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IDENTIFICATION OF OZONATION PRODUCTS OF PRODUCED WATER BY GC-MS

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IDENTIFICATION OF OZONATION PRODUCTS OF PRODUCED WATER BY GC-MS

1. BACKGROUND

Produced water, which is created in an oil pumping process, is seawater contaminated with several toxic organic compounds. Ozonation is one of many methods that can be used to eliminate these substances from produced water. Ozonation studies of produced water were performed at Oak Ridge National Laboratory (ORNL). Preliminary Gas Chromatography - Mass Spectrometry (GC-MS) analysis of produced water both before and after ozonation showed disappearance of several peaks and formation of others. The objective of this study is to identify the organic compounds in produced water before, during, and after ozonation, by using GC-MS.

2. INTRODUCTION

2.1 Ozonation

Ozone is an unstable reactive gas and has widely been used as an oxidant in water/wastewater treatment processes. It reacts with organic substances in two different mechanisms: direct reaction with ozone and indirect reaction with free hydroxyl radicals that are produced by ozone decomposition. The direct reactions with ozone can be classified into two ways: an electrophilic addition and a cyclo-addition. The electrophilic addition occurs at the electron rich parts of organic molecules like carbon-carbon double bonds at neutral to acidic conditions. The cyclo-reaction is selective to unsaturated carbon-carbon double bonds and forms carbonyl compounds (aldehydes or ketones). The reactivity of ozone depends on the electron density at the reaction sites. At alkaline conditions ozone decays mostly to hydroxide radicals and by chain reactions to other radicals, which effect an unspecific radical reaction with organic substances.

2.2 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography (GC) is a common analytical technique for separating volatile compounds and can provide a representative spectral output. The advantages of GC are speed of analysis, resolution, ease of operation, excellent quantitative results, and moderate costs. GC is unable,

however, to verify the identity or structure of any peaks, and therefore GC data alone cannot be used to identify compounds (McNair and Miller, 1998). Mass spectrometry (MS) on the contrary provides quantitative data as well as qualitative identification of unknown compounds. Furthermore, MS is easily coupled to a GC system.

When a sample is injected into a GC system, it will be vaporized. The different chemical and physical characteristics of molecules determine how each substance in the sample interacts with the GC column surface. The column allows the various substances to partition themselves. After the compounds emerge from the column, they enter the ionization chamber. A 70 eV electron beam draws out electrons from a tungsten filament. These high-energy electrons strike the neutral analyte molecules, causing ionization and fragmentation. Each fragment is charged and travels to the accelerator as an individual particle. In a quadrupole mass analyzer, the ions are separated according to their mass-to-charge (m/z) ratio by electric field. Depending on the produced electric field, only ions of a particular m/z will be focused on the detector.

GC-MS has been employed in several investigations. Feigel and Holmes used GC-MS to analyze waste and wastewater for low-level contaminants such as polyaromatic hydrocarbons (PAH). Glover and Bullin (1989) examined seven unweathered heavy residual oils by using both GC and GC-MS and compared the results to source samples for identification purposes. The long-side-chain alkylaromatics in crude oil were also investigated using GC-MS by Dutta and Harayama (2000). Maldonado et al. (1999) studied the presence of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. Zeng et al. (2000) focused on an integrated treatment of benzo[*a*]pyrene involving sequential chemical oxidation and biological degradation. The qualitative and quantitative determinations of benzo[*a*]pyrene, intermediates, and reaction products were carried out by GC and GC-MS.

Since the produced water is generated in the oil production, it is expected to contain hydrocarbon compounds. Toluene and xylenes are common compounds found in any crude oil and oil products. The present study used toluene, xylenes, and combinations of both as standard solutions for reference. The temperature program was obtained by considering the separation of standard solutions and compounds in the samples, as well as by examining temperature programs

found in the literature. The optimal temperature program chosen was the one that gave the best results.

3. EXPERIMENTAL INSTRUMENTS AND PROCEDURE

3.1 Test Apparatus and Instruments

The specifications of the major apparatus and instruments used in this study are listed below:

- An HP 6890 series gas chromatograph (Hewlett Packard Co., CA, USA).
- An HP 5973 mass selective detector (MSD) (Hewlett Packard Co., CA, USA).
- An HP 6890 series injector and autosampler (Hewlett Packard Co., CA, USA).
- An HP-5MS 5% Phenyl Methyl Siloxane capillary column (30 m × 0.25 mm I.D. × 0.25 μm film thickness, Hewlett Packard Co., CA, USA). The column length of 30 m provides a good compromise between resolution and speed of analysis. The column diameter of 250 μm represents the best concession between resolution, speed, sample capacity, and ease of operation. A standard film thickness of 0.25 μm represents a compromise between the high resolution attainable with thin films and the high capacity available with thick films.
- An HP Chemstation software (Hewlett Packard Co., CA, USA).
- A 10 μL autosampler syringe.
- 2 mL vials.
- 4 mL wash vials.

