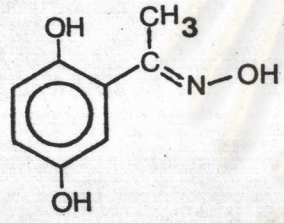
CHAPTER III

EXPERIMENTALS, RESULTS AND DISCUSSION

3.1 Preparation, Purification and Identification of Synthesised Oximes

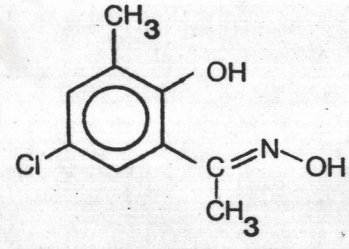
3.1.1 Preparation of the 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime

The proposed structures of the above mentioned two oximes are as follows respectively :



$C_8H_9NO_3$

M.W. 167.17



$C_9H_{10}ClNO_2$

M.W. 199.63

Reagents

(1) Hydroquinone (Analar, Merck) 99 % m.p. = 170-173°C

(2) 4-Chloro-o-cresol (HPLC grade, Fluka) 95 % m.p. = 45-48°C

(3) Acetic anhydride (Laboratory grade, Merck) b.p. = 140°C

(4) Concentrated sulfuric acid (Analar, Merck) 95-97 % density = 1.18 g/mL

(5) Ethanol (Analar, Merck) 99.8 % b.p. = 78.5°C

(6) Anhydrous calcium chloride (Laboratory grade, Fluka) 97 %

(7) Anhydrous aluminium chloride (Laboratory grade, BDH) 98 %

(8) Concentrated hydrochloric acid (Analar, Merck) 37 %
density = 1.19 g/mL

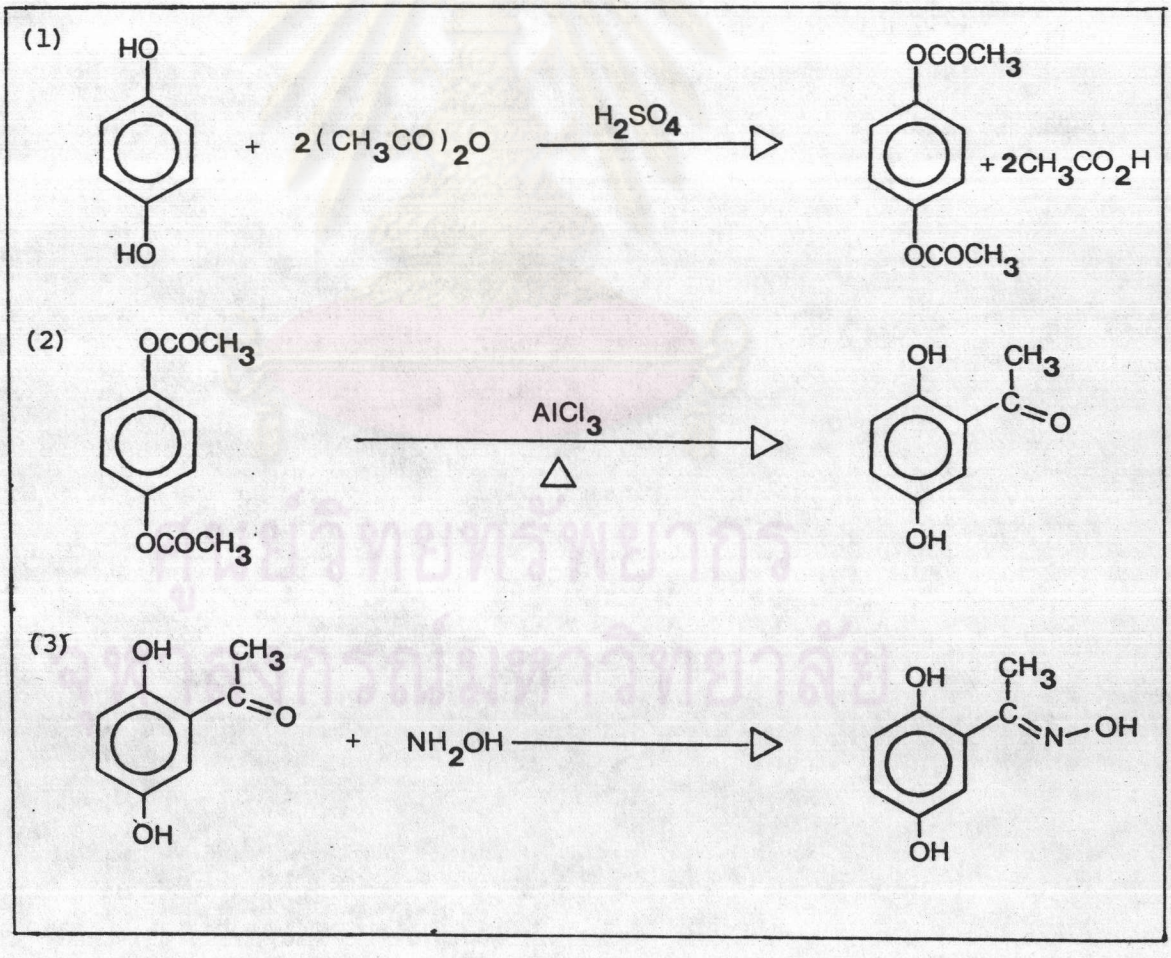
(9) Hydroxylamine hydrochloride (Analar, Seelze Hannover) 99 %

(10) Sodium hydroxide (Laboratory grade, BDH) 96 %

(11) Acetone (Analar, BDH) b.p. = 56.0 - 56.5°C

3.1.1.1 Preparation of 2,5-dihydroxy acetophenoxime

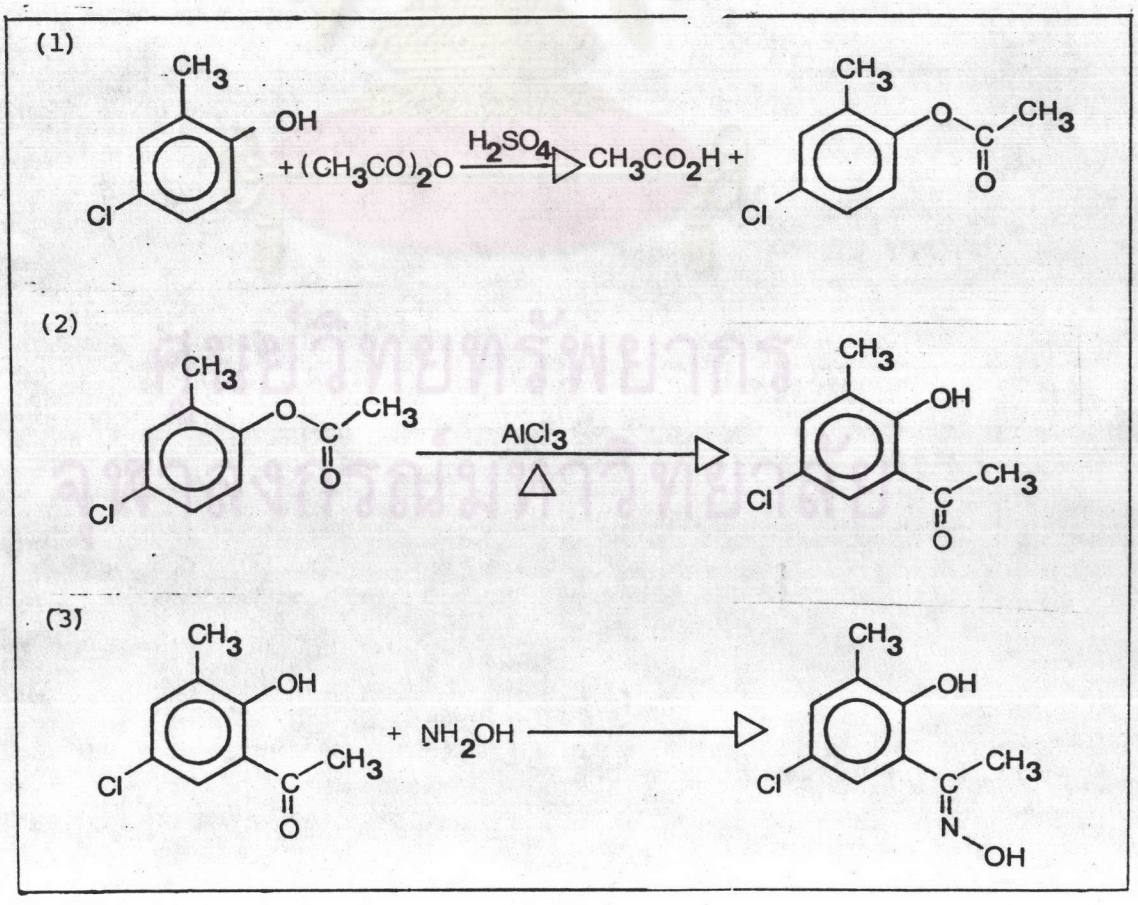
2,5-dihydroxy acetophenoxime could be prepared from hydroquinone as starting material. The method of the preparation of the reagent is schematically described below.



Hydroquinone (M.W. = 110.11, m.p. = 170-173°C) was acetylated with acetic anhydride to give hydroquinone diacetate (M.W. = 194.19, m.p. = 121 - 122°C) (28). The Fries rearrangement by the use of $AlCl_3$ gave 2,5-dihydroxy acetophenone (M.W. = 152.15, m.p. = 202 - 203°C) (29). The ketone was oximated to give 2,5-dihydroxy acetophenoxime. It was recrystallised several times from water and acetone mixture. It was dried and kept in a vacuum dessicator. (56 % yeild of the last step, M.W. = 167.17, m.p. = 149 - 150°C)

3.1.1.2 Preparation of 5-chloro-2-hydroxy-3-methyl aceto-phenoxime

The oxime could be prepared from 4-chloro-o-cresol. The prepation is schematically described below.



(1) 4-Chloro-2-methyl phenylacetate. One drop of concentrated sulfuric acid was added to a mixture of 30 g (0.21 mole) of 4-chloro-o-cresol and 25 mL (0.25 mole) of freshly redistilled acetic anhydride in 250-mL Erlenmeyer flask. The mixture was stirred gently ; it warmed up very rapidly, and the 4-chloro-o-cresol dissolved. After 5 minutes the clear solution was poured into about 150 mL of distilled water in 250 mL separatory funnel. Then the solution was washed with another portion of water (about 100 mL.) The brown liquid in the lower layer was dried with porous anhydrous calcium chloride. The nearly pure product (characteristic terrible smell), 4-chloro-2-methyl phenyl acetate ester was obtained (33.2 g, 86 %), b.p. 243-246^{o}C.

(2) 5-Chloro-2-hydroxy-3-methyl acetophenone. A mixture of 30 g (0.16 mole) of dry 4-chloro-2-methyl phenyl acetate ester and 47 g (0.35 mole) of anhydrous aluminium chloride (finely powdered in a mortar) was introduced into a dry 100-mL round bottomed flask fitted with a water condensor and connected to a gas absorption trap. The flask was placed in a silicone oil bath which was heated slowly from room temparature (30^{o}C) so that at the end of about 30 minutes the temparature of the oil reach 110 - 120^{o}C, at which point the evolution of hydrogen chloride began. The temperature was then raised slowly to 150^{o}C and maintained at that point for about 5 hours ; at the end of about 4 hours the evolution of hydrogen chloride became very slow and the mass assumed a dark green colour and pasty in consistency. The flask was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was dissolved in 250 mL of ethanol and the excess aluminium chloride was decomposed by adding 500 mL of distilled water and 20 mL of concentrated hydrochloric acid. The brown solid obtained in collected on a Büchner funnel and washed with 100 - 150 mL of

distilled water. The brown solid was collected, and then subjected to further recrystallisations (3 times) from ethanol-water to yield the brown needles, 5-chloro-2-hydroxy-3-methyl acetophenone (19.7 g, 67 %), m.p. 68 - 70°C.

(3) 5-Chloro-2-hydroxy-3-methyl acetaphenoxime. A mixture of 10 g (0.054 mole) of 5-chloro-2-hydroxy-3-methyl acetophenone, 5 g (0.072 mole) of hydroxylamine hydrochloride, 20 mL of ethanol, 5 mL of distilled water was placed in a 100-mL round-bottomed flask. To this was added in portions, with shaking, 8 g (0.2 mole) of sodium hydroxide pellets. If the reaction became too vigorous, cooling with tap water might be necessary. After all the sodium hydroxide has been added, the flask was connected to a reflux condensor, heated to boiling, and refluxed for 5 minutes. After cooling the content was poured into a solution of 12-13 mL of concentrated hydrochloric acid in 100 mL of distilled water. The brown solid separated. It was collected on a Whatman filter paper No. 42 and recrystallised 4 times with ethanol and water mixture. The product, 5-chloro-2-hydroxy-3-methyl acetophenoxime, was collected as brown plates (5.6 g, 52 %), m.p. 168-171°C

3.1.2 Purity Verification of the Synthesised Products

The synthesised oximes, 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime, were readily purified by recrystallization several times. Besides their sharp melting points, purity of these reagents was verified by applying methods of thin layer chromatography with many solvent systems and elemental analysis. Experiments and results of the methods are described in the following section.

3.1.2.1 Thin layer chromatography of the synthesised products

About 0.005 g of a dry synthesised product or starting reagent was dissolved in 5 mL of ethanol (Analar, Merck). The prepared ethanolic solution (10 µl) was spotted on 4 x 10 cm fluorescent silica gel-coated plastic sheet (silica gel 60 F_{254}, Merck, layer thickness 0.2 mm). Many solvent systems of n-hexane (Analar, BDH), chloroform (Analar, BDH) and ethanol (Analar, Merck) were used for developing the chromatogram by varying ratio of the three organic solvents in the component of mobile phase. The polarity range of these solvent systems was between 7.3 - 11.2. Comparision of R_f values of the starting reagent and synthesised products were exhibited in Tables 3.1 and Table 3.2

Table 3.1

composition ratio of the mobile phases			R_f values (solvent front = 8.0 cm)			
$n\text{-}C_6H_{14}$	$CHCl_3$	C_2H_5OH	(1)	(2)	(3)	(4)
10	-	-	0.01	0.01	0.01	0.01
9	1	-	0.01	0.02	0.04	0.03
8	2	-	0.01	0.02	0.05	0.03
7	3	-	0.01	0.02	0.07	0.03
6	4	-	0.01	0.03	0.08	0.04
5	5	-	0.02	0.03	0.09	0.04
4	6	-	0.02	0.03	0.09	0.05
3	7	-	0.02	0.04	0.10	0.05
2	8	-	0.02	0.04	0.11	0.05
1	9	-	0.03	0.05	0.11	0.05
-	10	-	0.03	0.05	0.12	0.06
-	9	1	0.35	0.80	0.57	0.46
-	8	2	0.59	0.86	0.78	0.69
-	7	3	0.66	0.89	0.81	0.76
-	6	4	0.78	0.96	0.95	0.85
-	5	5	0.86	0.96	0.96	0.93
-	4	6	0.94	0.96	0.96	0.96
-	3	7	0.95	0.97	0.97	0.97
-	2	8	0.96	0.97	0.97	0.96
-	1	9	0.96	0.96	0.96	0.96
-	-	10	0.96	0.97	0.97	0.96

Remark : (1) = hydroquinone

(2) = hydroquinone diacetate

(3) = 2,5-dihydroxy acetophenone

(4) = 2,5-dihydroxy acetophenoxime

Table 3.2

composition ratio of the mobile phase			R_f values (solvent front = 8.0 cm)			
$n\text{-}C_6H_{14}$	$CHCl_3$	C_2H_5OH	(1')	(2')	(3')	(4')
10	-	-	0.02	0.05	0.10	0.03
9	1	-	0.03	0.14	0.24	0.04
8	2	-	0.07	0.29	0.39	0.10
7	3	-	0.10	0.46	0.57	0.15
6	4	-	0.14	0.47	0.54	0.22
5	5	-	0.17	0.50	0.57	0.25
4	6	-	0.21	0.56	0.60	0.24
3	7	-	0.25	0.62	0.66	0.24
2	8	-	0.36	0.70	0.73	0.38
1	9	-	0.36	0.70	0.74	0.43
-	10	-	0.44	0.75	0.78	0.43
-	9	1	0.65	0.79	0.79	0.70
-	8	2	0.77	0.85	0.88	0.83
-	7	3	0.86	0.90	0.90	0.87
-	6	4	0.88	0.92	0.92	0.88
-	5	5	0.86	0.89	0.89	0.86
-	4	6	0.87	0.89	0.89	0.87
-	3	7	0.89	0.90	0.90	0.88
-	2	8	0.88	0.88	0.88	0.88
-	1	9	0.89	0.90	0.90	0.89
-	-	10	0.89	0.89	0.89	0.89

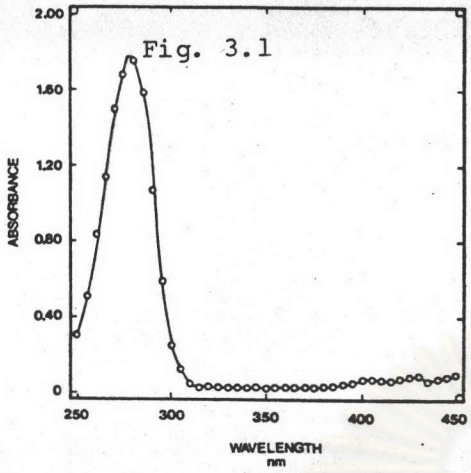
Remarks : (1') = 4-chloro-o-cresol

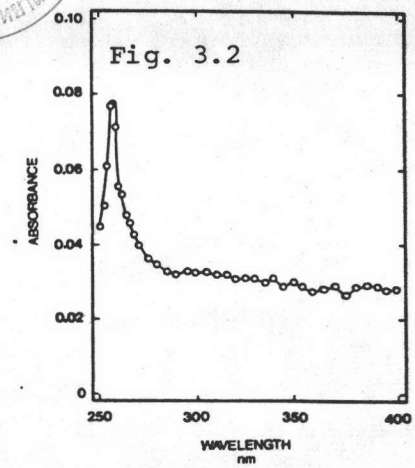
(2') = 4-chloro-2-methyl phenyl acetate ester

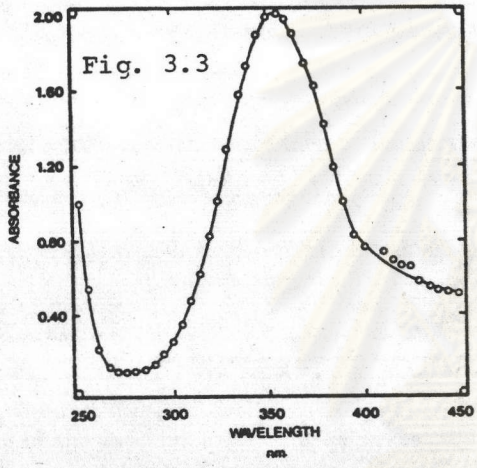
(3') = 5-chloro-2-hydroxy-3-methyl acetophenone

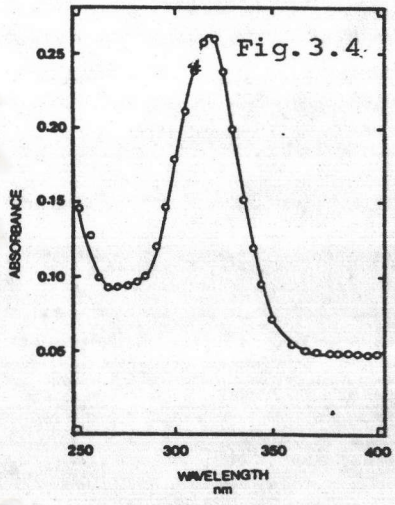
(4') = 5-chloro-2-hydroxy-3-methyl acetophenoxime

