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Screening Analysis of Volatile Organic Contaminants in Industrial Wastewater of GIDC Ankleshwar, Gujarat (India)

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Abstract: **Gas chromatography with mass spectrometry (GC-MS) detection is sensitive and selective to detect volatile organics in low concentrations. This study has detected volatile organic contaminants in industrial wastewater of Ankleshwar GIDC industrial area (Gujarat, India). The organic pollutants were extracted in CH_2Cl_2 and detected by GC-MS technique. The detected organics are 2-Propanol 1-dibutylamino, 4-Bromobenzenamine, 4, 7-methanoiso benzo furan, endosulphon, 2-propanol 1-dibutyl amino, m-chloropropinophenone, benzoic acid 4-chloro, 3-cyclohexene-1-ol-3-methyl, 2, 4 Pentadione 3(2-propenyl), Di-n-octyl phthalate etc. The detected organics were found to be carcinogenic and create harmful effect on the human body as well as on the environment. The identified organic compounds affect adversely the ground water and soil quality of the area.**

abstract must be a concise yet comprehensive reflection of what is in your article. In particular, the abstract must be self-contained, without abbreviations, footnotes, or references. The abstract should not be more that 200 words. Be sure that you adhere to these limits; otherwise, you will need to edit your abstract accordingly. The abstract must be written as one paragraph, and should not contain displayed mathematical equations or tabular material. Ensure that your abstract reads well and is grammatically correct. (Times New Roman, Font Size 9, Bold, Justified)

Index Terms: **Enter Wastewater, Volatile organic contaminants, Gas chromatography, Mass spectrometry, Fragmentation.**

I. Introduction

Environmental pollution is a global, public health problem. Because of industrialization and widespread use of pesticides, vast quantities of chemicals are released and dispersed into the environment each year. Environmental pollutants are constant threat to human health. As a consequence, these pollutants are ubiquitous and are found in air, water, soil, food sources and other biological materials (Enrique, M., et al.,2002). Many of the heavy metals, organochlorine and organophosphate pesticides are neurotoxicants (Schettler, T., et al.,2000; USEPA,1998; USEPA, 1998) and have direct effects on neuronal proliferation, migration, differentiation, synaptogenesis and apoptosis (Monnet, T.F., et al.,1998). They also interfere with hormones, neurotransmitters or neunotrophic growth factors that affect brain development (Cameron, H.A., et al.,1998). However, an increasing number of children with developmental, learning and behavioral difficulties have been noted recently, suffering from mental retardation, learning disability, attention deficit, hyper activity disorders and autism. A variety of environmental pollutants and toxins can contribute to these disorders even at low levels of exposure (Gillberg, C., et al.,1999; US Census1994). A report from the National Academy of Sciences found that 50% of US pregnancies result in birth defects or neurological complications and other chronic development problems are resulted from pollutants in water (Sonawane, H., et al.,2007). Although a potential for natural, accidental a intentional contamination of raw water sources and drinking water has always existed. The technology for developing and implementing contamination warning systems (CWSs) for drinking water security has been intensified significantly (Gullick, R.W., et al.,2003; Hasan, J., et al.,2004; USEPA, 2005). Michael, et al described these technologies as a state of art for detection of chemical, microbiological and radiochemical contaminations (Michael, P., et al.,2009).

The identification and determination of organic byproducts in wastewater and surface water are rather difficult tasks. As these compounds are of no use and have no economic value, little effort has been made to gather information about their physical and chemical properties, their toxicity and environmental fate. Their structures are often unknown or only tentatively known and reference compound are seldom available. The functional groups of such compounds are detected by FTIR technique.

FTIR absorbance spectra of extracted mass solid samples were obtained through KBr technique, with the analysis performed on

Perkin-Elmer make IR instrument in the wave number range of 4000-400 cm^{-1}.

Vapi and Ankleshwar (India) have the places in top ten of dirty thirty- The world's worst polluted places [14], Vapi and Ankleshwar area were declared critically polluted by the central pollution Board of India in 1994. It was observed that the waste products, discharged contain heavy metals, cyanides, pesticides, complex aromatic compounds such as polychlorinated biphenyls and other toxics (Blacksmith Institute,2007). Efforts have been made for the detection and identification of organic compounds in industrial waste in western countries (Schirmer, M., et al.,2008; Focazio, M. J., et al.,2006). However, less effort is under taken in India therefore this study was undertaken to detect and identity organic pollutants in industrial wastewater in GIDC industrial area Ankleshwar (Gujrat).

Gas chromatography with mass spectrometry (GC-MS) detection is an appropriate method for screening analysis of volatile compounds. GC-MS is sensitive and selective enough to detect volatiles in low concentrations and has high degree of automation for practical routine analysis (Kolb, B., et al.,2006;

Shen, H.Y., 2005). With mass spectrometer as a detector, the identification of unknown compounds is possible and false-positive misidentification can be reduced.

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Define abbreviations and acronyms the first time they are used in the text, even after they have already been defined in the abstract. Do not use abbreviations in the title unless they are unavoidable (for example, "TCP/IP" in the title of the article).

II. MATERIAL AND METHODS

A. Wastewater sampling

Two industrial wastewater samples were collected as per standard procedures (Greenberg, A.E., 1989) from Panoli, GIDC Ankleshwar, Gujarat (India). The organics were extracted from the effluent dichloromethane. Extracted organic layer was concentrated into a small mass.

