European Journal of Chemistry 2 (2) (2011) 163-167

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Comparative analysis of ZnO-catalyzed photo-oxidation of *p*-chlorophenols

Umar Ibrahim Gaya

Department of Pure and Industrial Chemistry, Bayero University Kano, 3011, Kano State, Nigeria

**Corresponding author at: Department of Pure and Industrial Chemistry, Bayero University Kano, 3011, Kano State, Nigeria. Tel.: +234.803.9169418; fax: +234.64.665904. E-mail address: umargaya2000@yahoo.com (U.I. Gaya).*

ARTICLE INFORMATION

Received: 09 December 2010
Received in revised form: 07 February 2011
Accepted: 03 March 2011
Online: 30 June 2011

KEYWORDS

Oxidation
Mechanism
Chlorophenol
ZnO
Photodegradation
Intermediates

ABSTRACT

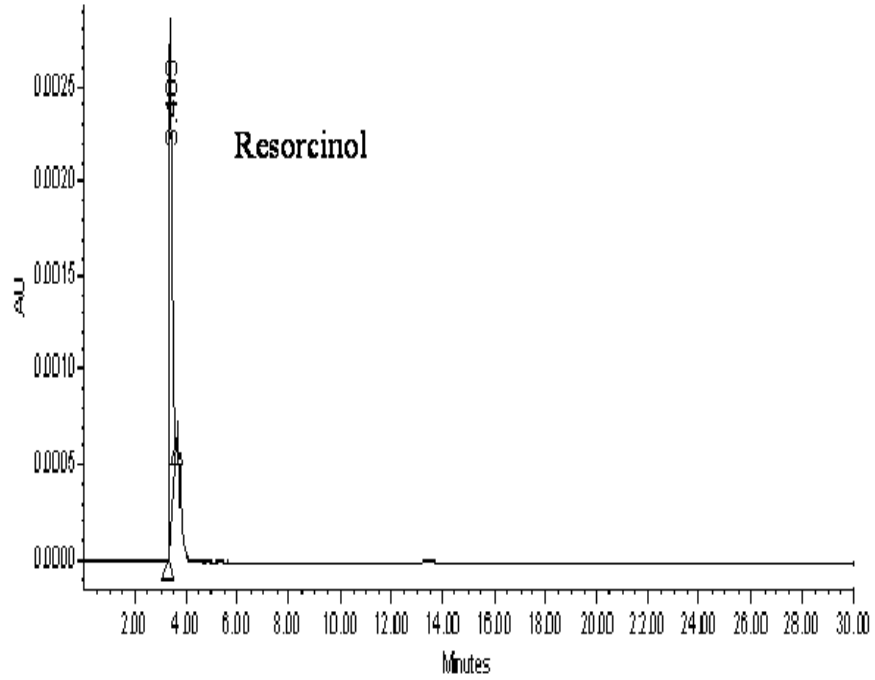
The present study compares for the first time the photocatalytic oxidation of three *p*-chlorophenols (4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol) in irradiated ZnO suspensions. The effect of operating parameters such as catalyst and concentration doses on the decomposition rate of these *p*-chlorinated compounds has been studied and optimized. The optimal feed concentration for each of the chlorinated phenolic compounds is 50 mg/L whereas the ZnO doses decreased as the number of chlorine substituent is increased. Kinetic profiles on the decomposition of chlorophenols over ZnO agreed with the pseudo-zeroeth order rate scheme with rate constants following the order 2,4,6-trichlorophenol > 2,4-dichlorophenol > 4-chlorophenol. The validity of the pseudo zero order model could be linked to the initial doses of the chlorophenols used vis-à-vis the catalyst. The study revealed stable intermediates of photocatalytic chlorophenol transformation by high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) technique. A combined mechanism is given to account for the photocatalytic destruction of the chlorophenols.

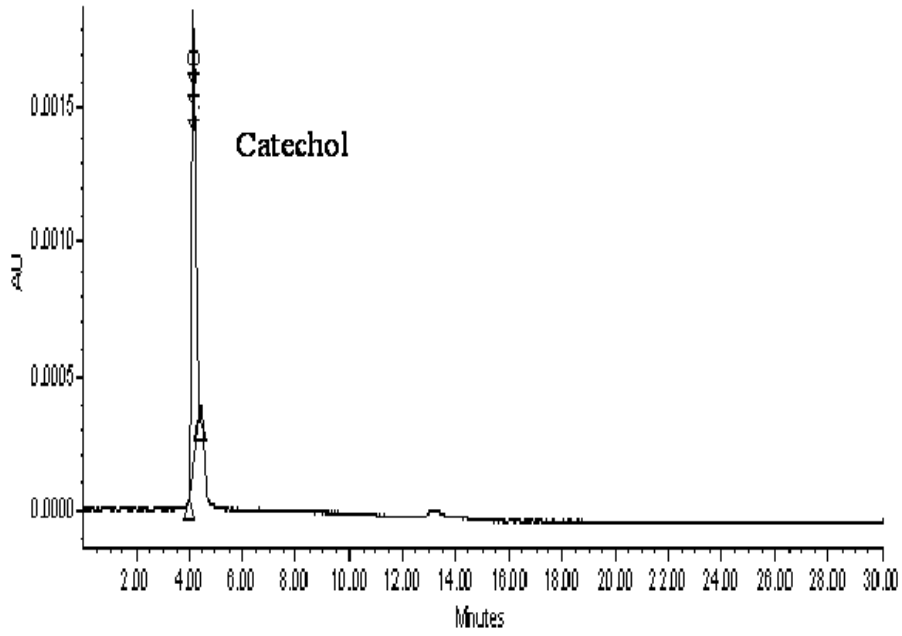
Supplementary Material

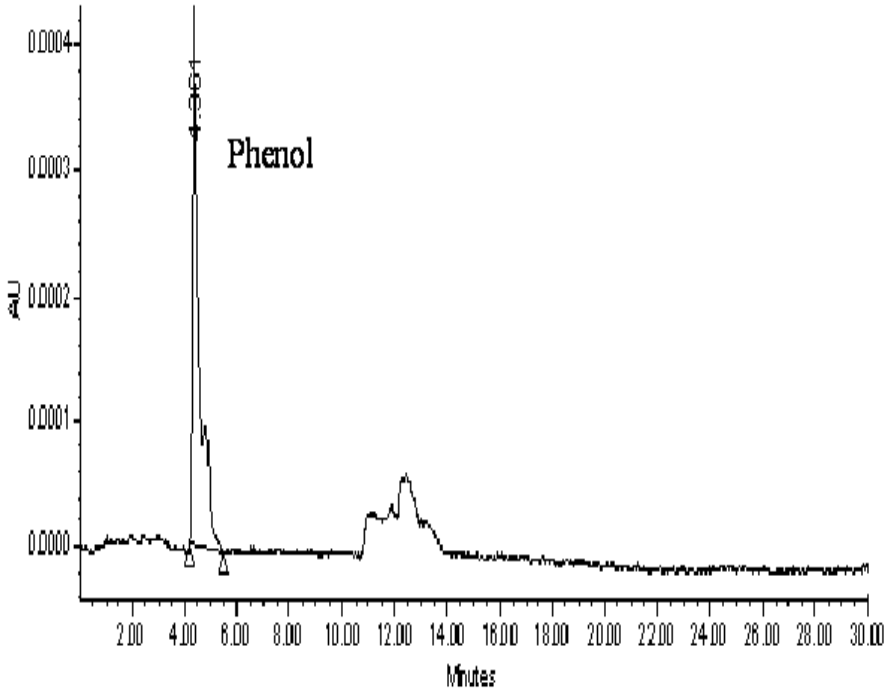
ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
DOI:10.5155/eurjchem.2.2.163-167.369