3.2 Chemicals and Samples

- Helium gas was employed as a carrier gas.
- The HPLC grade dichloromethane (Aldrich Chemical Co., MI, USA) was used as a solvent.
- As toluene and xylenes were expected to be present in the samples, they were used to prepare standard solutions. Oak Ridge National Laboratory (ORNL) provided pure toluene and xylenes.
- All the samples were provided by ORNL. Eight samples of produced water were categorized into three groups: non-ozonated samples indicated with O_2, partially

oxidized samples indicated with O_3, and completely oxidized samples indicated with O_3O_2. These samples came from three companies: Company A, Company B, and Company C. The samples from Company A and Company B included all three groups, while those from Company C included only non-ozonated and completely oxidized samples. In addition, four of completely oxidized Company-A samples ozonated for different time periods were provided to study the effect of ozonation time on the chemical composition in the sample.

3.3 Experimental Procedure

This study consisted of two phases:

I. Identifying the parent compounds, intermediates, and oxidation by-products in the non-ozonated samples, partially oxidized samples, and completely oxidized samples.
II. Comparing the compounds in the samples that underwent oxidation by ozone for different time periods.

The principal procedures included the following steps:

1. Preparing 1000 ppm stock standard solutions by spiking chemicals into 10 mL of dichloromethane. Diluting the solutions with dichloromethane to 20 ppm and filling them in 2 mL vials. These solutions were used as reference.
2. Varying the temperature program, pressure, and helium gas flow rate by considering temperature programs from the literature. The goal was to achieve the optimal program that gives the best results.
3. Employing the autosampler to inject 1 μL of solution into the GC-MS system.
4. Identifying organic compounds in the sample by using the NBS75K library.

The performance of the GC-MS system was verified with the experimental configuration and conditions summarized in Table 1. The quadrupole mass selective detector was operated under the scan mode to obtain spectral data for identifying the compounds.

Table 1: Instrument Conditions

Gas Chromatograph	
Oven Program:	38°C, 4 min; 10°C/min to 250°C and hold for 2 min.

Carrier Gas:	Helium, 1.2 mL/min
Injector Temperature:	250°C
Mass Spectrometer	
Ion Source Temperature:	230°C
Quadrupole Temperature:	160°C
Solvent Delay:	4 min
Electron Energy:	70 eV
Mass Range:	50-550 a.m.u.
Scans/sec:	1.5

The experimental results were obtained by using the ChemStation integrator and the default integration events, shown in Table 2.

Table 2: Integration Events

Initial Area Reject:	1
Initial Peak Width:	0.02
Shoulder Detection:	OFF
Initial Threshold:	18

4. EXPERIMENTAL RESULTS

The experimental results were given in terms of the highest match quality. Some statistics values such as percent impurity, confidence factor, contamination factors can also be obtained by using the ChemStation software. Since these values followed the same trend as the match quality, only the highest match quality is shown in the results.

4.1 Standard Solutions

As toluene and xylenes are expected to be present in the samples, they were used to make standard solutions. Three solutions - (1) toluene solution, (2) xylenes solution, and (3) toluene-xylenes mixture - were prepared. Figure 1 shows the chromatogram of toluene separation. One

significant peak was found at retention time (RT) about 4.35 min. This peak was identified as toluene with 94% match quality. In addition, there are 6 very small peaks at 18.90, 20.62, 22, 23, 24, and 26 min. A similar chromatogram was obtained in the separation of xylenes solution as shown in Figure 2. The peak appeared at 7.37 min and the library recognized it as *p*-xylene with 97% match quality. Six small peaks were also observed but at a lower value of abundance as compared to those in toluene solution. Two high peaks are shown in Figure 3, which presents the chromatogram of toluene-xylenes mixture. The first one appeared at 4.36 min, which is toluene, while the second one appeared at 7.37 min, which is *p*-xylene. The separation of this mixture gave the same percent match quality as in the separation of the single compound solutions. Those six small peaks observed in the separation of toluene and xylenes solutions are still present in this chromatogram.

