect of marker dye 9, 10, 11 and 12 to commercial high-speed diesel

TEST ITEM	ASTM D	Results				
		Marked <u>9</u>	Marked <u>10</u>	Marked <u>11</u>	Marked <u>12</u>	Unmarked
1. API Gravity @ 60 °F	1298	40.3	40.3	40.3	40.3	40.4
2. Calculated Cetane Index	976	56.1	56.5	56.4	55.9	56.2
3. Kinematic Viscosity @ 40 °C, cSt	445	2.549	2.552	2.557	2.539	2.574
4. Pour Point, °C	97	-4	-4	-4	-4	-4
5. Sulphur Content, %wt	4294	0.05	0.05	0.05	0.05	0.05
6. Copper Strip Corrosion, Number (3hrs.@50 °C)	130	No. 1a	No. 1a	No. 1a	No. 1a	No. 1a
7. Flash Point, (P.M.), °C	93	60	60	60	60	60
8. Distillation: (Correct Temp.)	86					
IBP		164.1	163.3	163.3	161.3	163.1
10% rec., °C		193.5	194.3	194.4	191.9	193.3
50% rec., °C		266.3	267.6	267.1	264.9	266.3
90% rec., °C		349.9	350.5	349.5	350.9	350.1
End point		377.6	378.3	378.2	379.3	377.5
9. Color, ASTM	1500	<0.5	0.5	0.5	0.5	<0.5

4.5 The Suitable Extraction Systems

Several extraction solution systems were evaluated in extracting marker dyes from diesel oil into the aqueous phase. The extraction system should be basic because these marker dyes possess a phenolic group. The base forms a salt with the phenolic –OH, resulting in development of the color and also improving the solubility of the marker in such a way that it is substantially less soluble in petroleum and substantially more soluble in aqueous medium.

The extraction solvents of marked diesel oil were observed and compared with the unmarked diesel oil as a blank. All of the extraction solvents gave obvious yellow color in extracted phase of marked diesel oil and colorless in the extracted phase of unmarked diesel oil. Comparison of extract phase colors is shown in Figure B.

In addition to laboratory test, ultraviolet and visible spectrophotometer was used in determination. After leaving until the two layer completely separated which took about 3 minutes, the aqueous layer was transferred for the spectroscopic study at the wavelength of 350 nm to 700 nm using the extracted layer of unmarked oil as a reference.

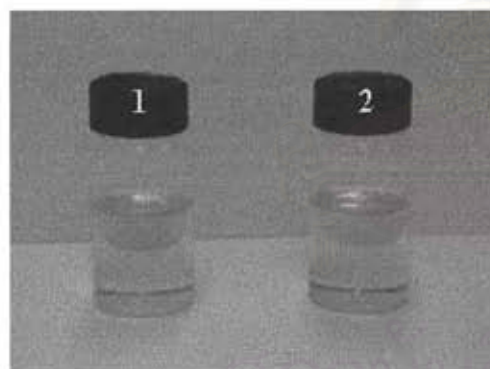


Figure A: Color of diesel oil

- 1) unmarked diesel oil.
- 2) marked diesel oil

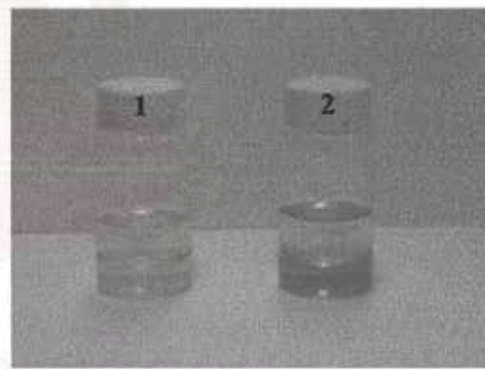


Figure B: Color of extracted phase

- (lower phase)
- 1) unmarked diesel oil
 - 2) marked diesel oil.

