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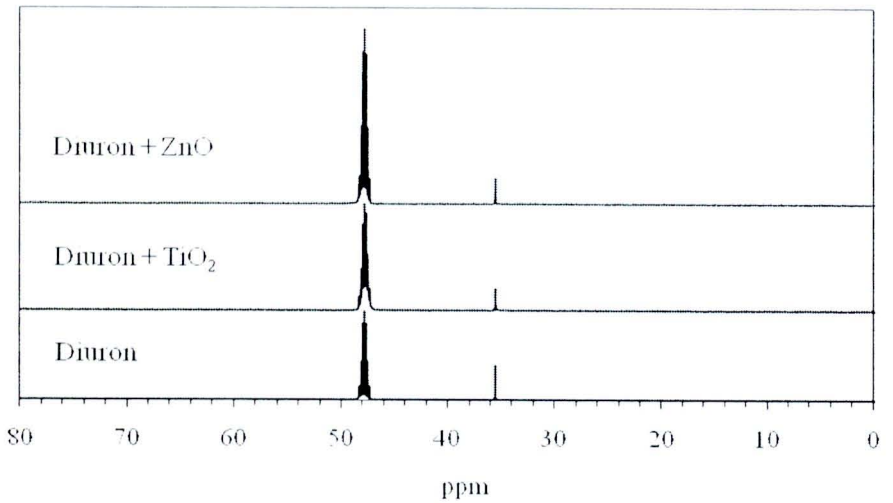
APPENDICES

APPENDIX A

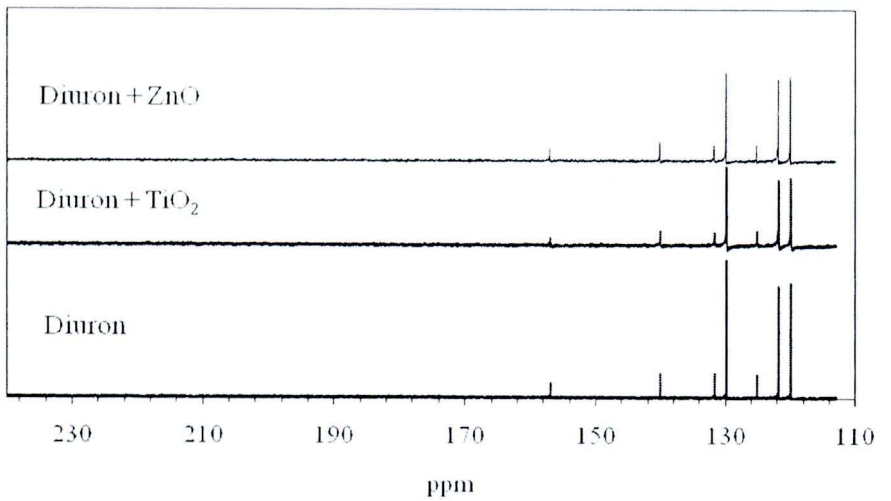
NMR STUDIES

^{13}C NMR analysis was conducted on the diuron solution to determine its chemical structure. Figure A.1 shows ^{13}C NMR spectra obtained from diuron solution in methanol (CD_3OD) and from diuron solution in methanol (CD_3OD) with the presence of TiO_2 and ZnO in the range of chemical shift from (a) 0-80 ppm and (b) 110-240 ppm. In general, all spectra show peaks in the resonance areas of alkyl carbon (0-50 ppm), o-alkyl carbon (50-110 ppm), aromatic carbon (110-160 ppm), and carbonyl carbon (150-220 ppm) [73]. The signal corresponding to carbon from methanol which was used as solvent appears at 48-49 ppm. For diuron, it has 9 atoms of carbon as shown in Figure A.2. The ^{13}C NMR results also indicate 9 atoms of carbon in the molecule. C_1 to C_6 are aromatic carbon corresponding to the chemical shift at 121.187, 141.321, 123.074, 132.915, 126.373, and 131.107 ppm, respectively. The chemical shift of C_7 appears at 158.133 ppm. C_8 and C_9 are alkyl carbon of which the signal appears at 36.732 ppm. The condition of diuron with TiO_2 and ZnO had not chemical shift compared diuron. Due to the NMR analysis, the aqueous suspension had to filter the catalyst from the diuron solution before analyze. It is indicated that, the reaction can not occur without light and catalyst.

Figure A.3 shows ^1H NMR spectra obtained from diuron solution in methanol (CD_3OD) and diuron solution in methanol mixed with TiO_2 and ZnO in the range of chemical shift from (a) 2.5 – 3.5 ppm, (b) 3.5 – 6.5 ppm, and (c) 7.2 -7.8 ppm. In the Figure A.3, the NMR lines in 3.39 – 5.0 ppm are due to CD_3OD as a solvent. The aromatic protons appeared at 7.29, 7.31, and 7.34 ppm [74, 75]. The signal of N,N-dimethyl group was observed at 2.99 ppm as a singlet [74]. The condition of diuron with TiO_2 and ZnO also had not chemical shift compared with diuron due to the NMR analysze as well.



(a)



(b)

Figure A.1 ^{13}C NMR spectra from diuron solution in methanol (CD_3OD), diuron solution in methanol (CD_3OD) with TiO_2, and diuron solution in methanol (CD_3OD) with ZnO in the chemical shift from (a) 0-80 ppm and (b) 110-240 ppm.

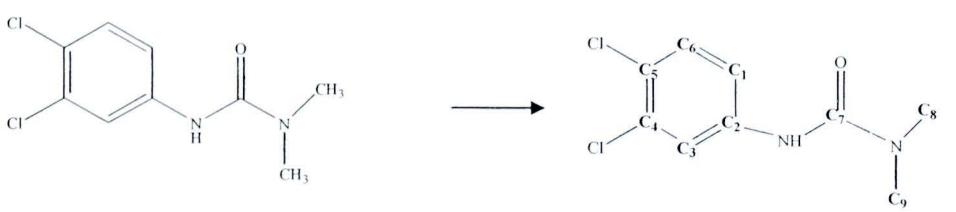


Figure A.2 Chemical structure of diuron.

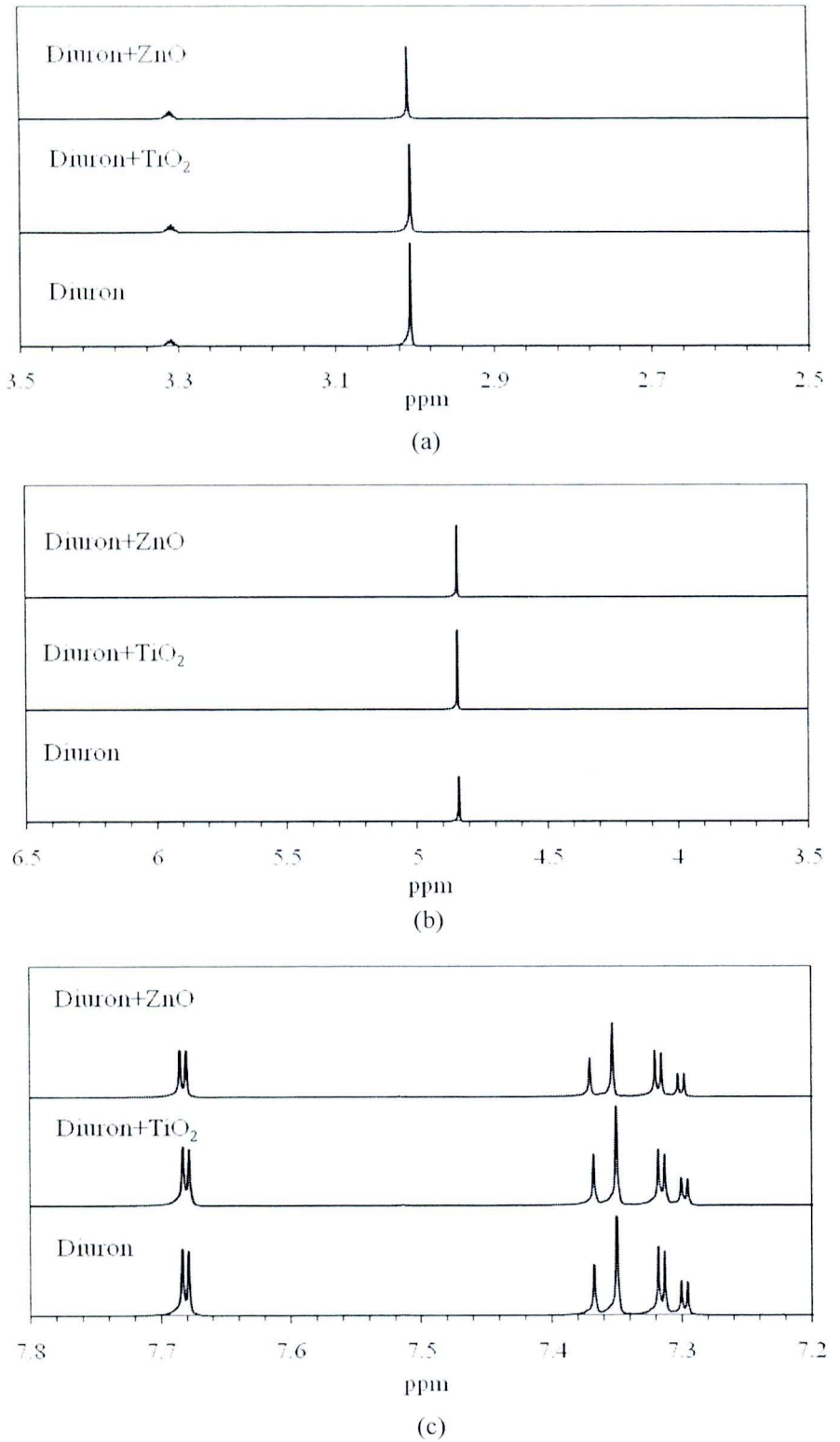


Figure A.3 ^{1}H NMR spectra from diuron solution in methanol (CD_3OD), diuron solution in methanol (CD_3OD) with TiO_2, and diuron solution in methanol (CD_3OD) with ZnO in the chemical shift from (a) 2.5-3.5 ppm, (b) 3.5-6.5 ppm, and (c) 7.2-7.8 ppm.

APPENDIX B

DIURON CALIBRATION CURVE

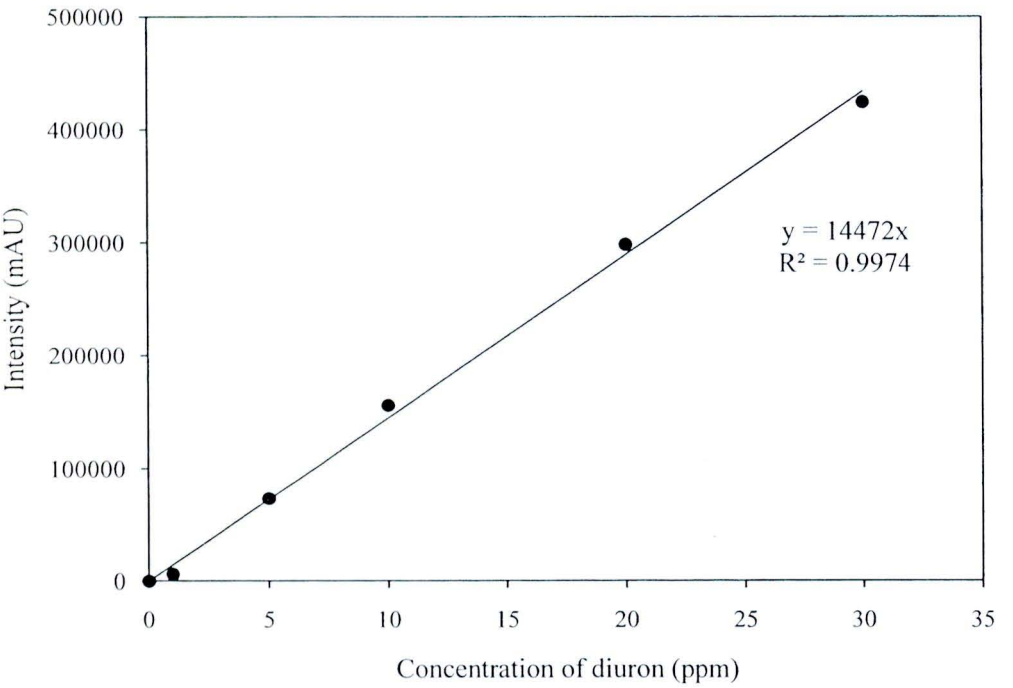


Figure B.1 The calibration curve of diuron.

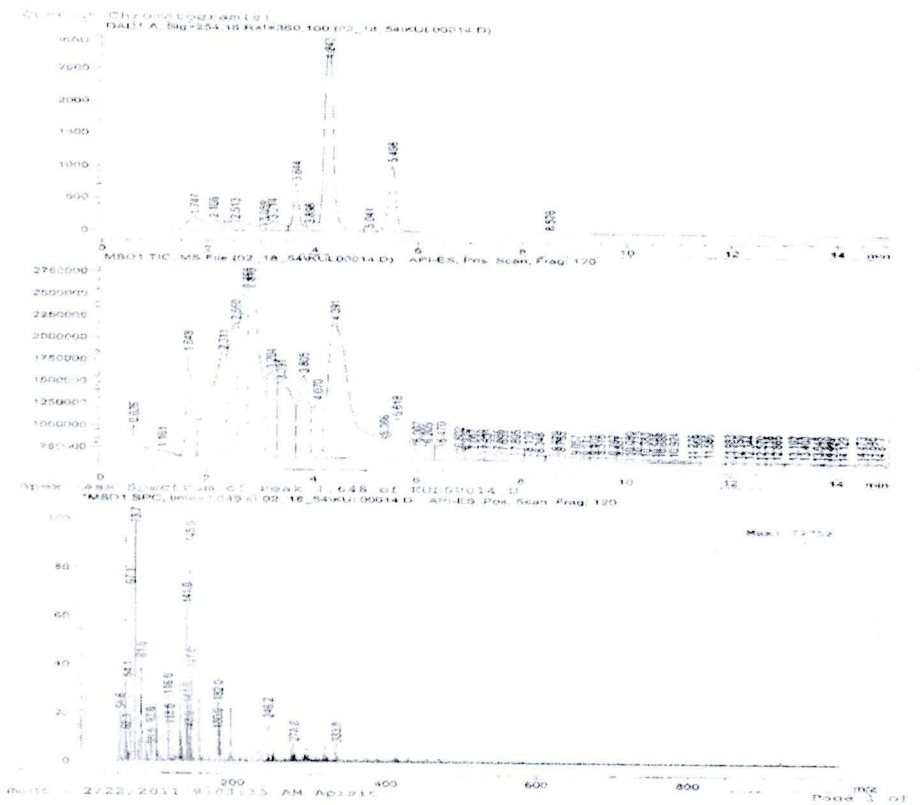
APPENDIX C

LC/MS MASS SPECTRUM

All samples were sent for analysis at Central Laboratory (Thailand) Ltd. Co. During a sample injection, three types of diagrams were obtained: chromatogram from UV detector, chromatogram from mass detector, and mass spectrum. Chromatogram from UV and mass detector spanned the LC runtime. The mass spectrum is obtained at a specific retention time

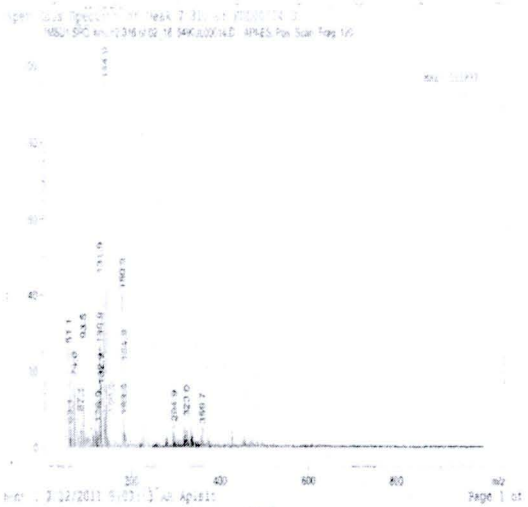
C.1 Mass spectrum of diuron solution from photodegradation by ZnO.

C.1.1 pH 3

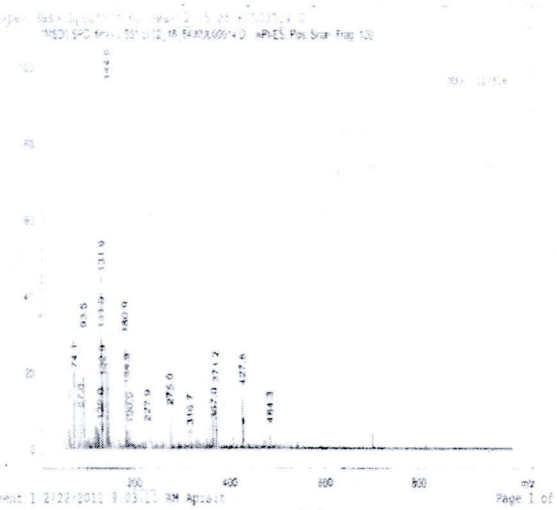


(a)

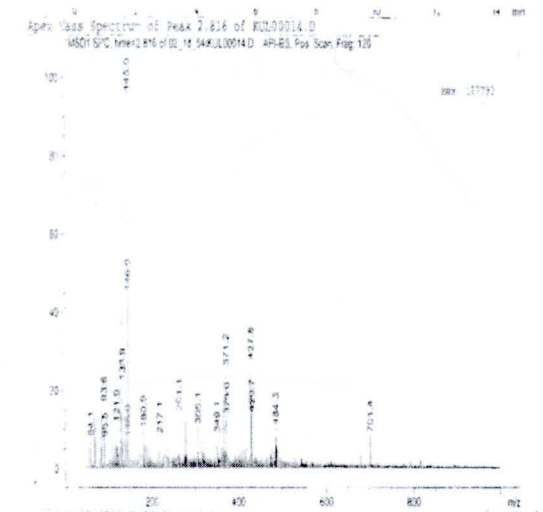
Figure C.1 Chromatogram of diuron solution photodegradation at pH3 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as sown in (a)-(p).



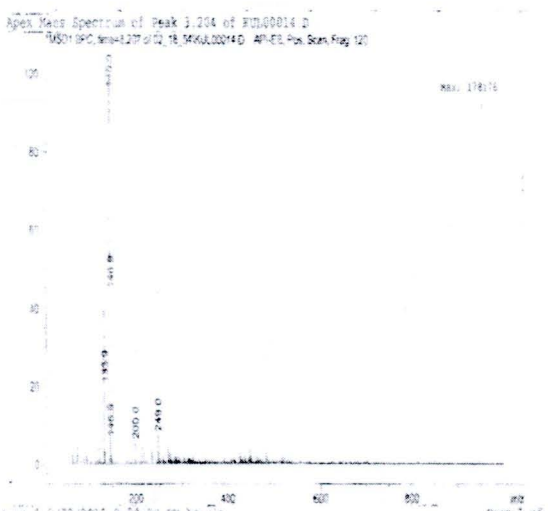
(b)



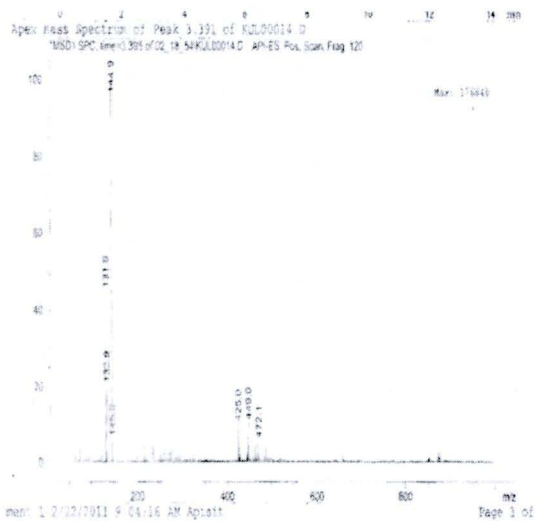
(c)



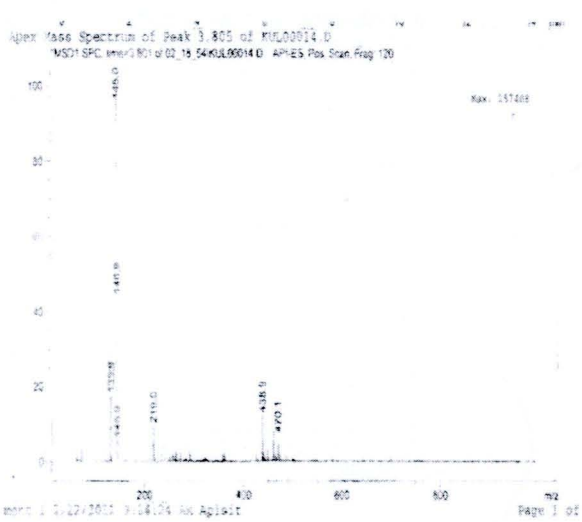
(d)



(e)

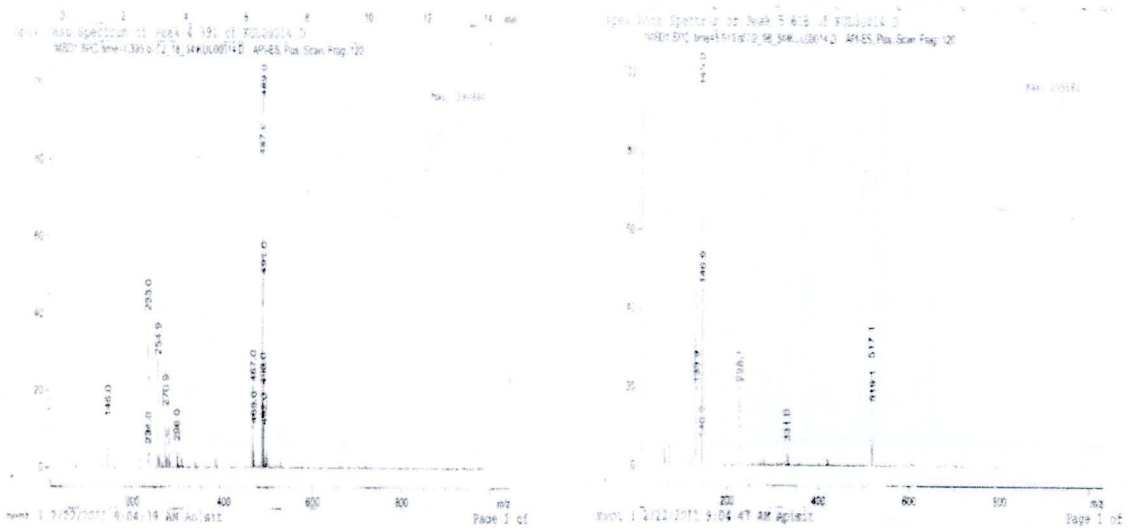


(f)

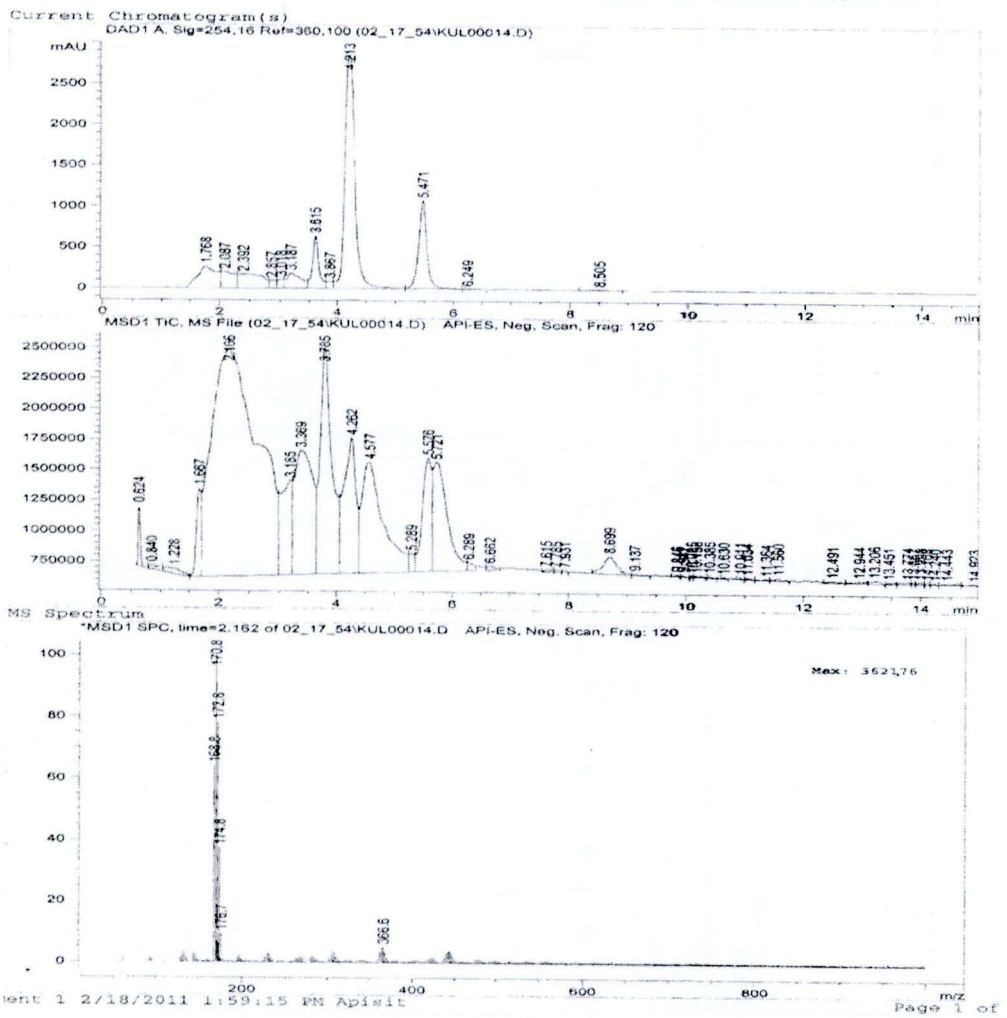


(g)

Figure C.1 (continued).