B. W FTIR and GC-MS

GC-MS was recorded on Hewlett- Packard make GC-MS spechophotometer. The mass spectrometer was a single quadrupole (Turbo mass, Perkin-Elmer, Germany). It was operated by election impact ionization with a voltage of 70 ev. The temperature of the ion source was 180^0c. Keeping sample and for 3 min, the analyses were performed in full scan mode (TIC) and in single ion recording mode (SIR) simultaneously. The full scan mode was used for identification and confirmation of detected compounds in the sample. The m/z range was 40-410 Da, with a scan time and 0.50 s. The compounds were identified by comparison of the experimental mass spectra with a mass spectra library (NBS 75K.L.). FTIR absorbance spectra of extracted mass solid samples were obtained through KBr technique, with the analysis performed on Perkin-Elmer make IR instrument in the wave number range of 4000-400 cm^{-1}.

III. . RESULTS AND DISCUSSION

A. FTIR analysis

The characteristic band and FTIR frequencies of sample 1 and 2 are given in Table 1 and 2 respectively. The characteristic FTIR bands indicate the presence of functional groups in the defected organic compounds by GC-MS.

Table 1. FTIR absorption bands of CH_2Cl_2 extracted mass of industrial wastewater sample-1.

Frequency [cm^{-1}]	**Characterization**
3363.5	-OH (Alcohol, Phenol, hydrogen bonded)
2966.3	Alkyl -C-H stretching
2930.7	-OH(carboxylic acid –H bonded)
2533.5	-OH(carboxylic acid –H bonded)
2874.7	Alkyl C-H stretching frequency
1734.1	-CHO-O ester linkage
1596.6	>C = C<
1387.8	-C $(CH_3)_3$
1026.3	C-O in ester group
926.6	Disubstituted alkene R-CH=CH-R(Trans)
761.5	Monosubstituted benzene
624.0	R-CH=CH-R Cis

Table 2. FTIR absorption bands of CH_2Cl_2 extracted mass of industrial wastewater sample-2

Frequency [cm^{-1}]	**Characterization**
3424.6	N-H stretching in amine.
2925.6	C-H stretching.
2859.4	C-H stretching.
1749.4	-C-O- ester linkage.
1652.6	>C = C < bond stretching frequency
1520.2	>C = C< in aromatic
1133.2	C-O stretching in –C -O group
1067.0	C-O stretching in –C-O group
761.5	Monosubstituted benzene
680.1	Metal disubstituted benzene

A. The VOC's

GC-MS allows the determination of different volatiles in aqueous samples such as halogenated hydrocarbons, trihalomethanes, ketones, acetic esters, fuel ether oxygenates and mono aromatic compounds in gasoline like benzene and its monomethyl-, dimethyl-, trimethyl- and monoethyl- derivatives Fig. 1 shows a total ion chromatogram (TIC) in which three organic pollutants were identified Table-3.

Table 3. Retention time and qualifier ion from SIR or extracted from TIC for overview screening of volatile compounds in aqueous sample 1 &2.

Sample	Name	CAS no.	RT [min]	Qualifier-ion
1.	4, 7 methano iso benzofuran	3369-52-6	10-52	94
	Endosulfan-II	33213-65-9	13.30	93
	Endosulfan	115-29-7	14.13	91
2	2-Propanol, 1- (dibuytyl amino)	2109-64-0	3.86	83
	Benzenomine 4-bromo	106-40-1	4.58	93
	m-chloropropiophenone	34841-35-5	5.01	94
	3-Cyclohexene-1-0l,3-methyl	53783-91-8	9.48	50
	2,4 Pentanedine, 3- (2-propenyl)	3508-78-9	11.88	38
	Cyclohexene (bromomethyl)	2550-36-9	12.15	43
	Endosulfan I	959-98-8	13.23	90
	1,2 benzenes Dicarboxylinic acid	27554-26-3	16.36	91

To improve the detection power for several analyses, a single ion recording (SIR) was used, which can be run simultaneously with the full scan mode. Therefore, a simultaneous acquisition of TIC and SIR increases the certainty in compound detection and decreases the uncertainty in compound identification and misinterpretation.

In figure 1 compound were detected with retention time of 10.52, 13.30 and 14.13 min. The mass spectra of these compounds with retention time 10.52 min has largest m/z peaks are 69 (abundance 32,000), m/z : 239 (abundance 6000), m/z: 85 (abundance 4000). The peak with 13.30 min retention time has largest m/z peaks are 195 (abundance 290000), m/z 170,241 (abundance 220000), m/z 159 (abundance 290000), m /z 243 (abundance 170000) which is mass spectra of Di-n-octyl phthalate (fig.2). The peak with retention time 14.13 min has largest m/z peaks 195 (abundance 1,30,000), m/z 159 (90,000) m/z 170, 237 (abundance 90000).

The total ion chromatogram of wastewater sample-2 was shown in fig.3, with peaks retention time at 3.86, 4.58, 5.01, 9.48, 11.88, 12.15, 13.23 and 16.36 min. The mass spectra of each peak in TIC were studied for different m/z peaks.