Table 4.15: The results of extraction of marker dye 9 at 5 ppm in commercial diesel oil. (Ratio of marked diesel oil: each solvent = 9:1 by volume)

No.	Extractant	Hue in aq. phase	Isolation between aq. phase and oil phase (Time/Quality)	Abs.
1	2% KOH in methanol	Pale yellow	Slow/Very good	0.235
2	5% KOH in methanol	Fair yellow	Slow/Very good	0.356
3	8% KOH in methanol	Fair yellow	Slow/Very good	0.479
4	2% KOH in ethylene glycol	Pale yellow	Fast/Good	0.101
5	5% KOH in ethylene glycol	Pale yellow	Fast/Good	0.197
6	8% KOH in ethylene glycol	Fair yellow	Fast/Good	0.285
7	10% KOH in ethylene glycol	Fair yellow	Fast/Good	0.325
8	10% KOH in methanol : ethylene glycol (1:1)	Fair yellow	Fast/Very good	0.385
9	10% morpholine + 50% ethylene glycol+40% of 10% KOH in methanol	Strong yellow	Fast/Very good	0.474
10	20% morpholine + 40% ethylene glycol+40% of 10% KOH in methanol	Strong yellow	Fast/Very good	0.602
11	30% morpholine + 30% ethylene glycol+40% of 10% KOH in methanol	Strong yellow	Fast/Very good	0.934
12	30% diisopropylamine + 30% ethylene glycol+40% of 10% KOH in methanol	Strong yellow	Fast/Very good	0.597
13	30% methylamine + 30% ethylene glycol+40% of 10% KOH in methanol	Strong yellow	Fast/Very good	0.512
14	2.5% FeCl ₃ in methanol	Colorless	-	-

The results in Table 4.15 showed that the increase in concentration of potassium hydroxide in solution had affected to the results of extraction, that was, the more amounts of potassium hydroxide used, the higher efficiency of extraction would be obtained. However, potassium hydroxide did not dissolved well in methanol and if the amount of potassium hydroxide was more than 8% in methanol, the solution became turbid. Ethylene glycol is a better solvent for potassium hydroxide than methanol and can be separated with diesel rapidly. In contrast, ethylene glycol forms emulsion with diesel oil and can have negative effect on detection procedure by UV-visible spectroscopy, and it extracted less dye than methanol. Therefore, the suitable extraction solution composed of a 1:1 methanol and ethylene glycol containing 10% by weight potassium hydroxide. The extraction solution, when had consisted of organic base would enable better extraction of marker dye from diesel oil. The solution system of ferric chloride in methanol could not extracted marker dye and it was colorless solution in extracted phase. Because only low concentrations of dye were added in oil, the phenolic group of dye did not enough to form complex with ferric chloride in methanol solution.

From these results, four solution systems (Table 4.16) were selected to study in details of detection procedure such as the suitable ratio of extraction system, λ_{max} of each solvent and absorption of each solvent. In order to choose the suitable concentration of marker dye in diesel oil, which was suitable for both the field test and laboratory inspection (Table 4.20). These results would be used for the quantitative determination (Table 4.22) and the other application.

Table 4.16: The solution systems for extraction of marker dyes 5 – 12

No.	Solvent
1	8% KOH in methanol
2	10% KOH in 1:1 of methanol: ethylene glycol.
3	30% diisopropylamine + 30% ethylene glycol + 40% of 10% KOH in methanol
4	30% morpholine + 30% ethylene glycol + 40% of 10% KOH in methanol

The results of extraction of 4 solvents at ratio 4:1, 7:1 and 9:1 were summarized in Table 4.17, 4.18 and 4.19, respectively.