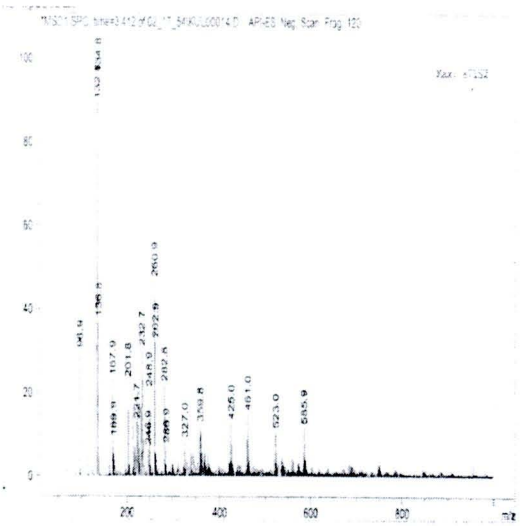


(h) (i)

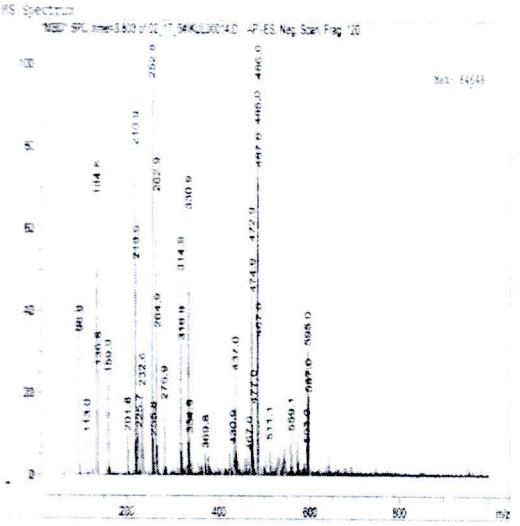


(j)

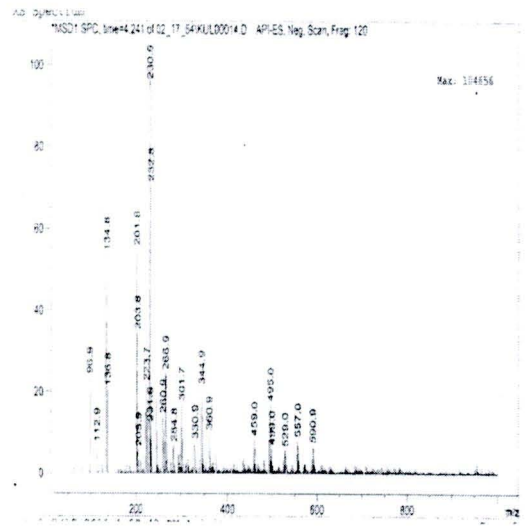
Figure C.1 (continued).



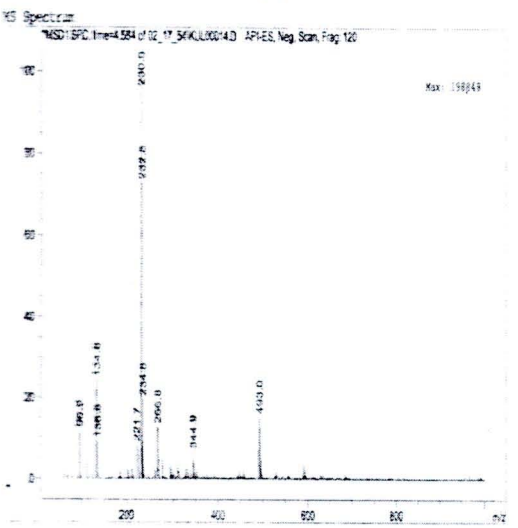
(k)



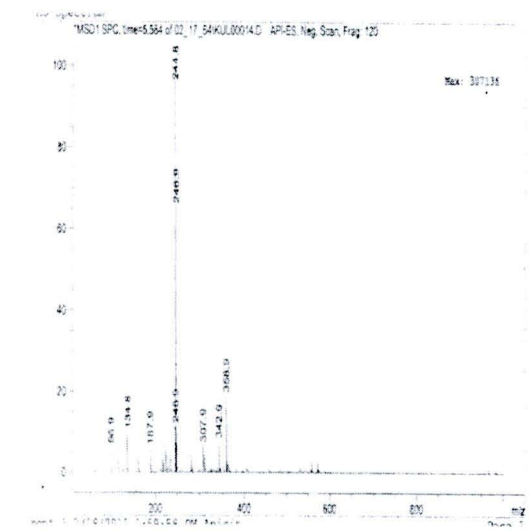
(l)



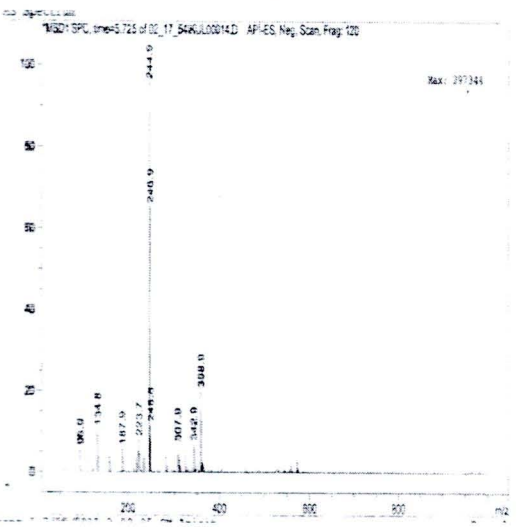
(m)



(n)



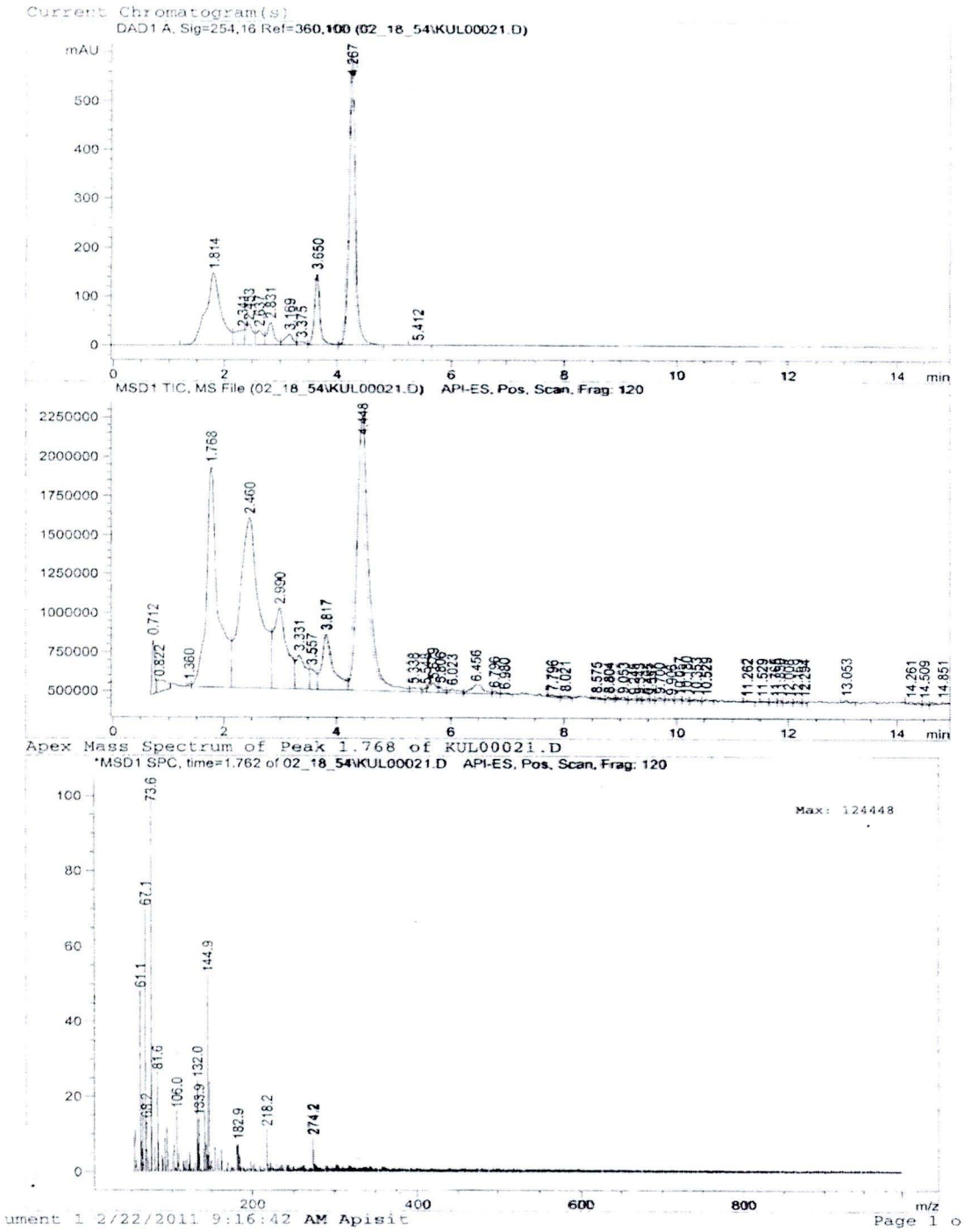
(o)



(p)

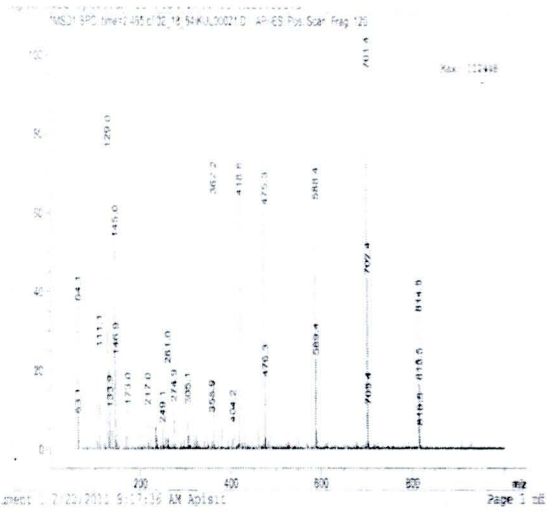
Figure C.1 (continued).

C.1.2 pH 7

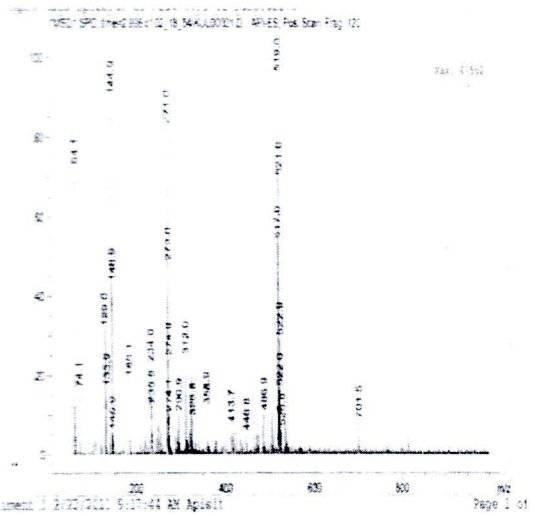


(a)

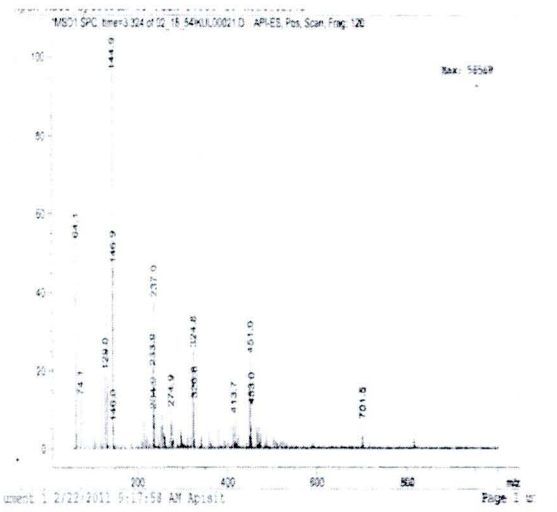
Figure C.2 Chromatogram of diuron solution photodegradation at pH7 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(q).



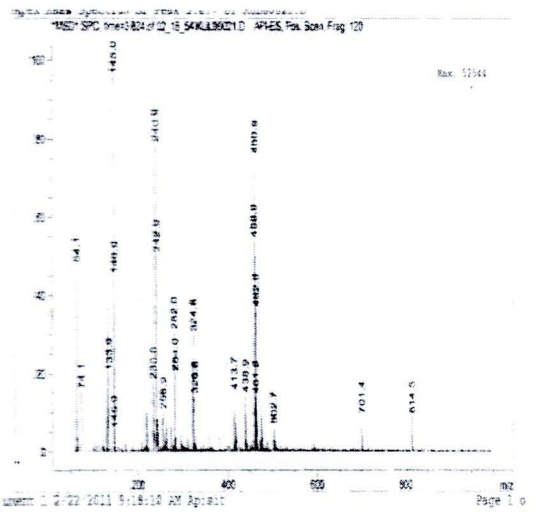
(b)



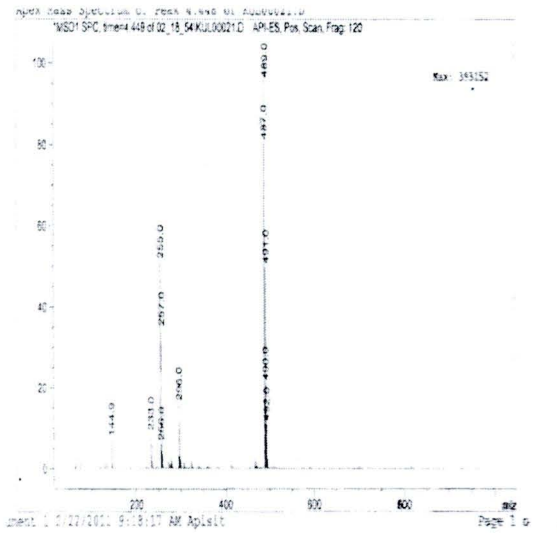
(c)



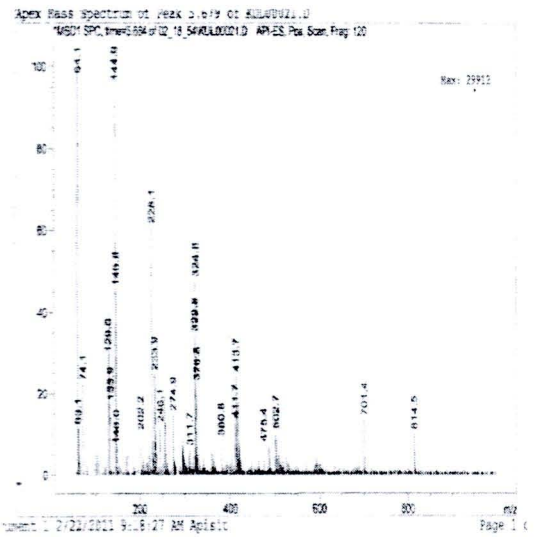
(d)



(e)

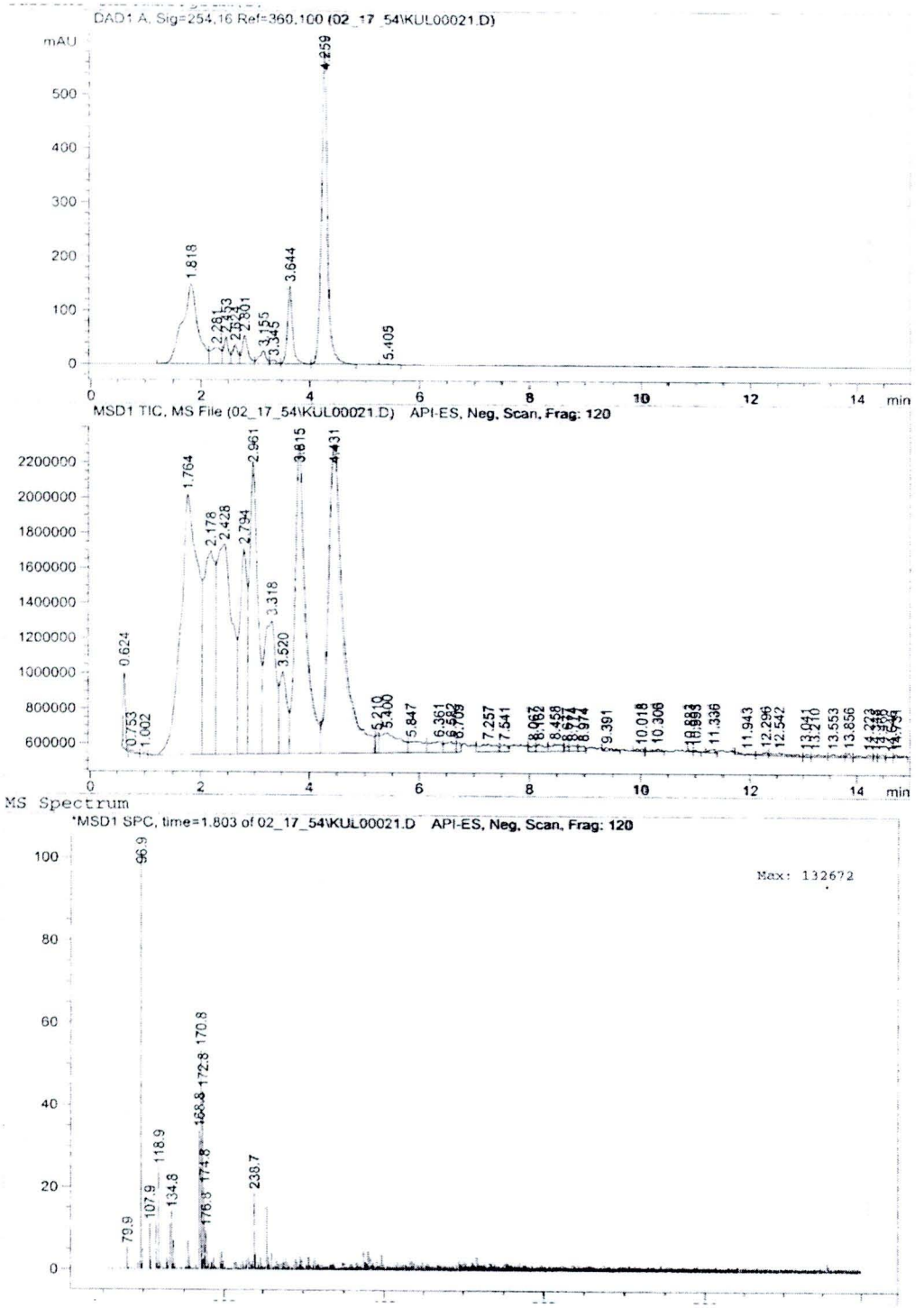


(f)



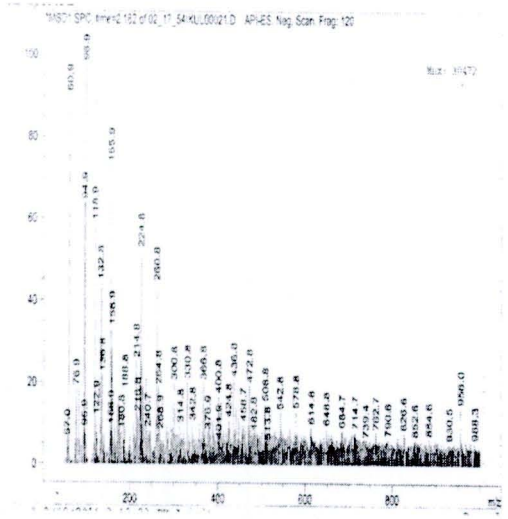
(g)

Figure C.2 (continued).

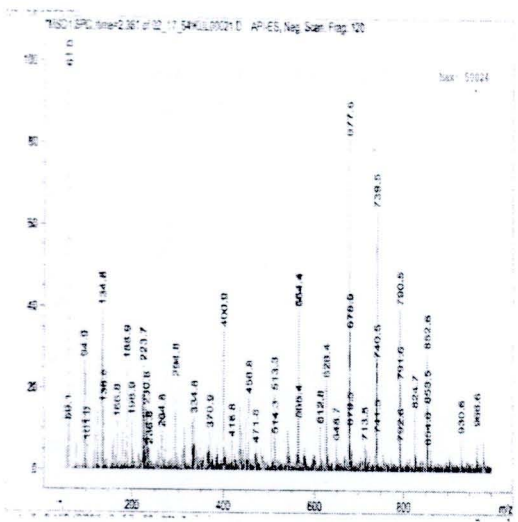


(h)

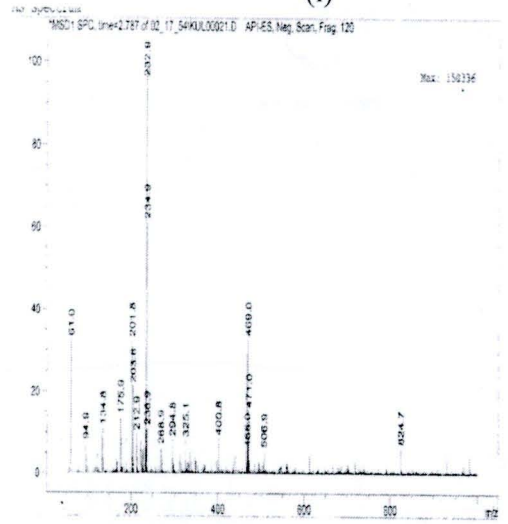
Figure C.2 (continued).