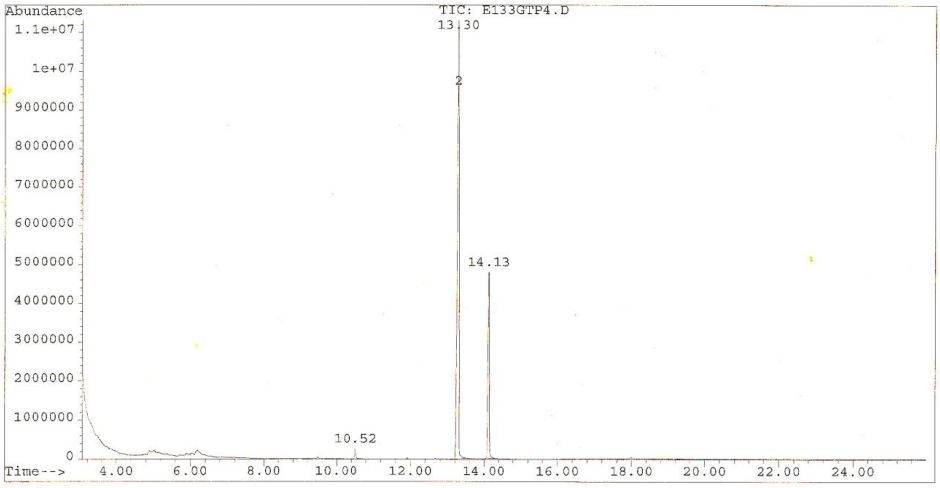


Fig. 1. Total ion chromatogram of wastewater sample number 1.

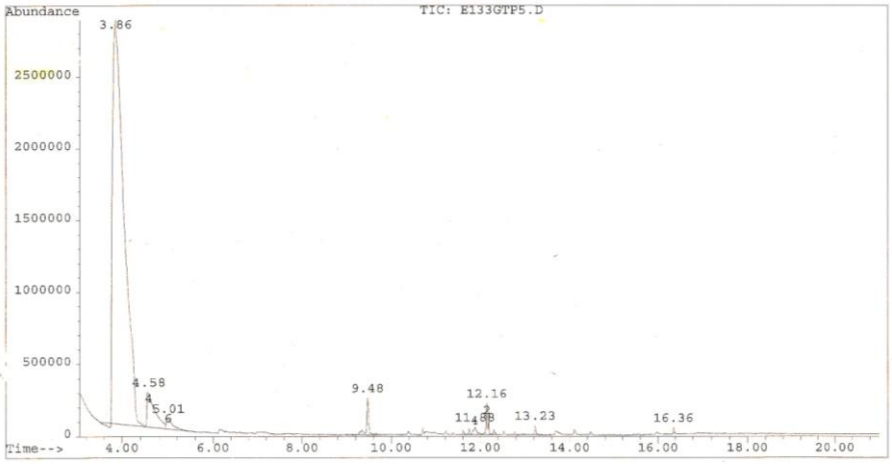


Fig.2. Total ion chromatogram of wastewater sample number 2.