Ascending TLC experiments of the synthetic products using all twenty-one developing solvent systems as described in the above tables were carried out. It was found that each synthesised products gave single regular round spot under UV radiation. By using the solvent system of 9:1 $CHCl_3$-C_2H_5OH as a mobile phase, these synthesised products, (1), (2), (3) and (4), showed most differences in R_f value among twenty systems while the other group of synthesised products, (1'), (2'), (3') and (4'), prefered less polar solvent system, 5:5 n-C_6H_{14}-$CHCl_3$. The UV absorption spectra (250 - 400 nm) of these spots (Fig. 3.1, 3.2, 3.3, 3.4, 3.6, 3.7, 3.8 and 3.9) were recorded by using Shimadzu TLC scanner. These spectra are compared with those belonged to the ethanolic solution of the same reagents (Fig. 3.5 and 3.10)









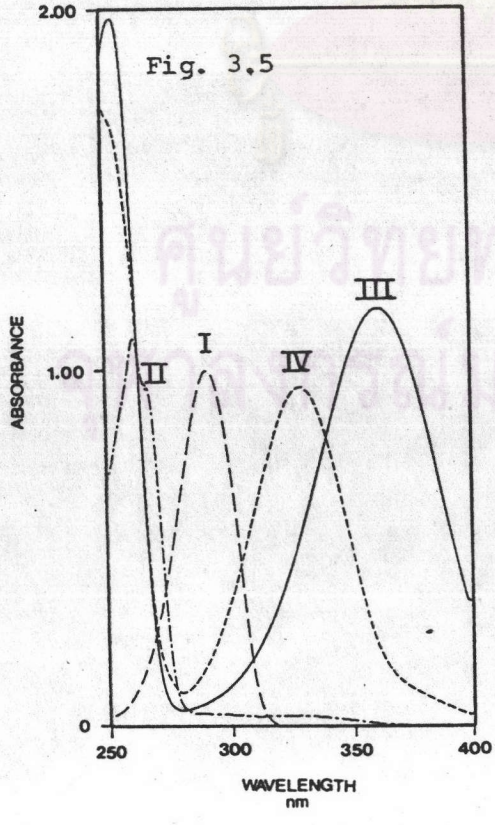


Fig.3.1 UV absorption of hydroquinone

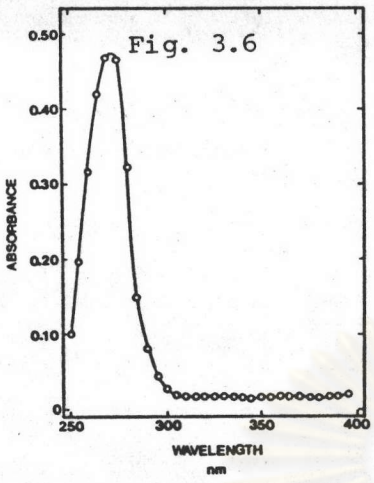
Fig.3.2 UV absorption of hydroquinone diacetate

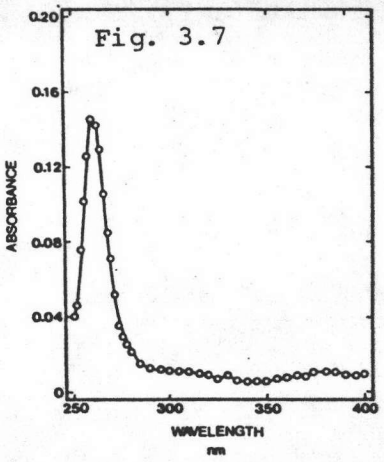
Fig.3.3 UV absorption of 2,5-dihydroxy acetophenone

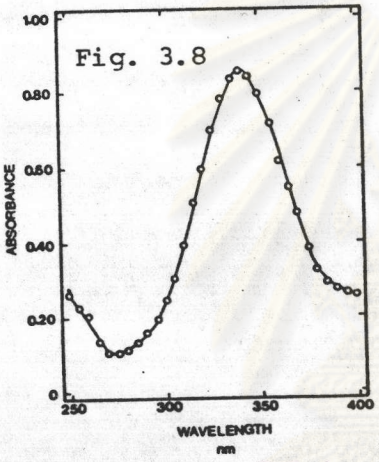
Fig.3.4 UV absorption of 2,5-dihydroxy acetophenoxime

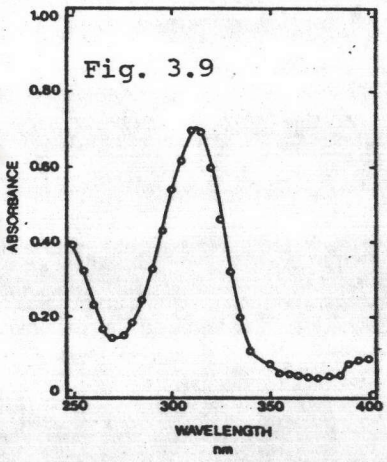
Fig. 3.5 UV absorption of ethanolic solutions of the synthesised products :

(I). hydroquinone
(II). hydroquinone diacetate
(III). 2.5-dihydroxy acetophenone an
(IV). 2.5-dihydroxy acetophenoxime









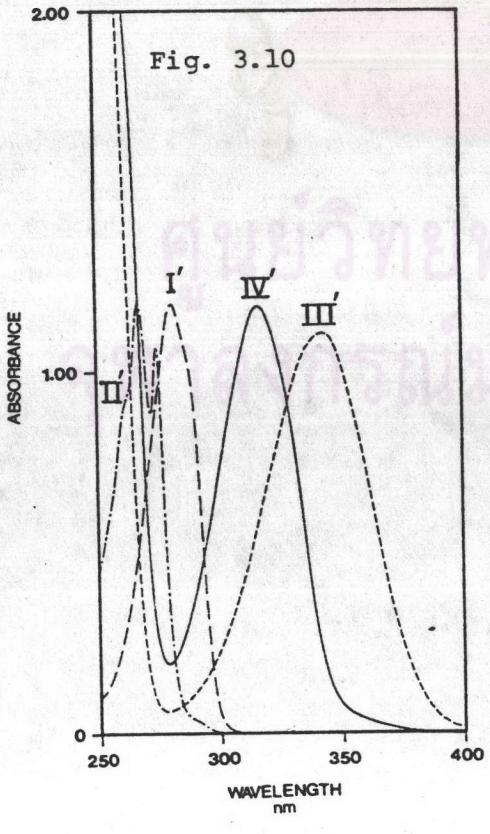


Fig.3.6 UV absorption of 4-chloro-O-cresol

Fig.3.7 UV absorption of 4-chloro-2-methyl phenyl acetate

Fig.3.8 UV absorption of 5-chloro-2-hydroxy-3-methyl acetophenone

Fig.3.9 UV absorption of 5-chloro-2-hydroxy-3-methyl acetophenoxime

Fig.3.10 UV absorption of ethanolic solutions of the synthesised products :

(I'). 4-chloro-O-cresol
(II') 4-chloro-2-methyl phenyl acetate
(III') 5-chloro-2-hydroxy-3-methyl acetophenone and
(IV') 5-chloro-2-hydroxy-3-methyl acetophenoxime

3.1.2.2 Elemental Analysis of the Synthesis Products

Purities of the synthesised products can also be verified by the method of elemental analysis. Percentage of carbon, hydrogen and nitrogen content in these substances were considered and compared with those calculated as shown in Table 3.3. It can be seen that the purity of the synthesised oximes were approximately 98 %.

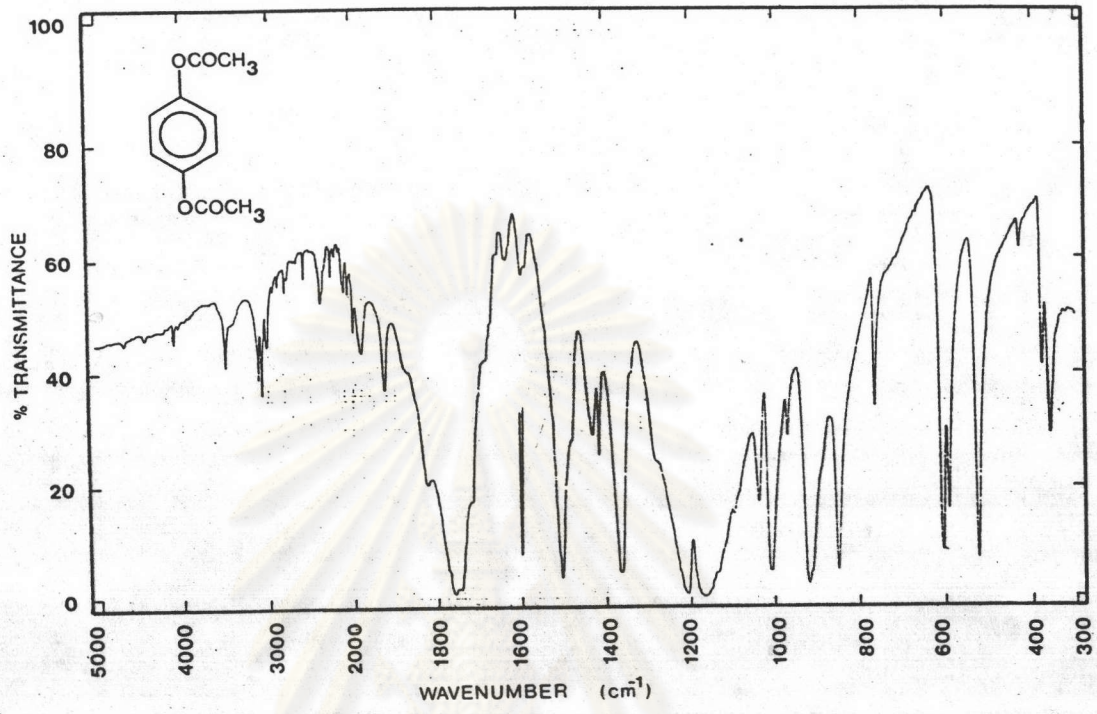
Table 3.3

Substance	% composition (w/w)								
	% C			% H			% N		
	cal.	exp.	Rel err.	cal.	exp.	Rel err.	cal.	exp.	Rel err.
Hydroquinone diacetate	61.85	61.54 ±0.03	0.50	5.19	5.13 ±0.03	1.16	-	-	-
2,5-dihydroxy acetophenone	63.15	62.62 ±0.03	0.84	5.30	5.24 ±0.02	1.13	-	-	-
2,5-dihydroxy acetophenoxime	57.48	57.67 ±0.17	0.33	5.43	5.32 ±0.01	2.02	8.38	8.31 ±0.08	0.84
4-chloro-2-methyphenyl acetate ester	58.55	57.84 ±0.07	1.21	4.91	4.78 ±0.02	2.65	-	-	-
5-chloro-2-hydroxy-3-methyl acetophenone	58.55	57.79 ±0.24	1.30	4.91	4.78 ±0.04	2.65	-	-	-
5-chloro-2-hydroxy-3-methyl acetophenoxime	54.14	53.63 ±0.21	0.94	5.05	4.96 ±0.05	1.80	7.01	6.89 ±0.06	1.71

3.1.3 Structural Elucidation of the Synthesised Products

3.1.3.1 By Infrared Spectroscopy. Infrared spectra is useful to interprete empirically the structure of the compounds by observing their functional group frequencies and finger prints. The spectra of these synthesised products were compared with spectra of similar skeletoned known compounds in Ref. 31. The IR spectra of these substances and their assignments of various important bands were given in the following paragraph below. They were obtained by using pure liquid or solid samples in potassium bromide pellets and were recorded on Shimadzu IR-440 infrared spectrophotometer. Figures 3.11 to 3.16 with Table 3.4 to 3.9 show the IR spectra and corresponding assignments of various synthesised products.

Fig. 3.11

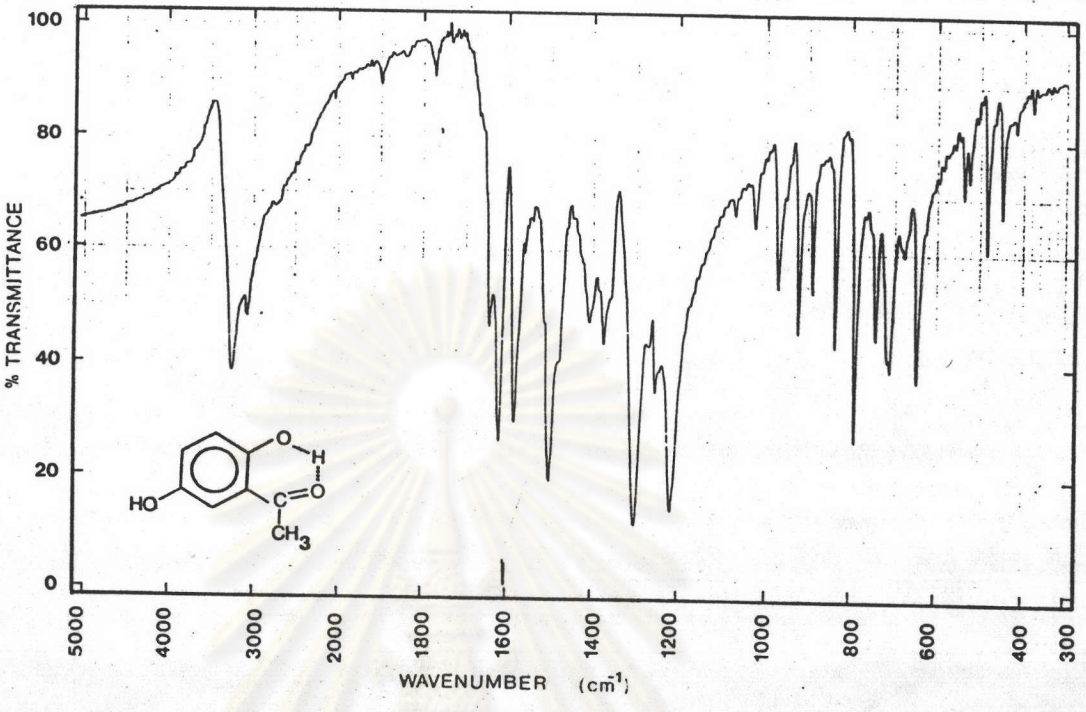


Assignment of the various important bands in the IR spectra of hydroquinone diacetate (value in cm^{-1})

Table 3.4

Bands	Tentative Assignments
1740 - 1780	C=O stretching, conjugated carbonyl to the aromatic ester
1505	aromatic-aliphatic C-C stretching
1363	C-H (methyl) bending
1160 - 1240	carbonyl C-O stretching
920	aromatic C-O stretching

Fig. 3.12

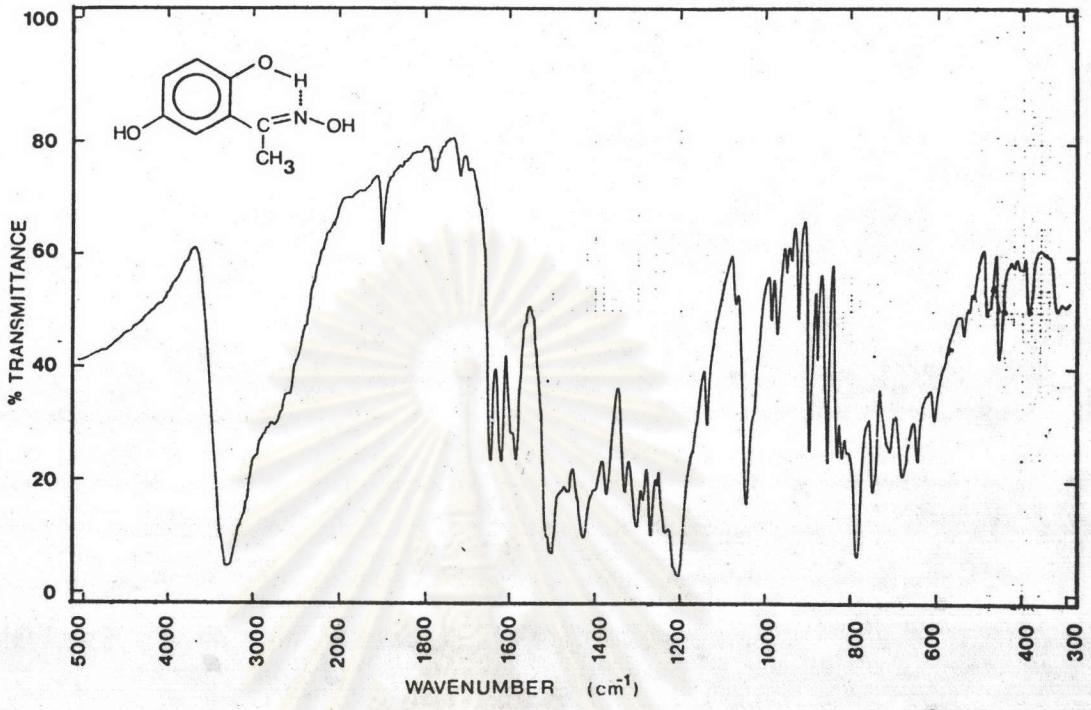


Assignment of the various important bands in the IR spectra of 2,5-dihydroxy acetophenone (value in cm^{-1})

Table 3.5

Bands	Tentative Assignments
3100 - 3250	O-H stretching, ortho position of acetophenone with hydrogen bonding between the carbonyl and hydroxyl group.
1610	C=O stretching, conjugated carbonyl of the aromatic ketone
1370 , 1400	C-H (methyl) bending
1300	aromatic C-O stretching

Fig. 3.13

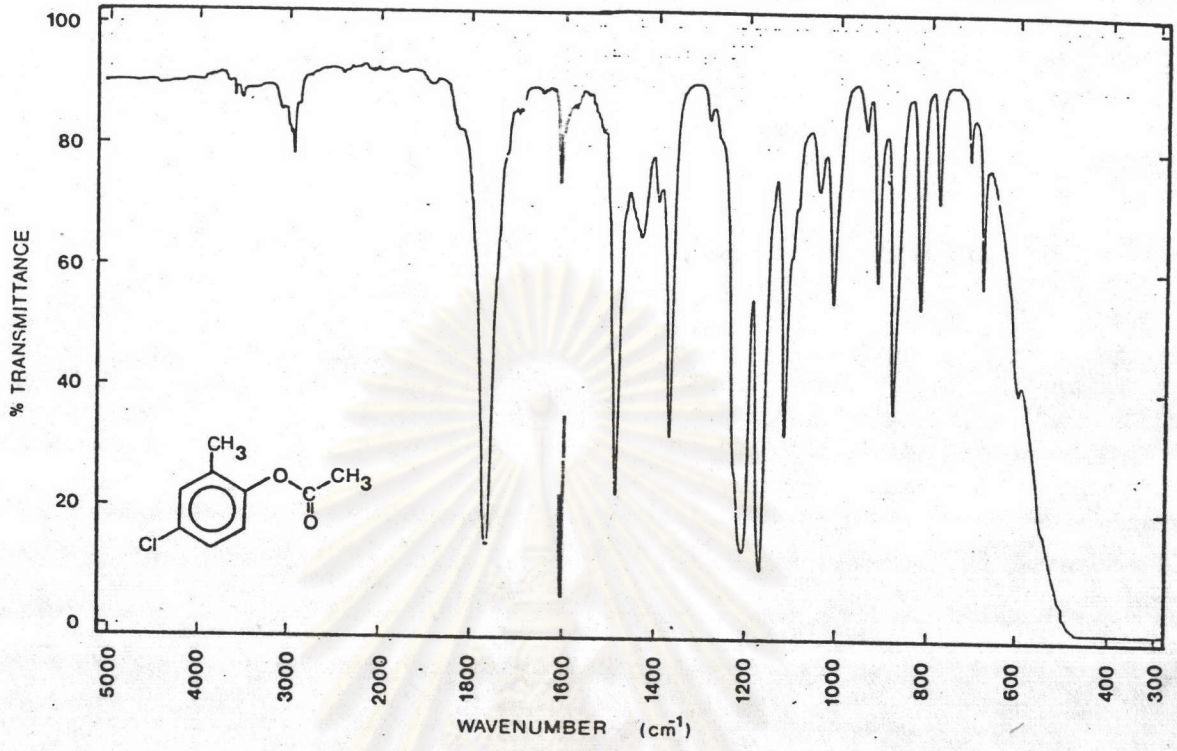


Assignment of the various important bands in the IR spectra of 2,5-dihydroxy acetophenoxime (value in cm^{-1})