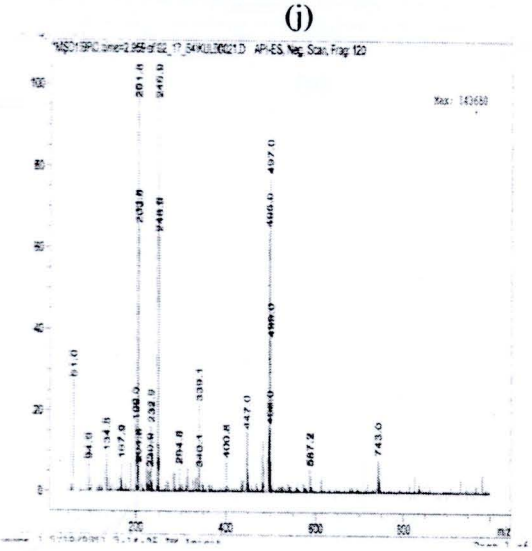
(i)



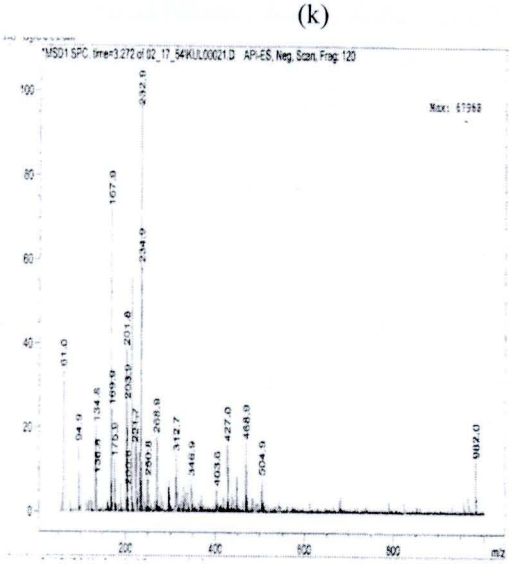
(j)



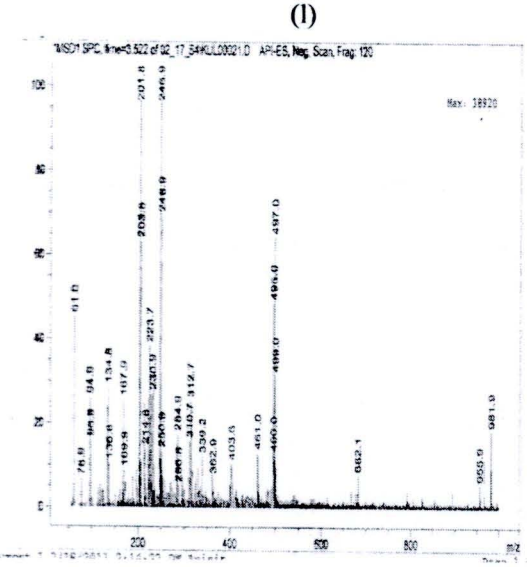
(k)



(l)

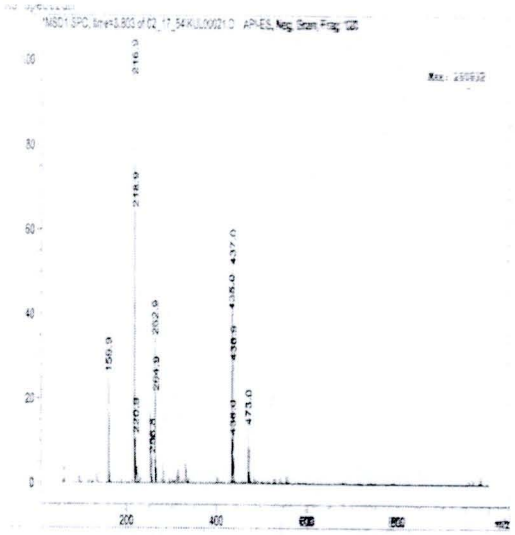


(m)

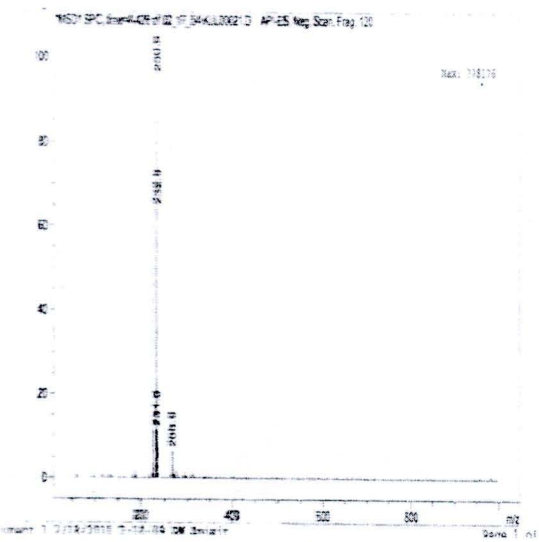


(n)

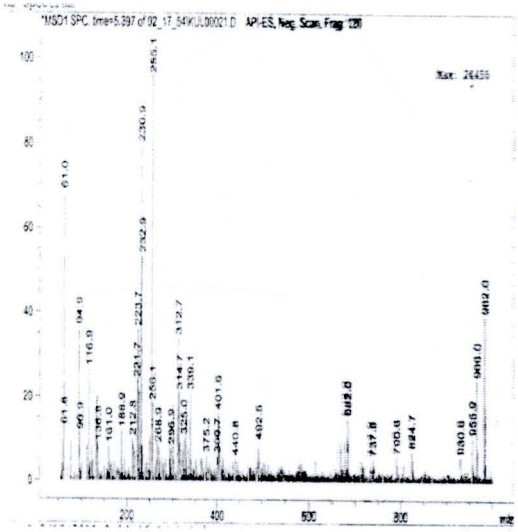
Figure C.2 (continued).



(o)



(p)



(q)

Figure C.2 (continued).

C.1.3 pH10

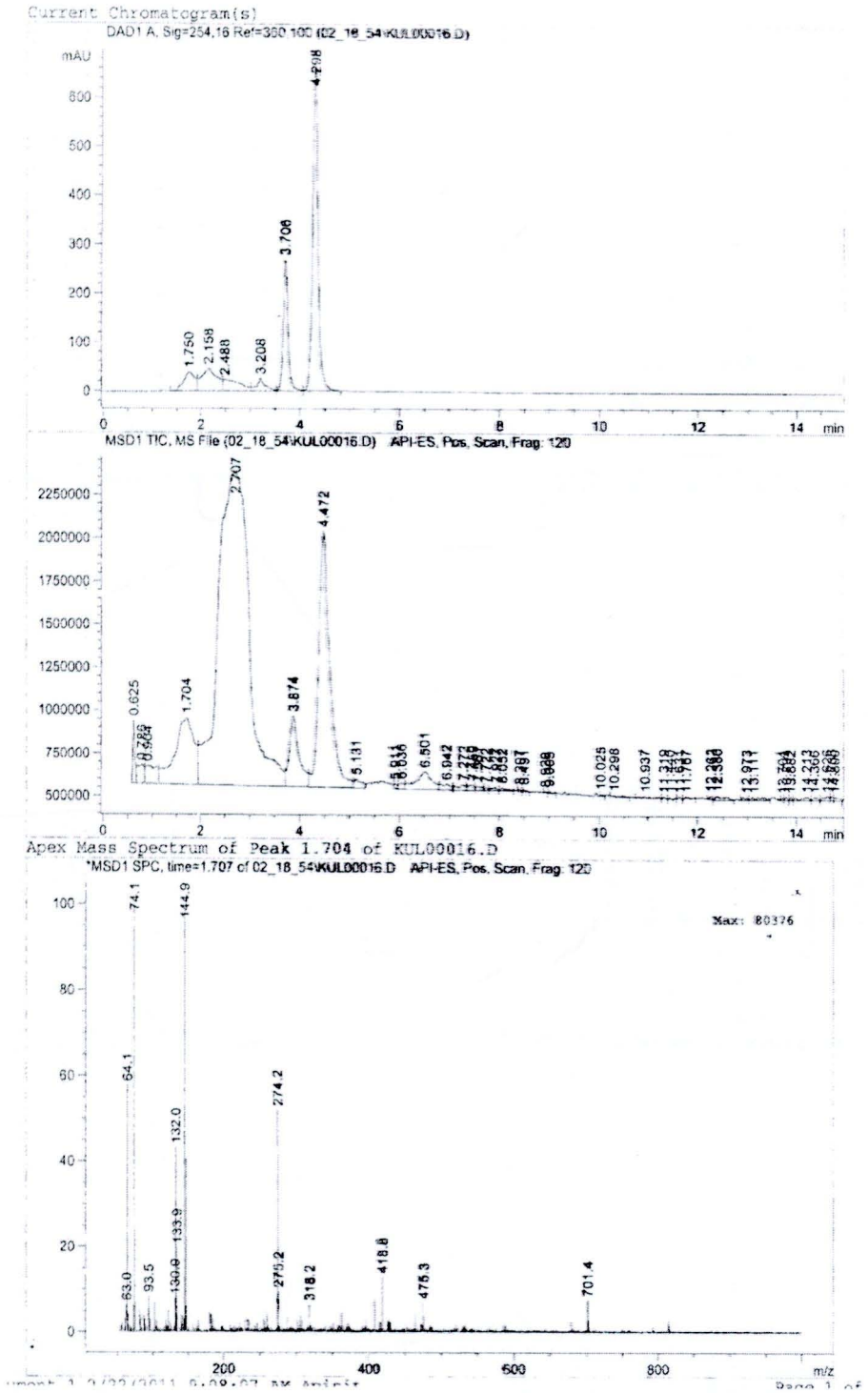
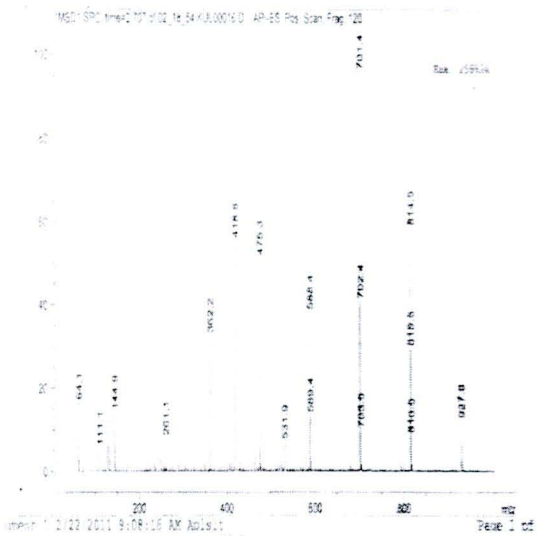
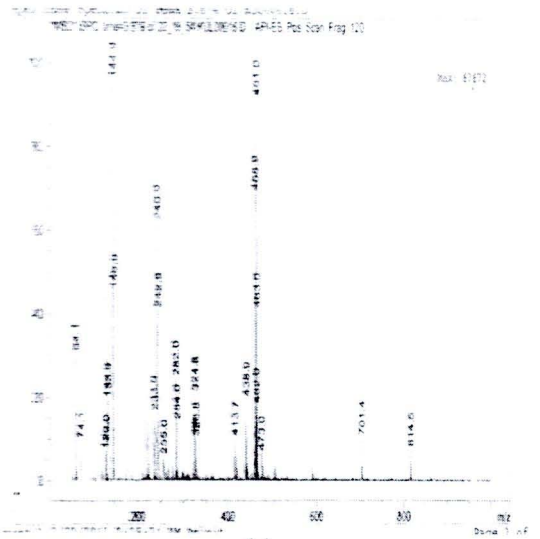


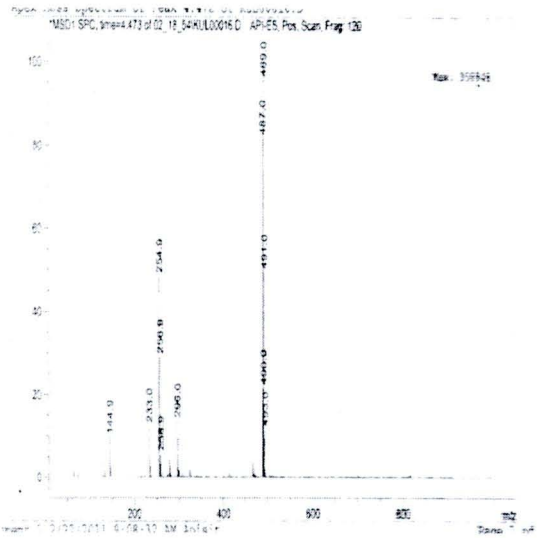
Figure C.3 Chromatogram of diuron solution photodegradation at pH10 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(n).



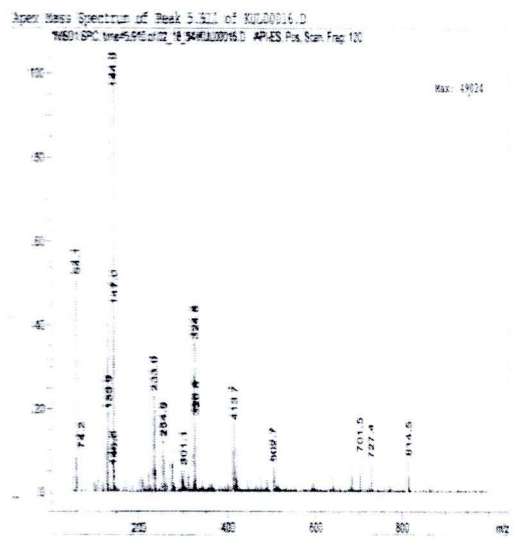
(b)



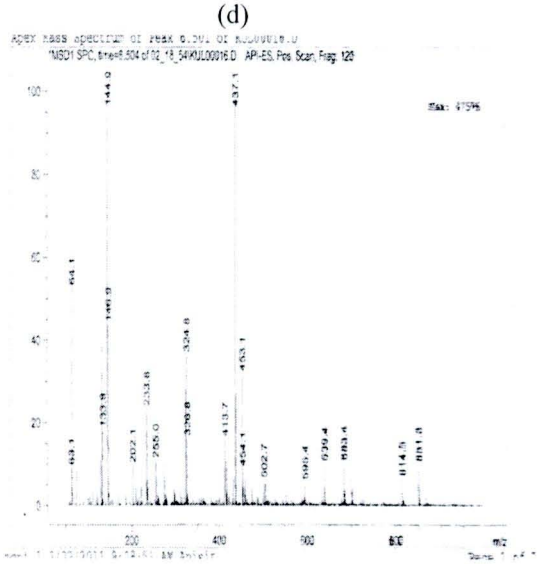
(c)



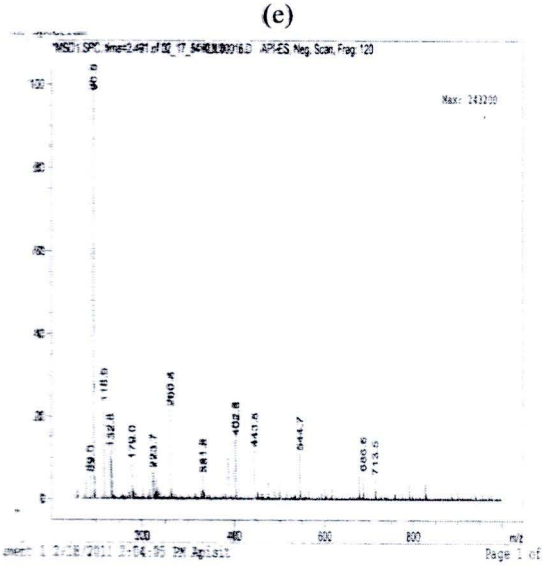
(d)



(e)

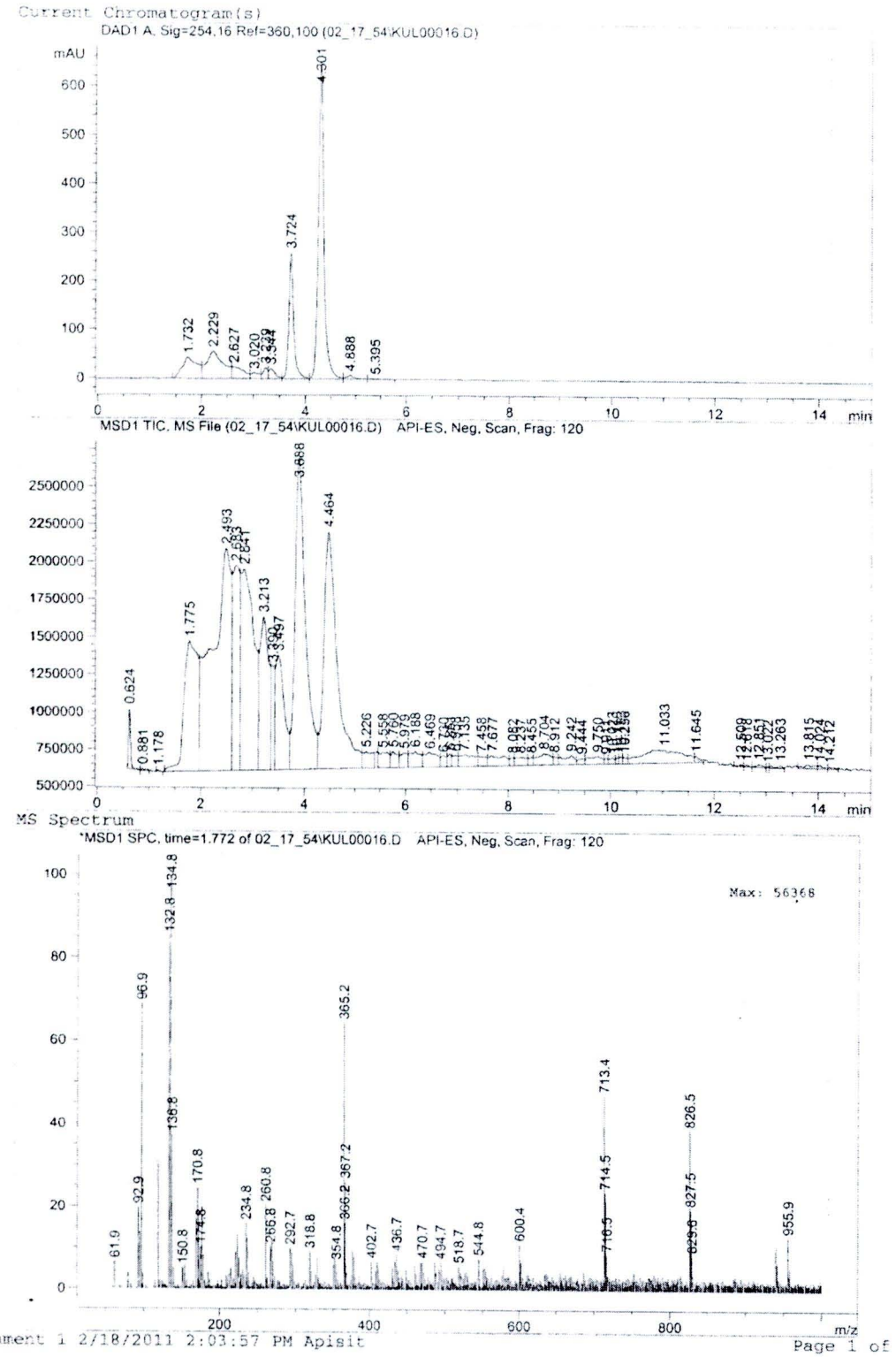


(f)



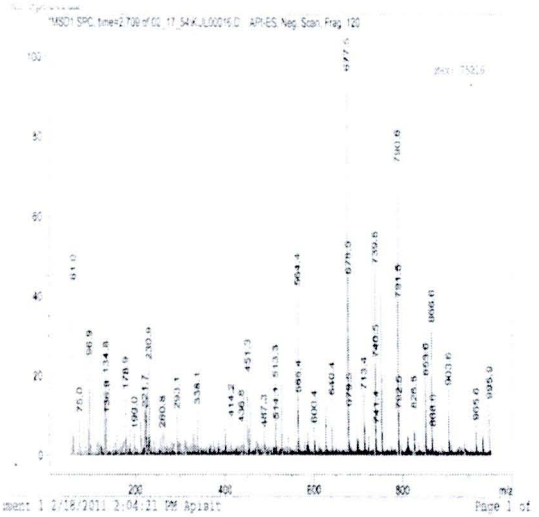
(g)

Figure C.3 (continued).

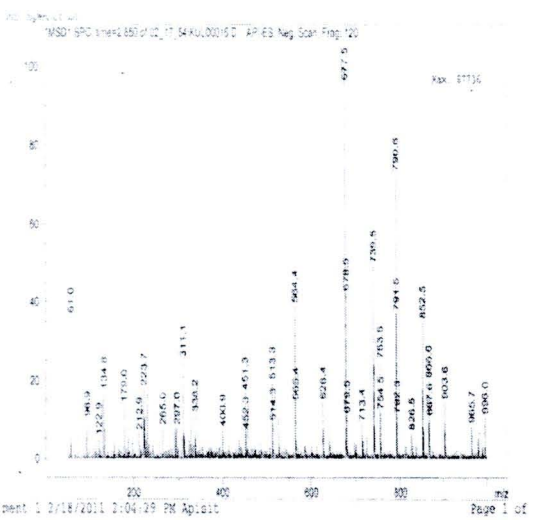


(h)

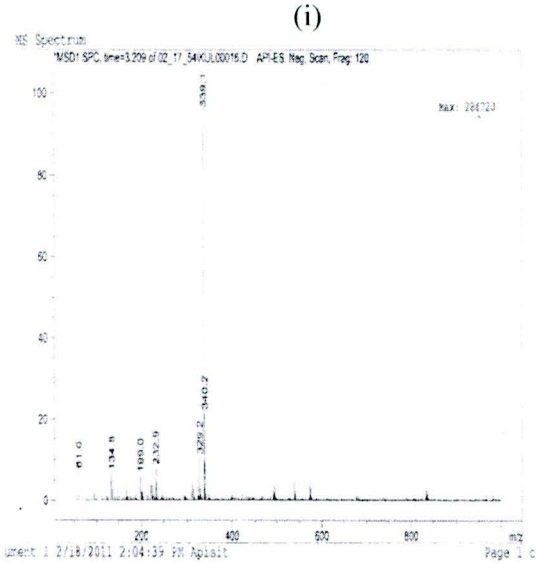
Figure C.3 (continued).