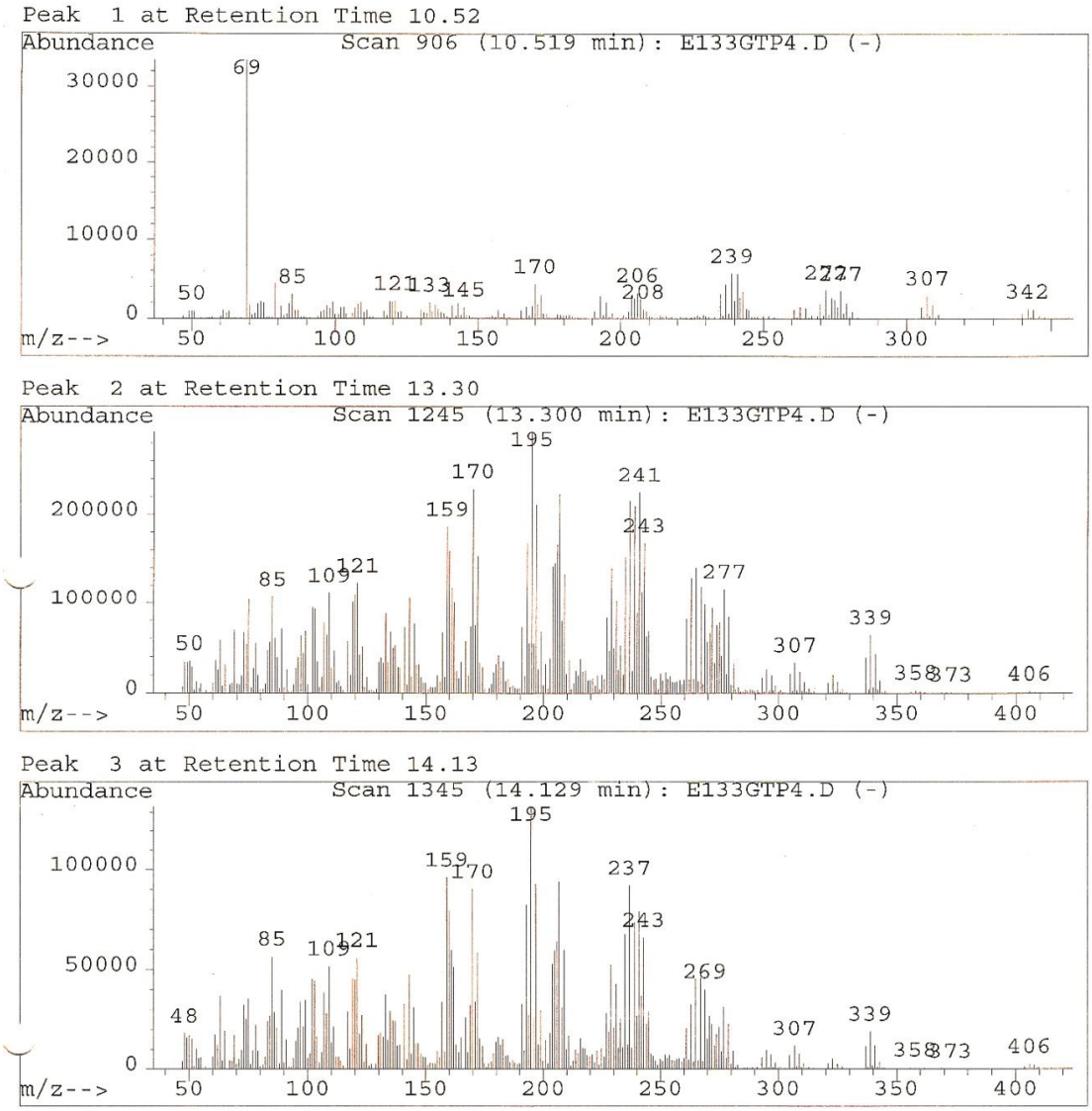
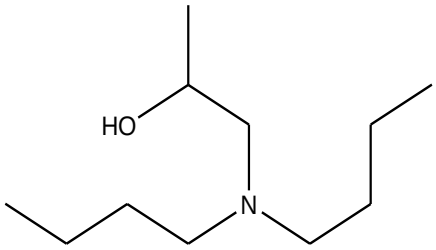
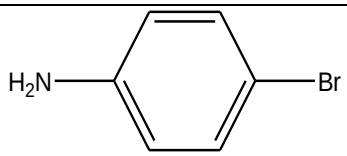
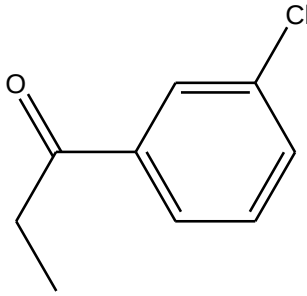
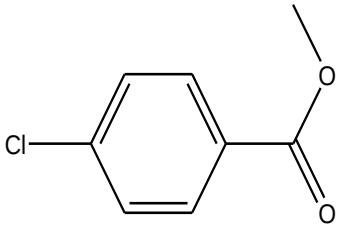
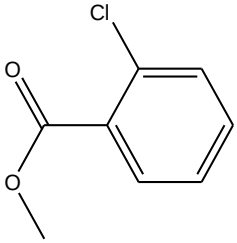
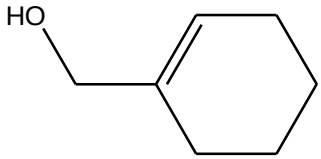
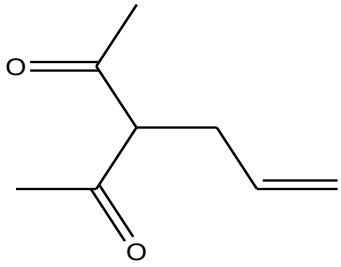
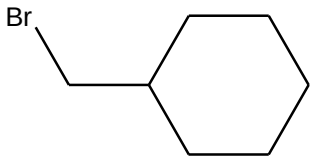


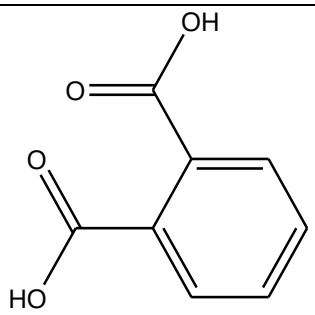
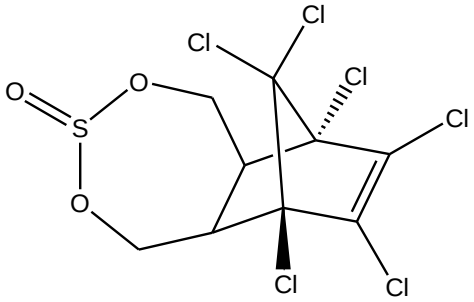
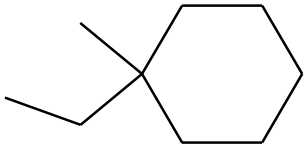
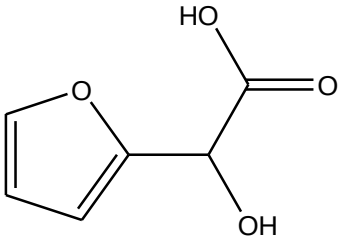
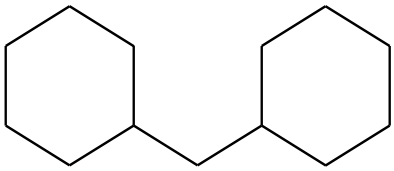
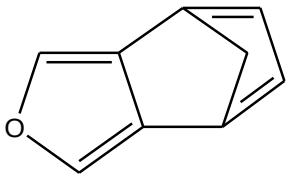
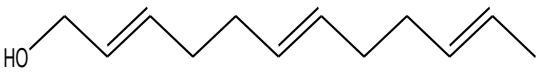
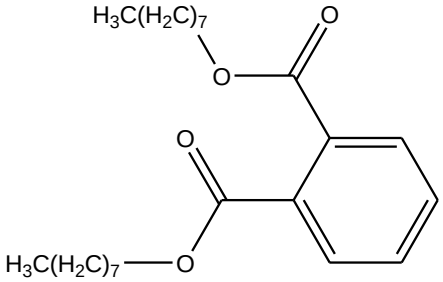
Fig.3. Mass spectra of residue with retention time 13.30 min. The largest m/z peaks are 195 (abundance 300,000), m/z 170, 214 (abundance 2,30,000).