Table 4.17: The results of marker dyes 5-12 when were extracted with solvent 1-4 at ratio 4:1

Ex. No. Ratio 4:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concentration in diesel fuel (ppm)	λ_{\max} (nm)	Abs.
1	M5	S1	Yellow	Weak yellow	Yellow	3	399.9	0.263
2	M5	S2	Yellow	Weak yellow	Yellow	3	397.8	0.267
3	M5	S3	Yellow	Almost colorless	Yellow	3	397.7	0.270
4	M5	S4	Yellow	Almost colorless	Yellow	3	404.4	0.270
5	M6	S1	Yellow	Weak yellow	Yellow	3	402.3	0.249
6	M6	S2	Yellow	Weak yellow	Yellow	3	401.9	0.327
7	M6	S3	Yellow	Almost colorless	Yellow	3	402.5	0.328
8	M6	S4	Yellow	Almost colorless	Yellow	3	409.2	0.330
9	M7	S1	Yellow	Weak yellow	Yellow	3	401.6	0.400
10	M7	S2	Yellow	Weak yellow	Yellow	3	397.8	0.478
11	M7	S3	Yellow	Almost colorless	Yellow	3	398.7	0.487
12	M7	S4	Yellow	Almost colorless	Yellow	3	404.4	0.501
13	M8	S1	Yellow	Weak yellow	Yellow	3	396.8	0.251
14	M8	S2	Yellow	Weak yellow	Yellow	3	394.7	0.239
15	M8	S3	Yellow	Almost colorless	Yellow	3	396.8	0.241
16	M8	S4	Yellow	Almost colorless	Yellow	3	401.6	0.259

Ex. No. Ratio 4:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concentration in diesel fuel (ppm)	λ_{\max} (nm)	Abs.
17	M9	S1	Weak yellow	Weak yellow	Yellow	5	407.1	0.186
18	M9	S2	Weak yellow	Weak yellow	Yellow	5	407.1	0.185
19	M9	S3	Yellow	Almost colorless	Yellow	5	410.2	0.204
20	M9	S4	Yellow	Almost colorless	Yellow	5	408.0	0.227
21	M10	S1	Yellow	Weak yellow	Yellow	5	408.1	0.204
22	M10	S2	Weak yellow	Weak yellow	Yellow	5	409.2	0.197
23	M10	S3	Yellow	Almost colorless	Yellow	5	411.2	0.214
24	M10	S4	Yellow	Almost colorless	Yellow	5	417.8	0.269
25	M11	S1	Yellow	Weak yellow	Yellow	5	406.1	0.305
26	M11	S2	Yellow	Weak yellow	Yellow	5	407.7	0.280
27	M11	S3	Yellow	Almost colorless	Yellow	5	409.3	0.316
28	M11	S4	Yellow	Almost colorless	Yellow	5	414.0	0.395
29	M12	S1	Yellow	Weak yellow	Yellow	5	405.0	0.274
30	M12	S2	Yellow	Weak yellow	Yellow	5	405.8	0.269
31	M12	S3	Yellow	Almost colorless	Yellow	5	407.1	0.284
32	M12	S4	Yellow	Almost colorless	Yellow	5	413.1	0.351

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Table 4.18: The results of marker dyes 5-12 when were extracted with solvent 1-4 at ratio 7:1

Ex. No. ratio 7:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concent- ration in diesel fuel (ppm)	λ_{\max} (nm)	Abs.
33	M5	S1	Yellow	Weak yellow	Yellow	3	400.4	0.501
34	M5	S2	Yellow	Weak yellow	Yellow	3	397.8	0.488
35	M5	S3	Yellow	Almost colorless	Yellow	3	397.7	0.572
36	M5	S4	Yellow	Almost colorless	Yellow	3	404.4	0.595
37	M6	S1	Yellow	Weak yellow	Yellow	3	404.4	0.671
38	M6	S2	Yellow	Weak yellow	Yellow	3	401.9	0.594
39	M6	S3	Yellow	Almost colorless	Yellow	3	402.5	0.521
40	M6	S4	Yellow	Almost colorless	Yellow	3	409.2	0.679
41	M7	S1	Yellow	Weak yellow	Yellow	3	400.6	0.759
42	M7	S2	Yellow	Weak yellow	Yellow	3	397.8	0.838
43	M7	S3	Yellow	Almost colorless	Yellow	3	398.7	0.910
44	M7	S4	Yellow	Almost colorless	Yellow	3	404.4	0.929
45	M8	S1	Yellow	Weak yellow	Yellow	3	396.8	0.478
46	M8	S2	Yellow	Weak yellow	Yellow	3	394.7	0.457
47	M8	S3	Yellow	Almost colorless	Yellow	3	396.8	0.523
48	M8	S4	Yellow	Almost colorless	Yellow	3	401.6	0.573