Table 3.6

Bands	Tentative Assignments
3300	O-H stretching (oxime)
2500 - 3000	phenolic O-H stretching, with intramolecular hydrogen bonding
1620	C=N stretching
1500	aromatic-aliphatic C-C stretching
1020	=N-O stretching

Fig. 3.14

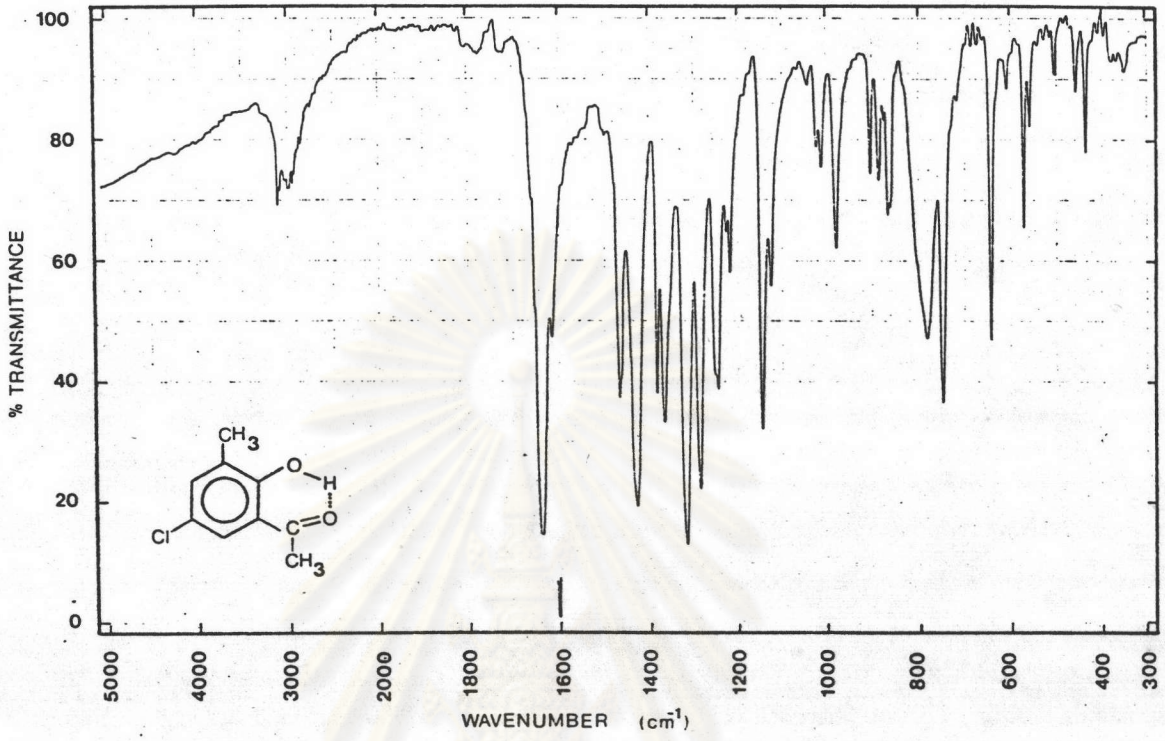


Assignment of the various important bands in the IR spectra of 4-chloro-2-methylphenyl acetate ester (value in cm^{-1})

Table 3.7

Bands	Tentative Assignments
1740 - 1770	C=O stretching, conjugated carbonyl of the aromatic ester
1420, 1482	aromatic-aliphatic C-C stretching
1370	C-H (methyl) bending
1160 - 1280	carbonyl C-O stretching
880	aromatic C-O stretching
780	aromatic C-Cl stretching

Fig. 3.15

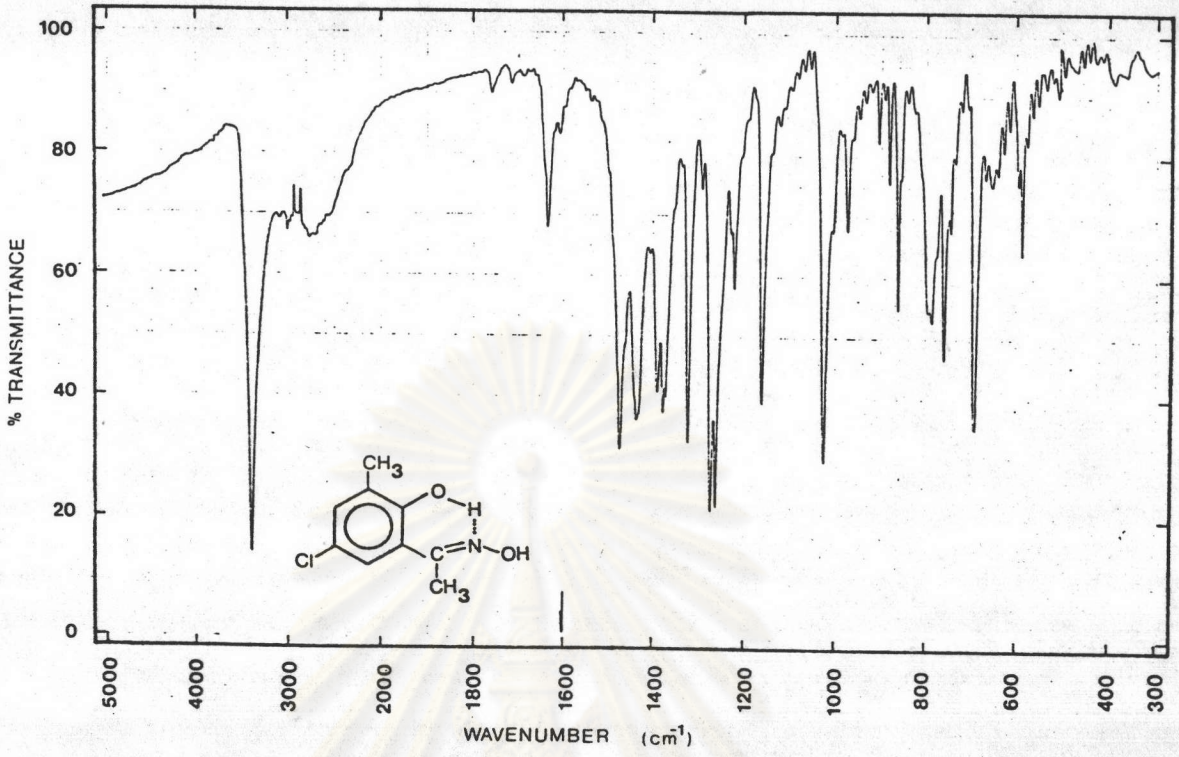


Assignment of the various important bands in the IR spectra of 5-chloro-2-hydroxy-3-methyl acetophenone (value in cm^{-1})

Table 3.8

Bands	Tentative Assignments
3000	O-H stretching, ortho position of acetophenone with hydrogen bonding between the carbonyl and hydroxyl group.
1645	C=O stretching, conjugated carbonyl of the aromatic ketone
1427, 1476	aromatic-aliphatic C-C stretching
1380	C-H (methyl) bending
1320	aromatic C-O stretching
790	aromatic C-Cl stretching

Fig. 3.16



Assignment of the various important bands in the IR spectra of 5-chloro-2-hydroxy-3-methyl acetophenoxime (value in cm^{-1})

Table 3.9

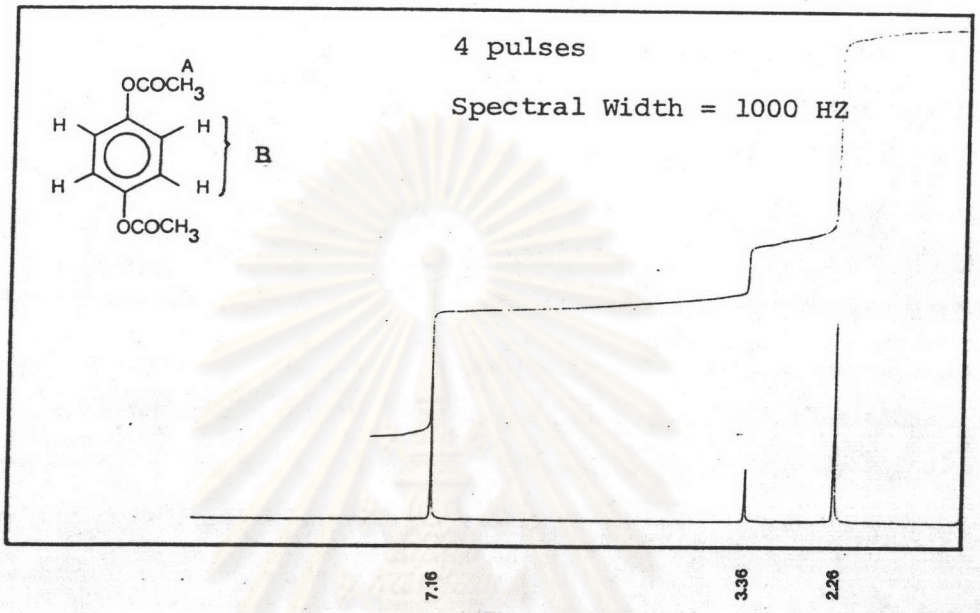
Bands	Tentative Assignments
3380	O-H stretching (oxime)
2800	phenolic O-H stretching, ortho position of acetophenoxime with hydrogen bonding between the oxime and hydroxyl group.
1615 - 1630	C=N stretching
1420 , 1480	aromatic-aliphatic C-C stretching
1380	C-H (methyl) bending
1312	aromatic C-O stretching
1022	= N-O stretching
790	aromatic C-Cl stretching
760	aromatic C-H bending (out of plane)

3.1.3.2 By Nuclear Magnetic Resonance Spectroscopy

Structures of the synthesised products can be elucidated by the useful proton and carbon 13 NMR spectroscopy. Suitable solvents were used for dissolving the samples. The proton NMR is able to characterize aliphatic and aromatic proton patterns complement while the carbon 13 NMR indicates the numbers of carbon atoms and their positions. These spectra are shown by using FX 90 Q Jeol Fourier transform NMR spectrometer.

NMR Spectra (both proton and C-13) with corresponding assignments of various synthesised products are shown in Fig.3.17 to 3.28 and Tables 3.10 to 3.21. (reference = TMS, solvent = DMSO-d_6 or DMSO-d_6 + $CDCl_3$).

Fig. 3.17

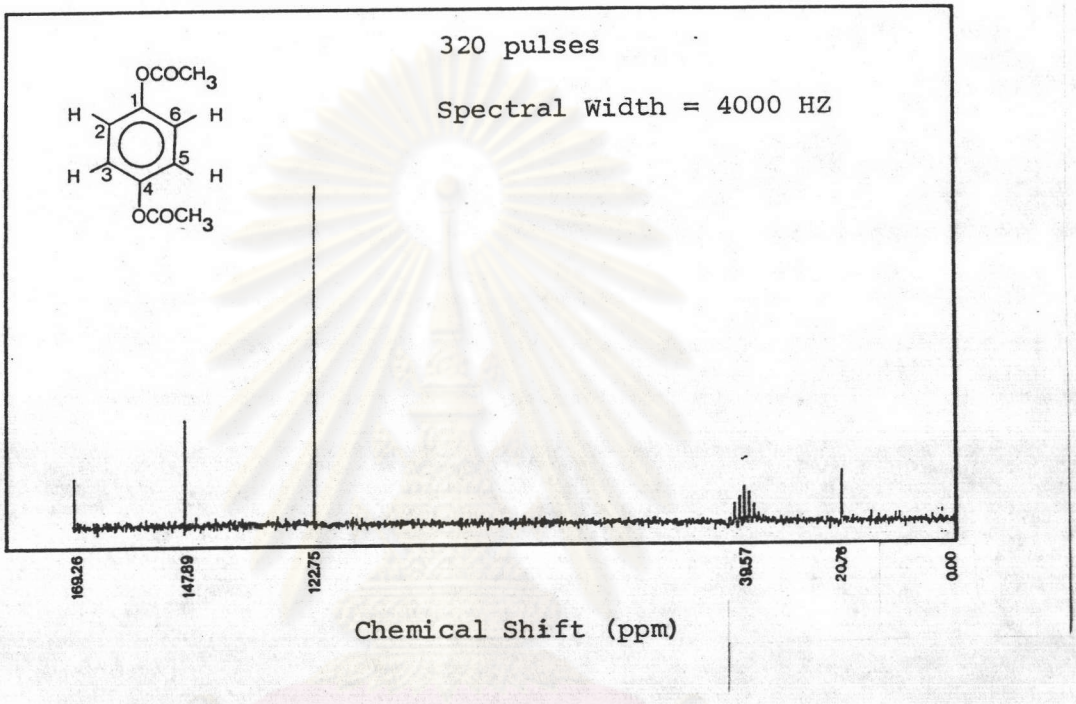


Assignment of the proton NMR signals of hydroquinone diacetate (DMSO-d_6 as solvent)

Table 3.10

Chemical Shift (ppm)	Multiplicity	Integration	Tentative Assignments
2.26	singlet	3	(A) methyl protons ($O-\overset{O}{\overset{\|}{C}}-CH_3$)
7.16	singlet	2	(B) aromatic protons
3.36	singlet		HOD as impurity in solvent

Fig. 3.18



Assignment of the carbon 13 NMR signals of hydroquinone diacetate (DMSO-d_6 as solvent)

Table 3.11

Chemical Shift (ppm)	Intensity Ratio	Tentative Assignments
20.76	1.0	2 x - CH_3
122.75	7.5	C_2,C_3,C_5,C_6
147.89	2.0	C_1,C_4
169.26	1.0	2 x C=O
39.57		DMSO-d_6 (multiplet)

Fig. 3.19 Assignment of the proton NMR signals of 2,5-dihydroxy acetophenone (DMSO-d_6 + $CDCl_3$ as solvent)

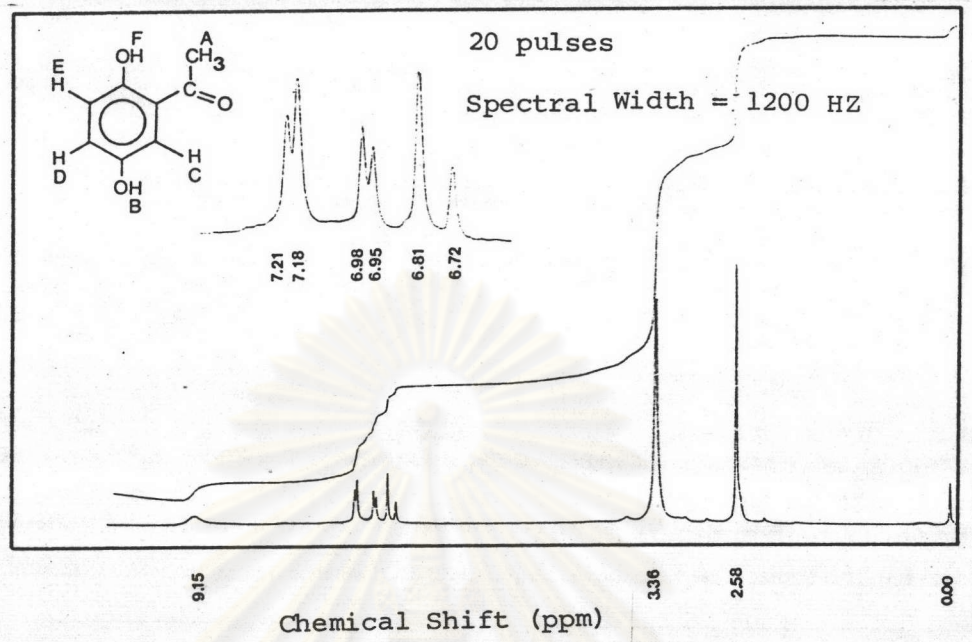
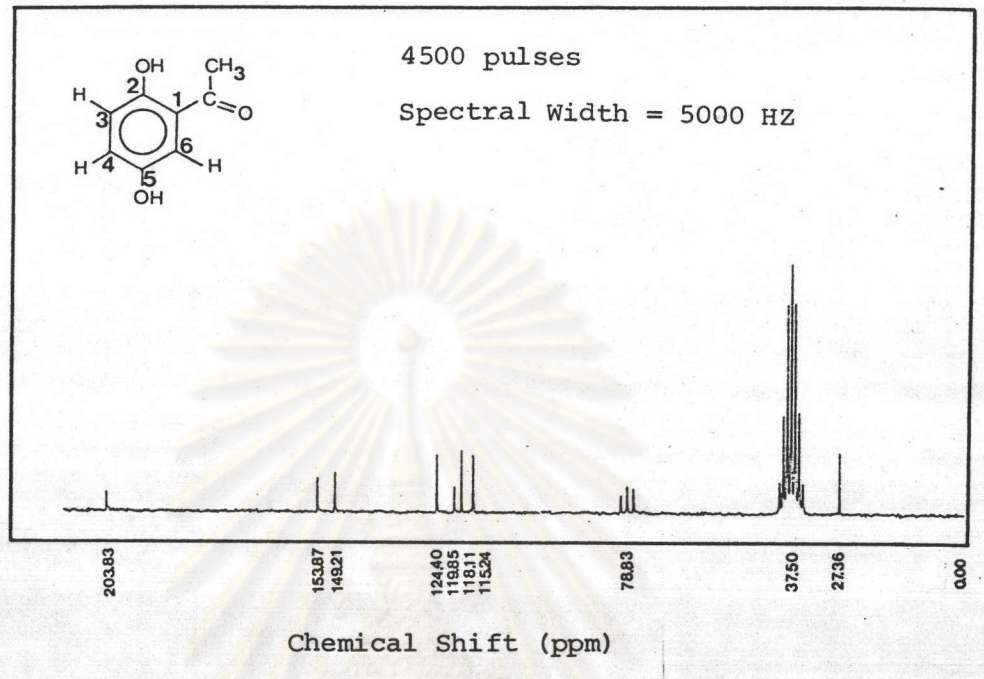


Table 3.12

Chemical Shift (ppm)	Multiplicity	Integration	Tentative Assignments
2.58	singlet	3	(A) methyl protons attached to the ketone group. (-C(=O)-CH_3)
6.72	singlet	1	(B) meta hydroxy proton of the ketone
6.81	singlet	1	(C) aromatic proton
6.95, 6.98 } 6.965	doublet with j = 0.03 ppm	1	(D) aromatic proton coupling with the vicinal proton (E)
7.18, 7.21 } 7.195	doublet with j = 0.03 ppm	1	(E) aromatic proton coupling with the vicinal proton (D)
9.15	broad line	1	(F) ortho hydroxy proton of the ketone with intramolecular hydrogen bonding
3.36	singlet		HOD as impurity in solvent

Fig. 3.20



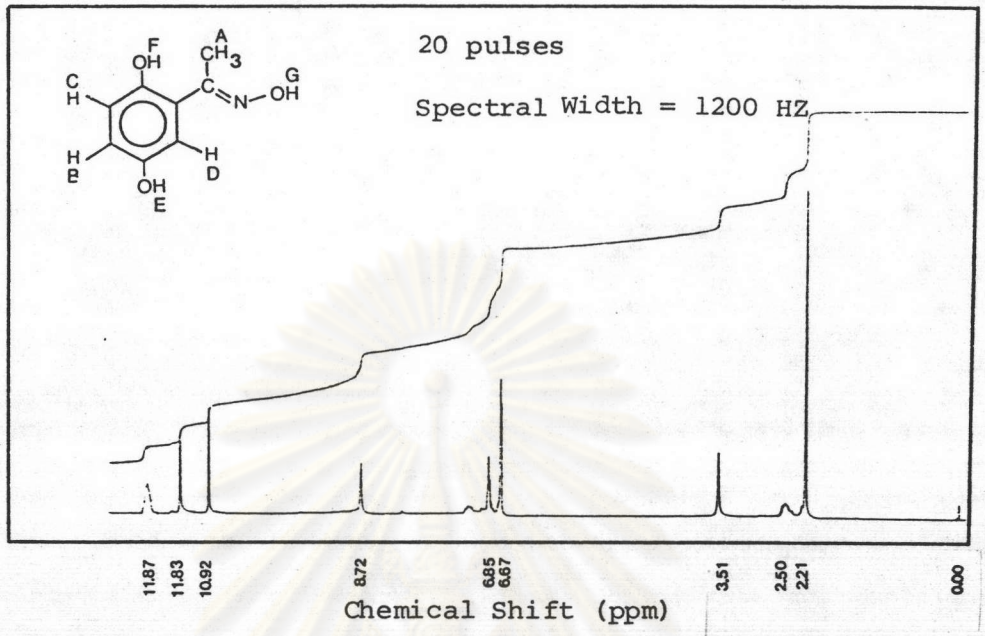
Chemical Shift (ppm)