The mass spectra of 2-propanol -1-(dibutyl amino) with retention time 3.85 min was shown in fig.4. The largest m/z peaks are 142 (abundance 1, 30,000), m/z 100 (abundance 6,00,000) m/z 58 (abundance 1,00,000) are observed. The detected organic compounds are given in Table-4. All these compounds are toxic, which impart taste and odour to water and are toxic to aquatic life.

Table 4: Organic compounds found in CH_2Cl_2 extracted mass of industrial wastewater (Sample No.1, 2) in G.I.D.C. Panoli, Ankleshwar

Sr. No.	Name of Organic Compound	Structure of Organic Compound	Molecular Formula	Mole. weight
1	2-Propanol 1-dibutylamino		$C_{11}H_{25}NO$	187

Sr. No.	Name of Organic Compound	Structure of Organic Compound	Molecular Formula	Mole. weight
2	4-Bromobenzenamine		C_6H_6NBr	171.2
3	m-Chloropropinophenone		$C_{10}H_{11}OC$ 11	182.5
4	Benzoic acid 4-chloro, methyl		$C_8H_7O_2Cl$	170.6
5	Benzoic acid 2-chloro, methyl		$C_8H_7O_2Cl$	170.6
6	3-Cyclohexene 1-01, 3 methyl		$C_7H_{12}O$	112
7	2,4 Pentanedione 3 (2-Propenyl)		$C_8H_{12}O_2$	140
8	Cyclohexane (Bromomethyl)		$C_7H_{13}Br$	177.1

Sr. No.	Name of Organic Compound	Structure of Organic Compound	Molecular Formula	Mole. weight
9	1,2 Benzene dicarboxylic acid		$C_8H_6O_4$	166
10	Endosulfan		$C_9H_6O_3Cl_6S$	406
11	Cyclohexane,1-ethyl-1-methyl		C_9H_{18}	124.1
12	2-furanaceticacid, alpha-hydroxy		$C_6H_6O_4$	142.1
13	Cyclohexane,1-(cyclohexyl methyl)		$C_{13}H_{24}$	180.3
14	4,7-Methanoisobenzofuran		$C_6H_6O_4$	130.1
15	2,6,10-Dodecatrien-1-ol		$C_{12}H_{20}O$	180.1
16	Di-n-octyl phthalate		$C_{24}H_{38}O_4$	390.5