4.2 Sample Solutions (Phase I)

4.2.1 Sample Solutions of Company A

Company-A O_2 sample represents produced water before ozonation. Several peaks were observed in the chromatogram, as shown in Figure 4. Most of them fall in the range of 10.39 to 19.36 min RT. As expected, toluene and *p*-xylene were found to be present in this sample. The baseline is unstable; it increased its slope at 10 min, decreased after 12.59 min, and then reached a stable state around 26 min. The percent match quality values are not as good as those obtained in the separation of standard solutions but they represent the best results of all the experimental runs for this sample. The results confirmed the presence of cyclopentanecarboxylic acid, cyclopentaneacetic acid, and cyclohexanecarboxylic acid in the sample.

Company-A O_3 sample represents produced water that was partially oxidized by ozone. Figure 5 shows that the peaks observed in the O_2 sample are still present in the O_3 sample, and about 10 new peaks are created. These new compounds have relatively high abundance as compared to the compounds found in the O_2 sample. The highest peak was identified as 2,4-dibromopentane. Toluene and xylenes were not detected in this chromatogram. The baseline has the same trend as in the O_2 sample.

Company-A O_3O_2 sample represents produced water after complete oxidation. Figure 6 illustrates that some compounds that were formed under partial oxidation still appear in this chromatogram, while some are gone especially the highest peak, 2,4-dibromopentane. The compounds found in the O_2 sample also disappeared. The small peaks, which were found in the toluene and xylenes solutions but not in Company-A O_2 and O_3 samples, appear in this case. The baseline of this chromatogram is stable.

4.2.2 Sample Solutions of Company B

The chromatogram of Company-B O_2 sample has an unstable baseline in the first 12 min and then reaches a stable state, as shown in Figure 7. Most of the peaks were also displayed in the first 12 min. Small peaks in the range of 18 to 26 min were also found, and some of them showed relatively high abundance. The results illustrate that the sample contains toluene and *p*-xylene. The compounds found in this sample are quite different from those found in the Company-A O_2 sample. The library identified that this sample contains propanoic acid, butanoic acid, and pentanoic acid.

Figure 8 demonstrates that new compounds were created in the Company-B O_3 sample. Most of them are similar to those created in the Company-A O_3 sample. Most of the peaks found in Company-B O_2 sample disappeared. Acids such as hexanoic acid, heptanoic acid, and octanoic acid were discovered while propanoic acid disappeared. However, butanoic acid and pentanoic acid were still present in the sample.

Figure 9, the chromatogram of the Company-B O_3O_2 sample, is similar to Figure 6. The difference is the level of abundance. Moreover, the Company-B O_3O_2 sample seems to show more peaks than the Company-A O_3O_2 sample.

4.2.3 Sample Solutions of Company C

Company-C O_2 sample displayed fewer peaks than the other O_2 samples, as shown in Figure 10. Toluene and *p*-xylene were found in this case. The highest peak was identified as 3-methyl-2-

buten-1-ol. The peaks at RT of 14.69, 16.91, 18.90, and 20.62 min, which were also identified in the Company-B O_2 sample, were found in relatively high abundance.

Company-C O_3O_2 sample has a similar chromatogram (Figure 11) as those of Company-A O_3O_2 and Company-B O_3O_2 samples, but with a smaller number of peaks than the Company-B O_3O_2 sample.

4.3 Sample Solutions (Phase II)

All of these samples came from Company A. They went through the ozone oxidation process for different time periods. Figure 12 displays the chromatogram of A18-2. Two peaks were discovered at 9.11 and 9.56 min RT and were identified as 2-ethyl-4-methyl-1,3-dioxolane and 1-bromo-3-methyl-2-butene, respectively.

The chromatograms of A18-6 and A18-10 (Figure 13 and 14) exhibited similar results but different from those of A18-2. There were three peaks at RT of 7.04, 7.47, and 9.20 min and were recognized as butanamide, 2,2-dichloropentane, and 1,3-dibromo-3-methylbutane, respectively. The chromatogram of A18-11 shown in Figure 15 presents almost the same results as those of A18-6 and A18-10 but has one peak less. The compounds found in this sample are butanamide and 2,2-dichloropentane. One can notice that these chromatograms have much fewer peaks than those of partially and completely ozonated samples.

5. DISCUSSION

Varying the temperature program, pressure, and flow rate has effect on the separation of compounds. The retention time and percent match quality depend on the conditions used. However, the shapes of all chromatograms for each sample are the same irrespectively of the conditions employed. The results presented in this report are the best results obtained based on the percent match quality.

5.1 Standard Solutions

The HP-5MS column exhibited a good capability to separate toluene and xylenes. Toluene was separated at temperature around 38.6°C while *p*-xylene was separated at 68.8°C. The small peaks observed in all chromatograms of standard solutions may come from the solvent itself or some contaminants in the column.