Assignment of the carbon 13 NMR signals or 2,5-dihydroxy acetophenone (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.13

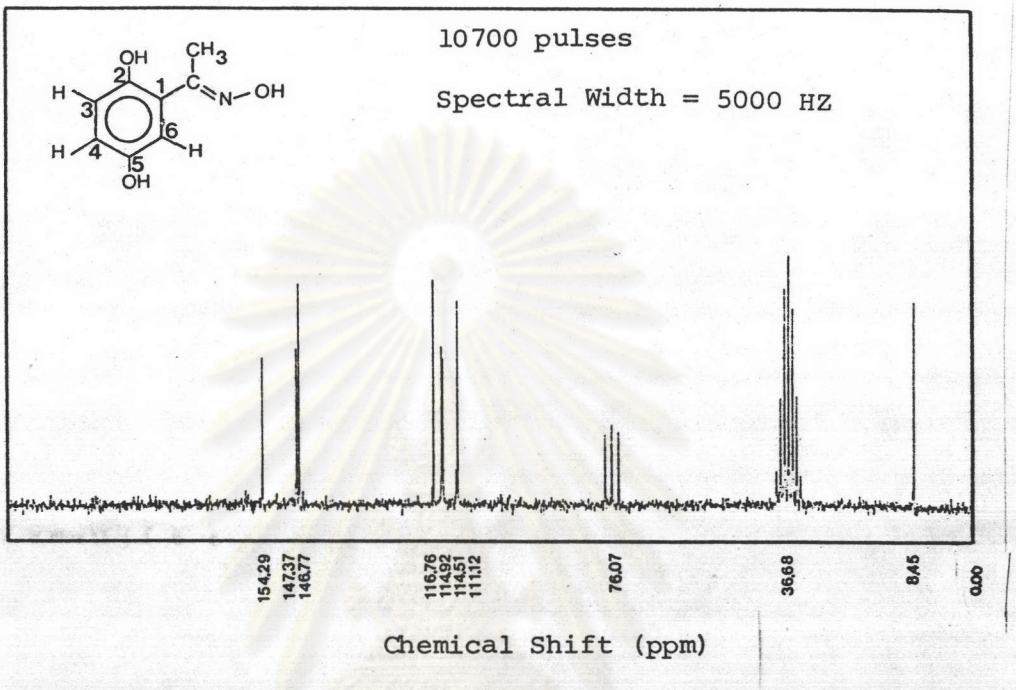
Chemical Shift (ppm)	Intensity Ratio	Tentative Assignments
27.36	3.2	$-CH_3$
115.24	3.0	C_1, C_3, C_4, C_6
118.11	3.2	
119.85	1.4	
124.40	3.0	
149.21	2.0	C_2, C_5
153.87	1.4	
203.83	1.0	$C=O$
37.50		DMSO-d_6 (multiplet)
78.83		$CDCl_3$ (triplet)

Fig. 3.21 Assignment of the proton NMR signal of 2,5-dihydroxy acetophenoxime (DMSO-d_6 + $CDCl_3$ as solvent)



Chemical Shift (ppm)	Multiplicity	Integration	Tentative Assignments
2.21	singlet	3	(A) methyl protons attached to the oxime group. $(-\overset{N-OH}{\overset{\|}{C}}-CH_3)$
6.67	approximate doublet	1	(B) aromatic proton coupling with the vicinal proton (C)
6.85	approximate doublet	1	(C) aromatic proton coupling with the vicinal proton (B)
8.72	singlet	1	(D) aromatic proton
10.92	singlet	1	(E) meta hydroxy proton of the aromatic oxime
11.33	singlet	1	(F) ortho hydroxy proton of the aromatic oxime
11.87	singlet (broad line)	1	(G) proton of the oxime group
2.50	broad line		DMSO
3.51	singlet		HOD as impurity in solvent

Fig. 3.22



Assignment of the carbon 13 NMR signals of 2,5-dihydroxy aceto-phenoxime (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.15

Chemical Shift (ppm)	Internsity Ratio	Tentative Assignments
8.45	1.4	- CH_3
111.12	1.4	C_1, C_3, C_4, C_6
114.51	1.0	
114.92	1.0	
116.92	1.5	
146.77	1.5	C_2, C_5
147.37	1.0	
154.29	1.0	C = N-OH
36.68		DMSO - d_6 (multiplet)
76.07		$CDCl_3$ (triplet)

Fig. 3.23 Assignment of the proton NMR signals of 4-chloro-2-methylphenyl acetate ester (DMSO-d_6 + $CDCl_3$ as solvent)

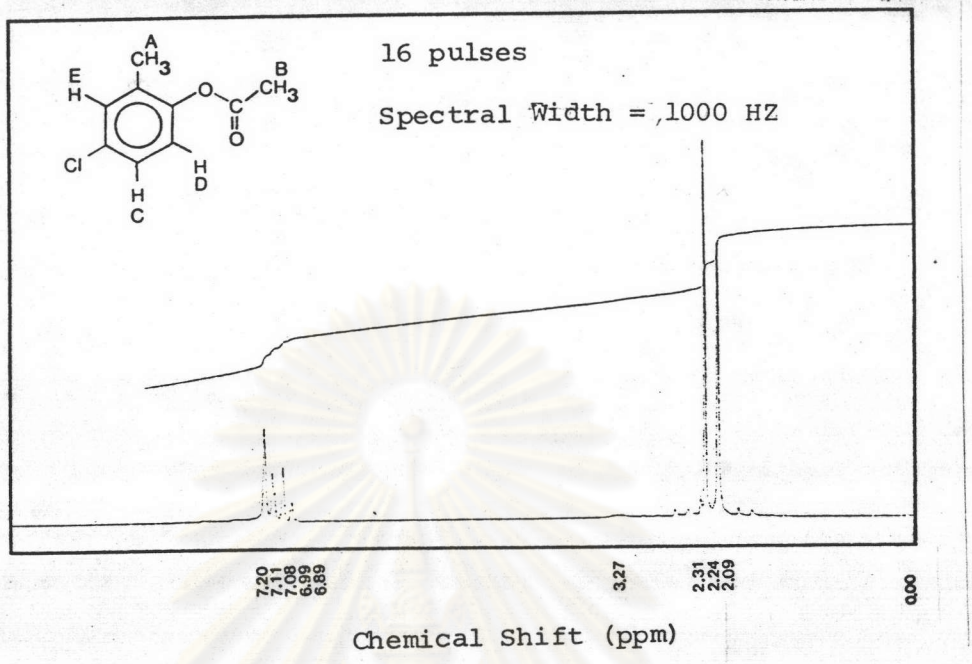
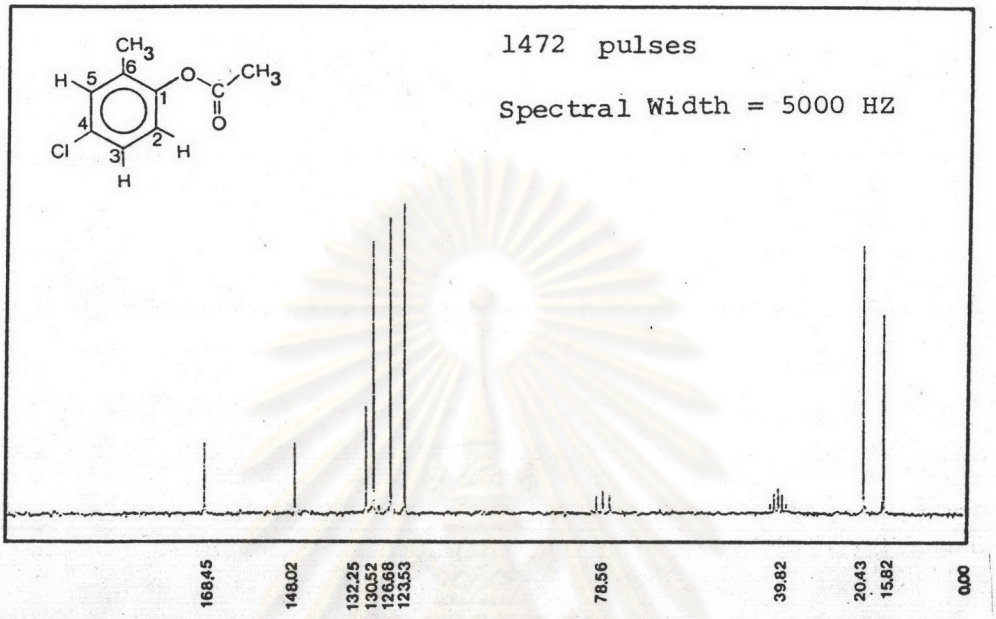


Table 3.16

Chemical Shift (ppm)	Multiplicity	Integration Ratio	Tentative Assignments
2.09	singlet	3	(A) methyl protons attached to the aromatic ring
2.24	singlet	3	(B) methyl protons attached to the ester group. ($O-\overset{O}{\overset{\|}{C}}-CH_3$)
6.89	approximate doublet	1	(C) aromatic proton coupling with the vicinal proton (D)
6.99	singlet	1	(E) aromatic proton
7.08, 7.11 } 7.095	doublet with j = 0.03 ppm	1	(D) aromatic proton coupling with the vicinal proton (C)
2.31	singlet		DMSO
3.27	broad line		HOD as impurity in solvent
7.20	singlet		$CHCl_3$ as impurity in solvent

Fig. 3.24

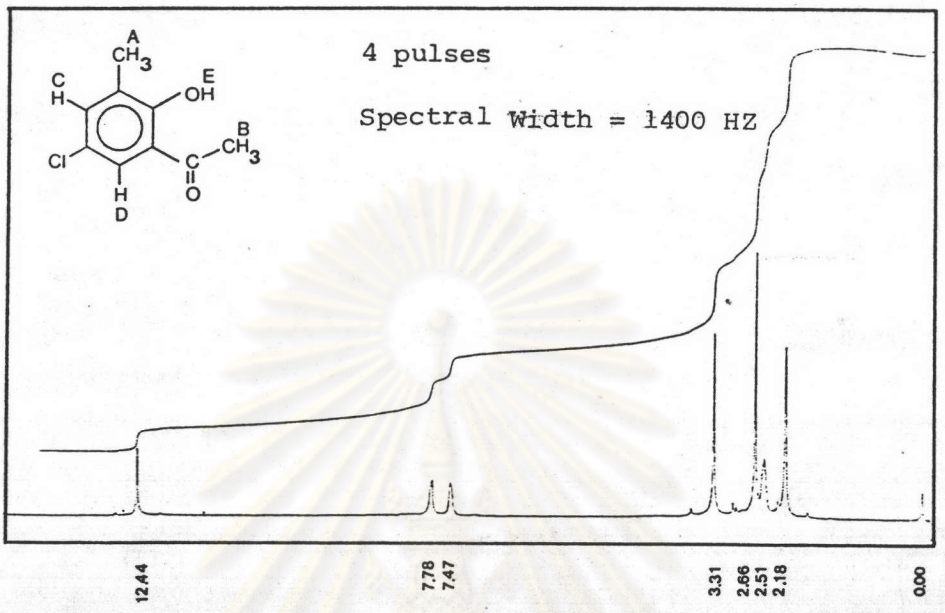


Assignment of the carbon 13 NMR signals of 4-chloro-2-methyl-phenyl acetate ester (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.17

Chemical Shift (ppm)	Intensity Ratio	Tentative Assignments
15.82	2.9	- CH_3
20.43	3.9	
123.53	4.6	C_1, C_3, C_4, C_6
126.68	4.4	
130.52	3.9	
132.25	1.5	C_2, C_5
148.02	1.0	
168.45	1.0	C = N-OH
39.82		DMSO-d_6 (multiplet)
78.56		$CDCl_3$ (triplet)

Fig. 3.25

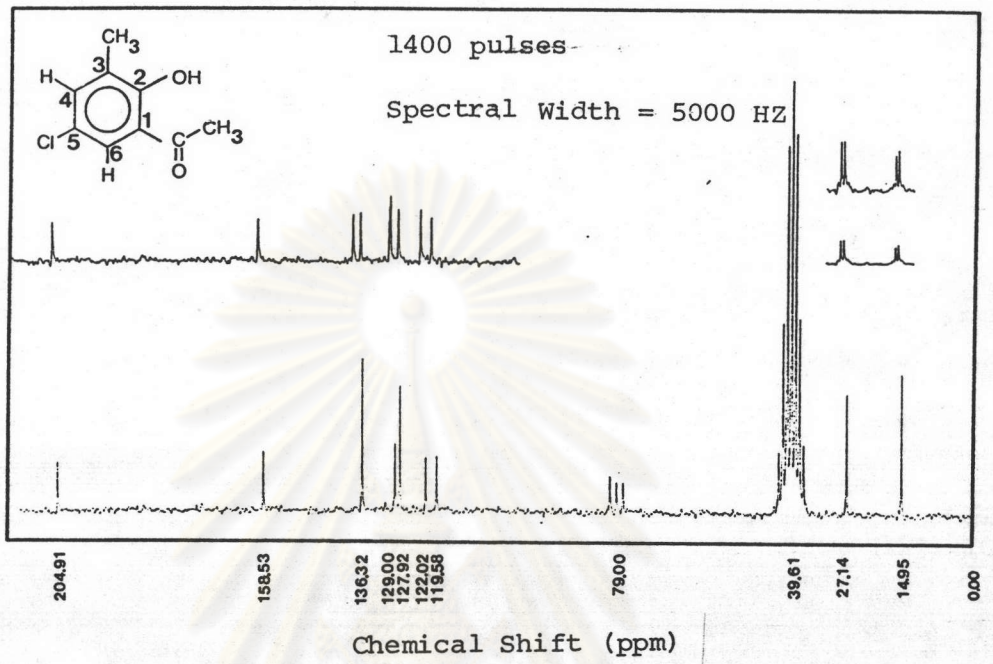


Assignment of the proton NMR signals of 5-chloro-2-hydroxy-3-methyl acetophenone (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.18

Chemical Shift (ppm)	Multiplicity	Integration Ratio	Tentative Assignments
2.18	singlet	3	(A) methyl protons attached to the aromatic ring
2.66	singlet	3	(B) methyl protons attached to the carbonyl group ($-\overset{O}{\overset{\|}{C}}-CH_3$)
7.47	singlet	1	(C) aromatic proton
7.78	singlet	1	(D) aromatic proton
12.24	singlet	1	(E) hydroxyl proton of the aromatic ring
2.51	singlet		DMSO
3.31	singlet		HOD as impurity in solvent

Fig. 3.26



Assignment of the carbon 13 NMR signals of 5-chloro-2-hydroxy-3-methyl acetophenone (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.19

Chemical Shift (ppm)	Intensity Ratio	Tentative Assignments
14.95	2.7	Ar - CH_3
27.14	2.3	$\underline{CH}_3$ - C=O
119.58	1.0	C_1, C_3, C_4, C_5, C_6
122.02	1.0	
127.92	2.4	
129.00	1.2	
136.32	2.8	
158.53	1.2	C_2
204.91	1.0	C=o
39.61		DMSO-d_6 (multiplet)
79.00		$CDCl_3$ (triplet)

Fig.3.23 Assignment of the proton NMR signals of 4-chloro-2-methylphenyl acetate ester (DMSO-d_6 + $CDCl_3$ as solvent)

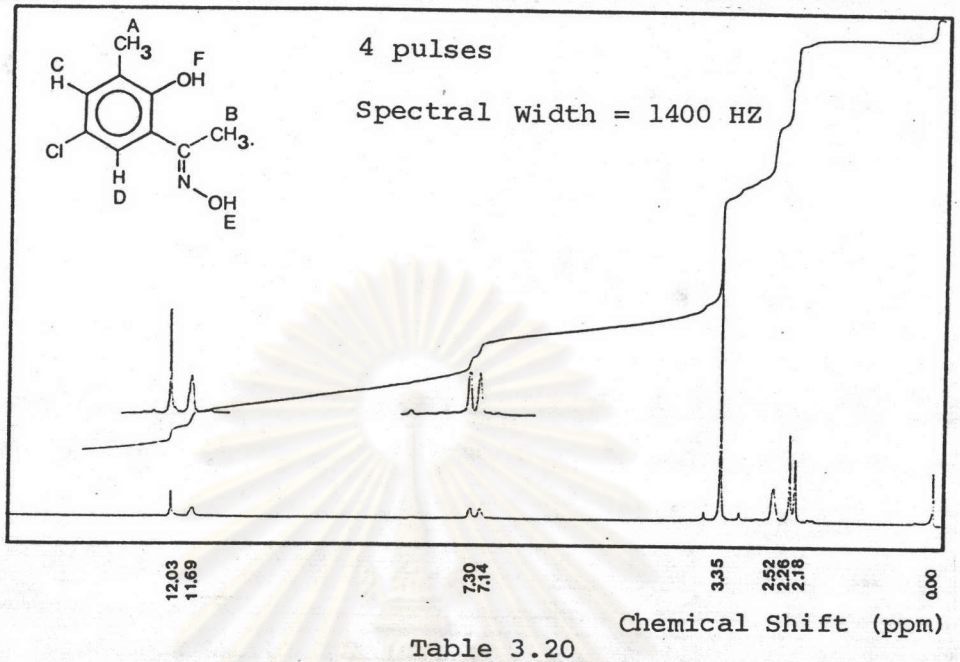
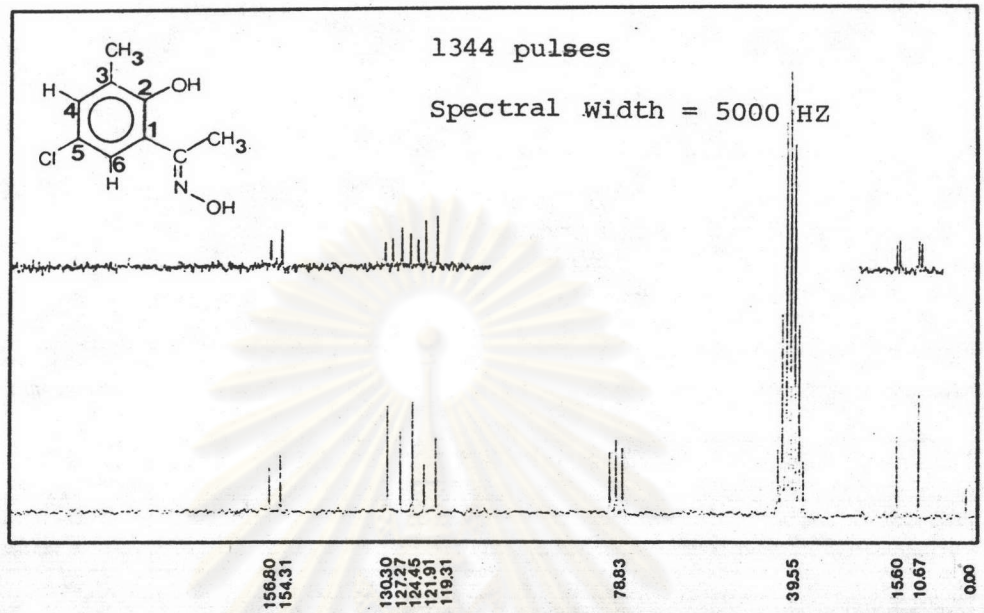


Table 3.20

Chemical Shift (ppm)	Multiplicity	Integration	Tentative Assignments
2.18	singlet	3	(A) methyl protons attached to the aromatic ring
2.26	singlet	3	(B) methyl protons attached to the oxime group. N-OH (-C-CH_3)
7.14	singlet	1	(C) aromatic proton
7.30	singlet	1	(D) aromatic proton
11.09	singlet (broad line)	1	(E) proton of the oxime group
12.03	singlet	1	(F) hydroxyl proton of the aromatic ring
2.52	singlet		DMSO
3.35	singlet		HOD as impurity in solvent

Fig. 3.28



Assignment of the carbon 13 NMR signals of 5-chloro-2-hydroxy-3-methyl acetophenoxime (DMSO-d_6 + $CDCl_3$ as solvent)

Table 3.21

Chemical Shift (ppm)	Intensity Ratio	Tentative Assignments
10.67	2.6	$\underline{C}H_3$- C = N-OH
15.60	1.7	Ar - CH_3
119.31	1.6	C_1, C_3, C_4, C_5, C_6
121.91	1.0	
124.45	2.3	
127.27	1.7	
130.30	2.2	
154.31	1.2	C_2, C = N-OH
156.80	1.0	
39.55		DMSO-d_6 (multiplet)
78.83		$CDCl_3$ (triplet)

3.2 Preliminary Studies of Metallochromic Property of 2,5-Dihydroxy Acetophenoxime and 5-Chloro-2-Hydroxy-3-Methyl Acetophenoxime

Reagents

1) The Oxime Solution. The two oximes (1.0×10^{-2}F) are slightly soluble in cold water. The oxime solution can be prepared by dissolving 1.67 g and 1.99 g of 2.5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime respectively in 1000 mL of ethanol (Analar, Merck, 99.8 %).