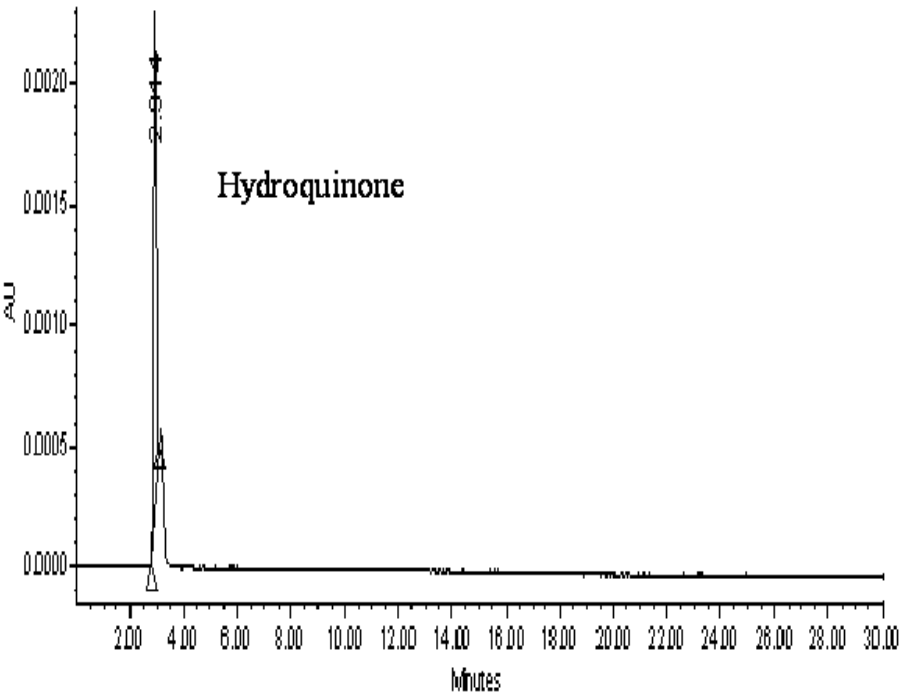
APPENDIX A
ORIGINAL CHROMATOGRAMS

1. HPLC Chromatograms of external standards (20 mg L^{-1}; 20 µL injection; 60:40 methanol-water) for 4CP degradation analysis

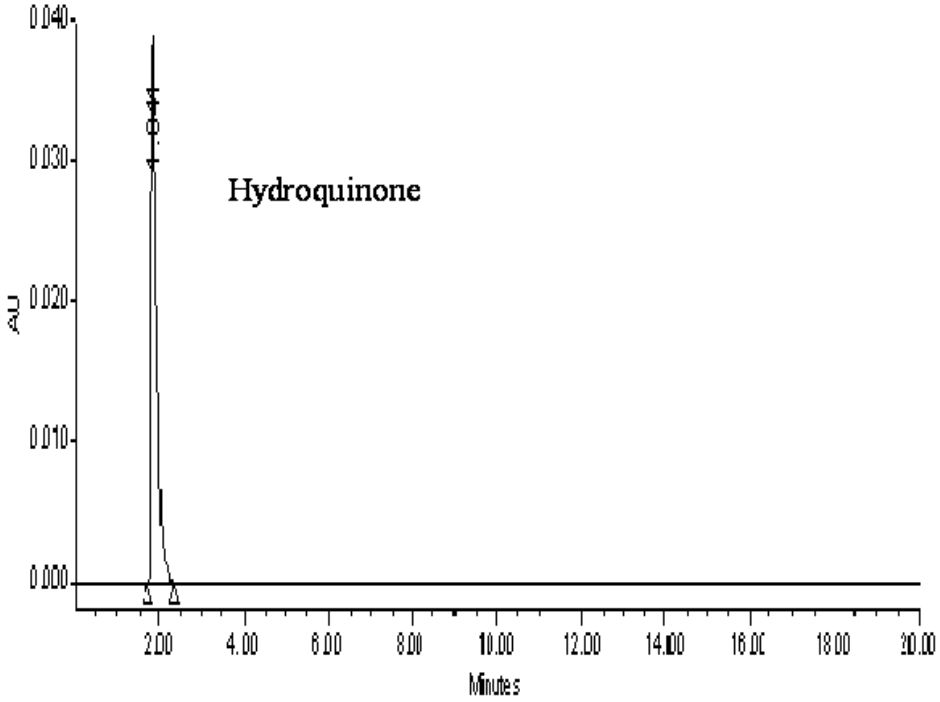


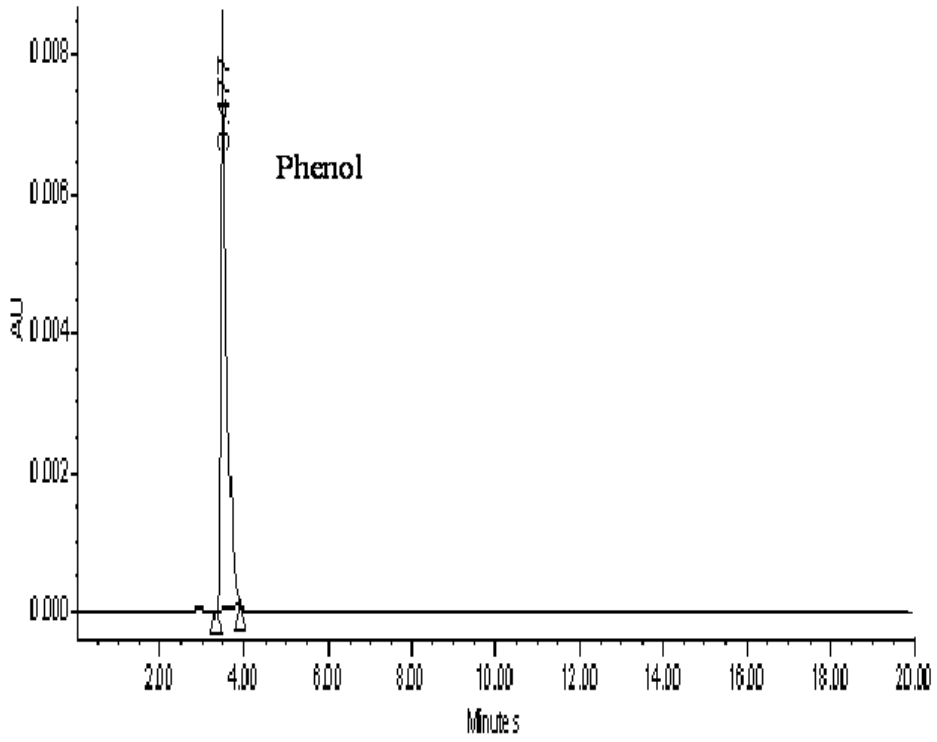


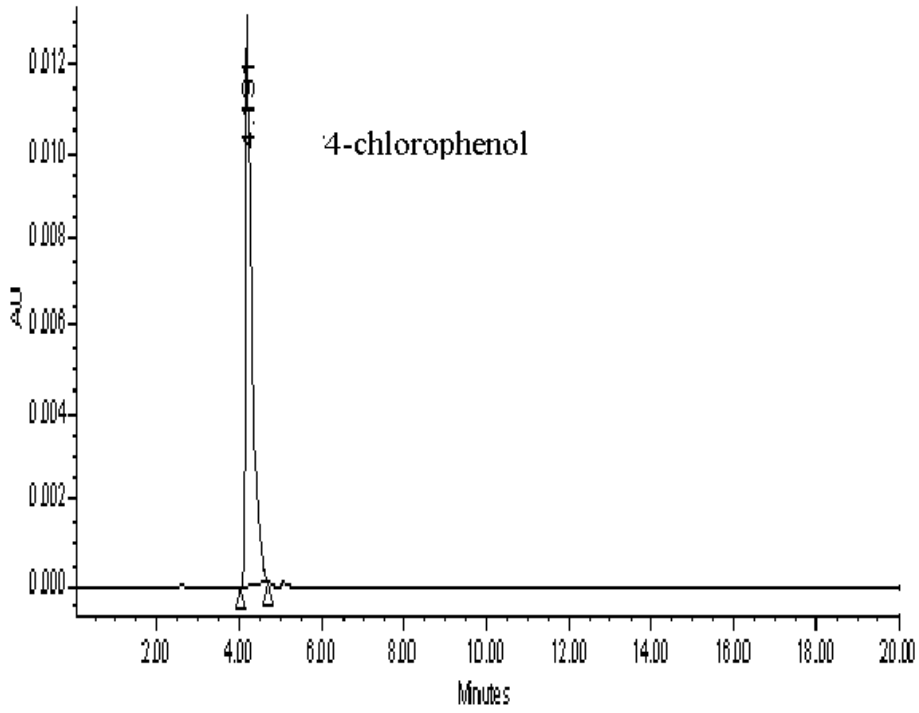

Phenol
4.361
AU
0.0004
0.0003
0.0002
0.0001
0.0000
2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00
Minutes