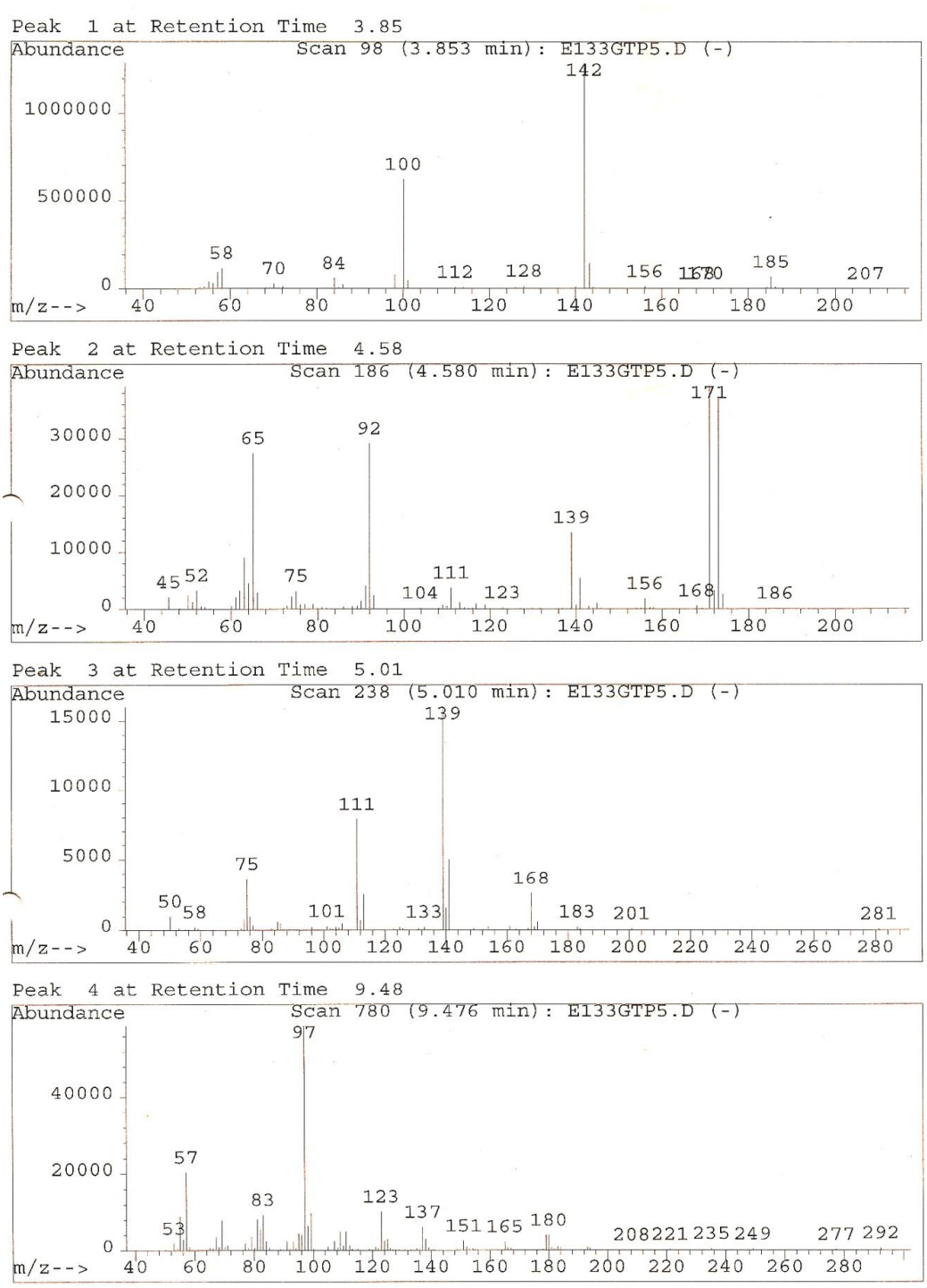


Fig.4. (a) Mass spectra of 2- propanol, 1- (dibutyl amino) with retention time 3.85 min. The largest m/z peaks are 142 (abundance 1,30,0000) m/z 100, (abundance 6,00,000) m/z 58 (abundance 1,00,000).

C. The Fragmentation patterns

Di-n-octyl phthalate has to show molecular ion (M^+) at m/z 391 ($C_{24}H_{38}O_4$) and has loss smaller chain moiety by fragmentation is thought to give rise to diagnostic ions at m/z 277 by loss of $C_{16}H_{21}O_4$ and m/z 113 loss of C_8H_{17}, m/z 233 by loss of $C_{15}H_{21}O_2$ and m/z 158 by loss of $C_9H_{17}O_2$, m/z 164 by loss of $C_8H_4O_4$ and m/z 113 by loss of C_8H_{17}, m/z 120 by loss of $C_7H_4O_2$ and m/z 105 by loss of C_7H_7O. The fragmentation pattern was shown in figure 5.