2) Metal Solutions. The stock metal ion solutions (1.0×10^{-2}F) were prepared by dissolving appropriate amounts of analytical grade of nitrate, chloride and sulfate salts of various metals.

3) EDTA Solution. The EDTA (1.0×10^{-2}F) was prepared by dissolving 0.372 g of ethylenediamine tetraacetic acid disodium salt in deionized water and dilute to 100 mL.

4) Solutions for pH Adjustment. Six solutions were prepared as followings:

Procedure

Preliminary studies of metallochromic property of the synthesis oximes were carried out at pH 2, 4, 7, 10, 11.5 and 12. Series of test tubes were required for blank, oxime alone, metal ion alone and metal ion with the oxime. All tested solutions were kept in 20 % v/v ethanol-water to prevent the precipitation of the oximes. The concentration of the oximes and metal ion in 5 mL of each tested solution was about 1×10^{-3} F. These tested solutions were pH controlled by adding 2-3 drops of suitable pH adjusting solutions listed in the Table 3.22 and tested again with pH paper (Whatman, BDH).

Table 3.22

pH	Solutions
2	2 F hydrochloric acid
4	acetate buffer : 25 mL of glacial acetic acid and 13.7 g of sodium acetate trihydrate are made up to 100 mL with deionized water.
7	20 % w/v sodium acetate trihydrate solution
10	ammonia-ammoniumchloride solution [7 g of NH_4Cl + 56.8 mL of NH_3 (sp.gr. = 0.880)] made up to 100 mL with deionized water
11.5	50 % v/v of ammonia solution (sp.gr. = 0.880) and deionized water
12	2 F sodium hydroxide solution

Colour change due to the complex formation of metal ions with the oximes were observed and compared with those of oxime alone and metal alone. The coloured or precipitated solutions were further tested with 3 to 5 drops of the EDTA solution.

Results

25 metal ions were studied with the two oximes as metallochromic reagents at various pH. The metal ions that showed no change after adding the reagent were :

Na (I), K (I), Ag (I),
Be (II), Mg (II), Ca (II), Zn (II), Sr (II), Zr (II), Mo (II),
Cd (II), In (II), Sn (II), Ba (II), W (II), Hg (II), Pb (II),
Bi (II), Cr (III) and Al (III)

whereas Mn (II), Co (II), Ni (II), Cu (II) and Fe (III) displayed some interesting colour development and coloured precipitates. These were investigated again at more specific pH values by the use of the pH adjusting solutions and the proper pH was tested by pH meter (pHM 83, Radiometer). The metallochromic properties of 2,5-dihydroxy acetaphenoxime (Reagent I) and 5-chloro-2-hydroxy-3-methyl acetophenoxime (Reagent II) with these metal ions are shown in Table 3.23 and 3.24 respectively.

Table 3.23

Reagent I + metal	Visual Observation	pH Range
reagent I alone	light yellow solution	9-12
Mn (II)	brown solution	7-10
Co (II)	brown solution	7-12
Ni (II)	green precipitate	7-9
Cu (II)	buff coloured precipitate	3-9
Fe (III)	dark coloured solution	3-6

Table 3.24

Reagent II + metal	Visual Observation	pH Range
reagent II alone	colourless solution	1-12
Mn (II)	brown solution	7-9
Co (II)	yellowish brown solution	6-12
Ni (III)	green precipitate	6-9
Cu (II)	buff coloured precipitate	3-9
Fe (III)	dark coloured solution	3-5

Only the complexes of the two oximes with Fe (III) showed colour change after adding EDTA from dark brown coloured to light yellow.

Many immiscible organic solvents ($CHCl_3$, CCl_4, C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, C_6H_{12} and petroleum ether) were used to extract Ni-oxime complexes. It was found that $CHCl_3$ showed the most visual intense colour.

3.3 Analytical Chloroform Extraction Spectrometric Studies of 2,5-Dihydroxy Acetophenoxime and 5-Chloro-2-Hydroxy-3-Methyl Acetophenoxime with Nickel II

In analytical chemistry, the solubilities of metal complex are of vital importance. The analytical selectivity of 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime arise from the low solubilities of their complexes with nickel and copper, whereas the corresponding complexes of all the other transition metals are quite soluble in 20 % (v/v) ethanol-water solution. It may be caused by the strong intramolecular hydrogen bonding of the -OH group in the planar Ni (II). Oxime complex makes it relatively difficult to co-ordinate water molecules and this can explain its readily extractability into chloroform. In the corresponding, but non-planar, cobalt (II) and Mn (II) complexes, the -OH group are avialable for bonding to solvent water or ethanol molecules, there by preventing extraction into chloroform.

Determination of nickel is of importance particularly in the fields of industrial metallurgy. Many spectrophotometric methods for nickel have been reported so far. Of these, the method based on extraction of nickel with dimethyl glyoxime was the most popular. The red nickel-dimethyl glyoxime complex (pH 7-12, λ_{max} = 366 nm, 465-470 nm) is only slightly soluble in chloroform leading to small sensitivity of the method. In the former study of 5-chloro-2-hydroxy-4-methyl acetophenoxime (pH 8, λ_{max} = 580 nm) gave more selective results but its sensitivity still was not satisfactory. In this work 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl aceto-phenoxime were examined as spectrometric reagents for determination

of nickel by chloroform extraction spectrophotometric method.

Apparatus

Visible spectra were recorded with a UV-240 Shimadzu UV-Visible Spectrophotometer with 10 mm-matched quartz cells and pHM 83 Radiometer pH meter were used for pH measurements.

Reagents

1) Water Deionized water was used for all solutions

2) Stock solutions of the oximes. The solutions of 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime (1.0×10^{-2} F) were prepared by dissolving 0.1672 g and 0.1996 g respectively in 100 mL of ethonal, 1.0×10^{-3} F and 0.5×10^{-3} F of oximes were prepared by further dilution of the 1.00×10^{-2} F solution.

3) Standard nickel solutions. The 1.00×10^{-2} F standard solution of Ni (II) solution was prepared by dissolving 0.1454 g of nickel nitrate hexahydrate in water, 1 mL of concentrated hydrochloric acid was also added to prevent hydrolysis and the content was diluted to 50 mL with water. A 1.00×10^{-3} F of Ni (II) solution was prepared by further dilution of the 1.00×10^{-2} F solution .

4) pH adjustment solution A 1.0×10^{-2} F hydrochloric acid and (or) a 1.0×10^{-2} F ammonia solution were employed for pH adjustment of the solutions.

3.3.1 Visible spectra of the chloroform extracted 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime at various pH

Procedure Twelve 2.0 mL-aliquots of 1.0 x 10^{-2}F ethanolic oxime solution were pipetted into a series of 20 mL mixer cylinders (Lidex).The pH of the solutions were adjusted to the desired value (1.0 - 12.0) by pH adjusting solutions suitable amount of water were added. The pH of the solutions were measured by a pH meter. The solutions were then made up to the mark of 10 mL with water. 10.0 mL pf chlorofrom (Analar, BDH) were pipetted into the solution. The cylinders were fitted with pistons which moved back and forth for 20 cycles. After leaving until the two layer completely separated, the chloroform layer was transfered for the spectra study at the wavelength of 400 nm to 800 nm using chloroform as reference. The gain of the spectrophotometer was set at -0.1 to 0.1, the slit width was 2.0 nm.

The absorption spectra of 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime at various pH are shown in Fig. 3.29 and Fig. 3.30 respectively. It was found that the extracted oxime in chloroform layer showed no significant absorption in visible range. The visible absorptions of the two oxime were studied again at the same pH range of the complex formations. The gain of the spectrometer was set at 0-0.1 with the same slit width. The absorption spectra of the two oximes at that pH range are shown in Fig. 3.32 and Fig. 3.34

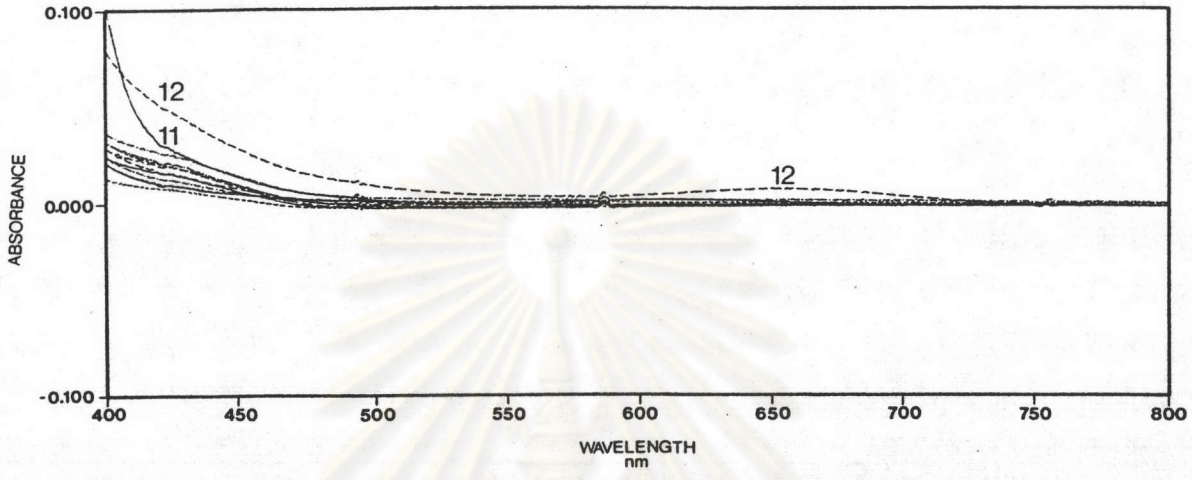


Fig. 3.29

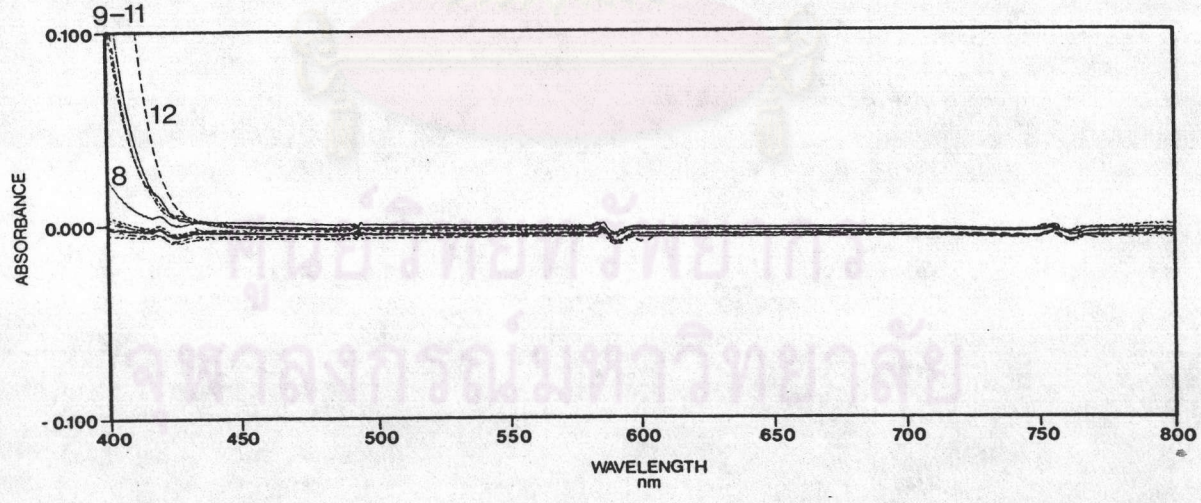


Fig. 3.30

3.3.2 Visible spectra of the chloroform extracts of 2,5-dihydroxy acetophenoxime nickel (II) complex and of 5-chloro-2-hydroxy-3-methyl acetophenoxime nickel (II) complex at various pH

Procedure Nine 0.5 mL aliquots of 1.0×10^{-2}F nickel (II) solution were pipetted into a series of 20 mL mixer cylinders containing exact 2.0 mL each of 1.0×10^{-2}F oxime solution. The pH of the solutions were adjusted to the desired pH (5.5 to 9.5 with the interval of 0.5) by using the pH adjusting solution. Suitable amount of water was added. The pH of the solution was measured by a pH meter. The pH probe was washed throughly with deionized water into the solution which was then made the volume to 10 mL. The solutions were left to stand for a peroid of 10 minutes to complete the complex formation. The green precipite was extracted with exact 10.0 mL of chloroform. The green chloroform layer was used for the spectra study at the wavelength of 530 - 700 nm using reagent blank treated in a similar manner as a reference. The gain of the spectrophotometer was set at 0-0.1, and the slit width was 2.0 nm. The absorption spectra of Ni (II)-2,5-dihydroxyacetophenoxime complex and Ni (II)-5-chlors-2-hydroxy-3-methyl acetophenoxime are shown in Fig. 3.31 and Fig. 3.33 respectively in comparisoin with those of the reagent blank as in Fig 3.32 and Fig. 3.34.

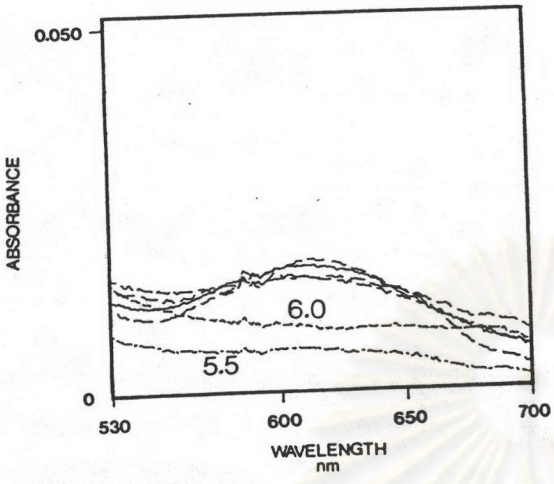


Fig. 3.31

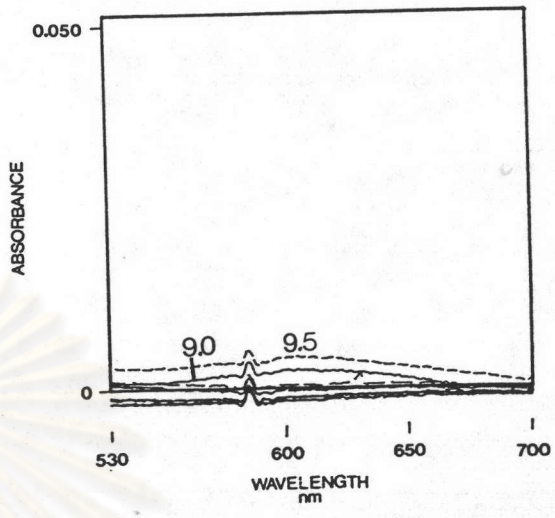


Fig. 3.32

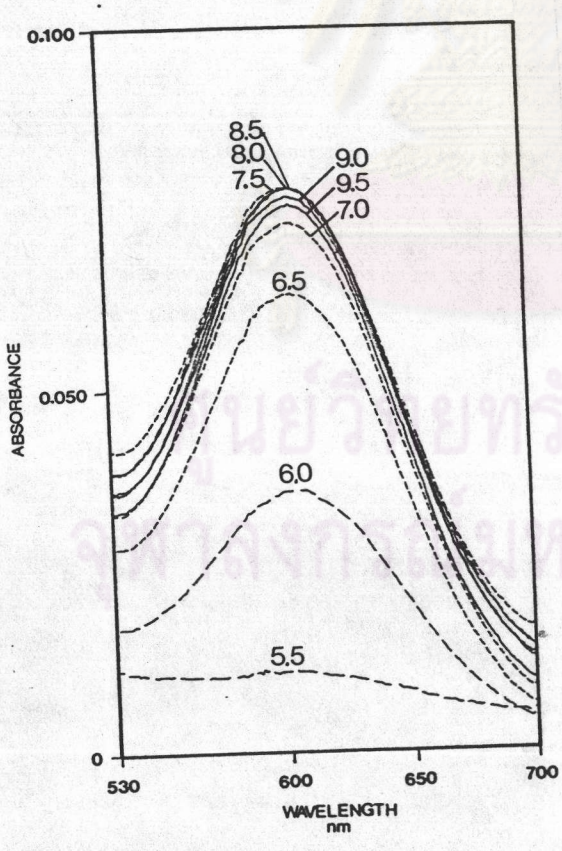


Fig. 3.33

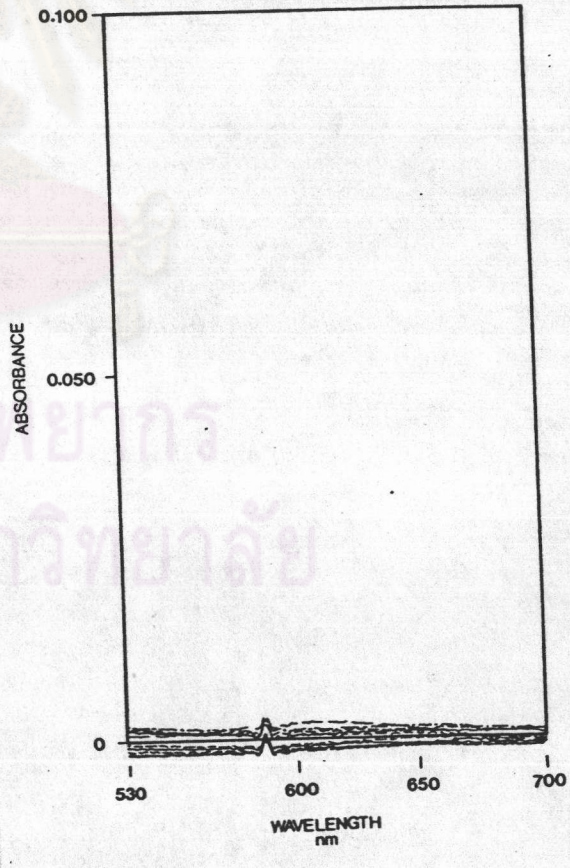


Fig. 3.34

3.3.3 Chloroform extraction spectrophotometric determination of nickel using 5-chloro-2-hydroxy-3-methyl acetophenoxime as spectrometric reagents.

Apparatus

The absorptions were measured with a Hitachi model 220 A spectrophotometer and a Shimadzu UV-240 recording spectrophotometer in a 10-mm quartz cell. A pHM 83 Radiometer pH meter, and the Lidex solvent extraction system were employed.

Reagents

1) Stock solutions of 5-chloro-2-hycroxy-3-methyl acetophenoximes (as described previously)

2) Standard nickel solutions (as described previously)

3) pH adjusting solutions (as described previously)

4) Diverse ion solutions. The solutions of diverse ions, 0.10 F, were prepared from most analytical grade and some laboratory grade of various ionic salts. Sodium or potassium salts were preferably employed in the case of anions while nitrate or chloride salts were used in the case of cations. The further dilutions of these solutions were made when required.

Procedure The optimal conditions of the chloroform extraction spectrophotometric determination of Ni by using 5-chloro-2-hydroxy-3-methyl acetophenoxime as complexing reagent were studied. They were carefully studied and established in order to obtain the highest sensitivity of the method. The experimental variables of the condition were carried out in the order of selected wavelenght, suitable pH, optimal amount of oxime added, sequence of reagent addition, waiting time, shaking time and standing time.