Ex. No. Ratio 7:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concentra- tion in diesel fuel (ppm)	λ_{\max} (nm)	Abs.
49	M9	S1	Yellow	Weak yellow	Yellow	5	406.8	0.309
50	M9	S2	Yellow	Weak yellow	Yellow	5	407.1	0.311
51	M9	S3	Yellow	Almost colorless	Yellow	5	408.8	0.364
52	M9	S4	Yellow	Almost colorless	Yellow	5	408.0	0.465
53	M10	S1	Yellow	Weak yellow	Yellow	5	408.9	0.300
54	M10	S2	Yellow	Weak yellow	Yellow	5	408.9	0.257
55	M10	S3	Yellow	Almost colorless	Yellow	5	409.7	0.298
56	M10	S4	Yellow	Almost colorless	Yellow	5	417.8	0.514
57	M11	S1	Yellow	Weak yellow	Yellow	5	407.5	0.502
58	M11	S2	Yellow	Weak yellow	Yellow	5	407.1	0.418
59	M11	S3	Yellow	Almost colorless	Yellow	5	407.3	0.498
60	M11	S4	Yellow	Almost colorless	Yellow	5	414.0	0.751
61	M12	S1	Yellow	Weak yellow	Yellow	5	405.0	0.440
62	M12	S2	Yellow	Weak yellow	Yellow	5	405.0	0.444
63	M12	S3	Yellow	Almost colorless	Yellow	5	406.1	0.425
64	M12	S4	Yellow	Almost colorless	Yellow	5	413.1	0.697

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Table 4.19: The results of marker dyes 5-12 when were extracted with solvent 1-4 at ratio 9:1

Ex. No. Ratio 9:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concentra- tion in diesel fuel (ppm)	λ_{\max} (nm)	Abs.
65	M5	S1	Yellow	Weak yellow	Yellow	3	398.0	0.682
66	M5	S2	Yellow	Weak yellow	Yellow	3	396.8	0.691
67	M5	S3	Yellow	Almost colorless	Yellow	3	397.7	0.754
68	M5	S4	Yellow	Almost colorless	Yellow	3	404.4	0.784
69	M6	S1	Yellow	Weak yellow	Yellow	3	405.4	0.854
70	M6	S2	Yellow	Weak yellow	Yellow	3	401.8	0.619
71	M6	S3	Strong yellow	Almost colorless	Yellow	3	402.5	0.913
72	M6	S4	Strong yellow	Almost colorless	Yellow	3	409.2	0.952
73	M7	S1	Strong yellow	Weak yellow	Yellow	3	400.6	1.094
74	M7	S2	Strong yellow	Weak yellow	Yellow	3	397.2	0.903
75	M7	S3	Strong yellow	Almost colorless	Yellow	3	398.7	1.025
76	M7	S4	Strong yellow	Almost colorless	Yellow	3	404.4	1.210
77	M8	S1	Yellow	Weak yellow	Yellow	3	396.8	0.611
78	M8	S2	Yellow	Weak yellow	Yellow	3	394.7	0.617
79	M8	S3	Yellow	Almost colorless	Yellow	3	396.8	0.678
80	M8	S4	Yellow	Almost colorless	Yellow	3	401.6	0.778