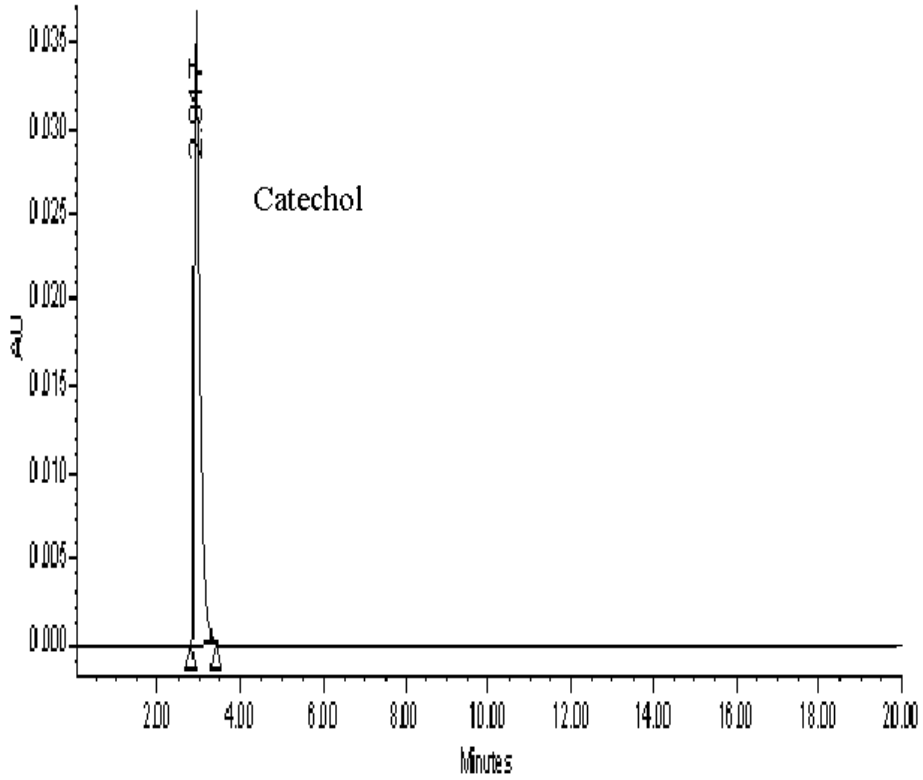

Hydroquinone
2.914
AU
0.0020
0.0015
0.0010
0.0005
0.0000
2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00
Minutes

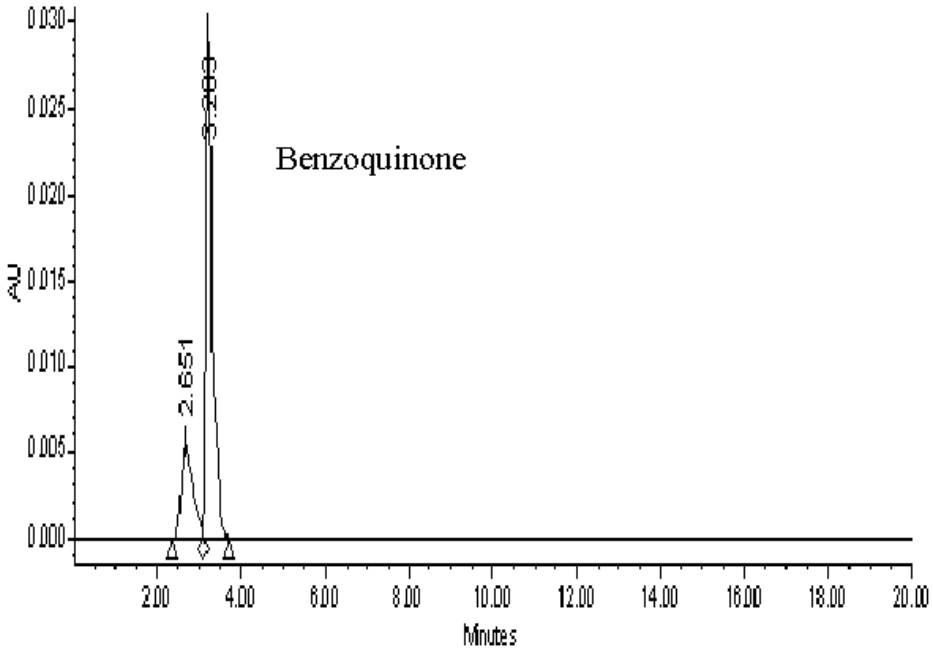
2. Chromatographic standards (20 mg L^{-1}) for 2,4-DCP photoproducts analysis