Selected Wavelength As shown in Fig. 3.33, the green complex of Ni and 5-chloro-2-hydroxy-3-methyl acetophenoxime displayed the absoption band with the highest sensitive wavelenght of 607.0 nm at pH range 6.0 - 9.5. Since the absorbance of the reagent blank at the same pH range were nearly kept on the base line. In this work, the absorption measurement was therefore carried out at wavelenght 607.0 nm.

Suitable pH The effects of pH on the complex formation and extraction were emamined. Series of the complex solutions were prepared in the same manner as the previous experiment. They were extracted with several portions of 10.0 mL choloroform. The obsorbances of the chloroform layers were measured at 607.0 nm against the reagent blank. The results obtained are shown in Table 3.25 and the coures-ponding plot appears in Fig. 3.35. The maximum and constant absorbances were obtained in a range of pH 7.3 - 9.0. Therefore, a pH of 8.0 was selected for all subsequent studies.

Table 3.25

pH	Absorbance at 607.0 nm.
5.5	0.011
6.0	0.037
6.5	0.063
7.0	0.071
7.5	0.076
8.0	0.077
8.5	0.077
9.0	0.075
9.5	0.073

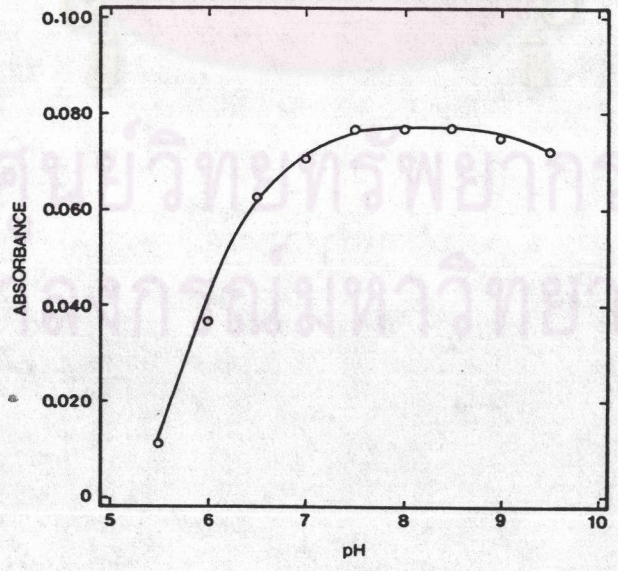


Fig. 3.35

Optimal Amount of Added Oxime The effect of the concentration of the added oxime was examined by adding various volume of 1.0×10^{-2}F (or 1.0×10^{-3}F if required) from 0.25 - 2.0 mL. A series of solutions containing 2.50×10^{-6} mole (0.14 mg) of Ni (II) were added with various amount of the oxime solution. The pH of each solution was adjusted to 8.0 ± 0.5 by addition of pH adjusting solution(s). The precipitate in the aqueous solution was extracted into 10 mL of chloroform. The absorbance of each solution was measured at 607.0 nm against the reagent blank using 10 mm quartz cells. The result appearing in Fig.3.36 shows the plot of absorbance of each solution against the added amount of the reagent. The maximum and constant absorbances were obtained above 0.5 mL of the oxime solution. Since the absorbance of the solution did not increase on addition of an excess volume of the oxime solution, 2.0 mL of 1.0×10^{-2}F. of the oxime solution was adopted throughout this experiment.

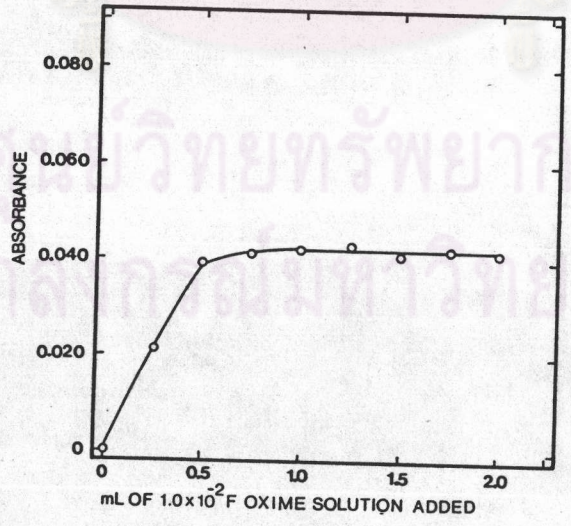


Fig. 3.36

Sequence of Reagent Addition The effect of sequence of reagent addition of all solutions used in the Ni-Oxime complex formation was studied. It is shown in Table 3.26 that the absorbance is constant in any sequency of addition. The subsequent experiments were performed in accordance with the chosen sequence No 1 Or No 5

Table 3.26

No.	Sequence of Addition	Absorbance at 607.0 nm
1.	metal, oxime, pH adjusting solution, diluting water.	0.040
2.	metal, pH adjusting solution, oxime, diluting water.	0.038
3.	metal, water, pH adjusting solution, oxime, diluting water	0.038
4.	oxime, pH adjusting solution, metal, diluting water.	0.040
5.	oxime, metal, pH adjusting solutions, diluting water.	0.040
6.	oxime, water, metal, pH adjusting solution, diluting water.	0.041

Waiting Time. The effect of waiting time for the complete complex formation of Ni (II) with the oxime was examined. The waiting time after vigorus stirring of the contents was obtained by measuring the absorbances of a series of the chloroform extracted complex solutions prepared in the same manner as previous experiment after the specified period of waiting. Result obtaining in Table 3.27 shows that the absorbance remained constant on waiting for more than 5 minutes. For the subsequent experiments, 10 minutes was therefore chosen for maximum complex formation.

Table 3.27

Period	Absorbance (at λ = 670 nm)
2 mins	0.021
4 mins	0.034
6 mins	0.039
8 mins	0.039
10 mins	0.040
20 mins	0.041
30 mins	0.041
1 hour	0.039
2 hours	0.040
1 day	0.042

Shaking Time The effect of shaking time on extraction of the complex with the immiscible chloroform was studied. The effective 20 mL Lidex solvent extraction system was used. To obtain the ultimate surface contact of two liquids, it is claimed that only one cycle of piston movement is equal to shaking in a separatory funnel 40 times. The optimum numbers of shaking cycle were determined. It is shown in Table 3.28 and Fig. 3.37. The constant and maximum absorbances were obtained above 10 cycles. Practically 20 cycles of shaking process was employed through out this work.

Table 3.28

Numbers of Shaking Cycle	Absorbance (at λ = 670 nm)
0	0.012
2	0.028
4	0.034
6	0.038
8	0.038
10	0.039
15	0.040
20	0.040
25	0.040
30	0.041

The recovery of Ni in the extraction process was determined by testing the amount of Ni (II) left in aqueous solution after being extracted into chloroform layer in the form of Ni-oxime complex. The left Ni (II) amount was compared with that of initial concentration of Ni (II) before extraction. This was determined by the method of atomic absorption spectrometry (using Shimadzu model AA 650 Atomic Absorption Spectrometer). Standard 20 % v/v ethanol-water 0.1-15.0 ppm Ni (II) solutions were prepared for a calibration curve. A series of aqueous layers of the various initial concentration of Ni (II) (2-40.0 ppm) was also prepared, these solutions were added with the excess amount of oxime to complete the complex formation, and then extrated with the portion of chloroform. The absorbances of these aqueous layer were measured at 607.0 nm. The concentration of Ni (II) left in the solution was then determined by the calibration method. The result is shown in Table 3.29 giving the reeovery in the range 99.7 - 100 %.

Table 3.29

Initial Ni Concentration	Left Ni Concentration	% Recovery
2 - 24 ppm	-	100.0
25 - 36 ppm	0.05 ppm	99.8 - 99.9
37 - 40 ppm	0.10 ppm	99.7 - 99.9

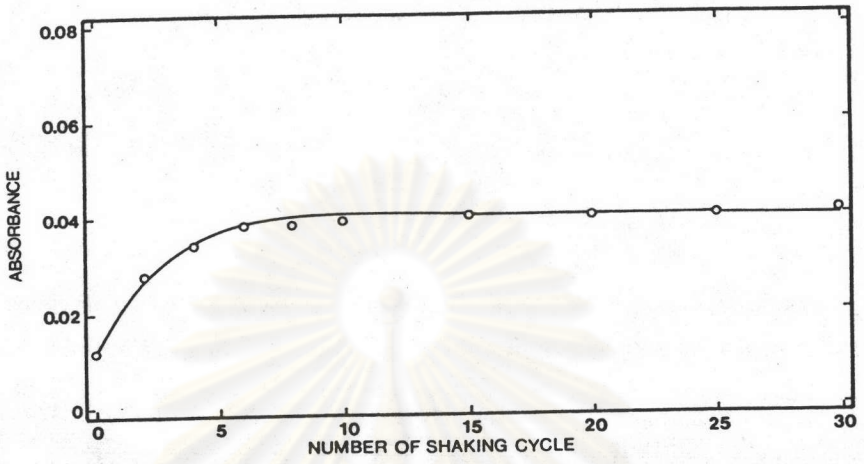


Fig. 3.37

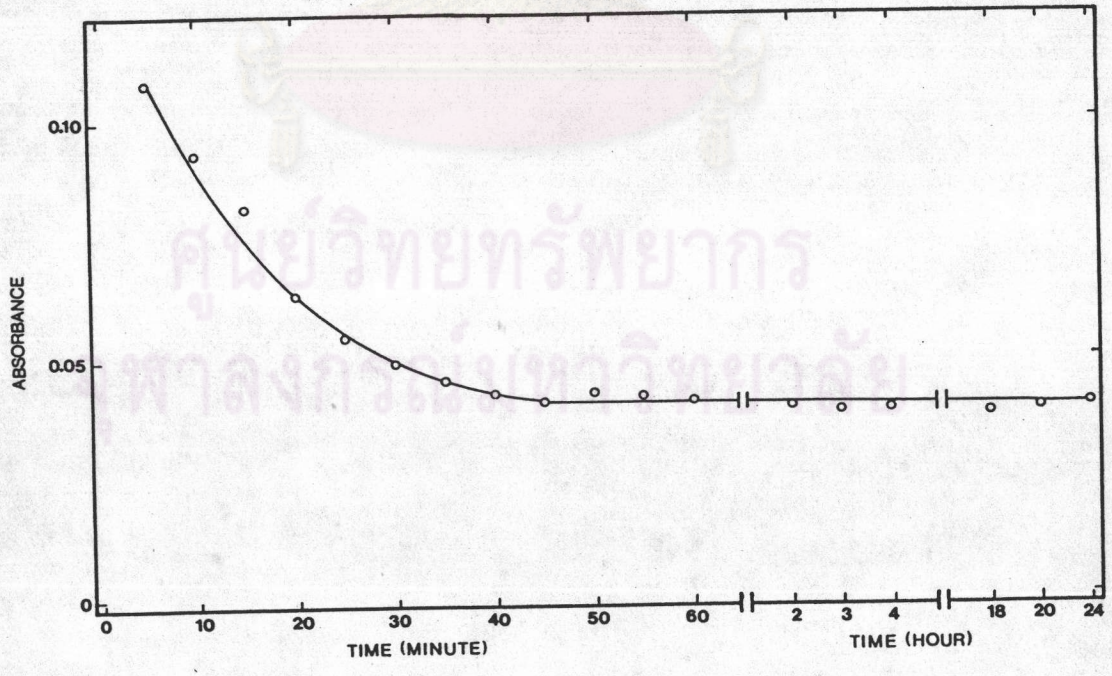


Fig. 3.38

Standing Time Standing time after shaking process was also studied. After set aside for a certain period of time, the chloroform layer was gradually separated from the aqueous one. The measurement of the absorbance should be performed after the complete separation of the two layers to avoid the light scattering from any immiscible droplets causing the decrease of transmittance. The absorbance of the chloroform extracted complex solutions were measured periodically at a specific time intervals after finishing the shaking process. Results are shown in Fig 3.38 and Table 3.30 the obtained result indicates that approximately 40 minutes is required for complete separation and the complex gives constant absorbance for at least 24 hours.

Table 3.30

Period	Absorbance (at 607.0 nm)	Period	Absorbance (at 607.0 nm)
5 mins	0.108	55 mins	0.042
10 mins	0.093	60 mins	0.041
15 mins	0.082	2 hours	0.040
20 mins	0.062	3 hours	0.039
25 mins	0.055	4 hours	0.039
30 mins	0.049	18 hours	0.038
35 mins	0.045	20 hours	0.039
40 mins	0.043	24 hours	0.040
45 mins	0.041		
50 mins	0.043		

Calibration Curve The calibration curve of the Ni (II)-5-chloro-2-hydroxy-3-methyl acitophenoxime complex was obtained by standard procedure. 0-4.0 mL of 100 ppm (1.7×10^{-3}F) standard solution of Ni(II)prepared from the 10 fold dilution of standard 1000 ppm Ni (II) (for AAS, BDH) were pipetted into a series of 20 mL mixer cylinders, containing 2.0 mL each of 1.0×10^{-2}F oxime solution. The pH of the solution were adjusted to 8.0 $\pm$ 0.5 by using a pH adjusting solution. Suitable amount of water was added. The pH of the solution was measured by the pH meter. The pH probe was washed throughly with water into the solution which was then made to the final volume of 10 mL. The solution was let to stand for 10 minutes. The green precipitate was extrated with the exact amount of chloroform (10.0 mL) with the movement of the fitted pistons for at least 10 cycles. The extracted contents were let to stand for an hour **for** complete separation. The absorbances of the chloroform layers in 1.0 cm quartz cell were subsequently measured at 607.0 nm using the reagent blank as reference. The obtained result is shown in Table 3.31 and Fig. 3.39. The calibration curve is linear in a range of 0-20 ppm of Ni (II). The molar absorptivity calculated from the slope is 1.60×10^{2} L $mol^{-1}cm^{-1}$ which was equivalent to the specific absorptivity of 2.73×10^{-3} mL g^{-1} and the sandell sensitivity of 0.3663 $\mu g\ cm^{-1}$. Reproducibility of the method was investigated by the mean absorbance for ten measurements at 12.0 ppm of Ni (II) was 0.040, the relative standard diviation being 2.5 % (= $\pm$ 0.001)

Calibration curve of Ni -5-chloro-2-hydroxy-3-methyl aceto-phenoxime complex. (0-40 ppm)

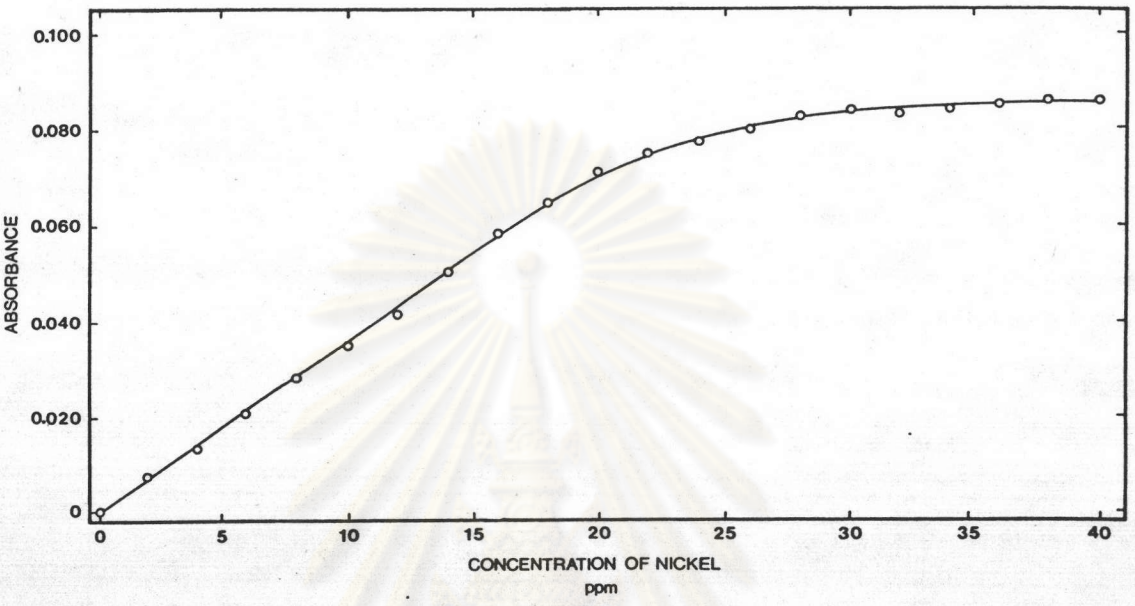
Reagent. - 0.2 mL - 4.0 mL of 100 ppm Ni^{2+} Std solution

- 2.0 mL of the reagent (2.0×10^{-5} mole)

Table 3.31

mL of the Ni^{2+} 100 ppm.	Conc. in ppm.	Absorbance
0.0	0.0	0.0002
0.2	2	0.0072
0.4	4	0.0132
0.6	6	0.0205
0.8	8	0.0276
1.0	10	0.0352
1.2	12	0.0415
1.4	14	0.0509
1.6	16	0.0587
1.8	18	0.0646
2.0	20	0.0716
2.2	22	0.0747
2.4	24	0.0773
2.6	26	0.0798
2.8	28	0.0828
3.0	30	0.0837
3.2	32	0.0830
3.4	34	0.0841
3.6	36	0.0848
3.8	38	0.0856
4.0	30	0.0853

Fig. 3.39



It was found that at the concentration of Ni (II) above 25 ppm, the green chloroform layers were not clear and some insoluble matters were observed. The absorbances of these turbid chloroform were obtained by masuring the filtrate (using Whatman paper No. 41). The solubility of the complex was calculated at this concentration of Ni to be 0.1950 g/L.

Effect of Coexisting Ions The effect of coexisting ions was examined at 12.0 ppm of Ni (II) concentration. 22 ionic salts and EDTA were individually present in various amount by adding their previously prepared 0.10 F, 1.0 x 10^{-2}F, or 1.0 x 10^{-3}F solutions for the molar ratio of the ions to Ni (II) being 200:1, 100:1, 50:1, 20:1, 10:1 and 1:1. The absorbances of the solutions were measured at 607.0 nm against a reagent blank using 1.0 cm quartz cells. Results are shown in Table 3.32. The absorbance of Ni alone(12.0 ppm)was 0.0400.

Table 3.32

present salts.	Absorbance at 607 nm of Ni (II) : salt					
	1:1	1:10	1:20	1:50	1:100	1:200
Ni alone	0.0400	0.0400	0.0400	0.0400	0.0400	0.0400
EDTA	0.0042	0.0043	0.0043	0.0041	0.0043	0.0049
NaCl	0.0418	0.0425	0.0400	0.0392	0.0409	0.0406
NH_4Cl	0.0403	0.0388	0.0381	0.0396	0.0410	0.0416
$MgCl_2$	0.0397	0.0395	0.0394	0.0398	0.0400	0.0406
$SrCl_2$	0.0405	0.0389	0.0392	0.0386	0.0392	0.0282
$CoCl_2$	0.0509,	0.1644	0.1753	0.1848	0.1832	0.1857
$CuCl_2$	0.0196	0.0084	0.0058	0.0060	0.0057	0.0063
$ZnCl_2$	0.0402	0.0250	0.0171	0.0118	-	-
$MnCl_2$	0.0399	0.0396	0.0385	0.0373	0.0395	0.4127
$Fe(NO_3)_3$	0.0417	0.0331	0.0011	-	-	-
$AgNO_3$	0.0432	0.0401	0.0426	0.0412	0.0375	0.0256
$Ba(NO_3)_2$	0.0422	0.0417	0.0394	0.0395	0.0379	0.0365
$Pb(NO_3)_2$	0.0406	0.0419	0.0397	0.0373	0.0402	0.0391
K_2SO_4	0.0418	0.0400	0.0407	0.0410	0.0415	0.0387
$AlK(SO_4)_2$	0.0313	0.0265	0.0131	0.0116	0.0072	0.0084
K_2CO_3	0.0394	0.0391	0.0393	0.0397	0.0383	0.0340
KI	0.0384	0.0417	0.0399	0.0394	0.0404	0.0224
$K_2C_2O_4$	0.0162	0.0133	0.0101	0.0091	0.0038	0.0018
K_2HPO_4	0.0381	0.0390	0.0382	0.0387	0.0374	0.0360
$NaOOCCH_3$	0.0413	0.0412	0.0397	0.0404	0.0421	0.0392
Na_2MoO_4	0.0399	0.0390	0.0379	0.0359	0.0316	0.0232
Na_2WO_4	0.0410	0.0393	0.0365	0.0347	0.0288	0.0266
NH_4Br	0.0420	0.0395	0.0377	0.0313	0.0242	0.0221

Remark Cu (II) showed coprecipitate with the reagent at this pH. The buff coloured precipitate could be extracted into chloroform and stayed as colloidal matter. The absorbances of the chloroform extracts were obtained by measuring the filtrates (using Whatmen paper No. 41).