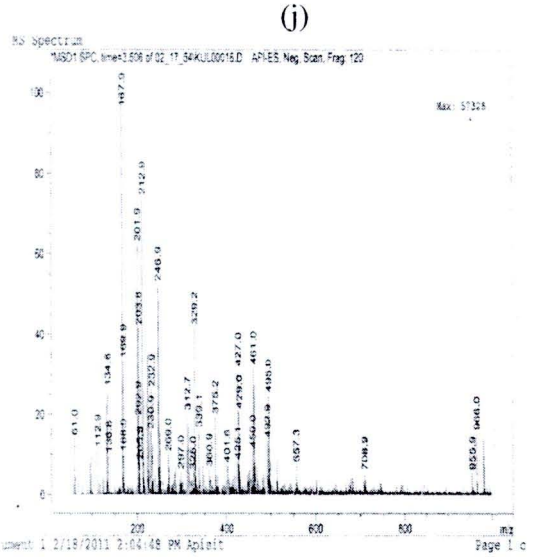
(i)



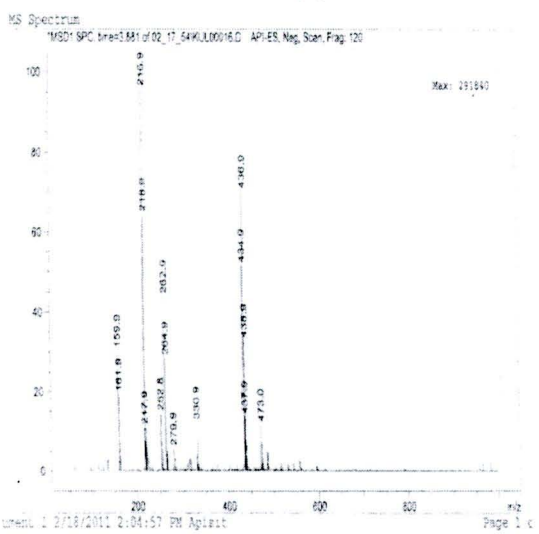
(j)



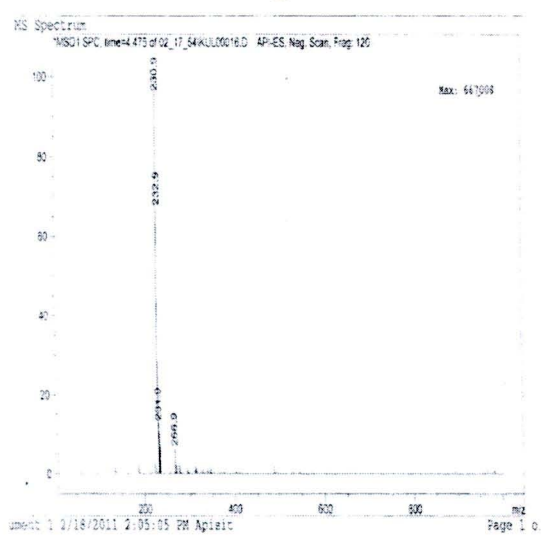
(k)



(l)



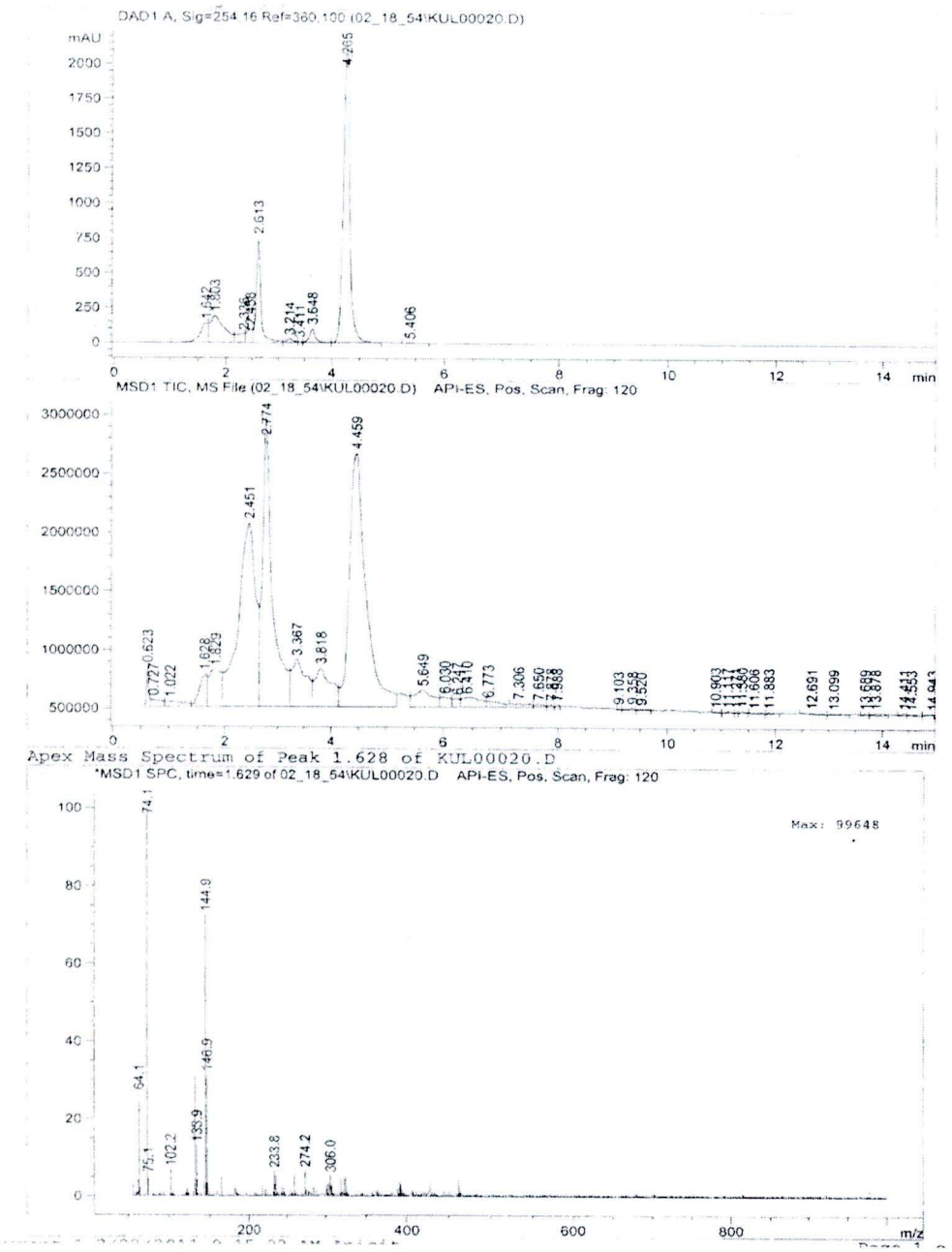
(m)



(n)

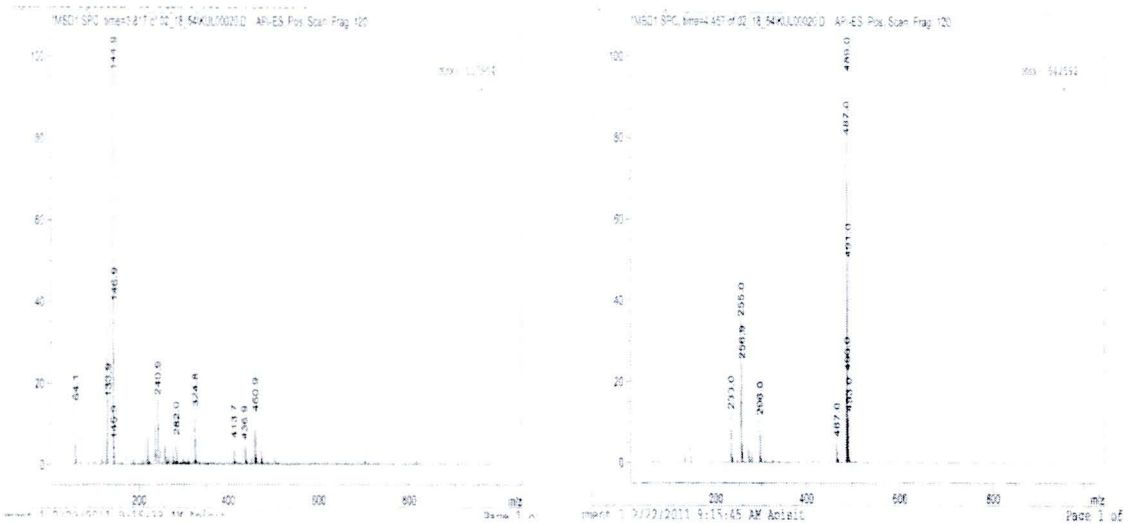
Figure C.3 (continued).

C.1.4 UV-C

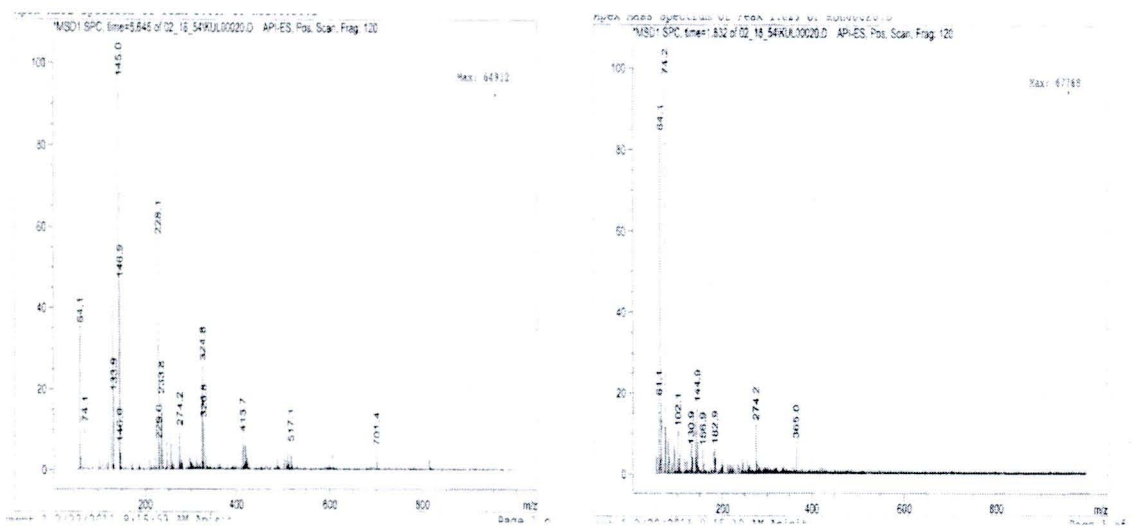


(a)

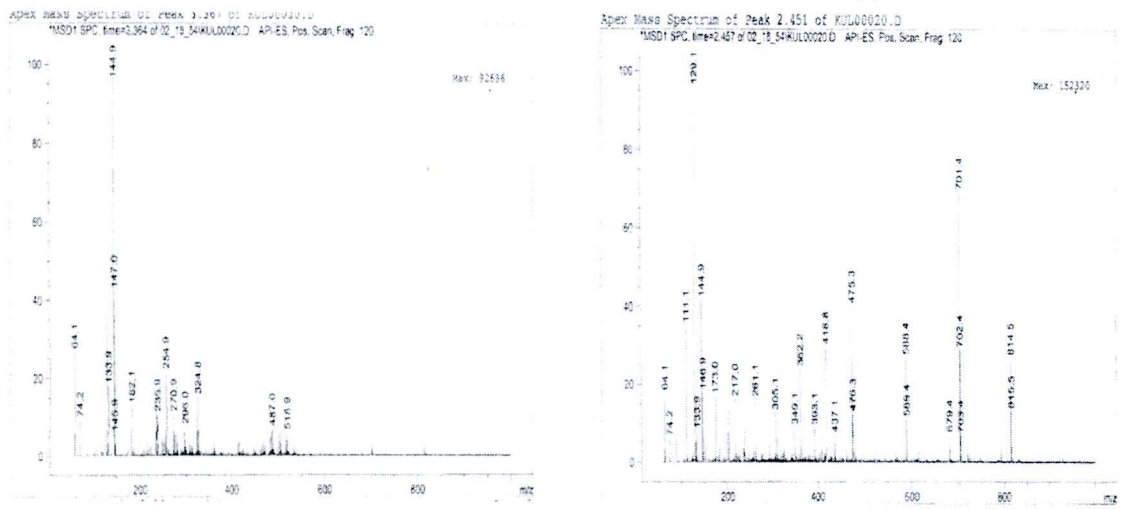
Figure C.4 Chromatogram of diuron solution photodegradation by UV-C obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(n).



(b) (c)

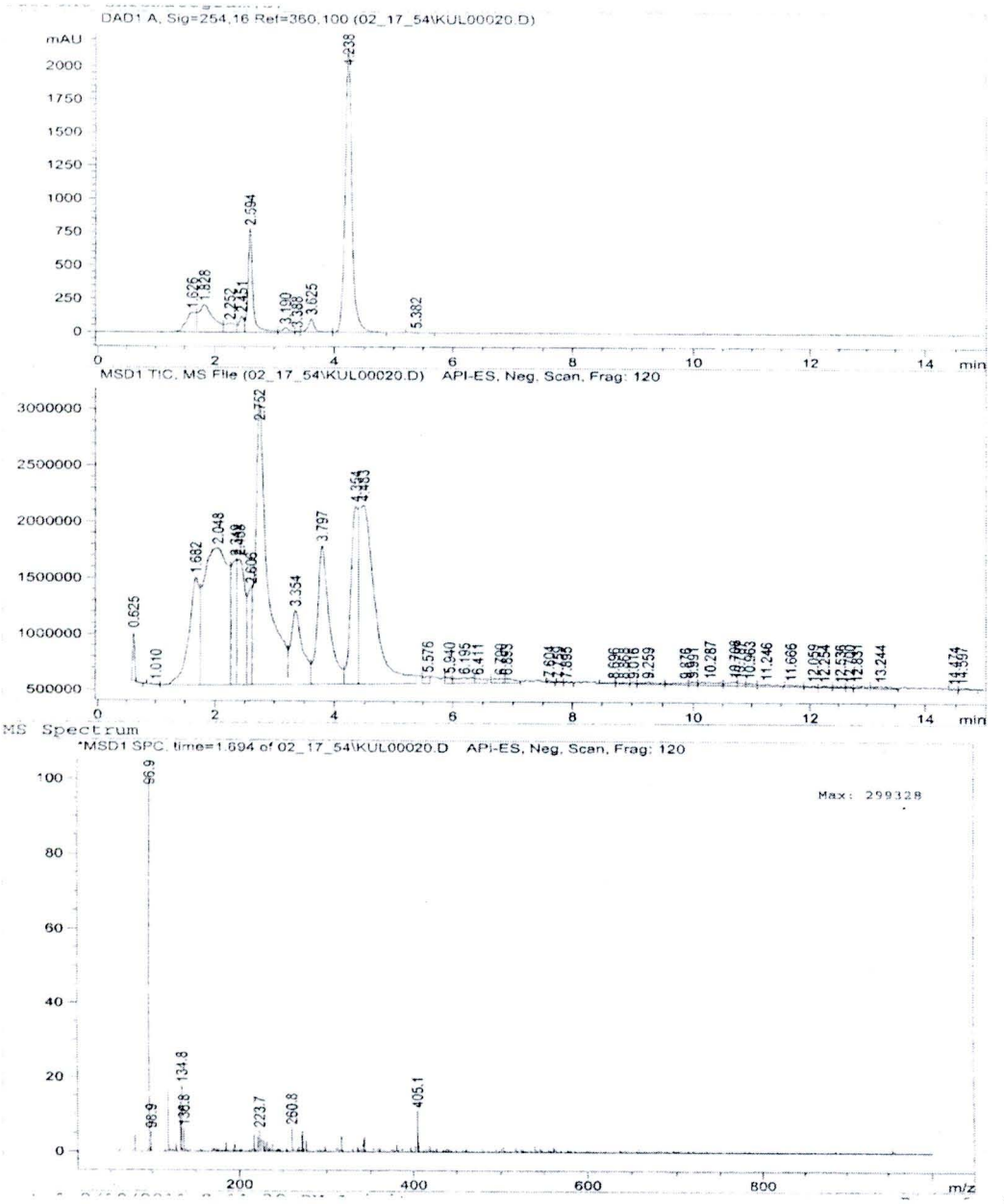


(d) (e)



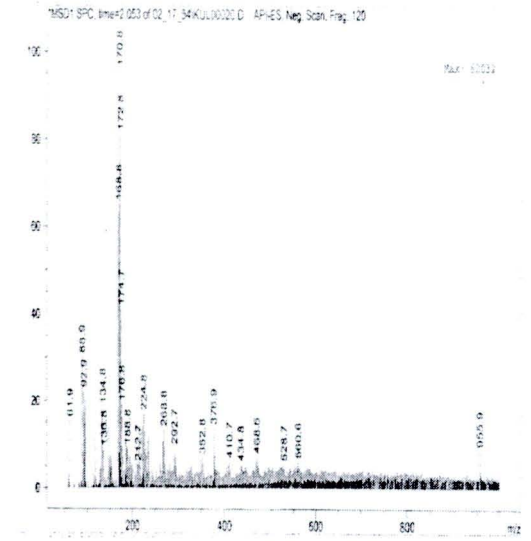
(f) (g)

Figure C.4 (continued).

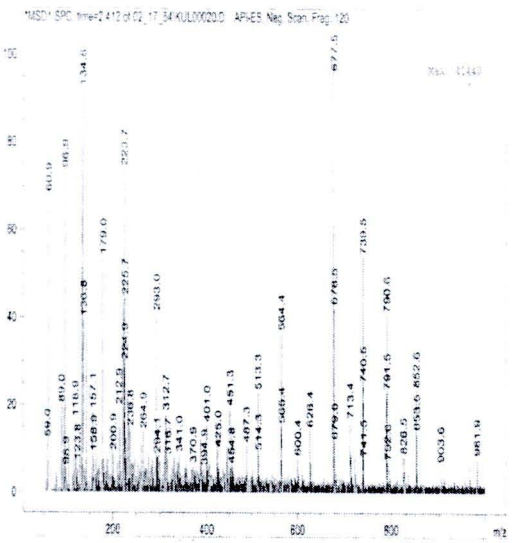


(h)

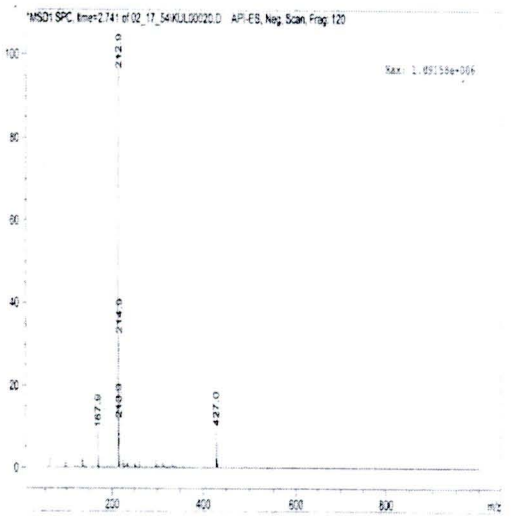
Figure C.4 (continued).



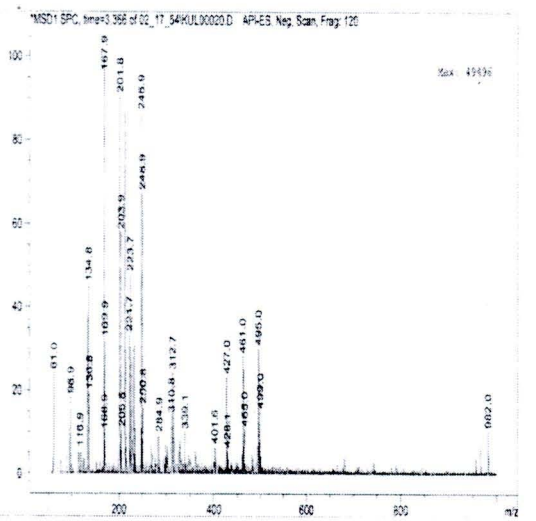
(i)



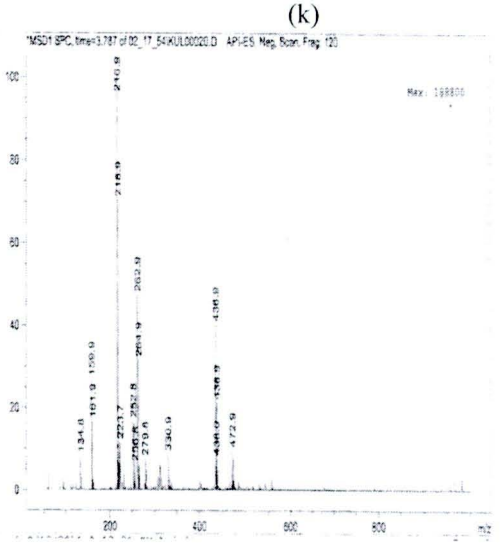
(j)



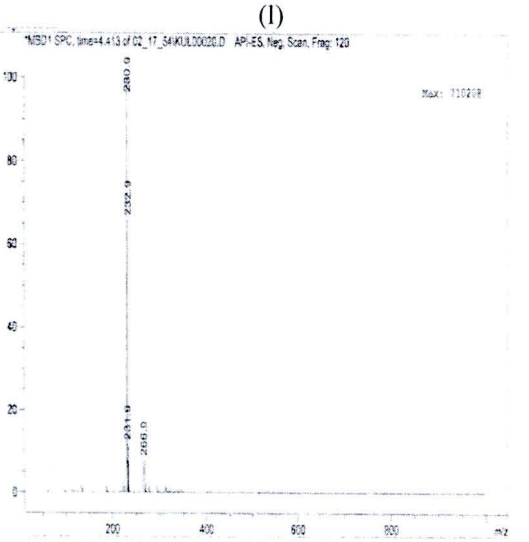
(k)



(l)



(m)

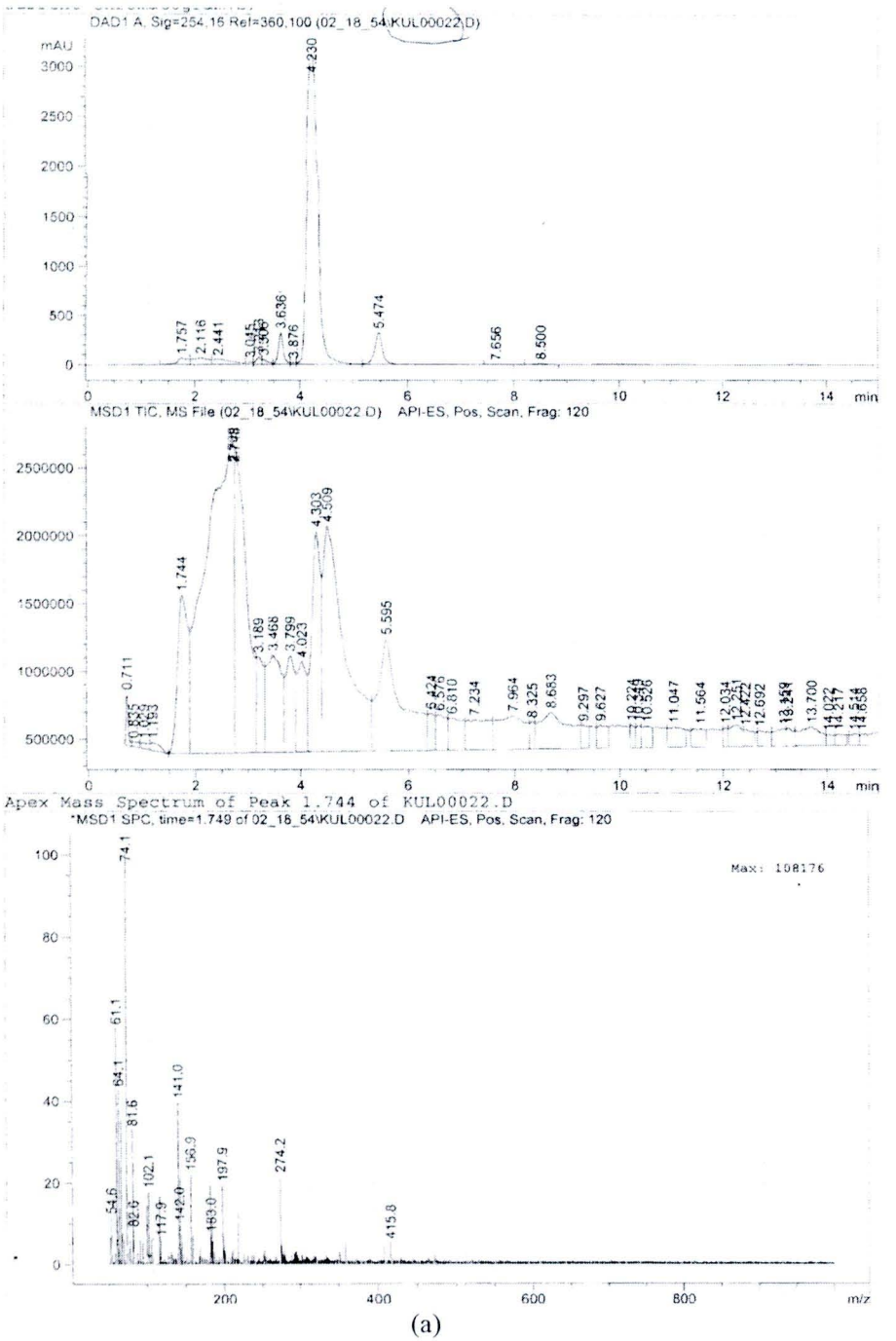


(n)

Figure C.4 (continued).