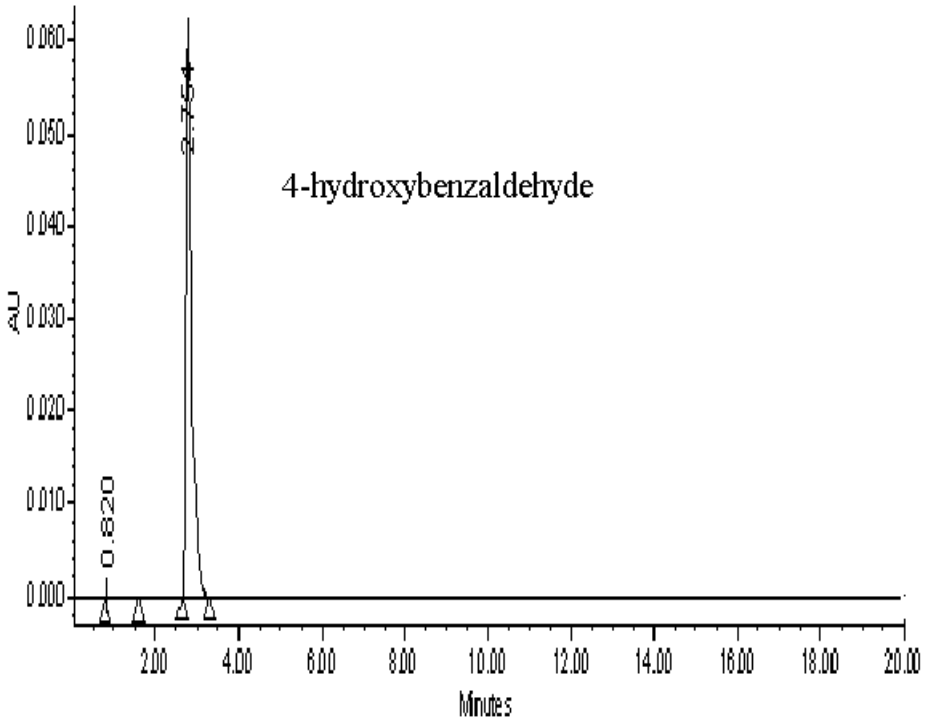




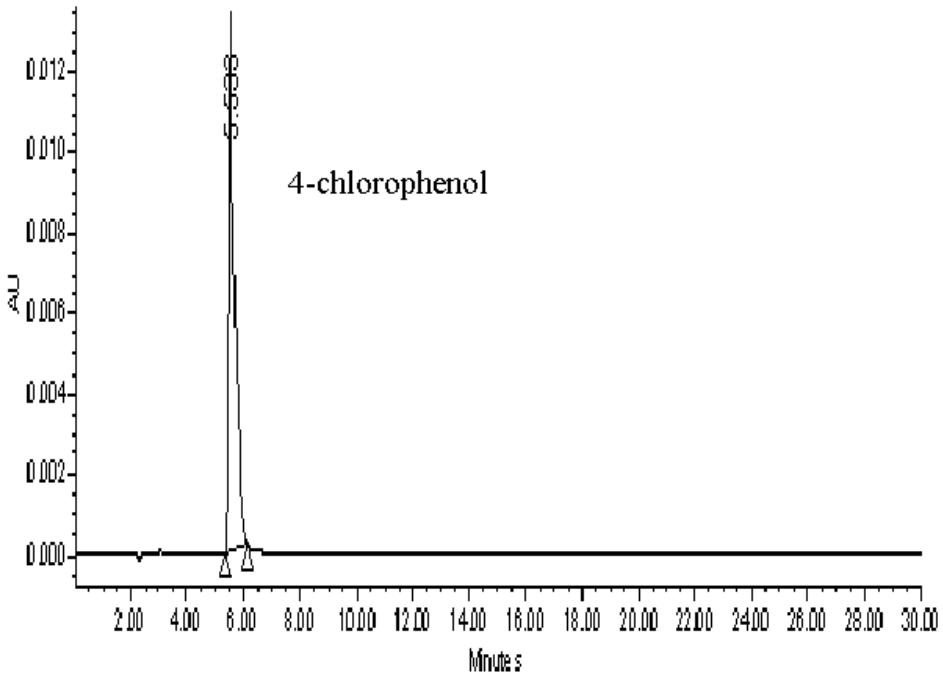

4-chlorophenol
AU
Minutes

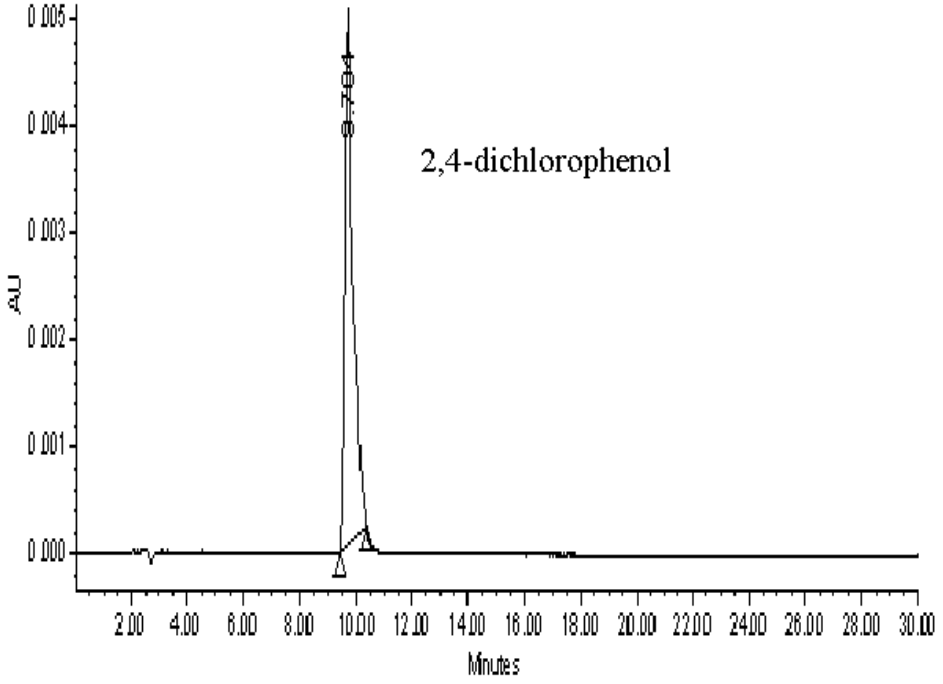

Catechol
AU
Minutes

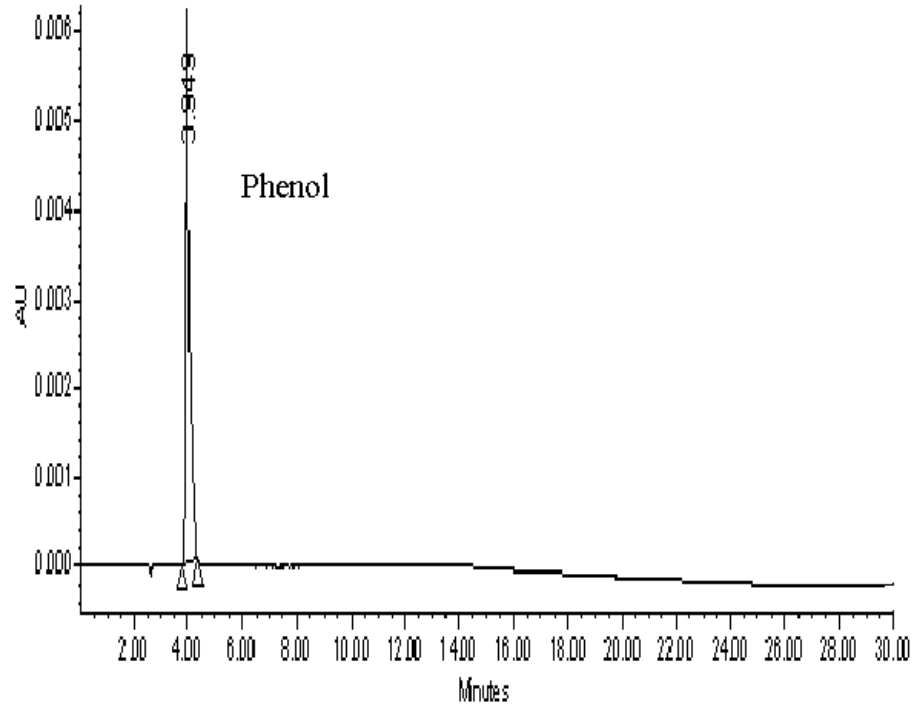

Benzoquinone
3.269
2.651
AU
Minutes

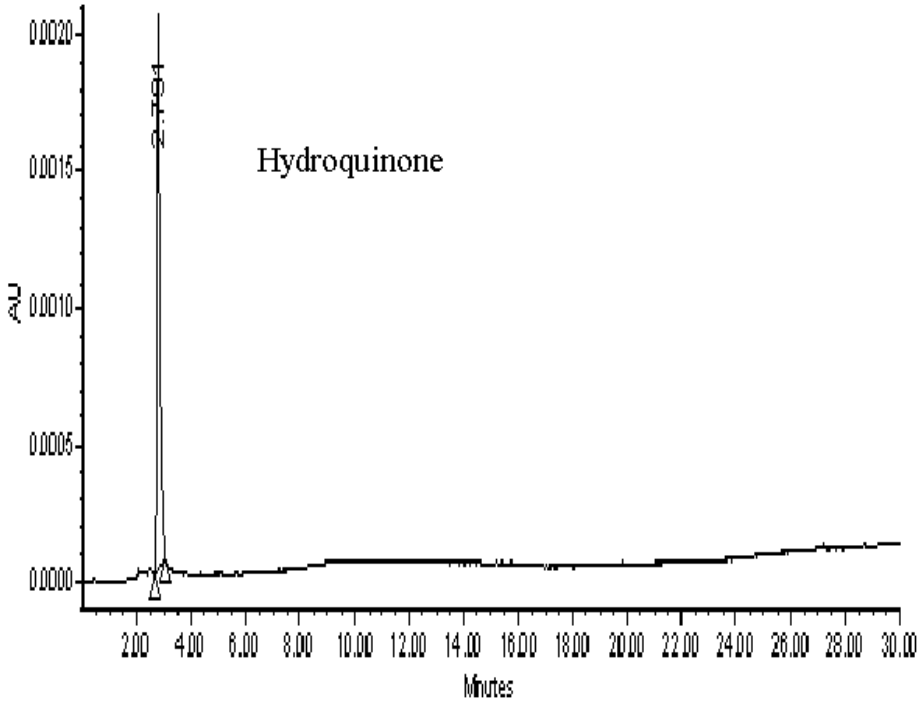

4-hydroxybenzaldehyde
2.754
0.820
AU
Minutes

3. Chromatograms of standards (20 mg L^{-1}) used during the analysis of intermediates of 2,4,6-TCP






3.949
Phenol
AU
0.006
0.005
0.004
0.003
0.002
0.001
0.000
2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00
Minutes


2.791
Hydroquinone
AU
0.0020
0.0015
0.0010
0.0005
0.0000
2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00
Minutes

Appendix B
ORIGINAL GC-MS SPECTRA

GC-MS chromatograms and spectra:
Spectra and chromatographic peaks of 4CP intermediates;