Ex. No. ratio 9:1	Marker Dye	Solvent	Hue of aqueous phase	Hue of oily phase after shaking	Hue of oily phase before shaking	Marker concentration in diesel fuel (ppm)	λ_{max} (nm)	Abs.
81	M9	S1	Yellow	Weak yellow	Yellow	5	406.8	0.479
82	M9	S2	Yellow	Weak yellow	Yellow	5	407.1	0.382
83	M9	S3	Yellow	Almost colorless	Yellow	5	404.9	0.597
84	M9	S4	Strong yellow	Almost colorless	Yellow	5	408.3	0.934
85	M10	S1	Yellow	Weak yellow	Yellow	5	408.0	0.460
86	M10	S2	Yellow	Weak yellow	Yellow	5	409.2	0.360
87	M10	S3	Strong yellow	Almost colorless	Yellow	5	408.8	0.570
88	M10	S4	Strong yellow	Almost colorless	Yellow	5	417.8	0.874
89	M11	S1	Strong yellow	Weak yellow	Yellow	5	405.4	0.705
90	M11	S2	Yellow	Weak yellow	Yellow	5	407.1	0.477
91	M11	S3	Strong yellow	Almost colorless	Yellow	5	407.3	0.751
92	M11	S4	Strong yellow	Almost colorless	Yellow	5	414.0	1.168
93	M12	S1	Yellow	Weak yellow	Yellow	5	404.0	0.557
94	M12	S2	Yellow	Weak yellow	Yellow	5	406.1	0.464
95	M12	S3	Strong yellow	Almost colorless	Yellow	5	407.1	0.562
96	M12	S4	Strong yellow	Almost colorless	Yellow	5	413.0	1.030

Table 4.17 – 4.19 showed that the higher ratio of marked oil added, the more distinctive color of extracted phase would be obtained. Therefore, laboratory determinations, the ratio 9:1 would be more appropriate because it would show a distinctive color. However, field tests, which require a quick and one-step test, a ratio 4:1 could be used in previous specify of sample commercial oil.

4.6 The Suitable Concentration of Marker Dyes in Commercial High-Speed Diesel

The results of extraction system indicated absorption of each solvent and marker dyes, so that the suitable concentration of marker dyes in commercial high-speed diesel oil were selected to give final absorption in the range of about 0.4-0.6. The suitable concentration of marker dyes 5 – 12, after extracted with solvent 1-4, were summarized in Table 4.20.

Table 4.20: The suitable concentration of marker dyes 5-12

Ex. No. Ratio 9:1	Marker Dye	Solvent	Hue of aqueous phase	Suitable concentration in diesel oil (ppm)	λ_{max} (nm)	Absorbance (± 0.03)
1	M5	S1	Yellow	3	398.0	0.68
2	M5	S2	Yellow	3	396.8	0.69
3	M5	S3	Yellow	2	397.7	0.49
4	M5	S4	Yellow	2	404.4	0.52
5	M6	S1	Yellow	2	405.4	0.55
6	M6	S2	Yellow	3	401.8	0.62
7	M6	S3	Yellow	2	402.5	0.60
8	M6	S4	Yellow	2	409.2	0.61
9	M7	S1	Yellow	1.5	400.6	0.56
10	M7	S2	Yellow	2	397.2	0.62
11	M7	S3	Yellow	1.5	398.7	0.51
12	M7	S4	Yellow	1.5	404.4	0.60
13	M8	S1	Yellow	3	396.8	0.62
14	M8	S2	Yellow	3	394.7	0.62
15	M8	S3	Yellow	2.5	396.8	0.58
16	M8	S4	Yellow	2	401.6	0.53
17	M9	S1	Yellow	5	406.8	0.48
18	M9	S2	Yellow	5	407.1	0.38
19	M9	S3	Yellow	4	404.9	0.48
20	M9	S4	Yellow	3	408.3	0.57

Ex. No. Ratio 9:1	Marker Dye	Solvent	Hue of aqueous phase	Suitable concentration in diesel oil (ppm)	λ_{\max} (nm)	Absorbance (± 0.03)
21	M10	S1	Yellow	5	408.0	0.46
22	M10	S2	Yellow	5	409.2	0.36
23	M10	S3	Yellow	5	408.8	0.57
24	M10	S4	Yellow	3	417.8	0.53
25	M11	S1	Yellow	3	405.4	0.42
26	M11	S2	Yellow	5	407.1	0.48
27	M11	S3	Yellow	4	407.3	0.58
28	M11	S4	Yellow	2	414.0	0.45
29	M12	S1	Yellow	5	404.0	0.56
30	M12	S2	Yellow	5	406.1	0.46
31	M12	S3	Yellow	5	407.1	0.56
32	M12	S4	Yellow	3	413.0	0.62

4.7 The Marker Dyes in Commercial Fuel Oil

Marker dye 5 was tested for tagging commercial fuel oil such as commercial diesel oil, of gasoline and kerosene. The results of extraction procedures were displayed in Table 4.21.