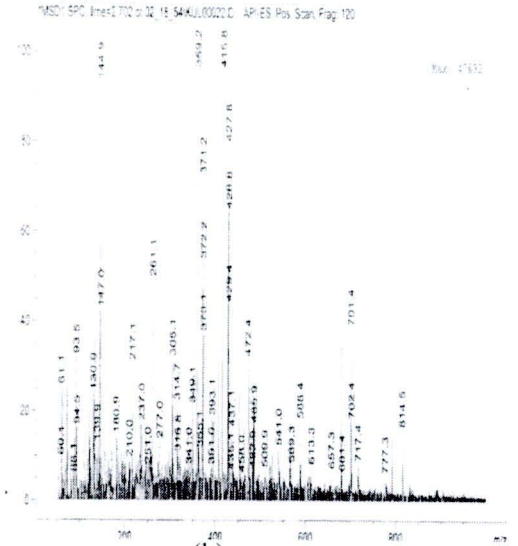
C.3 Mass spectrum of diuron solution from photodegradation by TiO_2.

C.3.1 pH 3

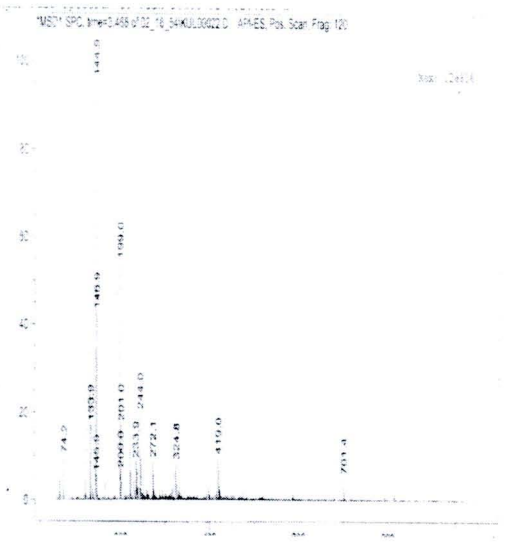


(a)

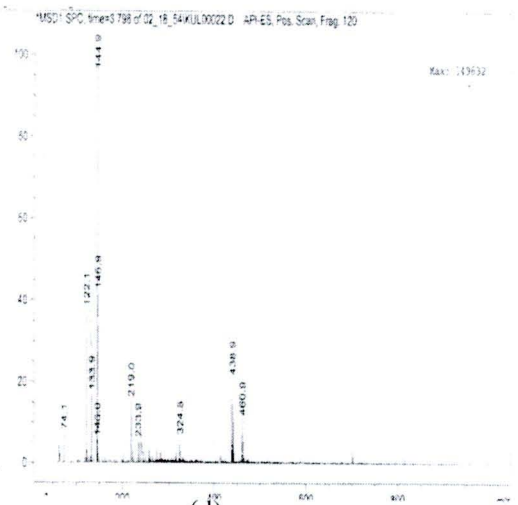
Figure C.5 Chromatogram of diuron solution photodegradation at pH3 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(p).



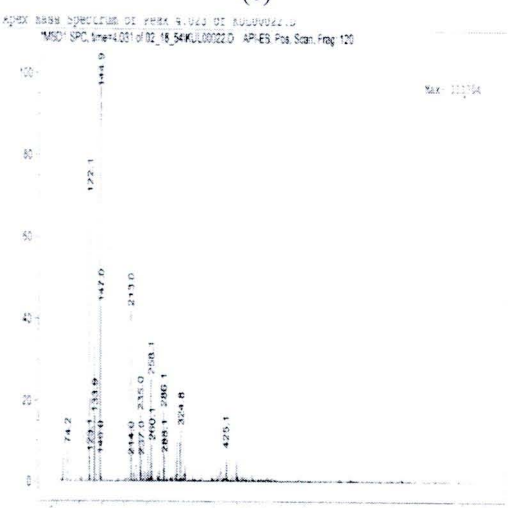
(b)



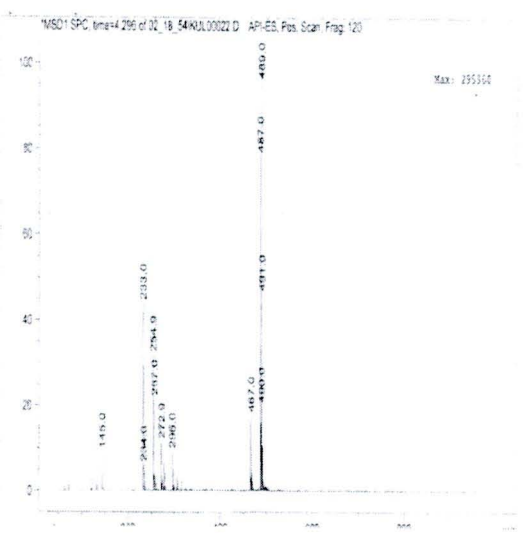
(c)



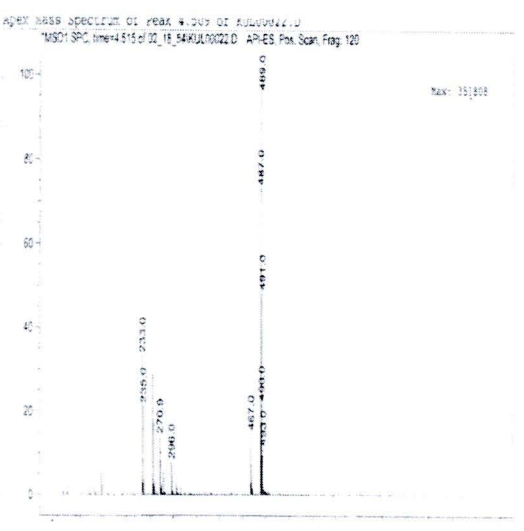
(d)



(e)

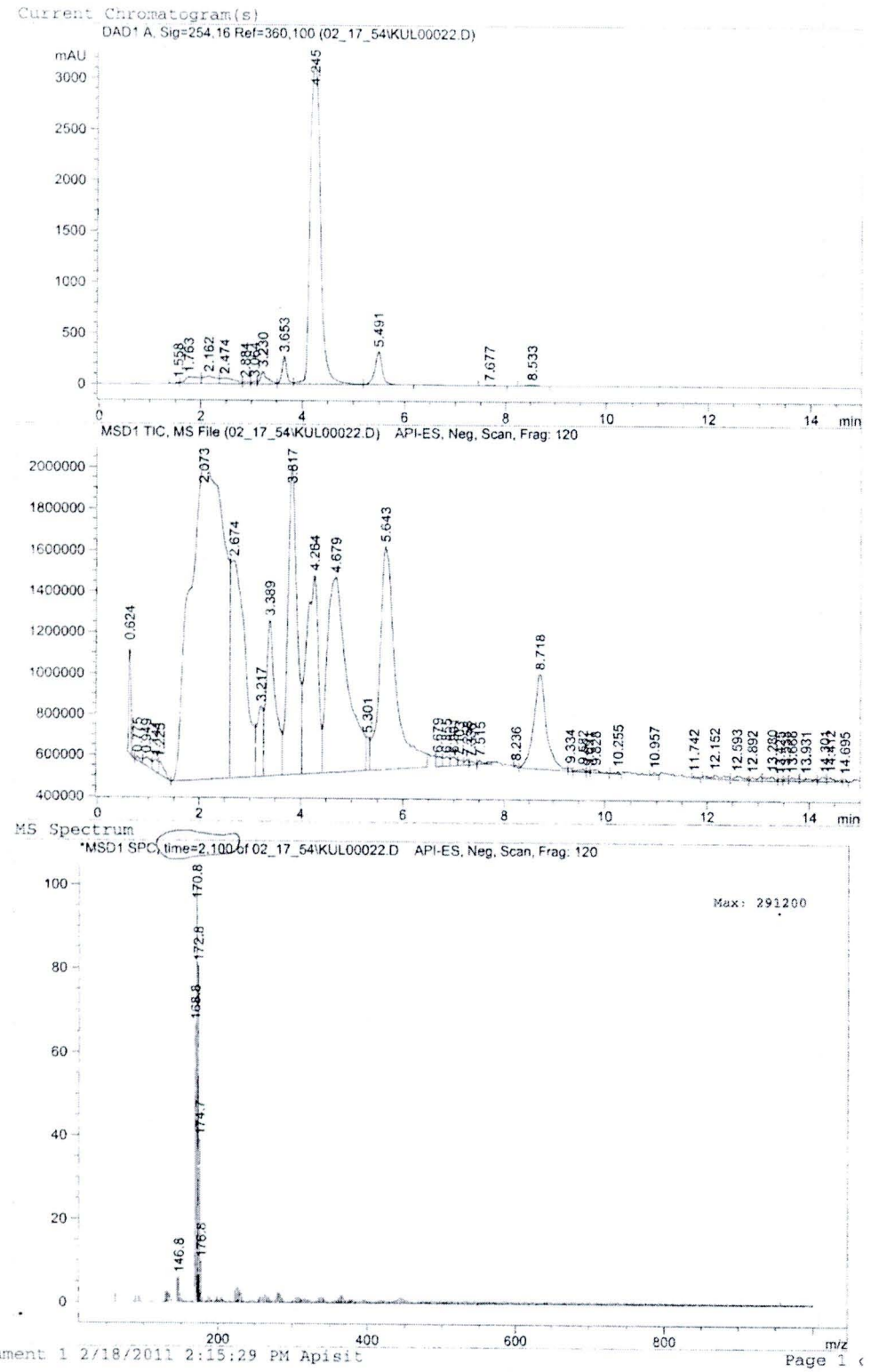


(f)



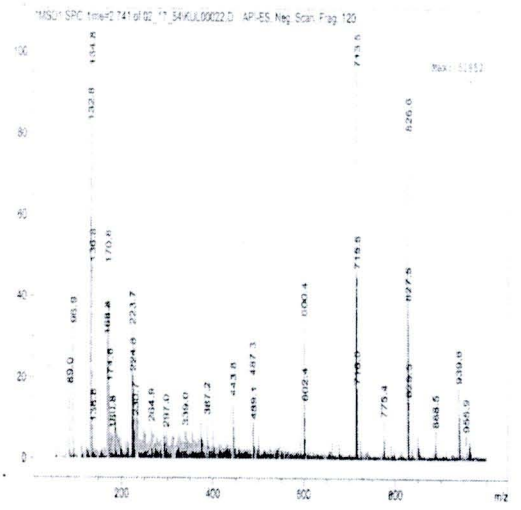
(g)

Figure C.5 (continued).

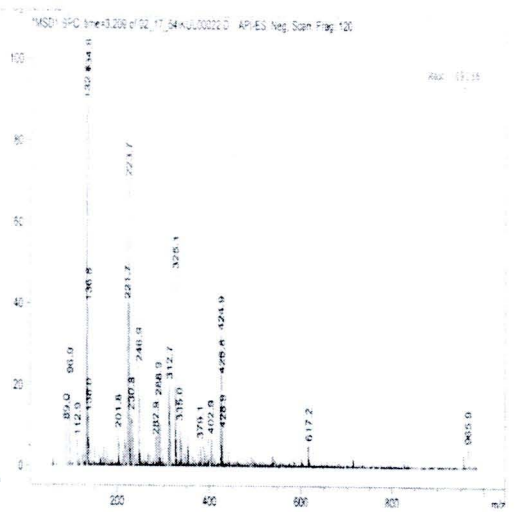


(h)

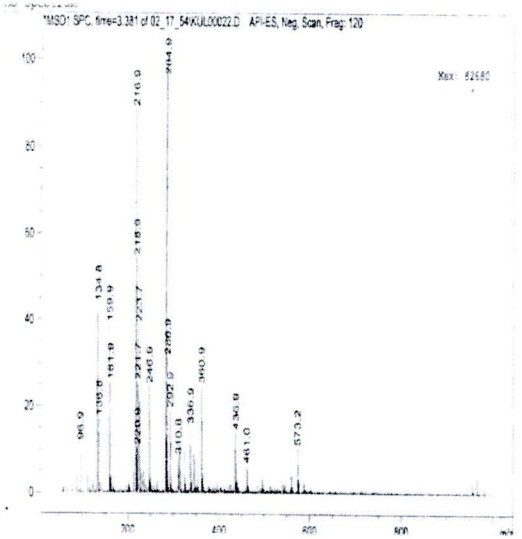
Figure C.5 (continued).



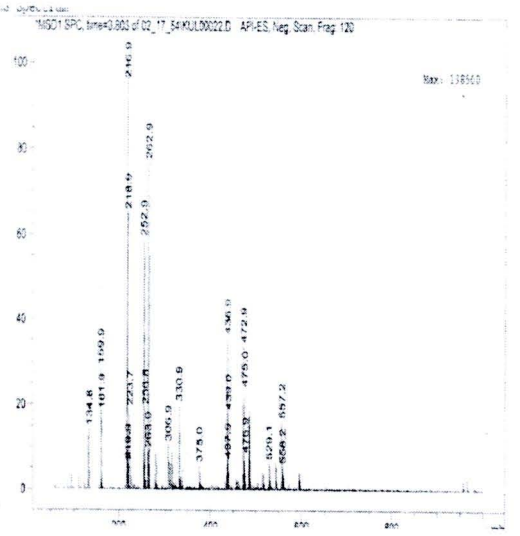
(i)



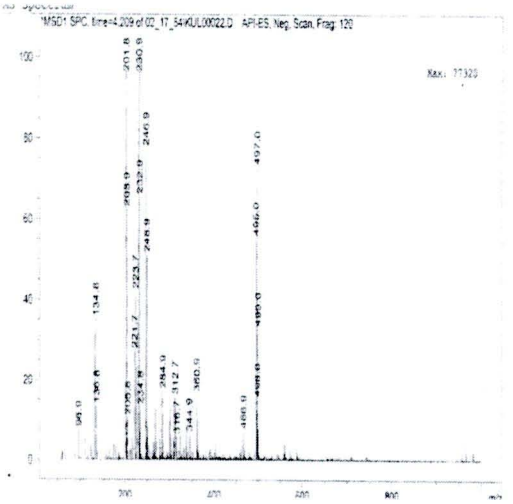
(j)



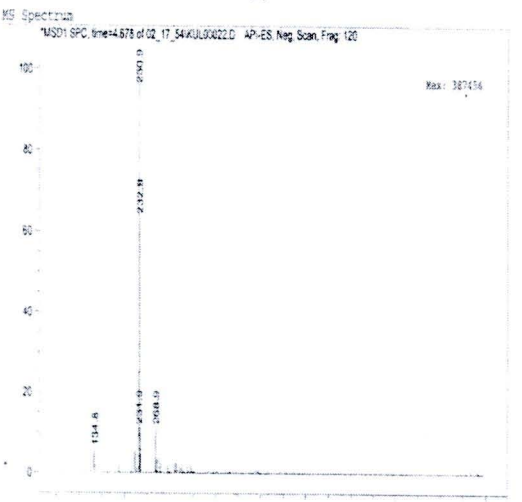
(k)



(l)

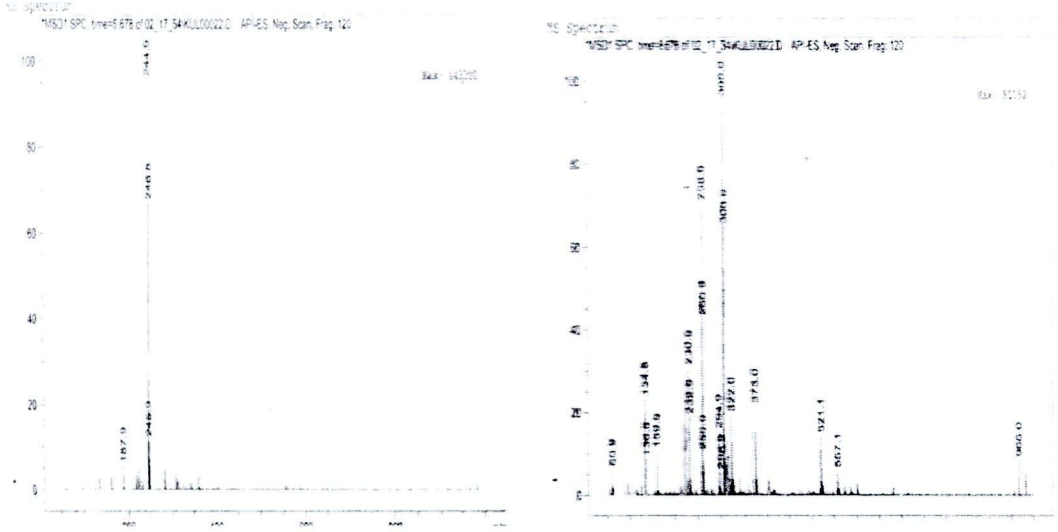


(m)



(n)

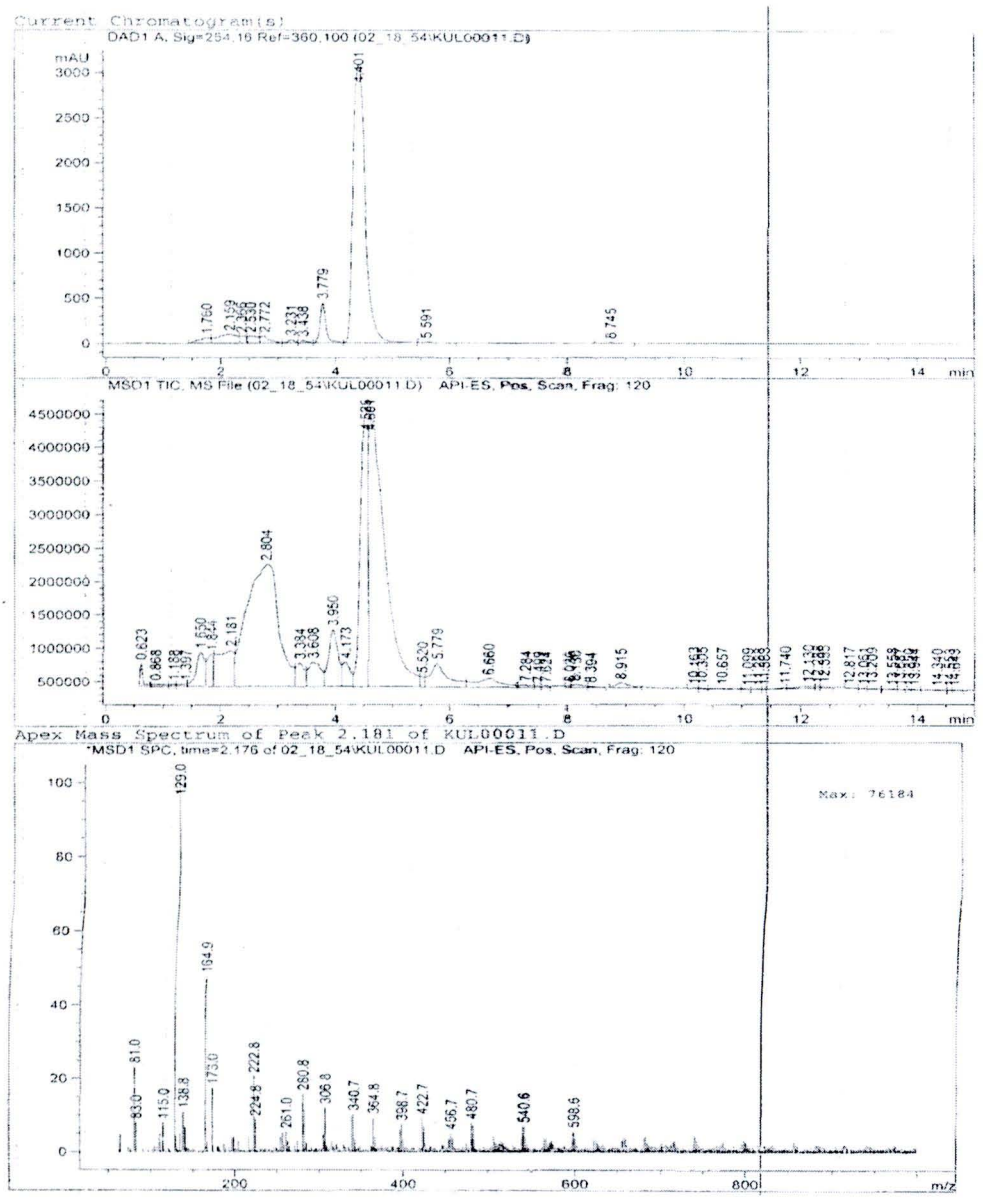
Figure C.5 (continued).



(o) (p)

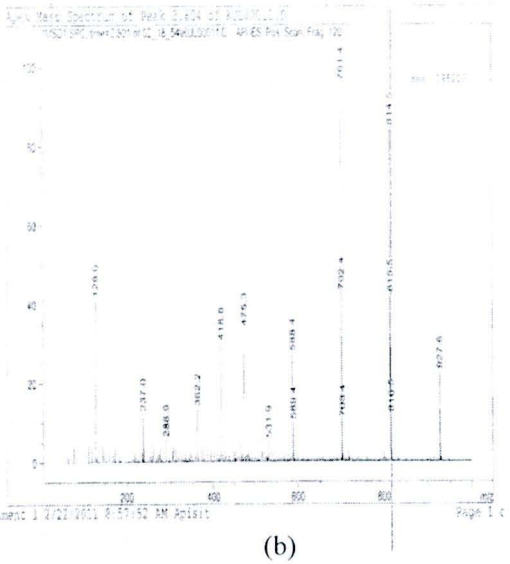
Figure C.5 (continued).