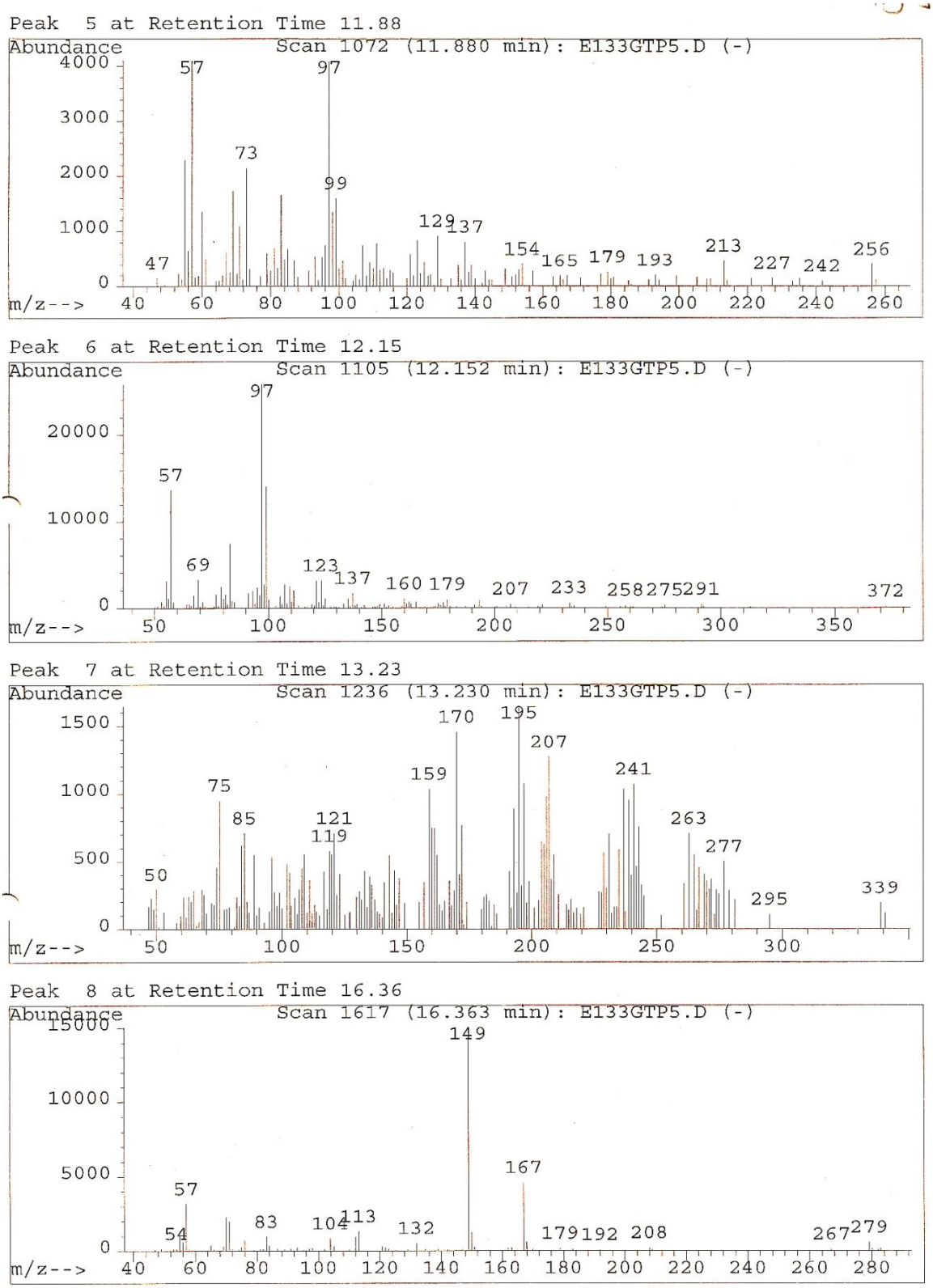


Fig.4. (b) shows the fragmentation pattern

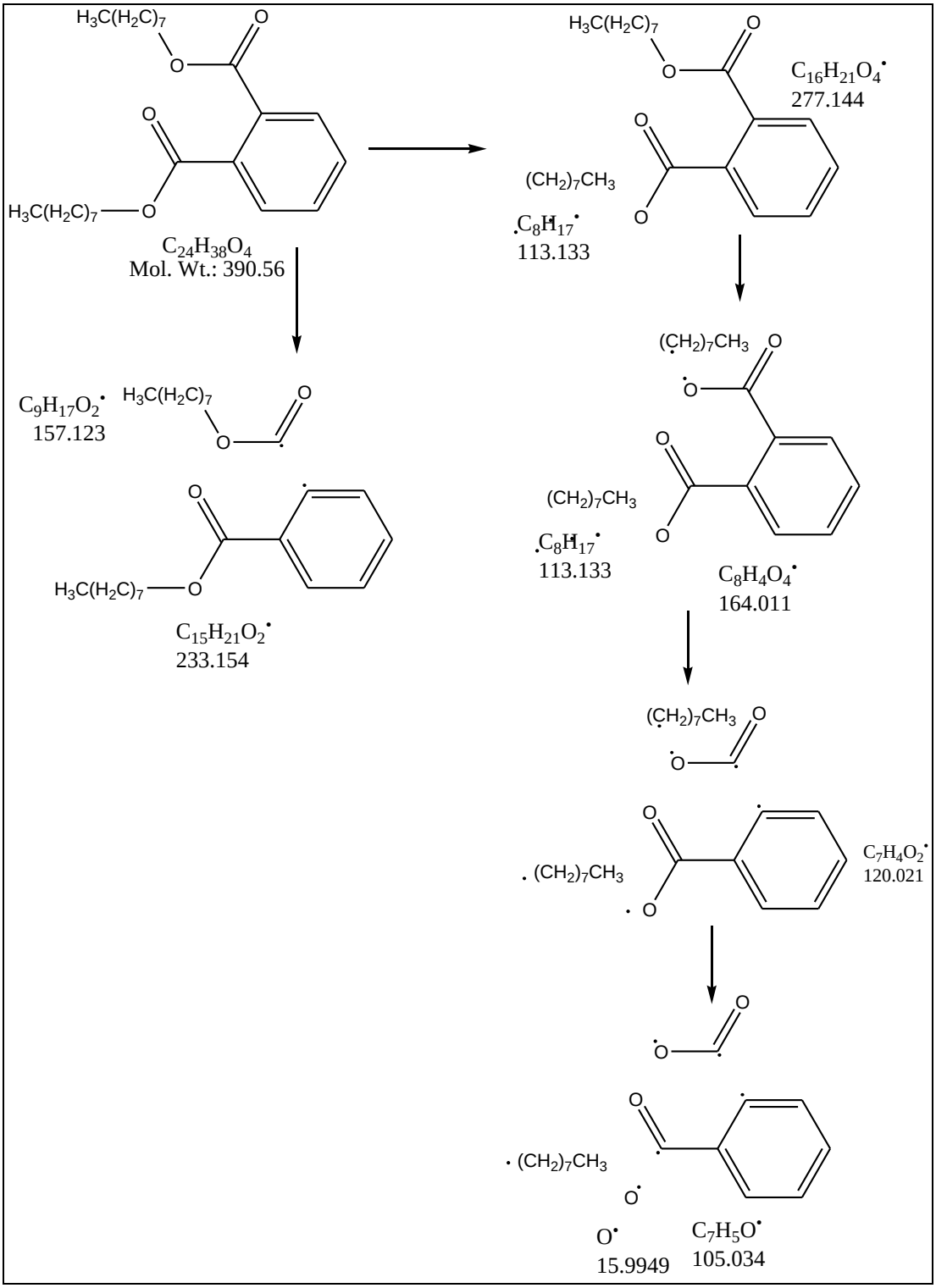


Fig.5. Fragmentation patterns of Di-n-octyl phthalate with retention time 13.30 min.

The 2,4 Pentanedione 3 (2-Propenyl) shows molecular ion (M^+) at m/z 142 ($C_8H_{12}O_2$) and has loss smaller chain moiety by fragmentation is thought to give rise to diagnostic ions at m/z 99 by loss of $C_5H_7O_2$, m/z 85 by loss of $C_4H_5O_2$, and C_3H_5, CH_3, m/z 71 by loss of C_4H_7O, m/z 43 by loss of C_2H_3O, m/z 27 by loss of C_2H_3 m/z 57 by loss of C_3H_5O, the fragmentation pattern was shown in figure 6.