Table 4.21: Marker dye 5 (3 ppm) in commercial fuel oil

Marker dye <u>5</u> 3 ppm in Commercial fuel oil	Results		
	Hue in aq. Phase Solvent 2	λ_{\max} (nm)	Absorbance (± 0.03)
Diesel			
PTT	Yellow	396.8	0.69
Caltex	Yellow	398.9	0.62
Shell	Yellow	399.7	0.61
Esso	Yellow	401.2	0.60
Gasoline (PTT)	Yellow	399.9	0.71
Kerosene (PTT)	Yellow	399.0	0.63

These results showed that these novel marker dyes could be used for tagging other commercial fuel oil. However, the extraction solvent system of each commercial fuel types should be further optimized because some extraction solvent systems were partially soluble in some petroleum products such as methanol was very immiscible with kerosene but it was some miscible with gasoline. In addition, the commercial diesel oil of shell was separated from methanol and base solution for a long time about 20 minutes. These problems of separation between oil and aqueous phase were solved by centrifuge before measurement. For this determination, solvent 2, which was a 50/50 by volume mixture of methanol and ethylene glycol containing 10% by weight KOH, was used because it could fairly extracted marker dye from tagged oil and it was just a petroleum-immiscible solution.

4.8 Quantitative Analysis of Marker Dyes 5 – 12

The quantitative analyses of marker dyes 5-12 were carried out by plotting calibration curve between concentration of marker dyes added and absorbance. The absorbance was obtained by extraction of the oil with an appropriate solvent and the absorbance was recorded to compare with its.

Table 4.22: The calibration of marker dyes 5 – 12 in diesel oil (Fig. 16-1 to 24-4)

No.	Marker dye	Solvent	Concentration (ppm)	Description
1	M5	S1	0, 2, 3, 4, 5	$Y = 3.333e-04 + 2.445e-01 * X$
2	M5	S2	0, 2, 3, 4, 5	$Y = 4.631e-03 + 2.291e-01 * X$
3	M5	S3	0, 1, 2, 3	$Y = 1.565e-02 + 2.161e-01 * X$
4	M5	S4	0, 1, 2, 3, 4	$Y = 2.012e-03 + 2.529e-01 * X$
5	M6	S1	0, 1, 2, 3	$Y = 1.667e-03 + 2.795e-01 * X$
6	M6	S2	0, 2, 3, 4	$Y = 1.000e-03 + 2.060e-01 * X$
7	M6	S3	0, 1, 1.5, 2, 2.5	$Y = -8.000e-04 + 3.046e-01 * X$
8	M6	S4	0, 1, 2, 3	$Y = -3.333e-04 + 3.105e-01 * X$
9	M7	S1	0, 1, 1.5, 2, 2.5	$Y = 1.898e-03 + 3.668e-01 * X$
10	M7	S2	0, 1, 2, 3	$Y = -5.921e-16 + 3.010e-01 * X$
11	M7	S3	0, 0.5, 1, 1.5, 2	$Y = -3.553e-16 + 3.414e-01 * X$
12	M7	S4	0, 0.5, 1, 1.5, 2	$Y = -1.308e-03 + 4.014e-01 * X$
13	M8	S1	0, 1, 2, 3, 4	$Y = -3.553e-16 + 2.031e-01 * X$