C.3.2 pH 7

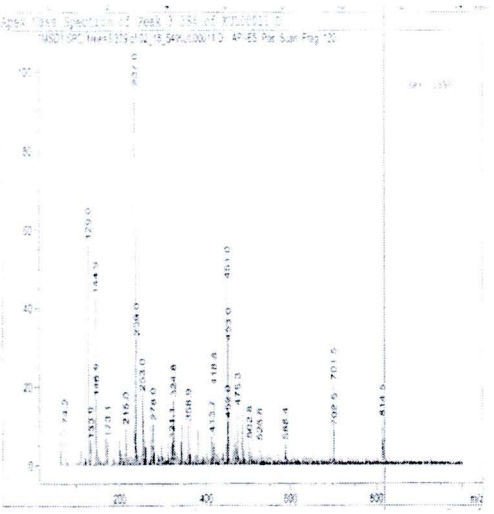


(a)

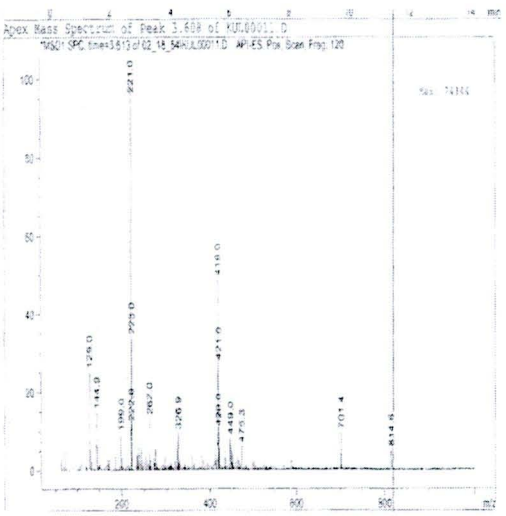
Figure C.6 Chromatogram of diuron solution photodegradation at pH7 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(r).



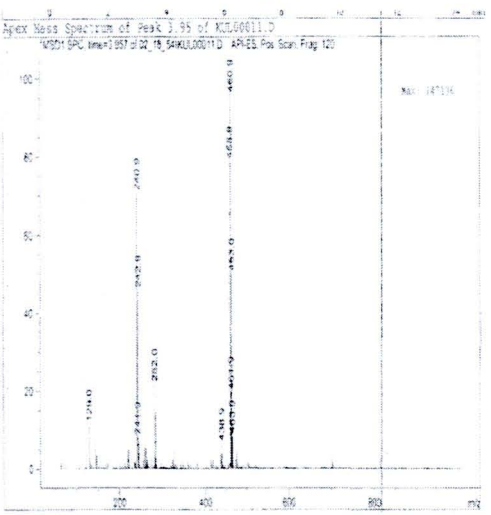
(b)



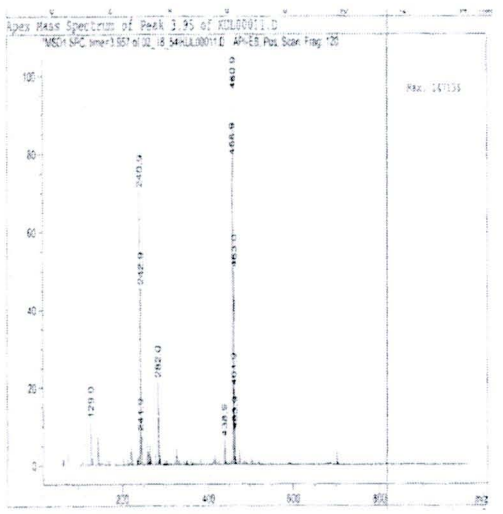
(c)



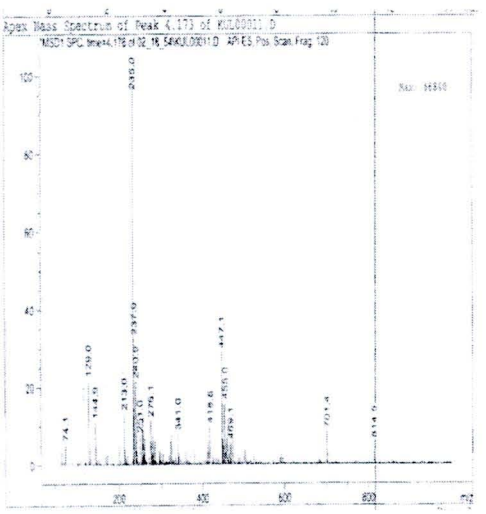
(d)



(e)

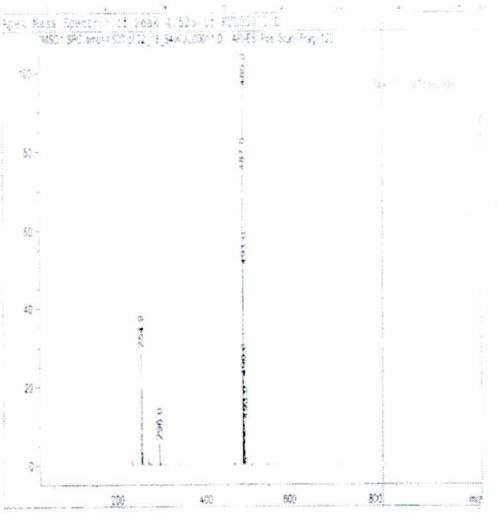


(f)

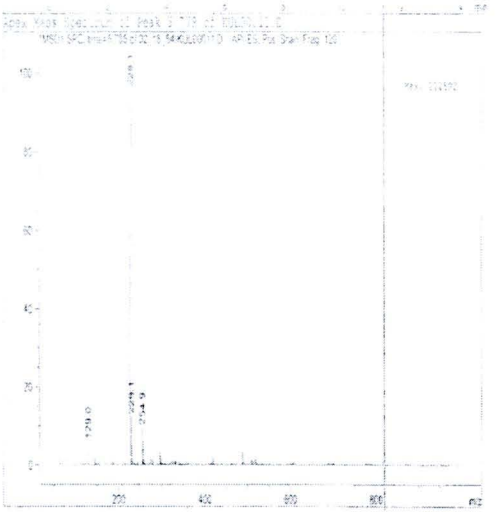


(g)

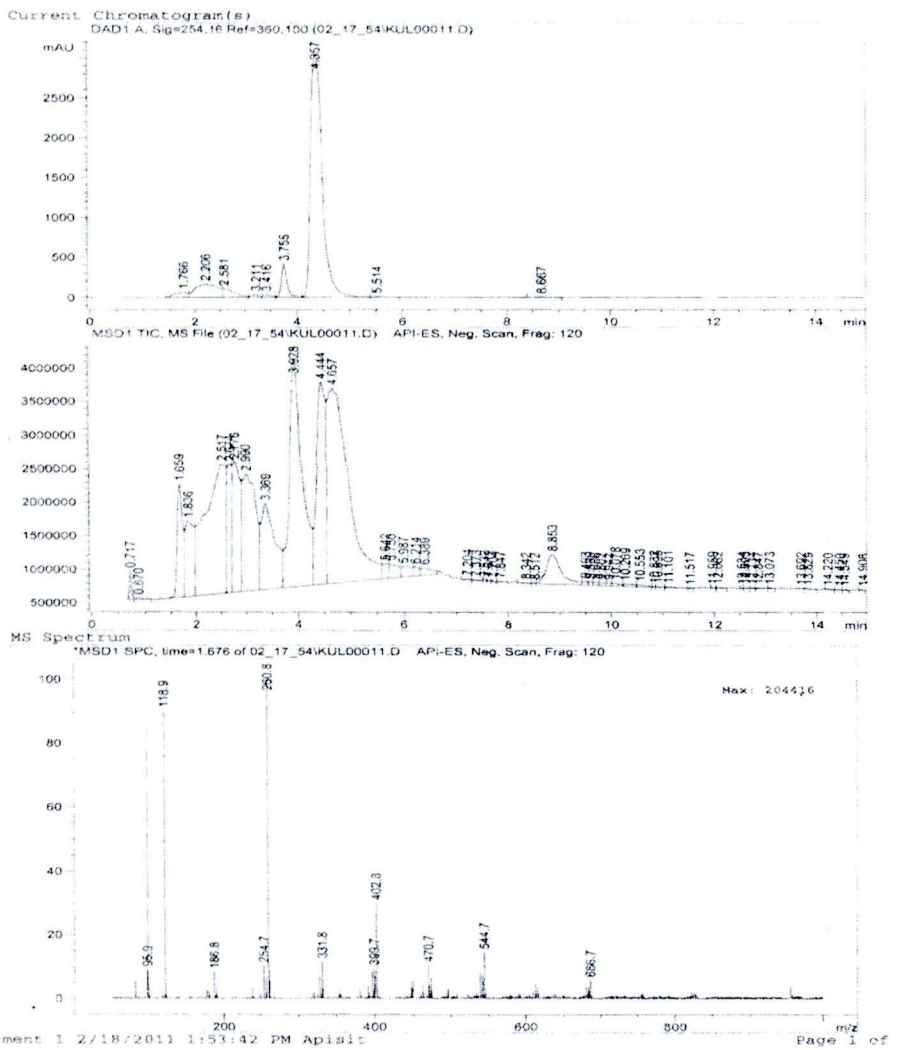
Figure C.6 (continued).



(h)

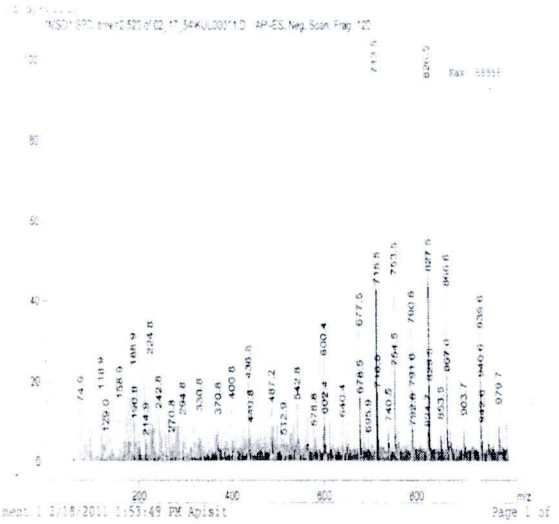


(i)

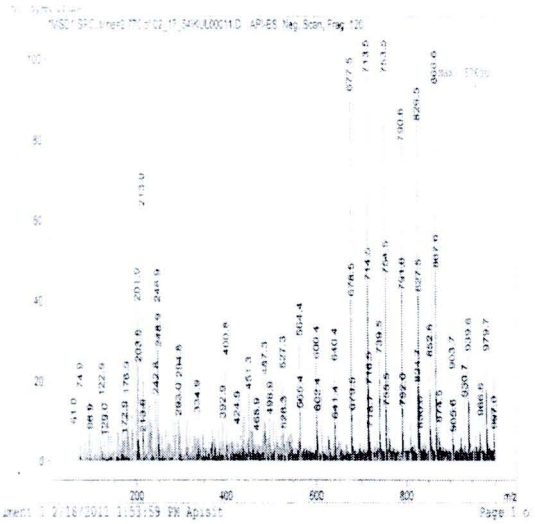


(j)

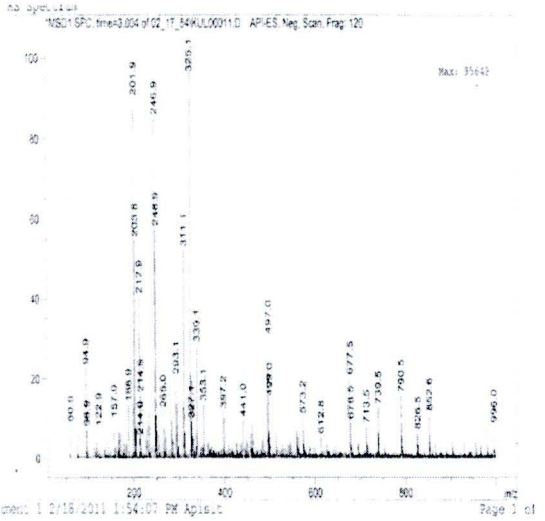
Figure C.6 (continued).



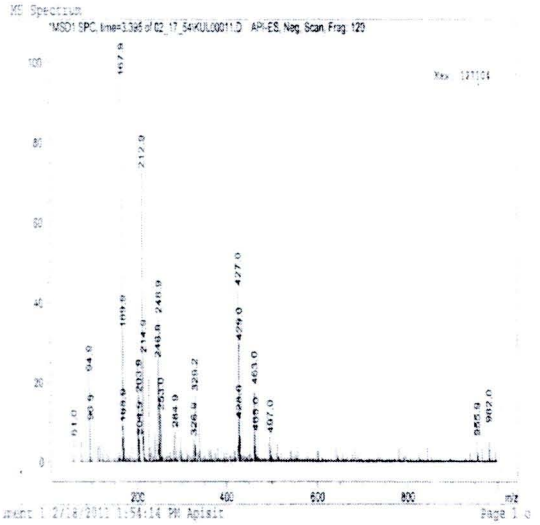
(k)



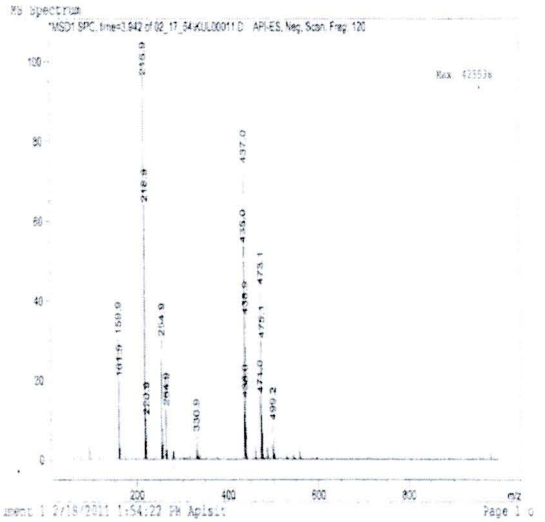
(l)



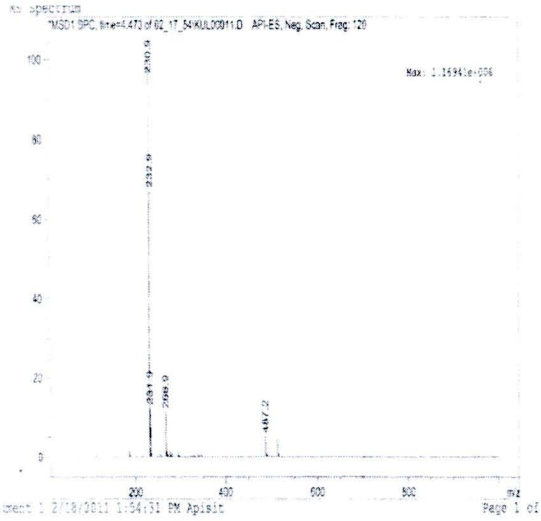
(m)



(n)

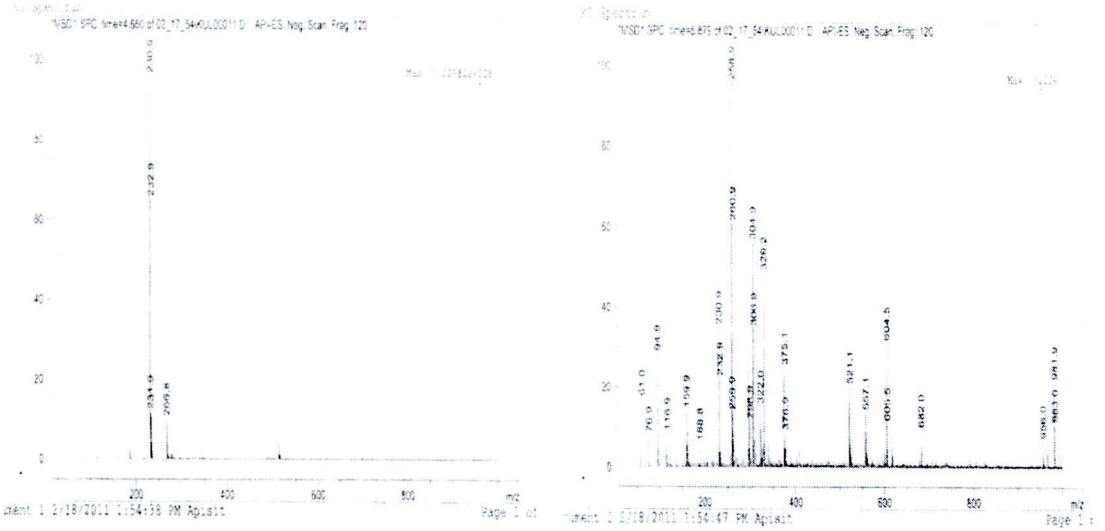


(o)



(p)

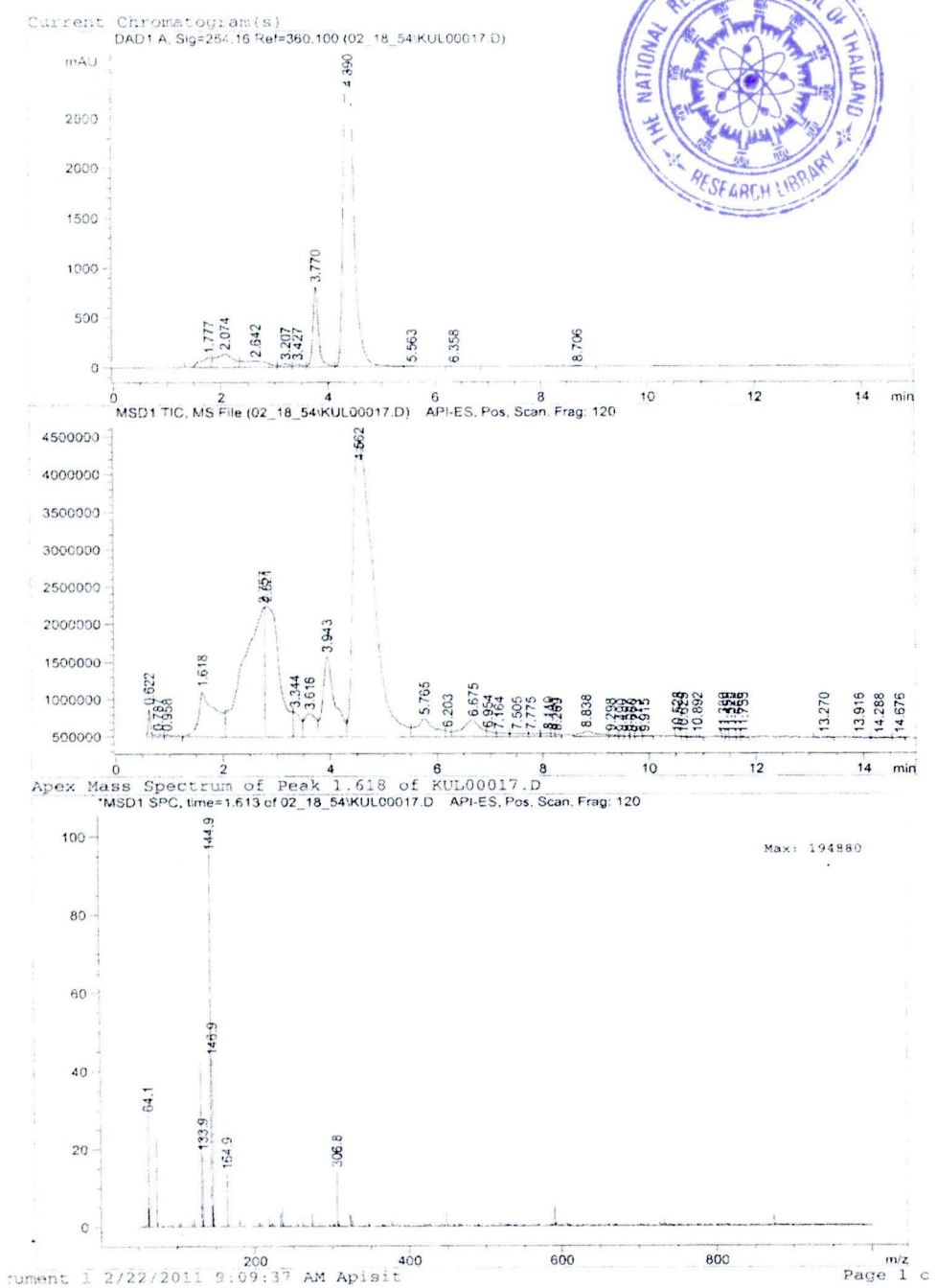
Figure C.6 (continued).



(q) (r)

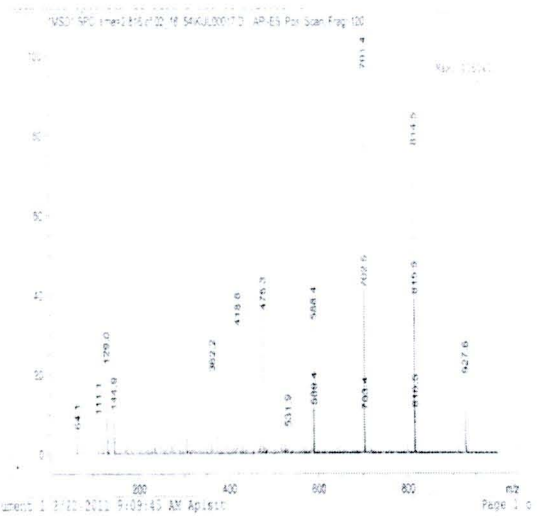
Figure C.6 (continued).

C.3.3 pH10

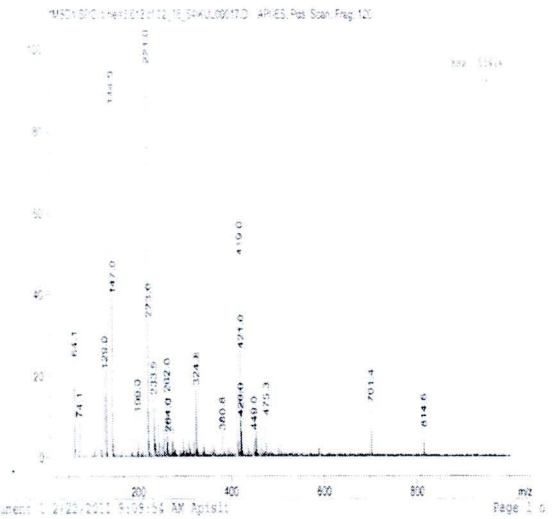


(a)

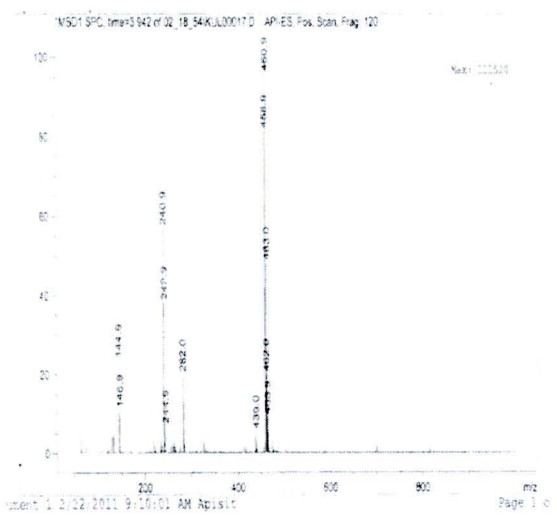
Figure C.7 Chromatogram of diuron solution photodegradation at pH10 obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(n).