It can be concluded from Table 3.32 based on the diviation ± 5.0 % from Ni (II) alone absorbance as Table 3.33.

Table 3.33

Cations	Anions	Tolerable amount (folds of Ni (II))
Na^+, K^+, NH_4^+, Mg^{2+} Pb^{2+}	Cl^-, NO_3^-, SO_4^{2-} $CH_3\ COO^-$	200
Sr^{2+}, Mn^{2+}	CO_3^{2-}, I^-	100
Ag^+, Ba^{2+}	PO_4^{3-}	50
-	MoO_4^{2-}, WO_4^{2-}, Br^-	10
Zn^{2+}, Fe^{3+}		1
Co^{2+}, Cu^{2+}, Al^{3+}	EDTA, $C_2O_4^{2-}$	seriously interfere

Determination of Ni (II) in the Presence of Cu (II) by Using 5-Chloro-2-Hydroxy-3-Methyl Acetophenoxime as Complexometric Reagent

As described previously, Cu (II) as the coexisting ions usually present in many Ni-determined samples can interfere seriously in the chloroform extraction spectrophotometric determination of Ni by using 5-chloro-2-hydroxy-3-methyl acetophenoxime. Since Cu (II) forms buff coloured complex with the oxime at pH 8 as the coprecipitate and is also extracted into chloroform, the absorbances of the Ni-determined solution can not be measured. As shown in Table 3.32, it is obviously seen that Cu (II) and Ni (II) competitively react with the oxime with K_f (complex formation constant) of Cu-oxime higher than that of Ni-Oxime. The chloroform extracted Cu-oxime complex were in the form of low soluble colloidal matter which caused the turbid chloroform. Fortunately, the coexisting Cu (II) could be eliminated by prior precipition with the excess oxime at the pH higher than 4 and filtering out the precipitate. After that, the solution was adjusted to pH 8 for precipitating Ni-Oxime complex which was readily extracted into chloroform without interference form Cu (II). On this experiment, the aqueous mixture of 1:1 Cu (II) and Ni (II) (each of 12.0 ppm) were prepared for Ni determination. The method of Ni determination is described as follows.

Reagents

1) Stock 1.0×10^{-2}F solution of 5-chloro-2-hydroxy-3-methyl acetophenoxime (as described previously)

2) Standard 100 ppm Ni (II) solution prepared from 10 fold dilution of standard 1000 ppm (1.70×10^{-3}F) Ni (II) solution (for AAS, BDH)

3) Standard 100 ppm. Cu (II) solution prepared from 10 fold dilution of standard 1000 ppm (1.57×10^{-3}F) Cu (II) solution (for AAS, BDH)

4) pH adjusting solutions (as described previously)

Procedure :

A 6.0 mL of 100 ppm Ni (II) (1.02×10^{-5} mole) and a 6.0 mL of 100 ppm Cu (II) (9.42×10^{-6} mole) were pipetted into a 50 mL beaker containing 5.0 mL of 1.0×10^{-2}F oxime solution (5.0×10^{-5} mole). The pH of the solution was adjusted to 4.0 ($\pm$ 0.5) with the suitable pH adjusting solution. The pH of the solution was measured by a pH meter. The pH probe was washed throughly with water into the solution. Buff coloured precipitate of Cu-oxime complex was formed in the vigorously stirred solution. After standing for a peroid of 15 minutes to complete the reaction, the precipitate was filtered with Whatman paper No, 41 and washed throughly with water. The filtrate was quantitatively transferred into a 25 mL volumetric flask. Small amount of water was added to the mark. The freshly prepared solution (5.0 mL) was pipetted into a 20 mL mixer cylinder containing accurate 2.0 mL of 1.0×10^{-2}F oxime solution. The pH of the content was adjusted to 8.0 ($\pm$ 0.5) by using the pH adjusting solution. Suitable amount of water was added. The pH of the solutions were measured by a pH meter. The pH probe was washed throughly with water into the solution which was then made the volume to 10 mL. The solution was left to stand for 10 minutes. The green precipitate of Ni-oxime complex was extracted into 10.0 mL of chloroform (by the condition of 20 cycled shaking and 1 hour standing). The absorbance of the chloroform was measured at 607.0 nm against the reagent blank. Mean absorbance for ten measurements

at this concentration of Ni (II) (12.0 ppm) was 0.0393, the relative standard diviation being 3.5 % (= ± 0.0014) The result was very close to the absorbance of 0.0400 ± 0.0010 belonging to the previous study.

Application of the Method to the Determination of Ni in Ni-Cu Alloy The usefulness of the method was applied to the determination of Ni in Ni-Cu alloy. The exact amount of the dry alloy (in this case 1.0191 g) was dissolved in 50 mL of the 1:1 concentrated nitric acid (65 % Analar, Merck, density = 1.40 g/mL.) and water mixture contained in a 250 mL beaker. After all the alloy dissolved in the acid solution, it was quantitatively transferred into a 250 mL volumetric flask and made up to the mark with water. The freshly prepared solution (0.05 mL) was pipetted into a 50 mL beaker. The Cu (II) ion present in the solution was then precipitated with an excess amount (5.0 mL) of 1.0×10^{-2}F oxime solution as Cu-oxime complex at pH 4. The insoluble matter was filtered. The filtrate was quantitatively collected and made up to the volume of 25 mL in a 25 mL volumetric flask. A 5.0 mL of the solution were pipetted into 20 mL mixer cylinder containing 2.0 mL of 1.0×10^{-2}F oxime solution. The Ni-oxime complex was precipitated at pH 8 and was extracted into 10 mL of chloroform. The detail of the experiment was the same as the previous one. The absorbance of the chloroform layer was measured at 607 nm against the reagent blank. Mean absorbance for 10 measurements was 0.0443, the relative standard diviation being 0.36 % (= ± 0.00016). The concentration of the measured solution was obtained by using calibration curve (Fig.3.39) being 12.4 ppm. The Ni content (% w/w) of this alloy

obtained from this experiment was calculated to be 30.42 % compared with 30.85 % of the true value. The relative error of the method was 1.39 %

3.3.4 Determination of Empirical Formula of the Ni-oxime Complex

3.3.4.1 Method of Elemental Analysis. The green silky needle of Ni-5-chloro-2-hydroxy-3-methyl acetophenoxime complex was prepared as follows. 1.0 mL of 1.0 x 10^{-2}F Standard Ni (II) and 10.0 mL of 1.0 x 10^{-2}F oxime solution were pipetted into a 250 mL beaker. This portion was diluted with water to 40 mL approximately. The pH of the solution was adjusted to the pH 8 ($\pm$ 0.5) by using the pH adjusting solution. The pH of the solution was measured by the pH meter. meter. Then the solution was made up to 50 mL. The green precipitate appeared and was filtered by using Whatman papers No. 41. It was washed with cold water in portion of 50 mL and finally washed with another portion of absolute ethanol. The green paste on the filter paper was dried in a desiccator and was recrystallized in chloroform. The crystal was analyzed for elemental composition by elemental analyzer. The results are shown in Table 3.34 in comparision with the colculated of 1:1 and 1:2 metal-ligand ratio.

Table 3.34

	% Composition (w/w)		
	%C	%H	%N
Calculated 1:1 metal-ligand ratio	41.84	3.87	5.42
Calculated 1:2 metal-ligand ratio	47.21	4.40	6.12
Experimental	46.74±0.26	4.29±0.02	5.92±0.01

3.3.4.2 Job's Method

A series of solution of Ni (II) and the oxime mixtures containing various mole fraction of Ni (II) from 0-1 was prepared. The sum of the concentration of Ni (II) and the oxime was kept constant at 1.0×10^{-5} mole/10 mL the solution were adjusted to the pH 8.0±0.5 and the complex was extracted into 10.0 mL of chloroform. The absorbance of each solution was measured at 610 nm against pure chloroform using 1.0 cm quartz cells. The job's plot is shown in Fig. 3.40. It shows that 1:2 metal ligand ratio complex is formed.

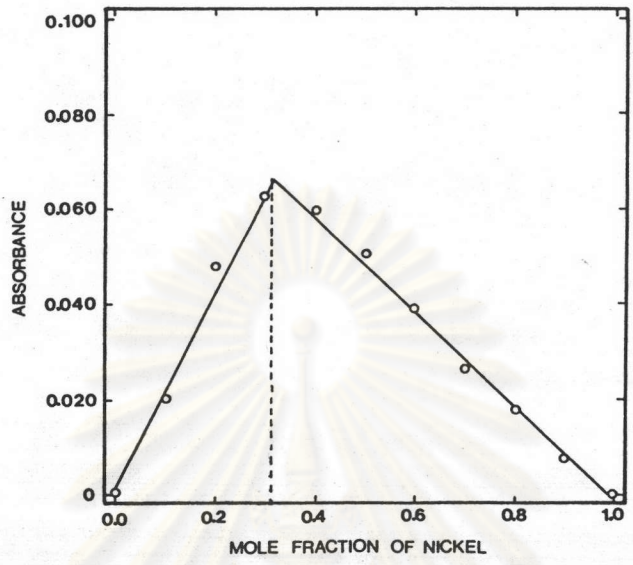


Fig. 3.40

3.3.4.3 The Molar Ratio Method

A series of solutions containing equal concentration of the metal fixed at 5.0×10^{-6} mole/10 mL but different concentration of oxime (0-2.0×10^{-5} mole/ 10 mL) were prepared. The pH of the solution was adjusted to 8.0 $\pm$ 0.5 and the ethanol-water content in the solution was kept at 20 %(v/v)for every solution. Each 10 mL solution was extracted with 10.0 mL of chloroform. The absorbances of these chloroform extracts were measured at 607.0 nm against pure chloroform using 1.0 cm quartz cells. The obtained result is shown in Fig.3.41 which is the plot of the absorbances against the mole fractions of Ni (II). The curve showed the deflection at a molar ratio of 1:2 metal-ligand complex.

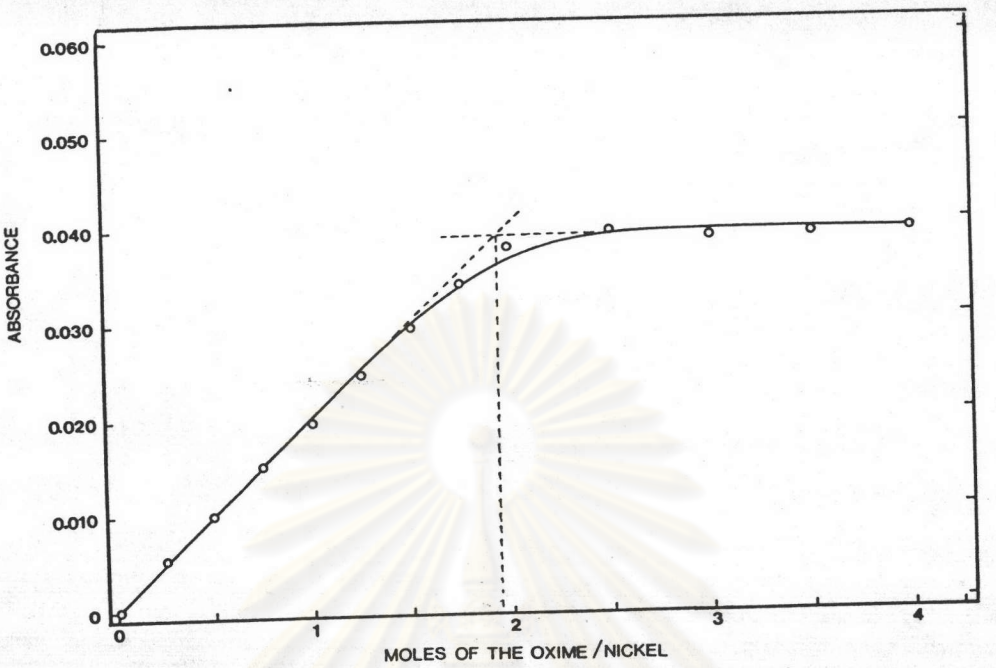


Fig. 3.41

3.3.4.4 The Slope Ratio Method

Two series of solutions were prepared for the study by this method. One was in the condition of excess Ni (II) concentration fixed at 2.0×10^{-5} mole/10 mL whereas the concentration of the oxime varied (0-5.0×10^{-6} mole/10 mL). The other one was in the condition of excess oxime concentration fixed at 2.0×10^{-5} mole/10 mL whereas the concentration of the Ni (II) varied (0-5.0×10^{-6} mole/10 mL). The pH of each solution was adjusted to 8.0 $\pm$ 0.5 and the ethanol-water content in the solution was kept at 20 % v/v. Each 10 mL solution was extracted with 10.0 mL of chloroform. The absorbances of these chloroform extracts were measured at 607.0 nm against pure chloroform using 1.0 cm. quartz cells. The obtained result is shown in Fig. 3.42 which is the plot of the absorbances against the added mL of the 0.5×10^{-2}F of oxime solution or Ni (II) solution. The ratio of the slope A/slope B was 2.063. It shows that 1:2 metal-ligand ratio complex is formed.

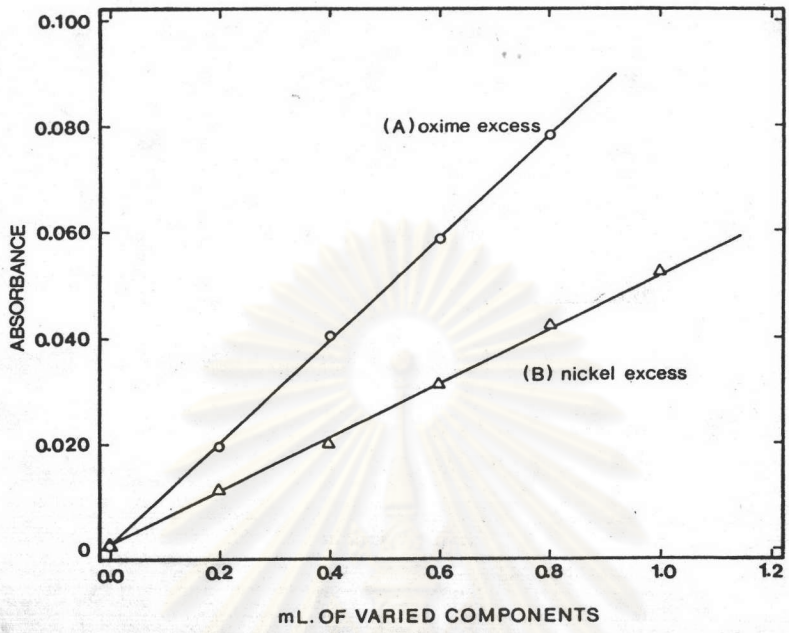


Fig. 3.42

3.4 Determination of Fe (III) by the Method of Direct EDTA Titration Using 5-Chloro-2-Hydroxy-3-Methyl Acetophenoxime as Indicator

It has been observed that 5-chloro-2-hydroxy-3-methyl acetophenoxime forms dark brown coloured complex with Fe (III) ion in 20 % v/v ethanol-water solution at pH 3-5 which is discharged by the addition of EDTA indicating that this reagent may be used as a metal indicator in complexometric determination of Fe (III). In the subsequent experiment, the complexometric tetration for Fe (III) is investigated.

Reagents

1) Standard Solutions of Fe (III) 0.10 F of Fe (III) solution was prepared by dissolving 40.40 g of dry $Fe(NO_3)_3 \cdot 9\ H_2O$ (Analar, Merck) in 1000 mL of water. To prevent hydrolysis and mould growth, this solution was prepared and kept in nitric acid(approximately 1 % v/v of concentrated nitric acid (Analar, Merck)). This solution was kept in polyethylene bottle. 0.05 F and 0.01 F of Fe (III) solutions were also prepared (if required) by further dilution of the 0.10 F with water. These Fe (III) solutions were standardized with secondary standard EDTA solution at pH 3 using Eriochrome black T as indicator.

2) Standard Solutions of EDTA 0.10 F of EDTA solution was prepared by dissolving 37.22 g of ethylenediamine tetraacetic acid disodium salt (dried in an oven at 80°C for at least 24 hours) in 1000 mL of water. The solution was kept in polyethylene bottle . This solution was standardized with primary standard calcium carbonate solution. 0.05 F and 0.01 F of EDTA solutions were prepared by further

dilution with water.

Standardization of the EDTA Solution with Primary Standard $CaCO_3$ Solution 2.5031 g of dry calcium carbonate (Analar, BDH) was dissolved in a smallest portion of 1.0 F hydrochloric acid and was made up to the mark of 250 mL volumetric flask with water. The concentration of the calcium (II) solution was 0.10 F. 10 mL of the Ca (II) was placed in a 250 mL Erlenmeyer flask. Ammonia ammonium chloride buffer solution was added to adjust the pH of the solution to pH 10. A pH meter was required for this pH measurement. A few drops of Eriochrome black T indicator solution were added. This content was titrated with the EDTA solution in the buret (pyrex 10 mL BS 846 No. 8558 min scale 0.02 mL) until the initial red colour of the solution changed to blue.

3) The Indicator Solution 0.2 % w/v of the indicator solution was prepared by dissolving 0.20 g of dry 5-chlors-2-hydroxy-3-methyl acetophenoxime in 100 mL of ethanol (Analar, Merck).

4) Acetate Buffer Solution for pH 4 Adjustment The solution was prepared by dissolving 25.0 mL of glacial acetic acid (Analar, BDH) and 13.7 g of sodium acetate trihydrate in deionized water and was made volume to 100 mL. For each titration, 2-6 mL of this buffer solution were required (1×10^{-2} mole of CH_3000^-). This amount of acetate ion was tested causing no change in colour. Other pH 4 adjustment solution were also tested to be valid for this pH control: Clark and Lubs buffer mixture (0.40 mL of 0.1 F NaOH + 50 mL of 0.1 F $KHC_8H_4O_4$ diluted to 100 mL of deionized water) or 0.5 F hydrochloric acid.

Procedure

Practically the following considerations are applied in the following complexometric tetrations.

1) Adjustment of pH Stability of the complex is dependent upon the pH of the solution for both metal-reagent complex and metal-EDTA complex. For the Fe (III)- oxime complex, the suitable pH of the solution should be 4-5 because of the most intense colour of the solution. Since Fe (III)-EDTA complex can exist at low pH while most of the divalent ions can not. To avoid the interferences form some divalent metal ions and to maintain the intensity of the colour of the solution, pH of the solution must be compromised. The pH 4 was shosen and was limitted to $\pm$ 0.5 diviation. To achieve these, a pH meter was recommended for this adjustment.

2) Concentration of the Metal Ion to be Titrated This titration was carried out with 1.0×10^{-3} to 1.0×10^{-6} mole (55.85 to 0.56 mg) of Fe concerned in a valume of 40 mL of solution in a 250 mL Erlenmeyer flask. It was tested that 40 mL of the solution in 250 mL of the container was the most effective volume for turbulent stirring (using magnetic stirrer) with no solution strewing and colour dilution effect.

3) Amount of the Indicator Many portions of Fe (III) ion and the indicator were tested for satisfactory colour in the volume of 40 mL of aqueous solution at pH 4.0 $\pm$ 0.5. The obtained result is shown in Table 3.35. The satisfactory amount of the indicator was at least 1.0×10^{-5} mole .