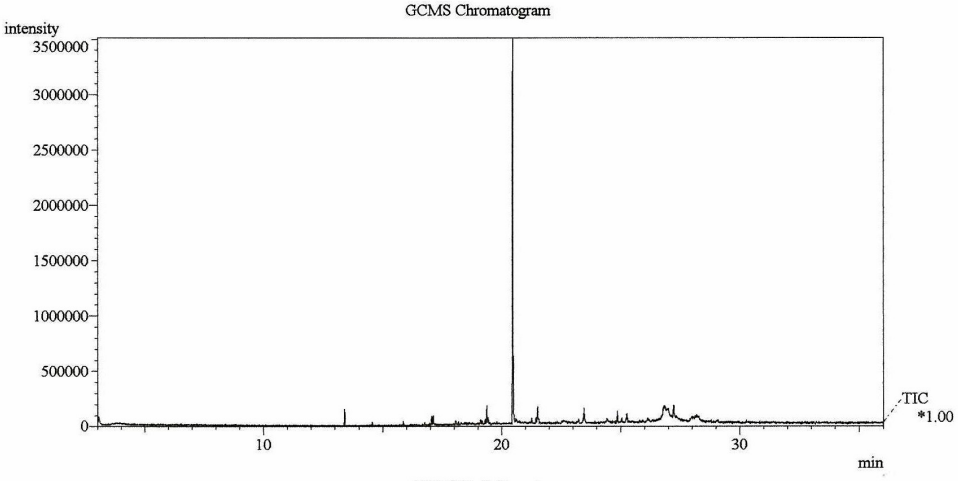
-

Solvent peak: Diethyl ether

GCMS Sample Information

Data Acquired by	: Admin, Jabatan Kimia, UPM
Acquisiton Date	: 2/4/08 1:02:33 PM
Sample Type	: Unknown
Level #	: 1
Sample Name	: Diethyl ether
Sample ID	: GS18309
IS Amount	: [1]=1.000
Sample Amount	: 1.000
Dilution Factor	: 1.000
Vial #	: 1
Injection Volume	: 1.000
Data File	: C:\GCMSsolution\Data\Halim\010208-deter2.qgd
Method File	: C:\GCMSsolution\Data\Halim\gc70310.qgm
Report File	: C:\GCMSsolution\Data\zaks\gcpotrait.qgr
Tuning File	: C:\GCMSsolution\System\Tune1\040208Elf2.qgt
Modified by	: Admin
Modified	: 2/4/08 1:38:38 PM