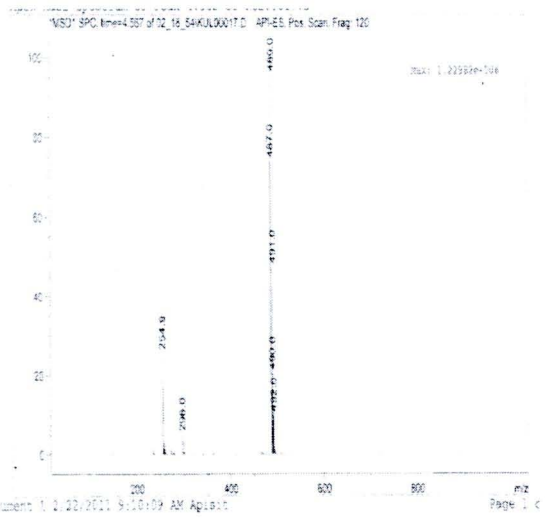
(b)



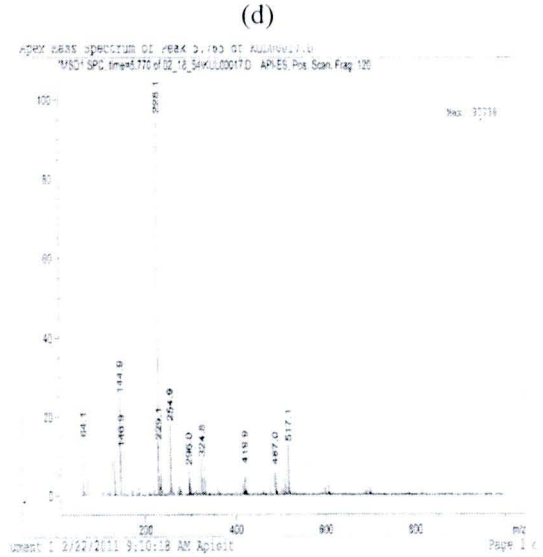
(c)



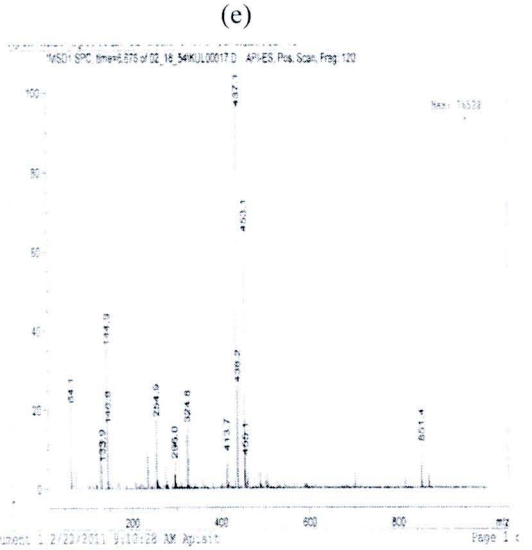
(d)



(e)

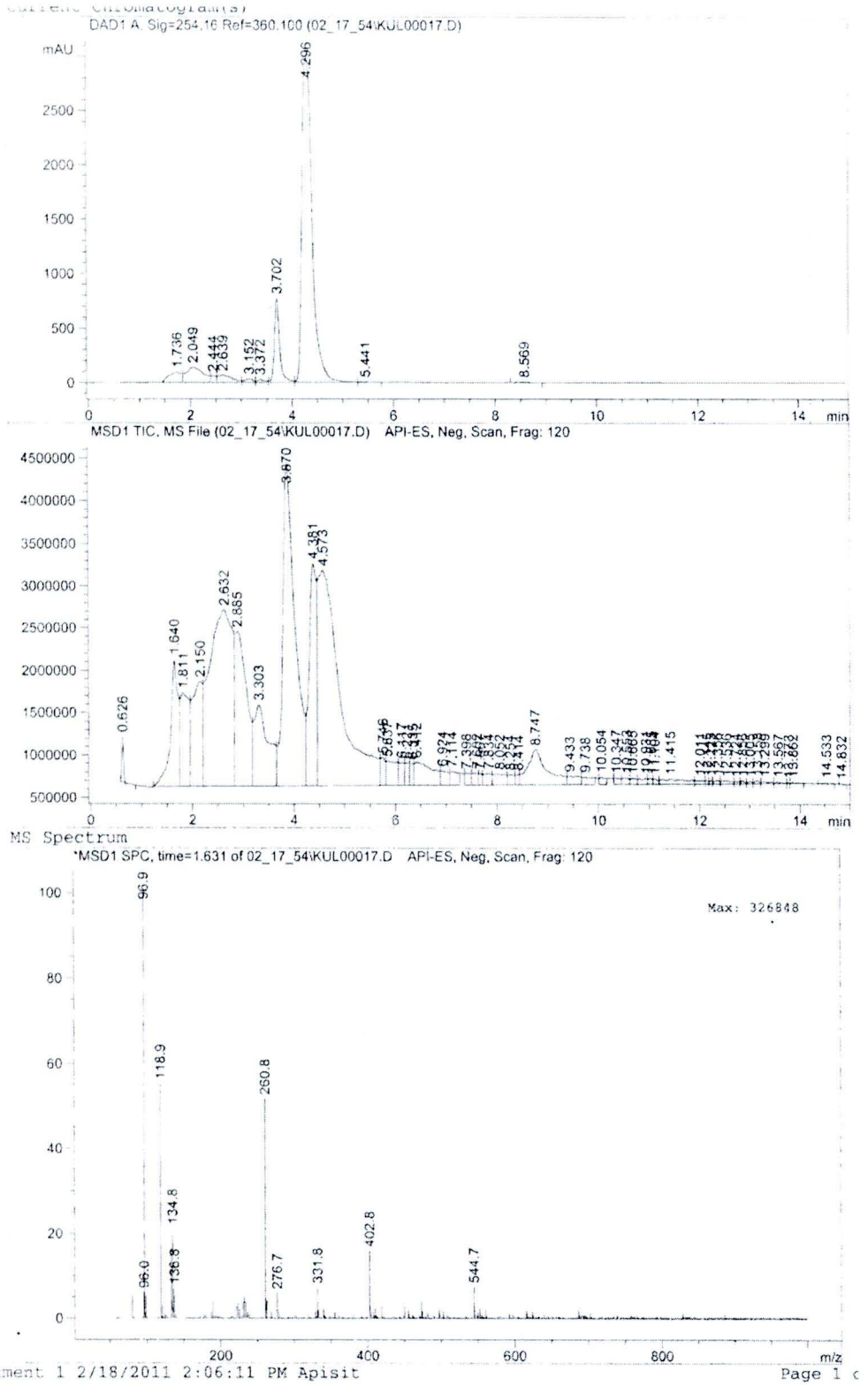


(f)



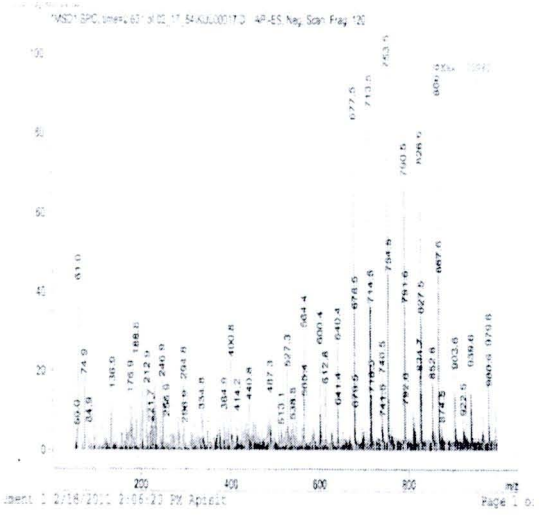
(g)

Figure C.7 (continued).

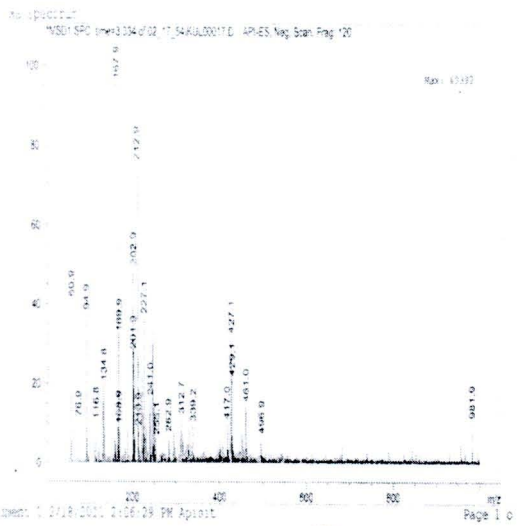


(h)

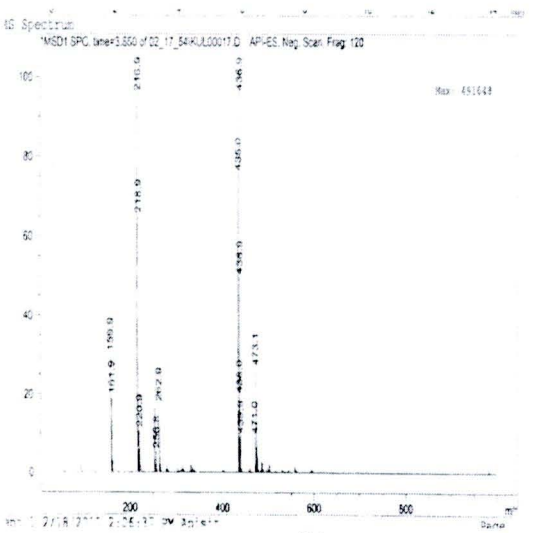
Figure C.7 (continued).



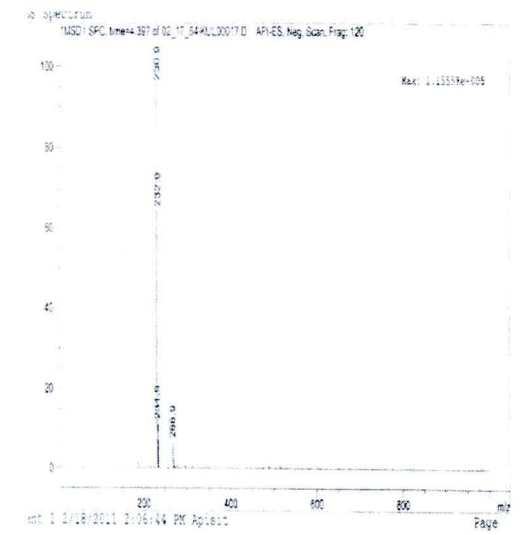
(i)



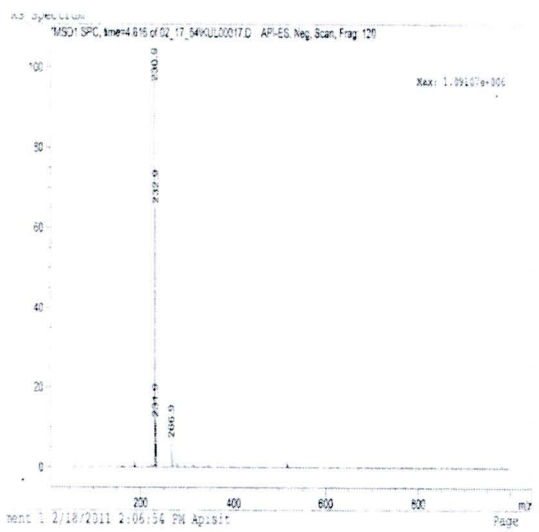
(j)



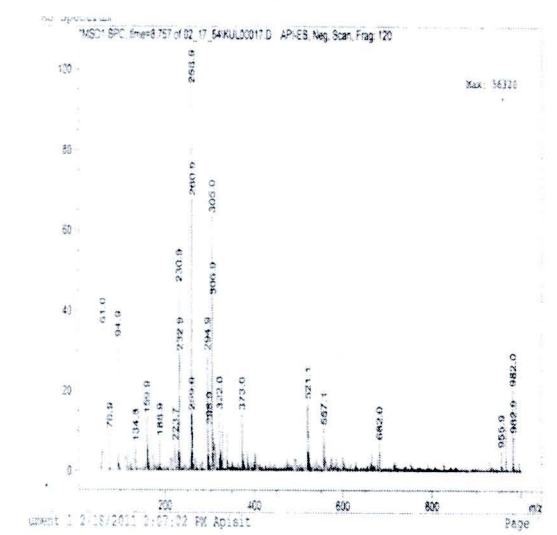
(k)



(l)



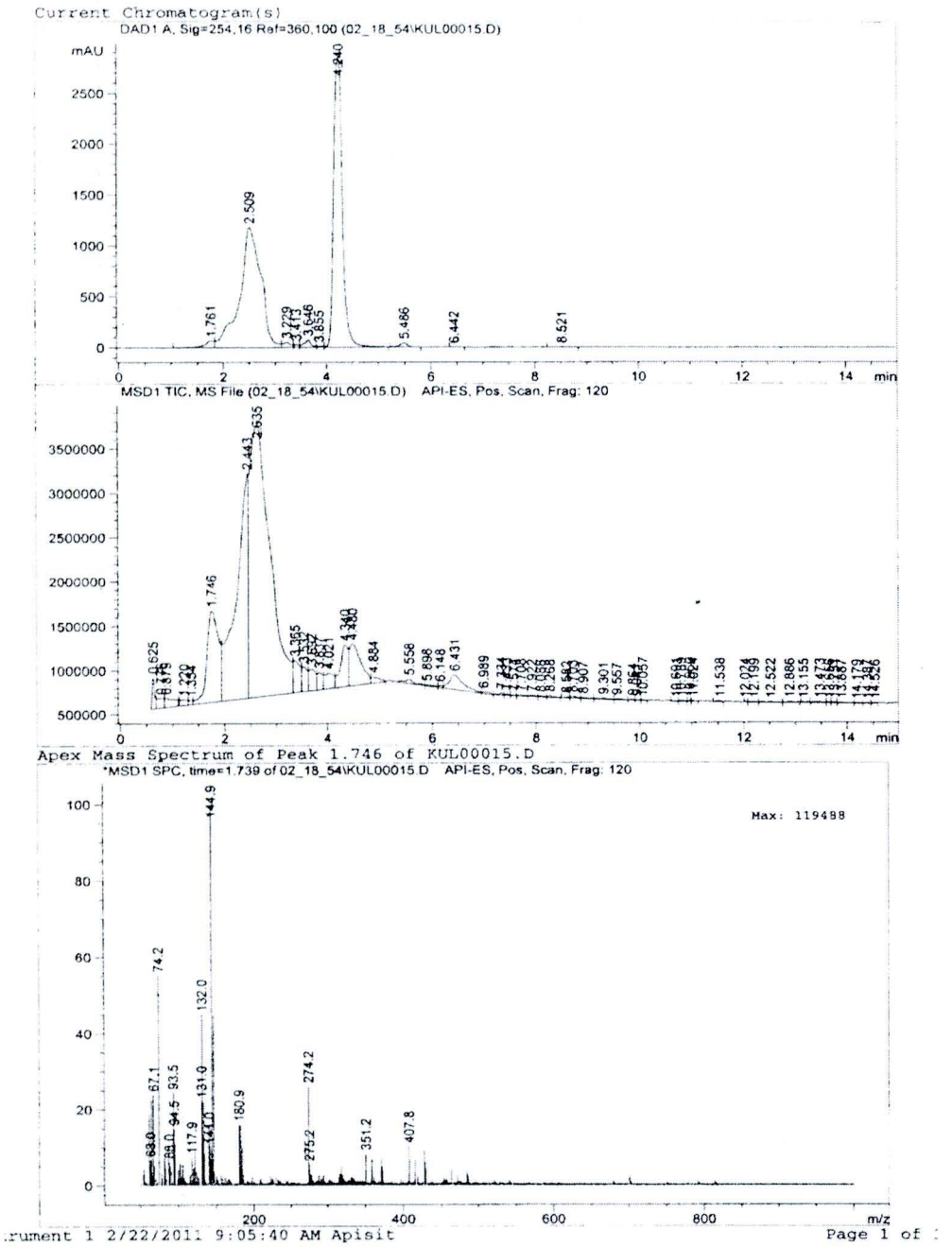
(m)



(n)

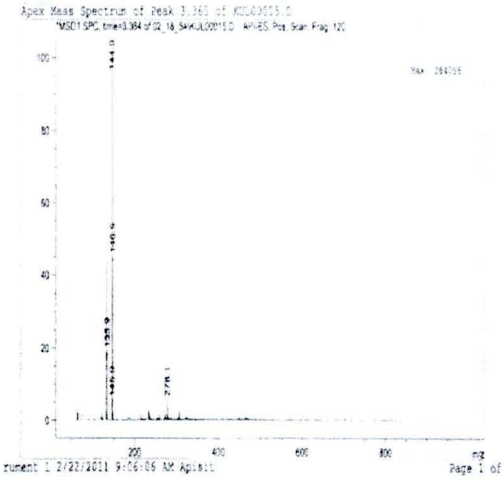
Figure C.7 (continued).

C.3.4 UV-C

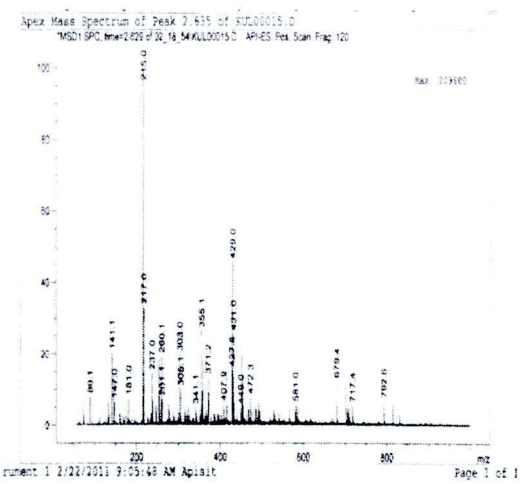


(a)

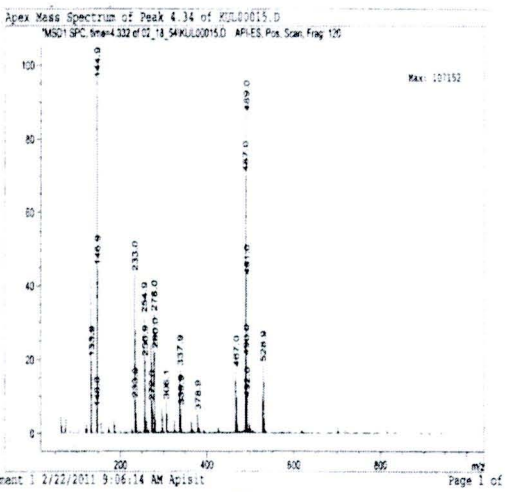
Figure C.8 Chromatogram of diuron solution photodegradation by UV-C obtained from UV detector and mass detector are displayed in (a). Mass spectrums were obtained using fragmentator of 120 V at various retention times as shown in (a)-(r).



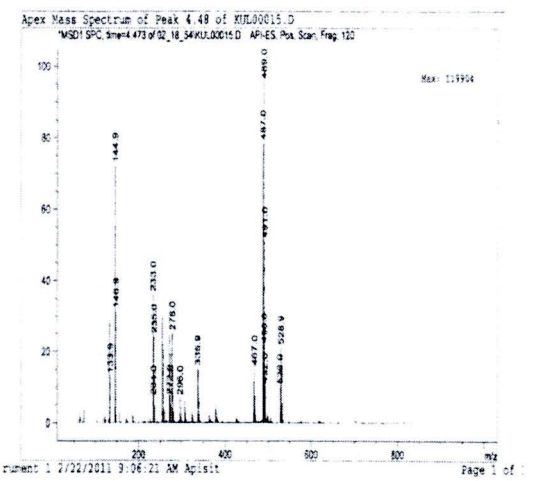
(b)



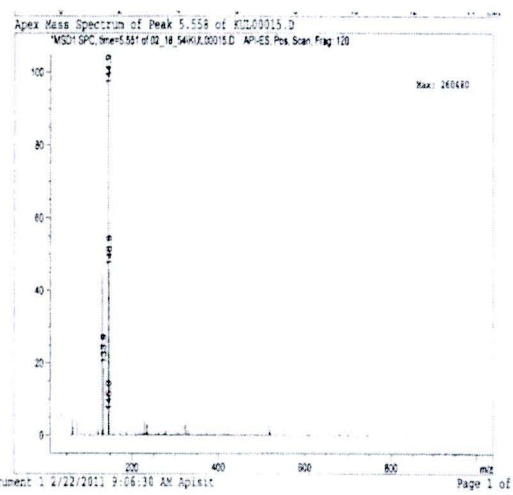
(c)



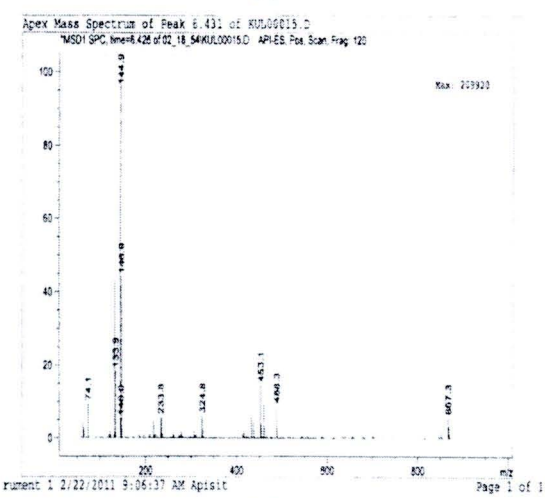
(d)



(e)

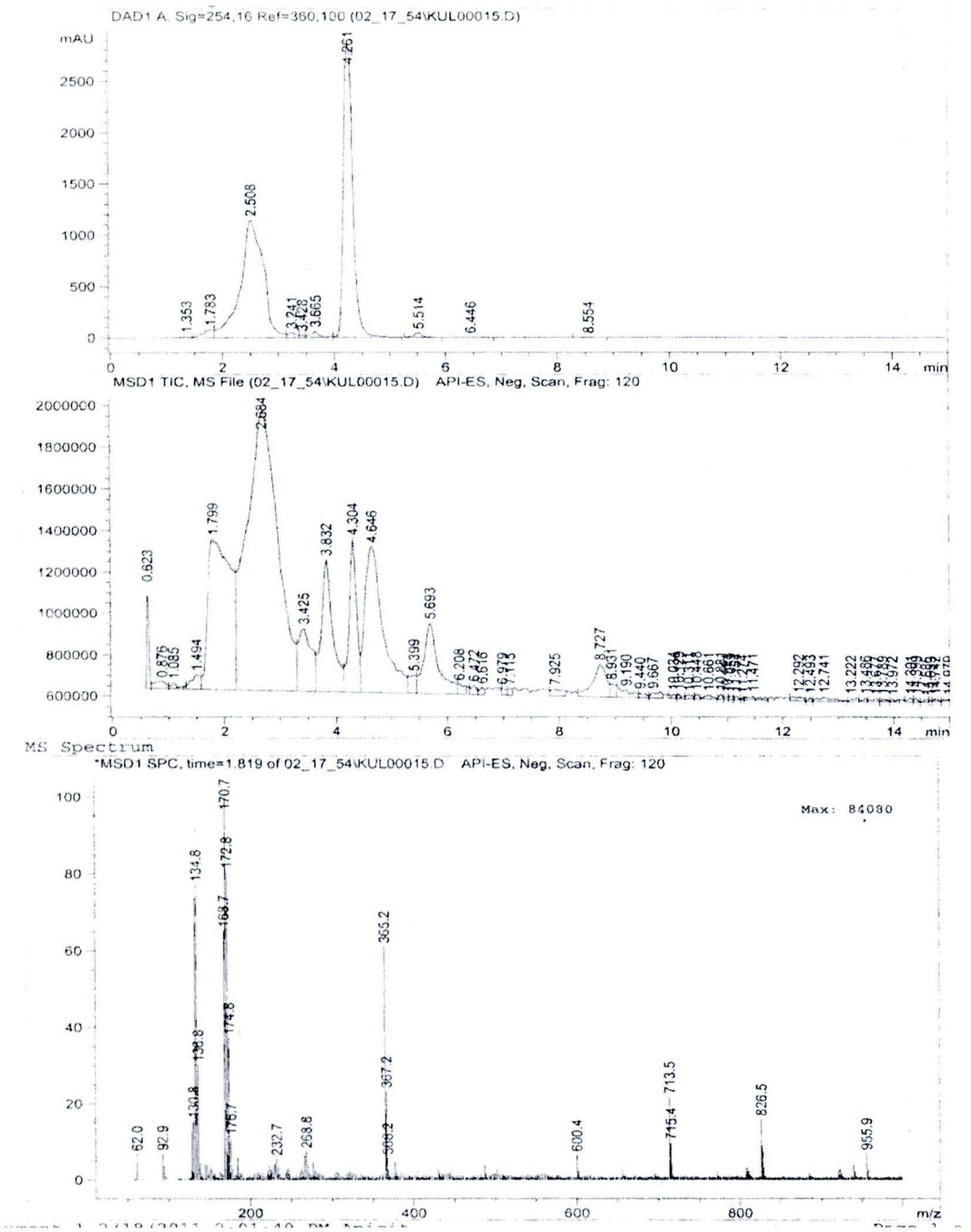


(f)



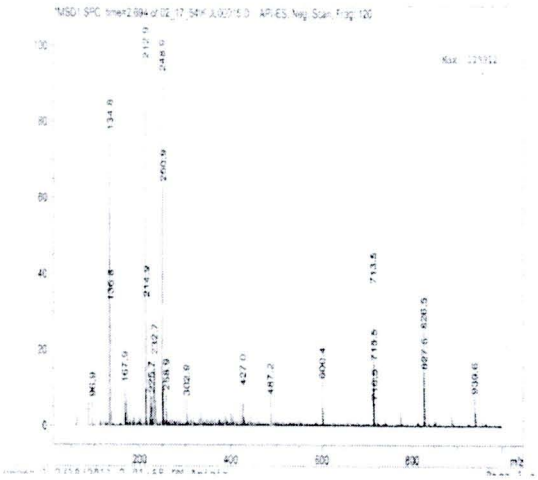
(g)

Figure C.8 (continued).