5.2 Sample Solutions (Phase I)

The intermediates and by-products of the ozone oxidation process were expected to include oxygen atom. One can see, however, that some of the intermediates and by-products of both partially and completely ozonated samples do not contain any oxygen atom. This phenomenon may be due to reactions between the solvent and the compounds in the samples, which cause replacement of the oxygen atom by some other substances contained in the solvent.

5.2.1 Sample Solutions of Company A

Most of the peaks in the chromatogram of the Company-A O_2 sample are able to separate in the range of temperature of 110°C to 165°C. The unstable baseline may be a result of contamination of the column or impurities in the sample. The small peaks could not be identified because their abundances are low as compared to other compounds in the sample. The obtained match quality showed that this column is unable to separate very well the unknown compounds in the sample.

The results of the Company-A O_3 sample showed that new compounds are created during the ozonation process while the compounds found in the Company-A O_2 sample are still present in the sample. Comparing these results to the results obtained in the separation of completely oxidized Company-A sample (Figure 6), one can see that some compounds that are created in the partial oxidizing step are gone but others are still present in the sample. This observation indicates that the compounds that have disappeared in the completely oxidized sample are intermediates. On the other hand, the compounds that are still present in the completely ozonated sample are considered as ozonation by-products.

In the completely oxidizing process, some new products that had not been found in the previous two samples are formed. These are considered as by-products as well. The intermediates of ozonation of Company-A samples are 2-ethyl-4-methyl-1,3-dioxolane, 1,3-dibromo-3-

methylbutane, and 4-nitrophenyl-ester-2-butenoic acid, and the by-products are 1-bromo-3-methyl-2-butene, dibromochloromethane, 2,3-dichloro-2-methylbutane, butanamide, tribromomethane, and 2,2-dichloropentane. Among the oxidation by-products only butanamide contains oxygen atom, while the others contain halogen atoms.

5.2.2 Sample Solutions of Company B

For Company B, the non-ozonated results are different from those of Company A. Most of the compounds were located in the temperature range of 35°C to 120°C. This sample contains fatty acids, which were not discovered in the Company-A sample. Some peaks in this chromatogram consist of silicon atom, which may come from the column itself. These peaks are also found in some of the other samples but at very low abundance. They appear in this chromatogram at very high concentration because the concentration of other compounds in the sample is low compared to the other samples.

The only compound, found in both non-ozonated and partial oxidized samples, is butanoic acid while the others are all gone. This result may be a consequence of the concentrations of compounds in the non-ozonated sample, which are greatly smaller than those in the partially oxidation sample. Some of the new compounds are similar to those found in the Company-A O_3 sample.

It is interesting to note that the disappeared substances in the partially oxidized sample are discovered in the completely oxidized sample. This phenomenon may be explained by the concentration effect. It can also be concluded that these chemicals cannot be destroyed by ozone. These compounds are toluene, *p*-xylene, and dimethyl-1,4-dioxane. The intermediates of ozonation for the Company-B samples are 1,4-dibromopentane, 1,3-dibromo-3-methylbutane, hexanoic acid, heptanoic acid, and octanoic acid. The by-products are 1-bromo-3-methyl-2-butene, dibromochloromethane, butanamide, tribromomethane, 2,2-dichloropentane, 2-piperidinone, and 3-hexen-2-one.

5.2.3 Sample Solutions of Company C

Substances that consist of silicon atom are found in the non-ozonated Company-C sample. All of them are also found in the non-ozonated Company-B sample. The reasons for that were discussed in Section 5.2.2.

Complete oxidization produces almost every compound as found with the Company B sample. The results confirmed that toluene and *p*-xylene are not destroyed under ozonation. Since there is no partially ozonation sample from Company C, the ozonation intermediates cannot be detected. The ozonation by-products are 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane.

5.3 Sample Solutions (Phase II)

The compounds found in A18-2 are dissimilar to those in A18-6, A18-10, and A18-11. However, when these compounds were compared to the substances in the partial and complete oxidation of Company-A samples, it was found that the first compound is an intermediate and the second one is a by-product. This result indicates that after the sample undergoes ozonation for a couple minutes, the intermediate, 2-ethyl-4-methyl-1,3-dioxolane, is formed as well as the by-product, 1-bromo-3-methyl-2-butene. By continuing the ozonation for several minutes, those compounds in the first sample are gone and other two products and another one intermediate are formed instead. These products are butanamide and 2,2-dichloropentane. The intermediate is 1,3-dibromo-3-methylbutane. The chromatograms of A18-6 and A18-10 are identical. Maintaining the ozonation for a longer time (A18-11), the intermediate is gone and the two by-products are still present in the sample.