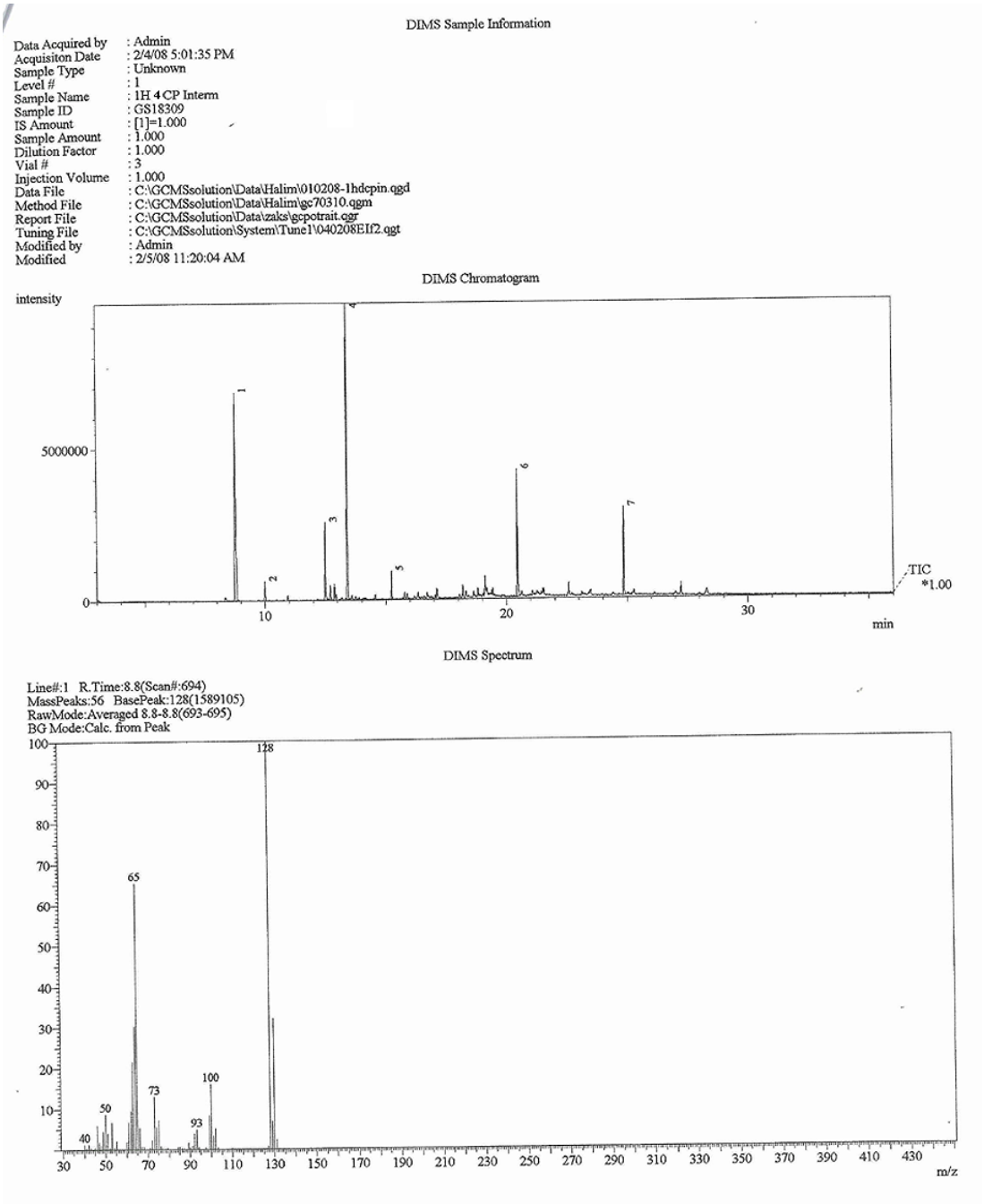
GCMS Chromatogram



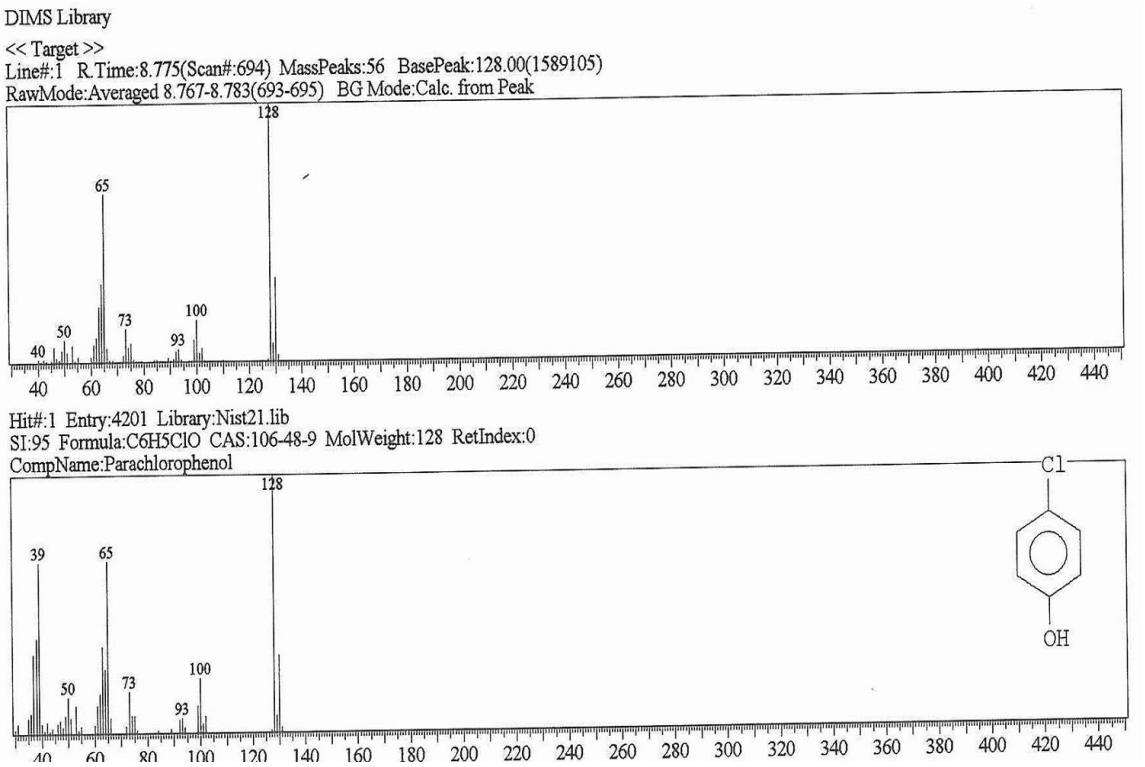
GCMS Peak Report

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
				0	0			0.00	

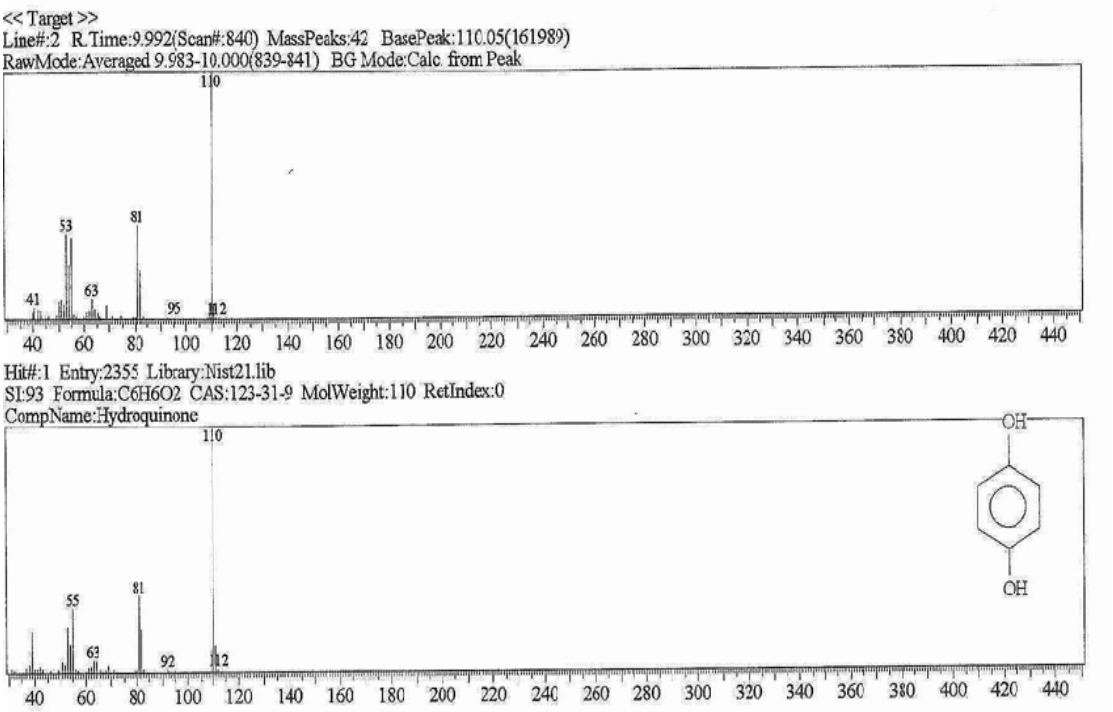
4. GC-MS of 4-chlorophenol and intermediates