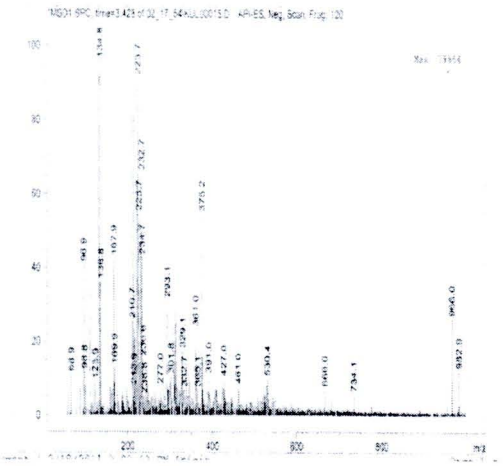


(h)

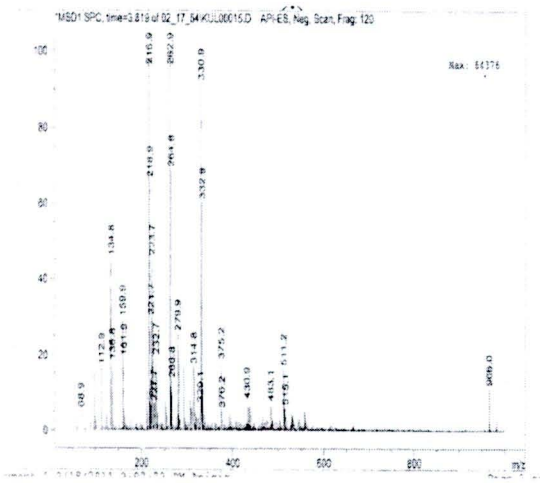
Figure C.8 (continued).



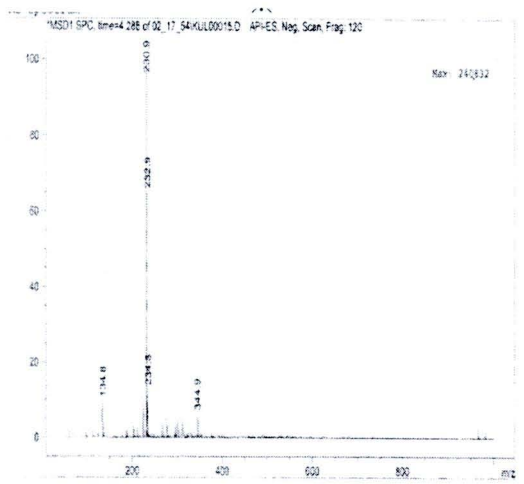
(i)



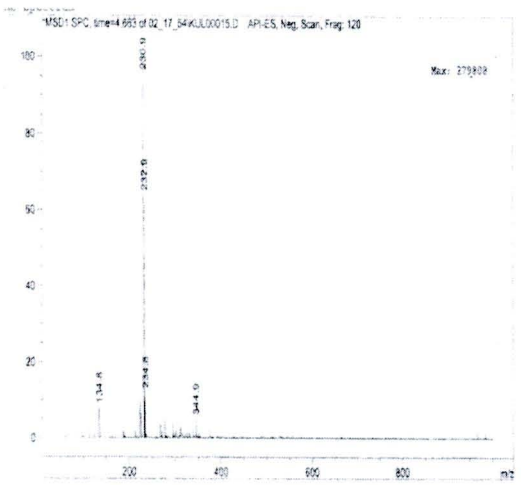
(j)



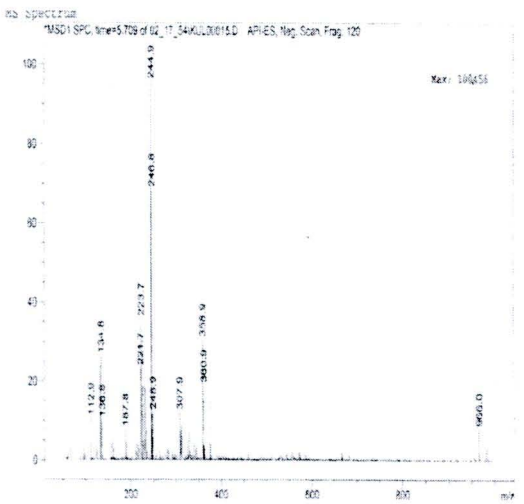
(k)



(l)



(m)



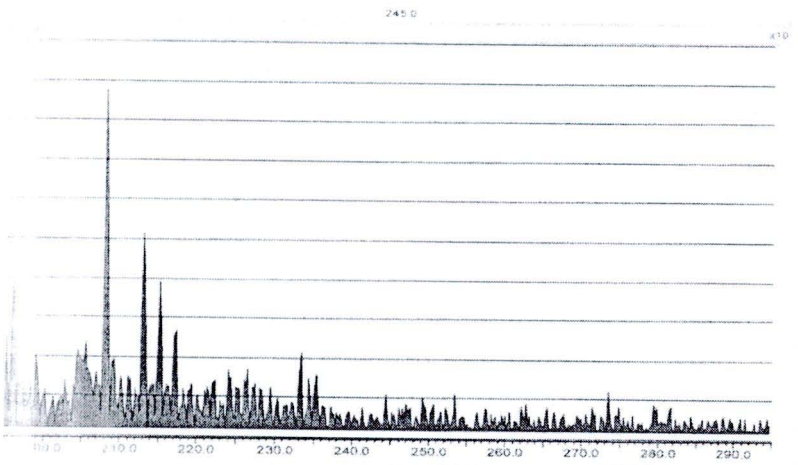
(n)

Figure C.8 (continued)

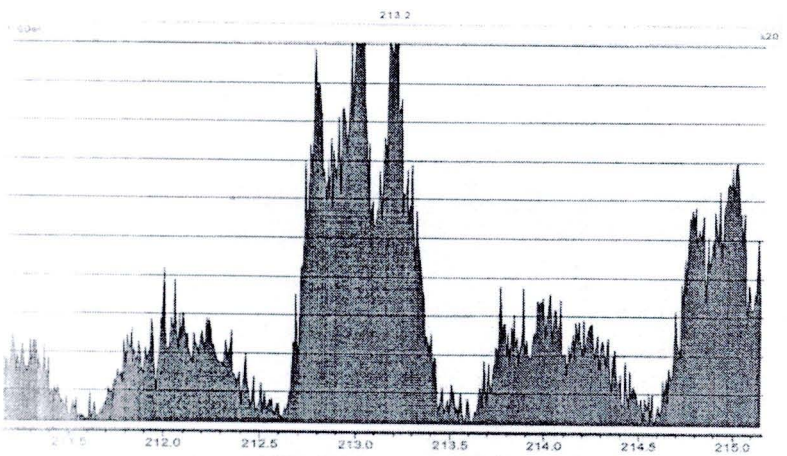
APPENDIX D

LC/MS/MS MASS SPECTRUM

D.1 Set mass spectrum of intermediates for analyzed by MS/MS detector

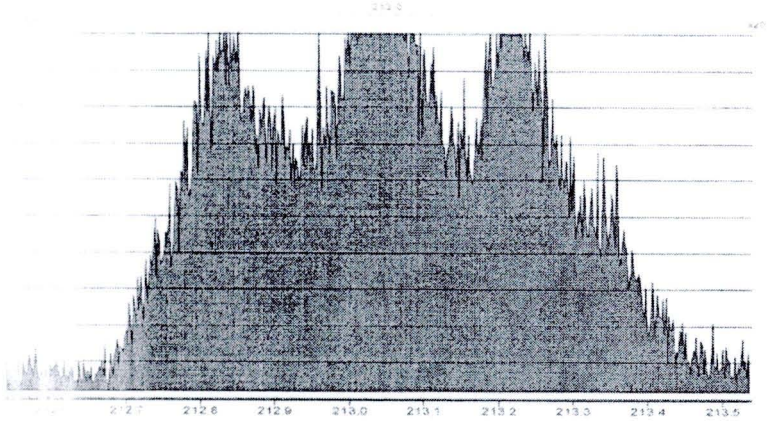


(a)

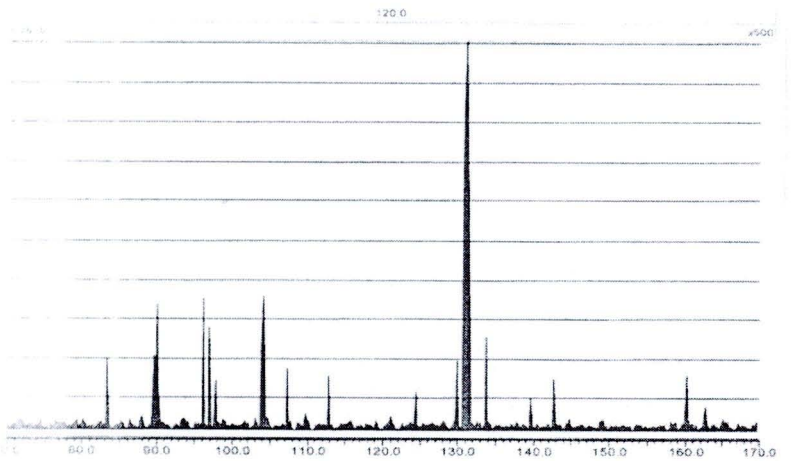


(b)

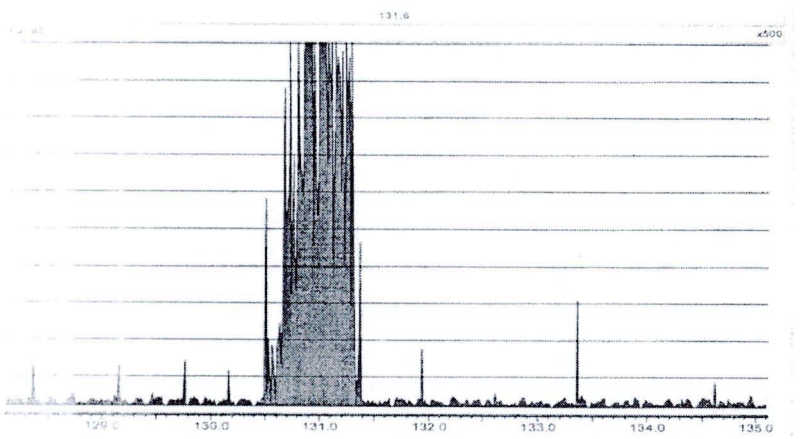
Figure D.1 Chromatogram of diuron solution photodegradation (set mass ~ 213) obtained from LC/MS/MS displayed in (a) (f).



(c)

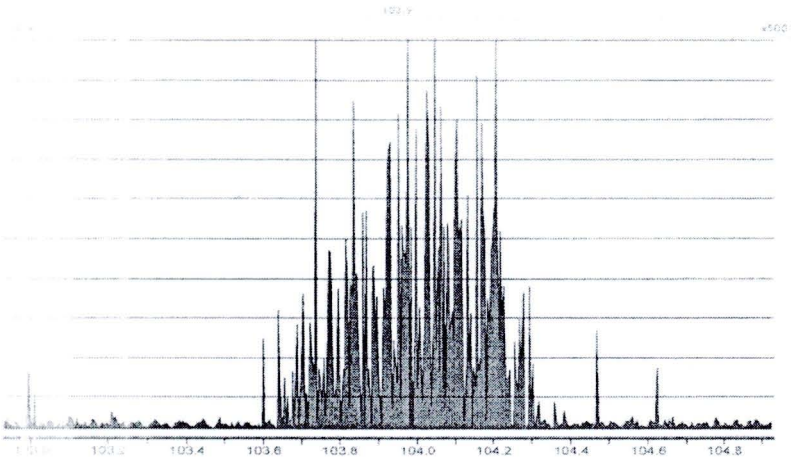


(d)



(e)

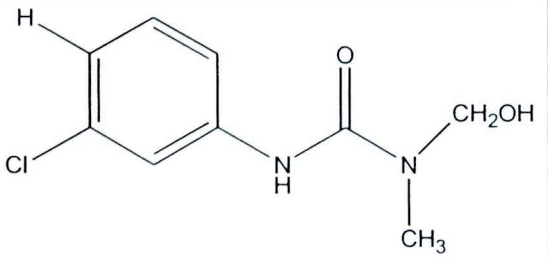
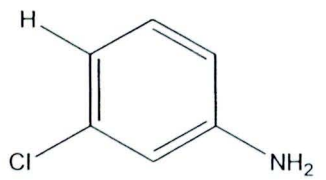
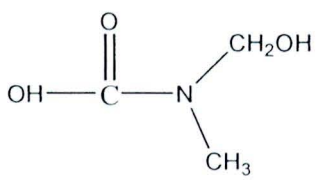
Figure D.1 (continued).



(f)

Figure D.1 (continued)

Table D.1 Mass spectral data for photocatalytic degradation of diuron as analyzed by LC/MS/MS.

Compound structure	m/z
	213 (parent ion)
	131 (daughter ion)
	104 (daughter ion)

APPENDIX E

ADSORPTION OF FILTER TEST

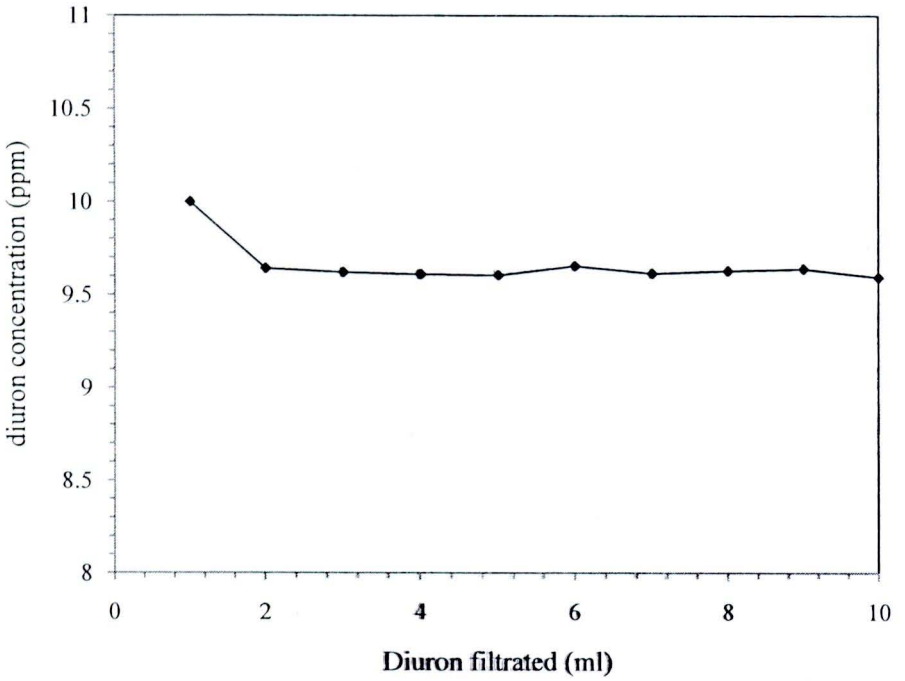


Figure E.1 Adsorption of diuron on filter.

APPENDIX F

TOXICITY OF SOME INTERMEDIATES

F.1 3,4-Dichloroaniline

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 545 mg/kg

Skin corrosion/irritation
Skin - rabbit - Severe skin irritation

Serious eye damage/eye irritation
Eyes - rabbit - Severe eye irritation

Respiratory or skin sensitization
May cause allergic skin reaction.

Causes sensitization.

Germ cell mutagenicity

Genotoxicity in vitro - Human - lymphocyte
Sister chromatid exchange

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	LC50 - Pimephales promelas (fathead minnow) - 7 - 10 mg/l - 96,0 h
Toxicity to daphnia and other aquatic invertebrates.	EC50 - Daphnia magna (Water flea) - 0,05 - 2,20 mg/l - 48 h
Toxicity to algae	EC50 - Pseudokirchneriella subcapitata (green algae) - 4,9 mg/l - 72 h
	Growth inhibition LOEC - Algae - 1 - 10 mg/l - 28 d

Persistence and degradability
Biodegradability — Result: - Not readily biodegradable.

Bioaccumulative potential
Bioaccumulation — Poecilia reticulata (guppy) - 48 h
Bioconcentration factor (BCF): 96

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects
Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

F.2 3,4-Dichlorophenol

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Ingestion	Harmful if swallowed.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye burns.

Signs and Symptoms of Exposure
Cough, Shortness of breath, Headache, Nausea, Vomiting, Tremors, Central nervous system depression, prolonged or repeated exposure can cause:, Damage to the eyes., To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: SK8800000

12. ECOLOGICAL INFORMATION

12.1 Toxicity

Toxicity to fish	LC50 - Oryzias latipes - 1,9 mg/l - 96 h
Toxicity to daphnia and other aquatic invertebrates.	EC50 - Daphnia magna (Water flea) - 2,77 mg/l - 24 h
Toxicity to algae	Growth inhibition EC50 - Pseudokirchneriella subcapitata - 3,2 mg/l - 96 h

12.2 Persistence and degradability
no data available

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
no data available

12.6 Other adverse effects
Toxic to aquatic life.
no data available

F.3 1-Methyl-3-phenylurea

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - rat - 3.440 mg/kg

Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitization
May cause sensitization by skin contact.

Germ cell mutagenicity

Genotoxicity in vivo - mouse - Oral
DNA inhibition

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to **0.1%** is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	Causes eye burns.

Signs and Symptoms of Exposure
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: YT8470000

12. ECOLOGICAL INFORMATION

12.1 Toxicity
no data available

12.2 Persistence and degradability
no data available

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

F.4 3,4-Dichlorophenyl isocyanate

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - rat - 91 mg/kg

LC50 Inhalation - rat - 4 h - 2.700 mg/m3
Remarks: Sense Organs and Special Senses (Nose, Eye, Ear, and Taste):Eye:Lacrimation. Behavioral:Ataxia. Gastrointestinal:Changes in structure or function of salivary glands.

Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitization
Prolonged or repeated exposure may cause allergic reactions in certain sensitive individuals.

May cause allergic respiratory and skin reactions

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
Inhalation - May cause respiratory irritation.

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	Harmful if inhaled. Causes respiratory tract irritation.
Ingestion	Toxic if swallowed.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes serious eye irritation.

Signs and Symptoms of Exposure
burning sensation, Cough, wheezing, laryngitis, Shortness of breath, Headache, Nausea, Vomiting, Repeated exposure may cause asthma., To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: NQ8760000

12. ECOLOGICAL INFORMATION

12.1 Toxicity
no data available

12.2 Persistence and degradability
no data available

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
no data available

12.6 Other adverse effects
no data available

F.5 1,2-Dichloro-4-nitrobenzene

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 953 mg/kg
Remarks: Nutritional and Gross Metabolic:Weight loss or decreased weight gain.

LC50 Inhalation - rat - 4 h - 10.000 mg/m3
Remarks: Sense Organs and Special Senses (Nose, Eye, Ear, and Taste) Olfaction:Other changes. Behavioral:Somnolence (general depressed activity). Nutritional and Gross Metabolic:Weight loss or decreased weight gain.

Skin corrosion/irritation
Skin - rabbit - Mild skin irritation - 24 h

Serious eye damage/eye irritation
Eyes - rabbit - Moderate eye irritation - 24 h

Respiratory or skin sensitization
May cause allergic skin reaction.

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity

Reproductive toxicity - rat - Oral
Maternal Effects: Other effects.

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	Harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	Causes eye irritation.

Signs and Symptoms of Exposure
Absorption into the body leads to the formation of methemoglobin which in sufficient concentration causes cyanosis. Onset may be delayed 2 to 4 hours or longer., To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: CZ5250000

12. ECOLOGICAL INFORMATION

Toxicity

no data available

Persistence and degradability

Bioaccumulative potential

Bioaccumulation	Oncorhynchus mykiss (rainbow trout) - 36 d Bioconcentration factor (BCF): 130

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects
no data available

VITA

Miss Wannipa Pradittakan was born on September 22, 1986 in Phang-nga Province, Thailand. She received the Bachelor Degree of Chemical Engineering from Faculty of Engineer, Mahidol University in 2009. She continued her Master's study at Chulalongkorn University in June, 2009.

LIST OF PUBLICATIONS

1. Wannipa Pradittakan, Esara Sadudeewong, Alisa S. Vangnai, and Varong Pavarajarn. "Comparative Study on Mechanism of Photocatalytic Degradation of Diuron on Titanium Dioxide and Zinc Oxide". The 17th Regional Symposium on Chemical Engineering (CRE384), Bangkok, November 22-23, 2010.

2. Wannipa Pradittakan, Esara Sadudeewong, Kamonrat Apichatsanee, Alisa S. Vangnai, and Varong Pavarajarn. "Comparative Study of Photocatalytic Degradation of Diuron on Titanium Dioxide and Zinc Oxide Nanoparticles". The CHEMECA 2011, Sydney, Australia, September 18-21, 2011.