No.	Marker dye	Solvent	Concentration (ppm)	Description
14	M8	S2	0, 2, 3, 4, 5	$Y = -1.613e-03 + 2.077e-01 * X$
15	M8	S3	0, 2, 2.5, 3	$Y = -4.737e-15 + 2.260e-01 * X$
16	M8	S4	0, 1, 2, 3	$Y = 3.933e-03 + 2.445e-01 * X$
17	M9	S1	0, 3, 5, 7, 9	$Y = 5.359e-04 + 9.468e-02 * X$
18	M9	S2	0, 3, 5, 7, 9	$Y = 7.946e-03 + 7.293e-02 * X$
19	M9	S3	0, 3, 5, 7	$Y = 1.667e-04 + 1.194e-01 * X$
20	M9	S4	0, 1, 2, 3, 4	$Y = -8.000e-04 + 1.875e-01 * X$
21	M10	S1	0, 3, 5, 7, 9	$Y = -2.300e-03 + 9.230e-02 * X$
22	M10	S2	0, 3, 5, 7, 9	$Y = 1.867e-02 + 6.800e-02 * X$
23	M10	S3	0, 3, 5, 7	$Y = 1.000e-03 + 1.140e-01 * X$
24	M10	S4	0, 1, 2, 3, 4	$Y = -9.060e-04 + 1.753e-01 * X$
25	M11	S1	0, 1, 3, 5, 7	$Y = 7.650e-04 + 1.410e-01 * X$
26	M11	S2	0, 3, 5, 7, 9	$Y = 1.689e-02 + 9.421e-02 * X$
27	M11	S3	0, 2, 4, 6	$Y = -3.333e-04 + 1.463e-01 * X$
28	M11	S4	0, 1, 2, 3, 4	$Y = -1.760e-04 + 2.329e-01 * X$
29	M12	S1	0, 3, 5, 7	$Y = -5.000e-04 + 1.150e-01 * X$
30	M12	S2	0, 3, 5, 7, 9	$Y = -1.101e-02 + 9.510e-02 * X$
31	M12	S3	0, 3, 5, 7	$Y = -5.000e-04 + 1.125e-01 * X$
32	M12	S4	0, 2, 3, 4	$Y = 1.833e-03 + 2.055e-01 * X$

4.9 The Stability of Marker Dyes 5 – 12 from Extraction with Solvent 1

The stability of marker dyes was determined by measuring the absorption of marker dyes in extracted phase for a specified period of time by UV-VIS spectroscopy and then the absorbance of extracted phase was compared with a standard calibration curve. The results of stability of marker dyes 5-12 were shown in Table 4.23.

The marked commercial diesel oil after storage in a dark container and dark place was measured for absorbance after twelve weeks by UV-VIS spectrophotometer and then the concentration was calculated from linear equation of its calibration curve. In Table 4.23 indicated that during twelve weeks, the amount of marker dye in fuel oil was not significantly different. Therefore, these marker dyes were stable for at least twelve weeks under storage conditions.

Table 4.23: Concentration monitoring of Marker dyes 5 – 8 and Marker dyes 9 – 12 from extraction with solvent 1

Marker dye	Conc. (ppm)	Concentration Average (ppm)											
		Week1	Week2	Week3	Week4	Week5	Week6	Week7	Week8	Week9	Week10	Week11	Week12
<u>5</u>	3.00	3.05	3.05	3.10	3.08	3.05	3.05	2.95	3.05	3.10	2.90	2.98	3.05
<u>6</u>	2.00	2.08	2.10	2.03	1.95	1.98	1.95	1.90	2.03	2.05	2.05	2.03	2.02
<u>7</u>	1.50	1.48	1.50	1.52	1.56	1.54	1.49	1.52	1.48	1.53	1.55	1.52	1.50
<u>8</u>	3.00	3.05	3.10	3.05	2.95	2.98	2.98	3.03	3.05	3.03	2.98	3.03	3.05
<u>9</u>	5.00	5.05	5.05	5.05	4.95	4.98	5.10	4.90	4.98	5.06	5.10	5.08	5.03
<u>10</u>	5.00	5.10	5.08	5.05	5.05	5.10	4.95	4.98	5.06	4.97	5.03	5.02	5.05
<u>11</u>	3.00	2.90	2.93	2.98	2.93	2.95	3.00	2.95	2.98	2.96	2.96	2.98	2.89
<u>12</u>	5.00	5.10	5.05	5.05	4.98	4.86	4.89	4.95	4.96	4.93	5.02	5.03	4.98