Table 3.35

Amount of the Oxime (in mole)	Amount of Fe (in mole)								
	$1.0x10^{-3}$	$5.0x10^{-4}$	$1.0x10^{-4}$	$5.0x10^{-5}$	$1.0x10^{-5}$	$5.0x10^{-6}$	$1.0x10^{-6}$	$5.0x10^{-7}$	$1.0x10^{-7}$
$1.0x10^{-3}$	very dark	very dark	dark brown	dark brown	light brown	brownish yellow	colour-less	colour-less	colour-less
$5.0x10^{-4}$	very dark	very dark	dark brown	dark brown	light brown	brownish yellow	colour-less	colour-less	colour-less
$1.0x10^{-4}$	dark brown	dark brown	dark brown	dark brown	light brown	brownish yellow	colour-less	colour-less	colour-less
$5.0x10^{-5}$	dark brown	dark brown	dark brown	dark brown	brownish yellow	brownish yellow	colour-less	colour-less	colour-less
$1.0x10^{-5}$	dark brown	dark brown	dark brown	dark brown	brownish yellow	brownish yellow	colour-less	colour-less	colour-less
$5.0x10^{-6}$	brownish orange	light brown	light brown	light brown	brownish yellow	brownish yellow	colour-less	colour-less	colour-less
$1.0x10^{-6}$	orange	pale orange	pale orange	pale orange	colour-less	colour-less	colour-less	colour-less	colour-less

4) Concentration of the EDTA Solution as Titrant EDTA forms 1:1 complex with Fe (III) at pH 4. It is therefore 1.0×10^{-3} to 1.0×10^{-6} mole of EDTA should be present in a suitable volume which was not affected by colour dilution when the solution of Fe (III)-oxime complex was titrated near the end point. The original volume (before the titration) was 40 mL so the final volume (at the end point) should not ever 60 mL. The suitable concentration of the titrant should be 0.05 F of EDTA.

5) Attainment of the End Point In this EDTA titration, the colour change from dark brown to yellow in the neighbourhood of the end point might be slow. The solution should be continuously stirred (a magnetic stirrer was recommended). 10 titrations were performed at the same amount of Fe (III) for statistical evaluation. The end point should be observed more precisely when the later titration undergoes by comparing the colour change with the former titration solution containing slight excess of EDTA.

6) Method for the Titration under the Described Condition
A certain amount of the standard solution of Fe (III) was pipetted into a 250 mL Erlenmeyer flask and was diluted to 30-35 mL with water. pH of the solution was adjusted to 4.0 by the addition of 2-6 mL of the acetate buffer solution ; the pH might be checked with a pH meter as it should lie between 3.5 and 4.5. 1 mL of the 0.2 % indicator solution was added for colour development. All the content was titrated with secondary standard 0.050 F EDTA solution contained in the buret until the colour change from dark brown to light yellow.
10 titration was performed for each amount of Fe (III). The result of the titrations is shown as Table 3.36 to Table 3.38

Table 3.38

#	experimental amount of std EDTA 0.0501 F used for determination of Fe																	
1	19.02	16.81	15.56	13.48	11.80	9.93	7.96	5.96	3.89	2.02	1.82*	1.62	1.42	1.21	1.00	0.82	0.60	0.40
2	18.92	16.27	13.91	13.74	11.76	9.99	7.95	5.98	3.94	2.00	1.82*	1.60	1.42	1.20	1.02	0.78*	0.62	0.42
3	18.51	16.86	14.23	13.70	11.52*	10.04	7.98	5.93	4.02	1.98	1.80	1.62	1.41	1.20	1.00	0.82	0.61	0.41
4	18.10	16.54	14.44	13.62	11.85	9.92	7.92	5.94	4.09	2.02	1.79	1.60	1.40	1.24*	0.98	0.80	0.62	0.42
5	18.66	17.14	13.86	13.78	11.96	9.92	7.88	5.94	3.94	1.96	1.78	1.60	1.38	1.21	1.00	0.82	0.62	0.40
6	19.61	17.66	14.68	13.59	12.04	9.96	7.88	5.92	3.98	1.98	1.80	1.62	1.38	1.22	0.99	0.81	0.58*	0.38
7	18.04	16.90	14.40	13,72	11.90	9.91	7.96	5.98	3.92	2.03	1.79	1.60	1.39	1.20	1.02	0.81	0.62	0.39
8	18.49	17.09	14.68	13.79	11.90	10.02	7.98	5.94	4.02	1.97	1.80	1.60	1.38	1.20	1.01	0.80	0.60	0.42
9	18.60	17.10	15.72	13.82	12.02	10.02	7.92	5.97	4.00	2.02	1.78	1.62	1.42	1.22	1.02	0.82	0.62	0.42
10	18.58	16.84	15.13	13.70	11.89	9.84	7.98	5.96	3.91	1.98	1.78	1.62	1.39	1.22	1.01	0.82	0.60	0.42
range	1.57	1.39	1.86	0.34	0.52	0.13	0.10	0.06	0.20	0.07	0.04	0.02	0.04	0.04	0.04	0.04	0.04	0.04
$\bar{X}$	18.65	16.92	14.66	13.69	11.90	9.96	7.94	5.95	3.97	2.00	1.79	1.61	1.40	1.21	1.01	0.81	0.61	0.41
Std diviation	0.45	0.37	0.64	0.10	0.09	0.06	0.04	0.02	0.06	0.03	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
true value	20.00	18.00	16.00	14.00	12.00	10.00	8.00	6.00	4.00	2.00	1.80	1.60	1.40	1.20	1.00	0.80	0.60	0.40

Table 3.39

#	experimental amount of Fe determined in mg.																	
1	53.22	47.03	43.54	37.72	33.02	27.78	22.27	16.68	10.88	5.65	5.09*	4.53	3.97	3.39	2.80	2.29	1.68	1.12
2	52.94	45.52	38.92	38.44	32.90	27.95	22.24	16.73	11.02	5.60	5.09*	4.48	3.97	3.36	2.85	2.18*	1.73	1.18
3	51.79	47.17	39.81	38.33	32.23*	28.09	22.33	16.59	11.25	5.54	5.04	4.53	3.95	3.36	2.80	2.29	1.71	1.15
4	50.64	46.28	40.40	38.11	33.16	27.76	22.16	16.62	11.44	5.65	5.01	4.48	3.92	3.47*	2.74	2.24	1.73	1.18
5	52.21	47.96	38.78	38.56	33.46	27.76	22.05	16.62	11.02	5.48	4.98	4.48	3.86	3.39	2.80	2.29	1.73	1.12
6	54.87	49.41	41.07	38.02	33.69	27.87	22.05	16.56	11.14	5.54	5.04	4.53	3.86	3.41	2.77	2.27	1.62*	1.06
7	50.47	47.29	40.29	38.39	33.30	27.73	22.27	16.73	10.97	5.68	5.01	4.48	3.89	3.36	2.85	2.27	1.73	1.09
8	51.73	47.82	41.07	38.58	33.30	28.04	22.33	16.62	11.25	5.51	5.04	4.48	3.86	3.36	2.83	2.24	1.68	1.18
9	52.04	47.84	43.98	38.67	33.63	28.04	22.16	16.70	11.19	5.65	4.98	4.53	3.97	3.41	2.85	2.27	1.73	1.18
10	51.99	47.12	42.33	38.33	33.27	27.53	22.33	16.68	10.94	5.54	4.98	4.53	3.89	3.41	2.83	2.27	1.68	1.18
range	4.40	3.89	5.20	0.95	0.79	0.56	0.28	0.17	0.56	0.17	0.06	0.05	0.11	0.05	0.11	0.05	0.05	0.12
$\bar{X}$	52.19	47.34	41.02	38.32	33.30	27.86	22.22	16.65	11.11	5.58	5.01	4.51	3.91	3.38	2.81	2.27	1.71	1.14
Std diviation	1.27	1.04	1.78	0.29	0.26	0.18	0.11	0.06	0.17	0.07	0.03	0.03	0.05	0.02	0.04	0.02	0.02	0.04
true value	55.85	50.26	44.68	39.09	33.51	27.92	22.34	16.75	11.17	5.58	5.03	4.47	3.91	3.35	2.79	2.23	1.68	1.12
absolute error	3.66	2.92	3.66	0.77	0.21	0.06	0.12	0.10	0.06	0.00	0.02	0.04	0.00	0.03	0.02	0.04	0.03	0.02
Relative error	6.55	5.81	8.19	1.97	0.63	0.22	0.54	0.60	0.54	0.00	0.40	0.89	0.00	0.90	0.72	1.79	1.79	1.79

Table 3.38

Determined Amount of Fe (mg)	Amount of Fe (mg) Obtained from Experiment	Standard Diviation (mg)	Relative Error (%)	Standard Diviation of Added 0.05 EDTA solution (mL)
55.85	52.19	1.27	6.55	0.45
50.26	47.34	1.04	5.81	0.37
44.68	41.02	1.78	8.19	0.64
39.09	38.32	0.29	1.97	0.10
33.51	33.30	0.26	0.63	0.09
27.92	27.86	0.18	0.22	0.06
22.34	22.22	0.11	0.54	0.04
16.75	16.65	0.06	0.60	0.02
11.17	11.11	0.17	0.54	0.06
5.03	5.01	0.03	0.40	0.03
4.47	4.51	0.03	0.89	0.01
3.91	3.91	0.00	0.00	0.01
3.35	3.38	0.02	0.90	0.02
2.79	2.81	0.04	0.72	0.01
2.23	2.27	0.02	1.79	0.01
1.68	1.71	0.02	1.79	0.01
1.12	1.14	0.04	1.79	0.01

It has been observed that the end point of the titration at high concentration of Fe (III) was very difficult to observe because of large amount of Fe (III) ion at the equilibrium condition caused reddish yellow solution at the end point. At very low concentration of Fe (III) (less than 2.5 mg/40 mL) the initial visual colour of the solution could not be observed. The efficiency of the titration method was evaluated by the plot of determined amount of Fe against relative error (in %) as shown in Fig. 3.43. The result of the titration method was satisfactory in the range of 5-30 mg of the determined Fe (III) with accuracy of $\pm$ 1.0 %.

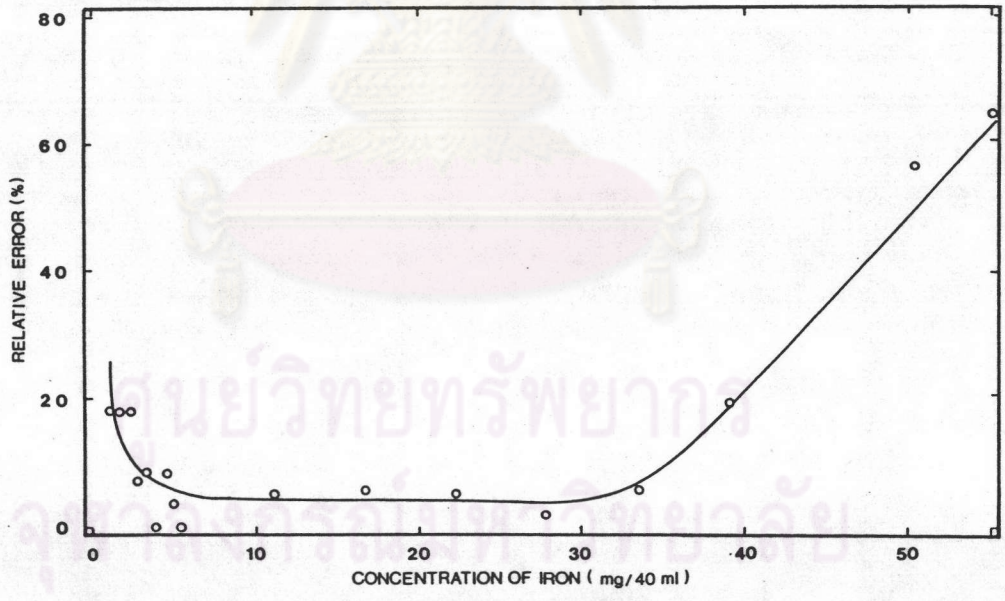


Fig. 3.43

7) Study of Coexisting Ions Effect on the Titration The Effect of coexisting ions was examined at 11.17 mg/40 mL of Fe (III) concentration. Sixteen cations and twelve anions wer individually present i various amount by adding their previously prepared 1.0 F, 0.1 F or 1.0×10^{-2} F solutions for the molar ratios of the ions to Fe (III) being 100:1, 50:1, 30:1, 10:1, 3:1, 1:1, 0.1:1 and 0.01:1.

Reagents

1. Standard Solution of Fe (III) (as described previously)
2. Standard Solution of EDTA (as described previously)
3. The Indicator Solution (as described previously)
4. Acetate Buffer Solution (as described previously)
5. Diverse Ion Solutions. (as described previously)

Procedure

A 2.0 mL of 0.10 F Fe(III) standard solution were placed in a 250 mL Erlenmeyer flask. A certain amount of the tested salt solution was added individually to be the foreign ions. Then the content was diluted to 30-35 mL with water. pH of the solution was adjusted to 4.0 by the addition of 2-6 mL of the acetate buffer solution. The pH of the solution was checked by using a pH meter as it should lie between 3.5 and 4.5. A 1 mL of the 0.2 % indicator solution was added for colour development. All the content was titrated with secondary standard 0.050 F EDTA solution contained in the buret. Any change that diviated from normal titration were noted. The titrations at the same ratio of Fe and the salt were carried out duplicately. Results of the titration that allowed to be at most $\pm$ 1.5 % deviation from the true value (employ the 0.050 F EDTA solution in the range of

3.94-4.06 mL) are treated as no interferences. These results are summarized and shown in Table 3.39 and Table 3.40

Table 3.39

Cations	Anions	Torlerable amount (folds of Fe (III))
Na^+, K^+, NH_4^+	NO_3^-, Cl^-, Br^-, I^-	100
Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}	CH_3COO^-, SO_4^{2-}, CO_3^{2-}	
Ag^+	-	30
Fe^{2+}	F^-, MoO_4^{2-}	3
Ni^{2+}, Cu^{2+}	PO_4^{3-}, WO_4^{2-}, $C_2O_4^{2-}$	0.1
Pb^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}	-	0.01

Table 3.40

Type of Interferences	Ions
1. Other colour development	Ni^{2+}(green), Cu^{2+}(blue), Co^{2+}(red)
2. Colour disappearance	Ag^+, F^-, MoO_4^{2-}, PO_4^{3-}, WO_4^{2-}, $C_2O_4^{2-}$
3. Using more amount of titrant	Fe^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}

8. Application of the Titration Method for Determination of Fe in Mineral Samples

8.1 Determination of Fe in Iron Ores Generally, Iron are contains large content of iron. Iron in the ore was converted to Fe (III) after dissolving in hydrochloric acid . Amount of insoluble matter such as Al_2O_3 and SiO_2 can be ignored in this titration.

Procedure

The exact amount of iron ore (1.0 g) of dry powdered or small granular ore (dried in an oven at 105°C for an hour and kept in an dessicator)was weighed out and dissolved in a smallest amount of concentrated hydrochloric acid (Amalar, Merck) by heating on a water bath (70-80°C) for 2 hours and made up to the mark in a 500 mL volumetric flask with water. 10.0 mL of this freshly prepared solution were pipetted into a 250 mL Erlenmeyer flask and was diluted to 25-30 mL with deionized water. pH of the content was adjusted to 4 by the addition of 6-10 mL of the acetate buffer solution. The pH meter was used to check pH of the solution. (between 3.5 and 4.5). 1-2 mL of the 0.2 % indicator solution was added for colour development. All the content was titrated with secondary standard 0.050 F EDTA solution until the colour change from dark brown to light yellow. Each 10 titrations of 3 persons was performed for statistical evaluation and personal error correction. The results are shown in Table 3.41 to Table 3.43

Table 3.41

A) Nimba iron ore

	ore weight (g)	mL of Std EDTA (0.0501 F) solution used in each titration									
		# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
1 st person	1.0016	4.72	4.75	4.76	4.70	4.72	4.74	4.78	4.72	4.76	4.76
2 nd person	1.0212	4.80	4.88	4.90	4.85	4.88	4.90	4.86	4.88	4.87	4.88
3 rd person	1.0314	4.92	4.68	4.89	4.88	4.91	4.92	4.88	5.00	4.88	4.90

Table 3.42

B) Brazilian iron ore

	ore weight (g)	mL of Std EDTA (0.0501 F) solution used in each titration									
		# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
1 st person	1.0045	4.92	4.95	4.96	4.89	4.96	4.96	4.88	4.98	4.96	4.92
2 nd person	1.0138	5.12	4.97	4.96	5.12	4.88	5.06	4.88	5.10	5.04	4.94
3 rd person	0.9916	4.76	4.88	4.94	4.88	4.90	4.91	4.79	4.94	4.80	4.86

Table 3.43

Sources	Methods	% Fe (w/w)
Nimba Iron Ore (a)	certified value	66.1
	1st person's titration	66.20 ± 0.35
	2nd person's titration	66.82 ± 0.23
	3rd person's titration	66.58 ± 0.51
Brazilian Iron Ore (b)	Certified value	69.1
	1st person's titration	68.71 ± 0.45
	2nd person's titration	69.09 ± 1.29
	3rd person's titration	68.82 ± 0.76

Note (a) Nimba Iron Ore (No. 172/2), Bureau of Analysed Samples, LTD, England, 1968.

Fe 66.09 %, SiO_2 2.58 %, Al_2O_3 1.08 %, others 0.2 %

(b) Brazilian Iron Ore (No. 17 b), Bureau of Analysed Samples, LTD, England, 1968.

Fe 69.1 %, SiO_2 0.47 %, P 0.019 %

8.2 Determination of Fe in Cerment and Barite Cement and barite contain small portion of iron so the larger amount of sample were recommended for the titration. Insoluble matters such as SiO_2 and Al_2O_3 in large amount should be filtered out to make the accurate volume in any dilution.

Procedure : The iron content of cement or barite was determined by weighing out certain amount (10.0 g) of dry powdered sample (dried in oven at 105^{o}C for an hour and kept in an dessicator) dissolving in smallest portion of concentrated hydrochloric acid by heating on a water bath (70-80^{o}C) for 2 hours with temporary vigorously stirring. The content was cooled to room temperature. A 20 mL of water were added with continuous stirring. The insoluble matters (such as SiO_2 and Al_2O_3) were filtered off from the solution by using Whatman paper No. 42. The filtrate was quantitatively collected in a 250 mL volumetric flask and then was made to the mark with water. A 25 mL of this already prepared solution was pipetted into a 250 mL Erlenmeyer flask. The pH of the content was adjusted to approximately 4 by the addition of 10-12 mL of the acetate buffer solution that had to lie between 3.5 and 4.5. 1-2 mL of the 0.2 % indicator solution was added for colour development. All the content was titrated with secondary standard 0.050 F EDTA solution until the colour change from dark brown to light yellow. Each 10 titration of 2 persons was performed for statistical evaluation and personal error correction. The results are shown in Table 3.44 to Table 3.46

Table 3.44

A) Portland cement

	sample weight (g)	mL of Std EDTA (0.0501 F) solution used in each titration									
		# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
1st person	10.0714	6.12	6.09	6.20	6.18	6.22	6.20	6.22	6.20	6.18	6.21
2nd person	10.0650	6.04	6.16	6.20	6.18	6.16	6.18	6.24	6.26	6.14	6.16

Table 3.45

B) Siamese barite

	sample weight (g)	mL of Std EDTA (0.0501 F) solution used in each titration									
		# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
1st person	10.0422	5.16	5.22	5.24	5.26	5.16	5.18	5.16	5.24	5.20	5.20
2nd person	10.0325	5.20	5.06	5.16	5.15	5.20	5.12	5.16	5.21	5.14	5.12

Table 3.46

Sources	Methods	% Fe (w/w)
Portland Cement (c)	Certifigated value	1.71
	1st person's titrations	1.72 ± 0.01
	2nd person's titrations	1.72 ± 0.01
Siamese Barite	ditermined by ICP spectro--metric method	1.42
	1st person's titration	1.45 ± 0.01
	2nd person's titration	1.44 ± 0.01

Note (c) Portland Cement (No. 24 b), Bureau of Analysed Samples, LTD, England, 1968.

Fe_2O_3 2.44 %, SiO_2 20.8 %, Al_2O_3 6.22 % , CaO 62.9 % MgO 2.56 %.