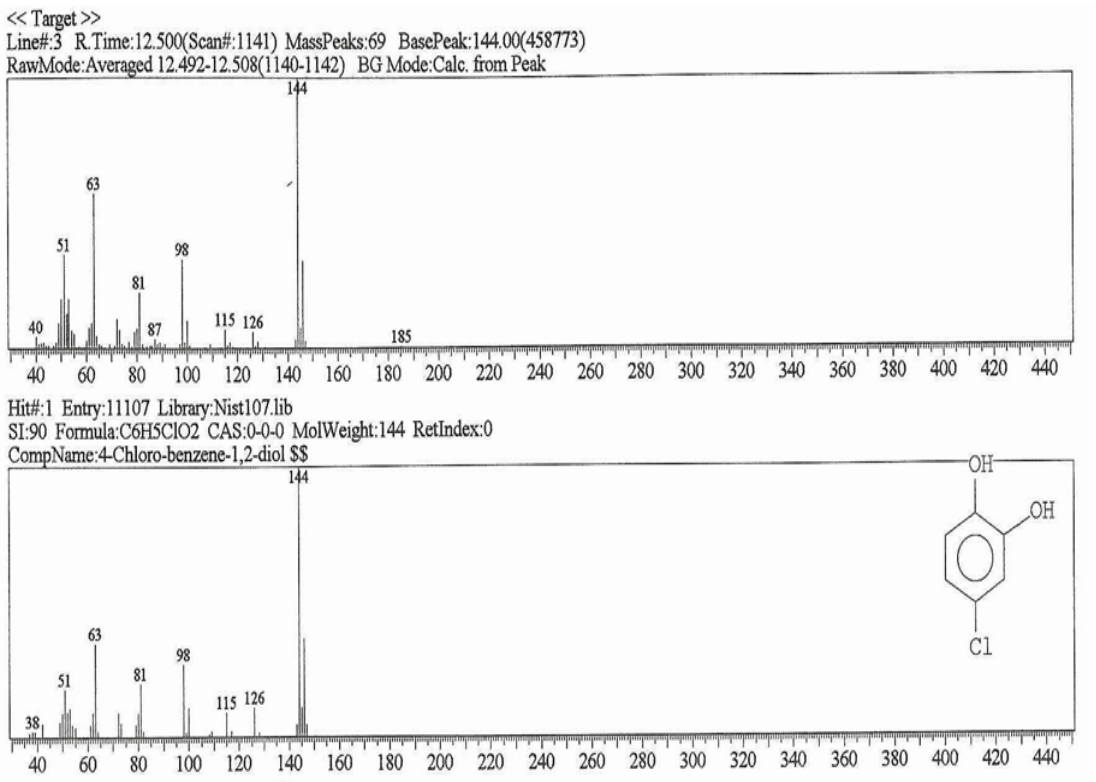
4-chlorophenol



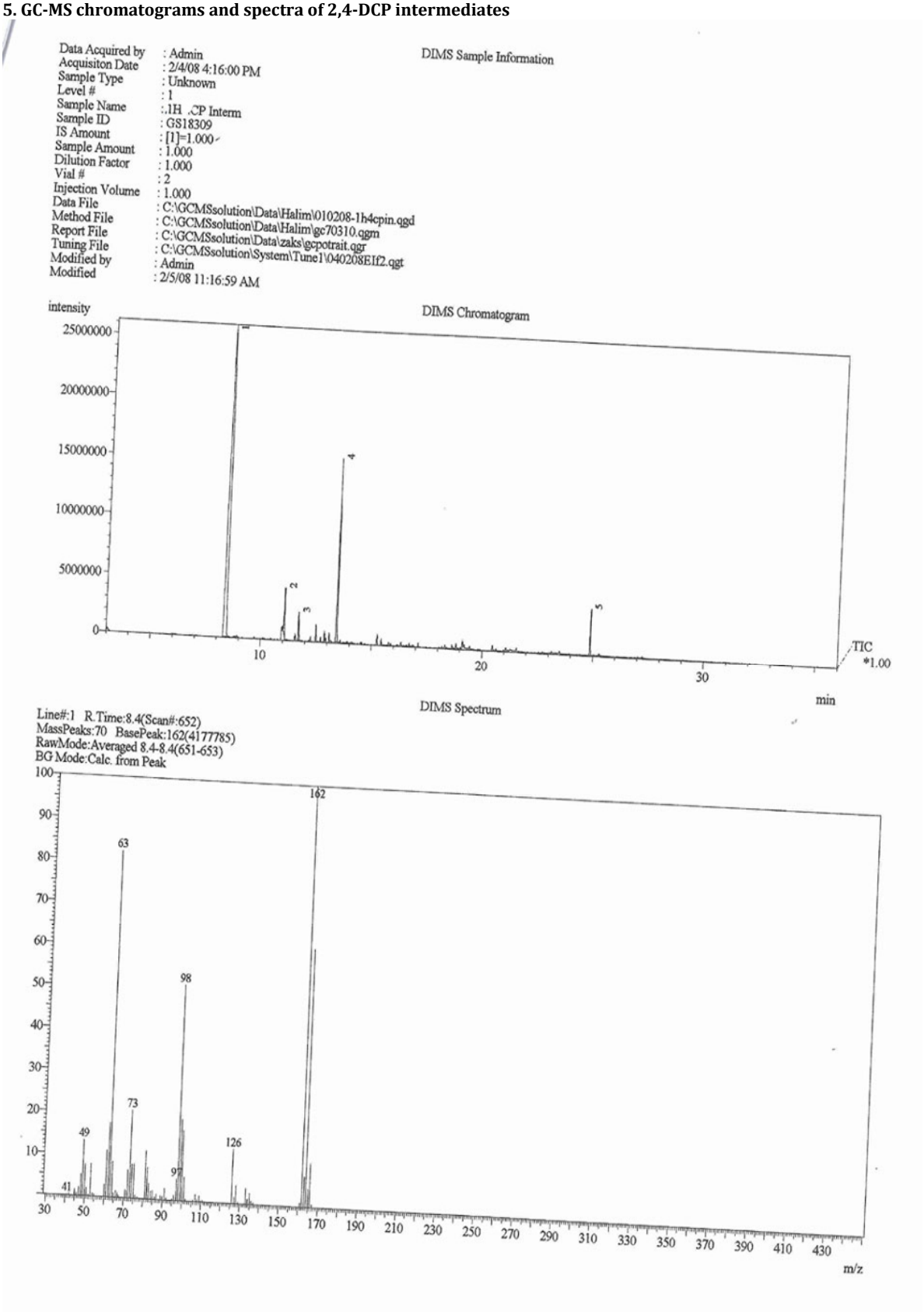
Hydroquinone



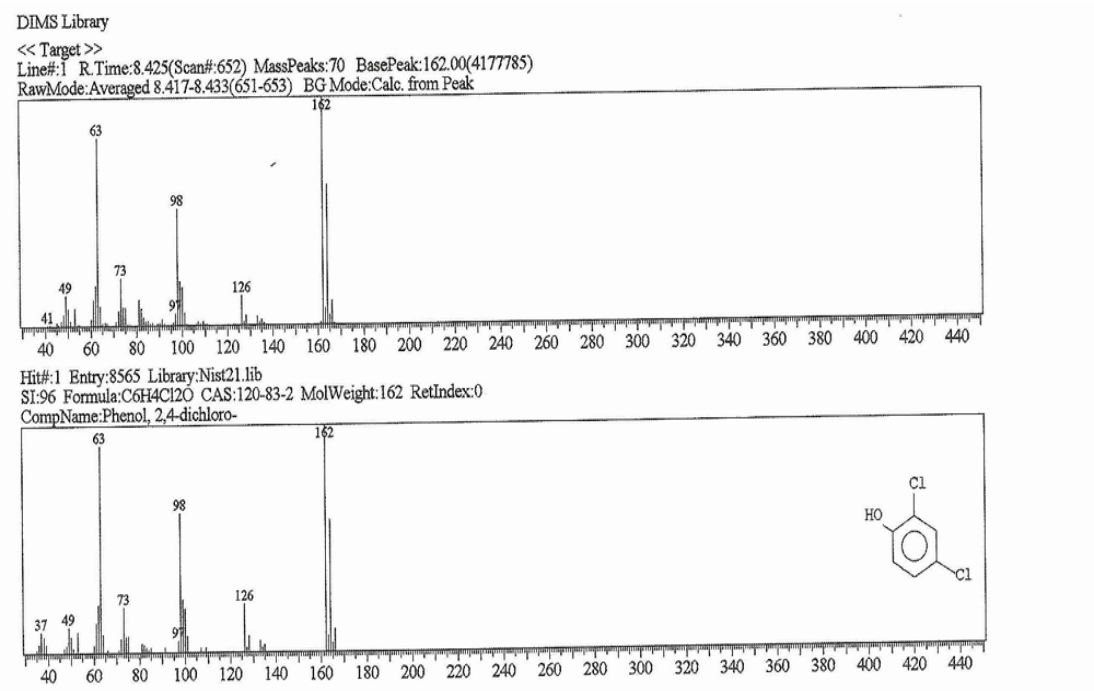
4-chlorocatechol


<< Target >>
Line#:3 R.Time:12.500(Scan#:1141) MassPeaks:69 BasePeak:144.00(458773)
RawMode:Averaged 12.492-12.508(1140-1142) BG Mode:Calc. from Peak
144
63
51
98
81
40
87
115
126
185
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440
Hit#:1 Entry:11107 Library:Nist107.lib
SI:90 Formula:C6H5ClO2 CAS:0-0-0 MolWeight:144 RetIndex:0
CompName:4-Chloro-benzene-1,2-diol $$
144
63
51
98
81
38
115
126
OH
OH
Cl
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440

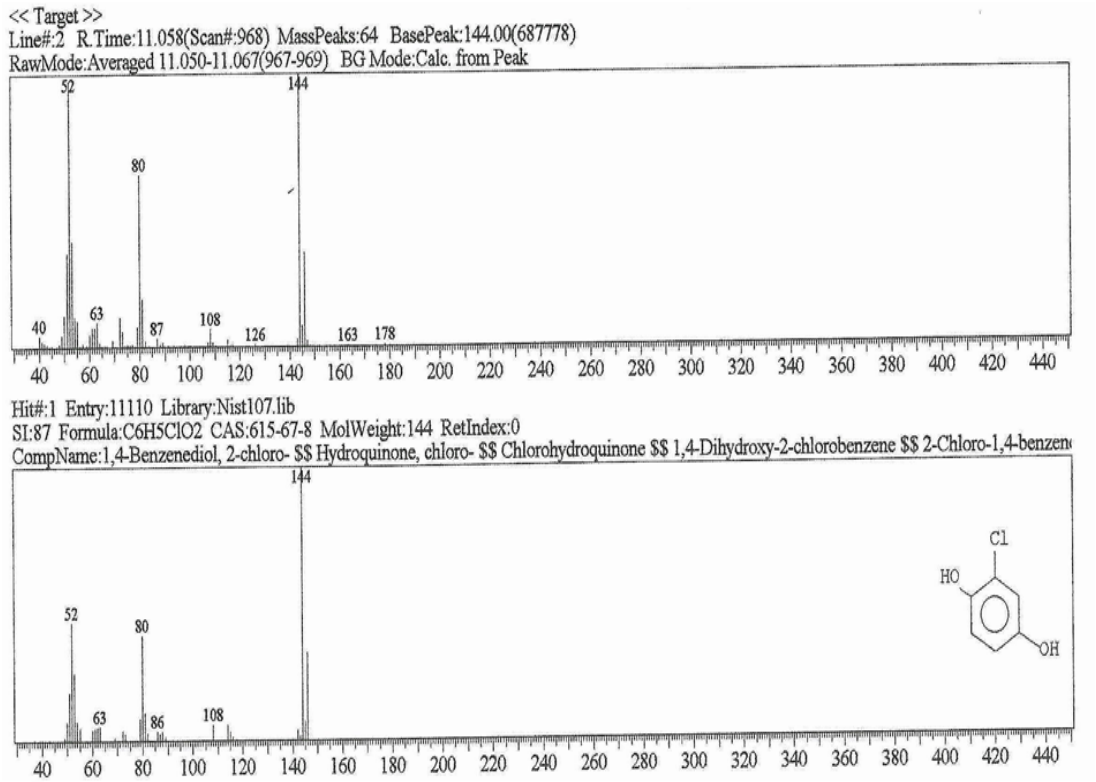
5. GC-MS chromatograms and spectra of 2,4-DCP intermediates