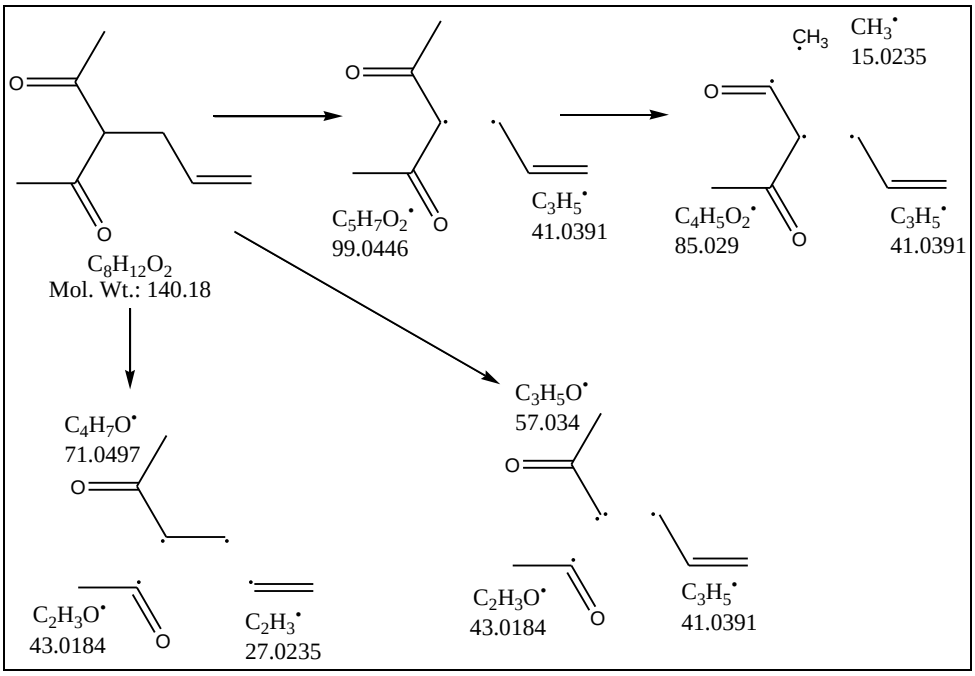


Fig.6. Fragmentation patterns of 2,4-Pentanedione-3-(2-propenyl) with retention time 3.85 min.

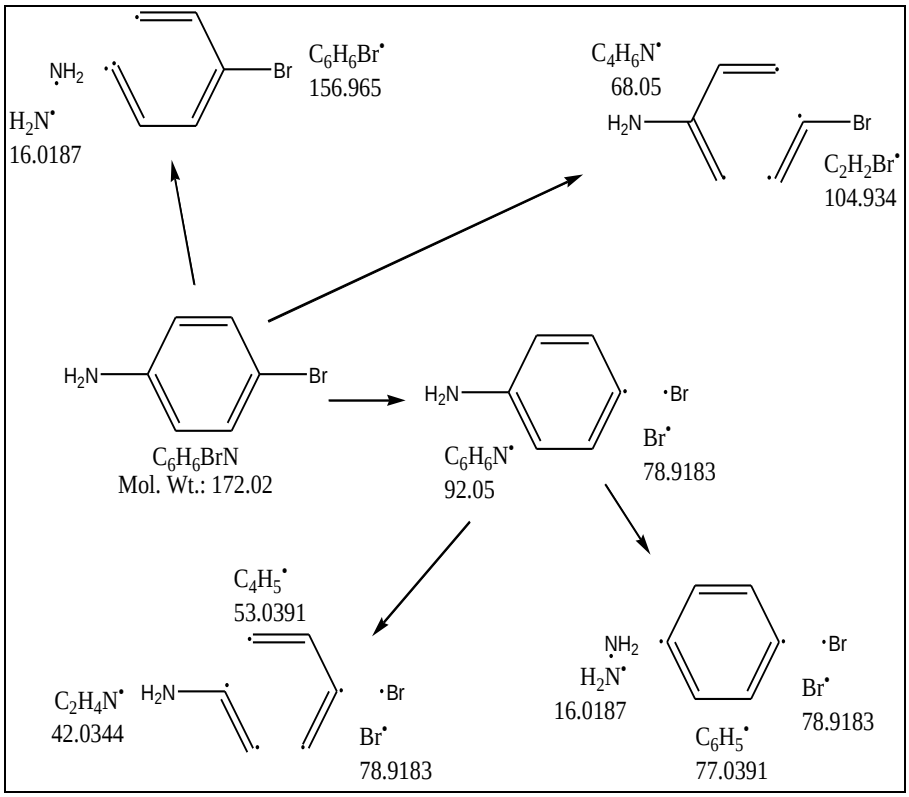


Fig.7. Fragmentation patterns of 4-Bromobenzenamine with retention time 4.58 min.

The 4-Bromobenzenamine shows molecular ion (M^+) at m/z 172 (C_6H_6Br N) and has loss smaller chain moiety by fragmentation is thought to give rise to diagnostic ions at m/z 156 by loss of C_6H_6Br and m/z 16 by loss of NH_2, m/z 104 by loss of C_2H_2Br, and m/z 68 by loss of C_4H_6N, m/z 92 by loss of C_6H_6N and m/z 78 by loss of Br,. m/z 53 by loss of C_4H_5 and m/z 42 by loss of C_2H_4N, m/z 77 by loss of C_6H_5 and m/z 16 by loss of NH_2,The fragmentation pattern was shown in figure 7.

CONCLUSIONS

Huge number of organic compounds are used in industries for different processes. The presence of these compounds in industrial wastewater, amended soil, may lead to the formation of the new substituted compounds. All the above compounds in industrial wastewater will be a complex mixture of the contaminants with the predominance of any type depending on effluents hydrology, discharge sources and general effluent condition. The presence of such organic compounds in the industrial waste, amended soil may be the cause of worry for the ecosystem, aquatic life, soils flora and fauna as well as the health and hygiene of people living in the surrounding area.

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