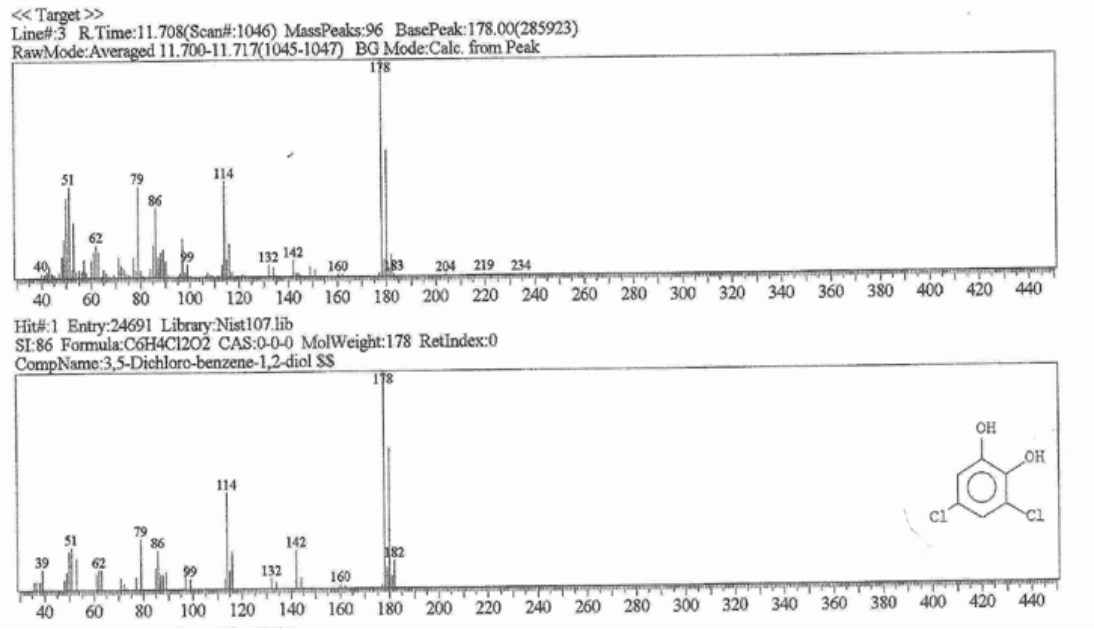
2,4-DCP



2-chlorohydroquinone



3,5-dichlorocatechol

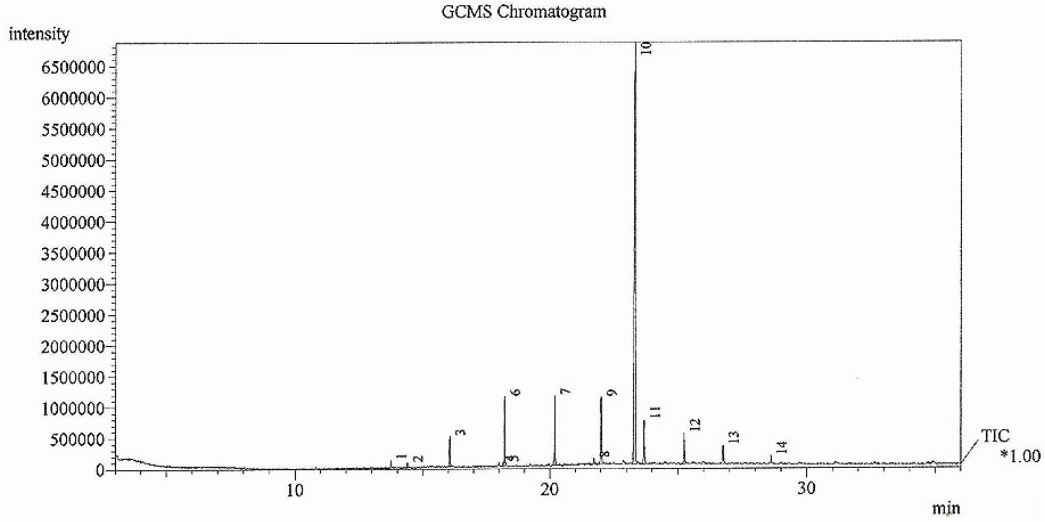

<< Target >>
Line#:3 R.Time:11.708(Scan#:1046) MassPeaks:96 BasePeak:178.00(285923)
RawMode:Averaged 11.700-11.717(1045-1047) BG Mode:Calc. from Peak
178
51
79
114
86
62
40
99
132
142
160
183
204
219
234
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440
Hit#:1 Entry:24691 Library:Nist107.lib
SI:86 Formula:C6H4Cl2O2 CAS:0-0-0 MolWeight:178 RetIndex:0
CompName:3,5-Dichloro-benzene-1,2-diol $$
178
114
79
51
86
142
39
62
99
132
160
182
OH
OH
Cl
Cl
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440

6. GC-MS chromatogram and spectra; 2,4,6-TCP intermediates

GCMS Sample Information

Data Acquired by	: Admin, Jabatan Kimia, UPM
Acquisiton Date	: 7/10/08 10:06:33 AM
Sample Type	: Unknown
Level #	: 0
Sample Name	: TCP 30
Sample ID	: GS18309
IS Amount	: [1]=0.000
Sample Amount	: 0.000
Dilution Factor	: 0.000
Vial #	: 1
Injection Volume	: 0.500
Data File	: C:\GCMSsolution\Data\Halim\1587-tcp_30.qgd
Method File	: C:\GCMSsolution\Data\Halim\gc70310.qgm
Report File	: C:\GCMSsolution\Data\zaks\gcpotrait.qgr
Tuning File	: C:\GCMSsolution\System\Tune1\090708EIf2.qgt
Modified by	: Admin
Modified	: 7/14/08 10:06:16 AM

GCMS Chromatogram



GCMS Peak Report

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	13.751	13.717	13.817	274772	120220	2.28		0.83	
2	14.390	14.342	14.433	125582	82628	1.51		0.38	
3	16.057	16.017	16.083	739963	498933	1.48		2.22	
4	18.002	17.983	18.050	81917	67925	1.20		0.25	
5	18.158	18.125	18.175	135896	71926	1.88		0.41	
6	18.214	18.175	18.242	1850964	1128774	1.63	V	5.57	
7	20.187	20.108	20.250	2210586	1130446	1.95		6.65	
8	21.726	21.700	21.775	133451	95724	1.39		0.40	
9	22.005	21.933	22.067	2117868	1090718	1.94		6.37	
10	23.322	23.225	23.400	21863215	6799099	3.21		65.74	
11	23.687	23.500	23.733	1655457	721096	2.29	V	4.98	
12	25.246	25.175	25.292	1073195	508035	2.11		3.23	
13	26.756	26.700	26.800	688257	300041	2.29		2.07	
14	28.613	28.558	28.675	305910	122481	2.49		0.92	
				33257033	12738046			100.00	

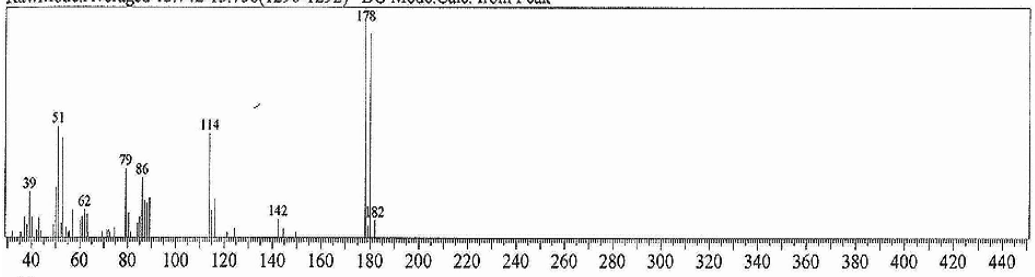
DIMS of 3,5-dichlorocatechol

GCMS Library

<< Target >>

Line#:1 R.Time:13.750(Scan#:1291) MassPeaks:49 BasePeak:178.10(16529)

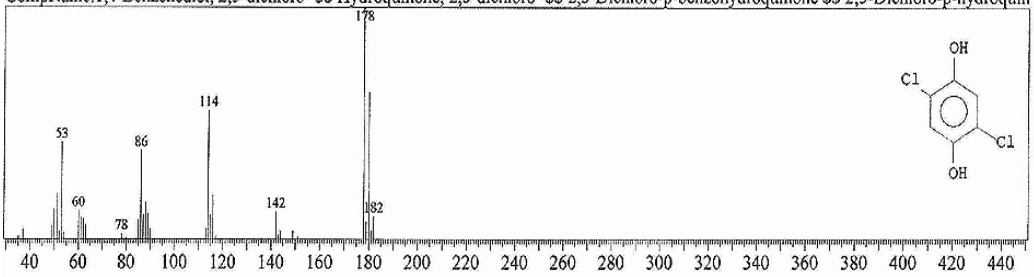
RawMode:Averaged 13.742-13.758(1290-1292) BG Mode:Calc. from Peak



Hit#:1 Entry:24694 Library:Nist107.lib

SI:82 Formula:C6H4Cl2O2 CAS:824-69-1 MolWeight:178 RetIndex:0

CompName:1,4-Benzenediol, 2,5-dichloro- $$ Hydroquinone, 2,5-dichloro- $$ 2,5-Dichloro-p-benzohydroquinone $$ 2,5-Dichloro-p-hydroquin



Hit#:2 Entry:24691 Library:Nist107.lib

SI:80 Formula:C6H4Cl2O2 CAS:0-0-0 MolWeight:178 RetIndex:0

CompName:3,5-Dichloro-benzene-1,2-diol $$