6. CONCLUSIONS

A GC-MS instrument accompanied with the HP Chemstation software and using the NBS75K library was employed in this study to identify ozonation products of produced water. The results were obtained by means of match quality. The quality of some identified compounds, however, was not high enough, which indicates that the HP-5MS capillary column is not the best column to separate these compounds and the samples themselves may have some impurities.

All the results demonstrate that ozonation may be used to destroy some organic compounds. On the other hand, ozonation also creates by-products. Some of the ozonation by-products of Company-A, Company-B, and Company-C samples are the same. The common ozonation by-products are 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane. There are some intermediates formed during the ozonation process. Each intermediate and by-product is formed at different ozonation periods. Toluene and *p*-xylene are not destroyed during the ozone oxidation process.

The non-ozonated Company-A sample includes the most compounds as compared to the other samples. The main compounds are cyclopentanecarboxylic acid, cyclopentaneacetic acid, and cyclohexanecarboxylic acid. The compounds of Company-B samples are fatty acids such as butanoic acid and pentanoic acid. The results of Company-C samples are pretty much the same as those of Company-B but with fewer compounds. None of the fatty acids is found in any of the Company-C samples.

An interesting point is the formation of compounds that contain halogen atoms rather than oxygen atom. This result is presumed to be due to the extraction procedure with dichloromethane; some compounds originally in the sample interact with halogen atoms in the solvent. In addition, some of the compounds formed during ozonation give up the oxygen atom and bond to halogens in the solvent instead.

7. REFERENCES

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APPENDIX A

CHROMATOGRAMS OF ALL SAMPLES

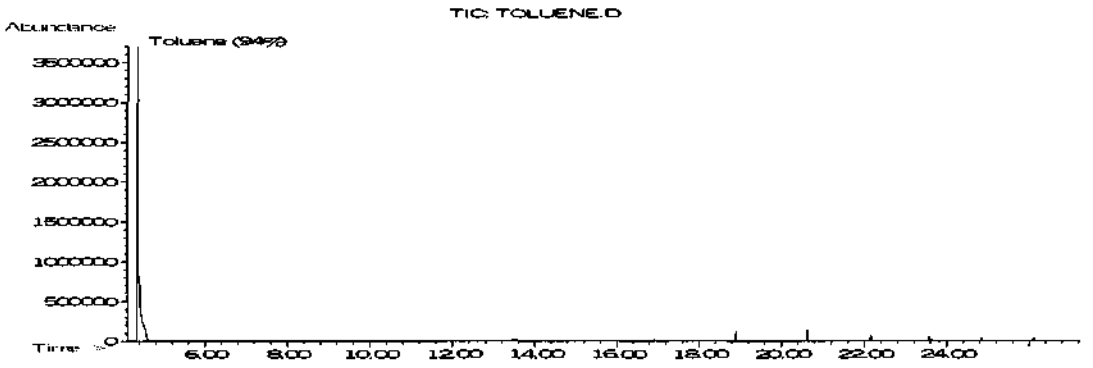

Figure 1. Chromatogram of toluene solution.

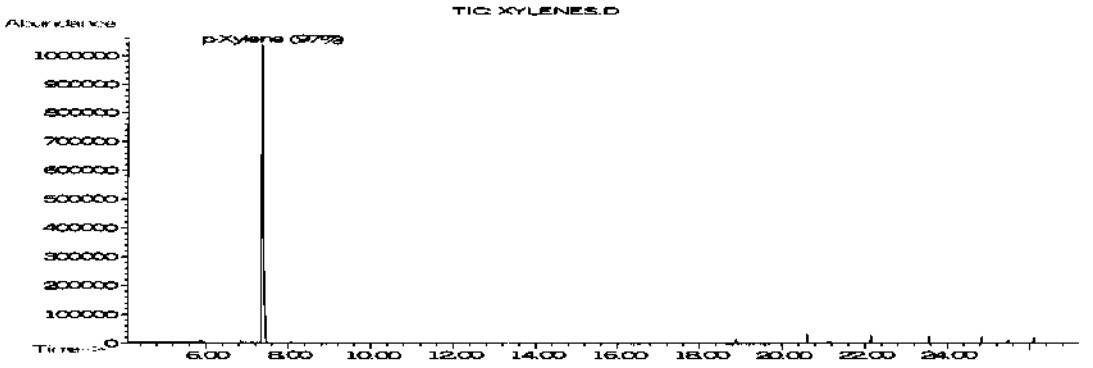

Figure 2. Chromatogram of xylenes solution.

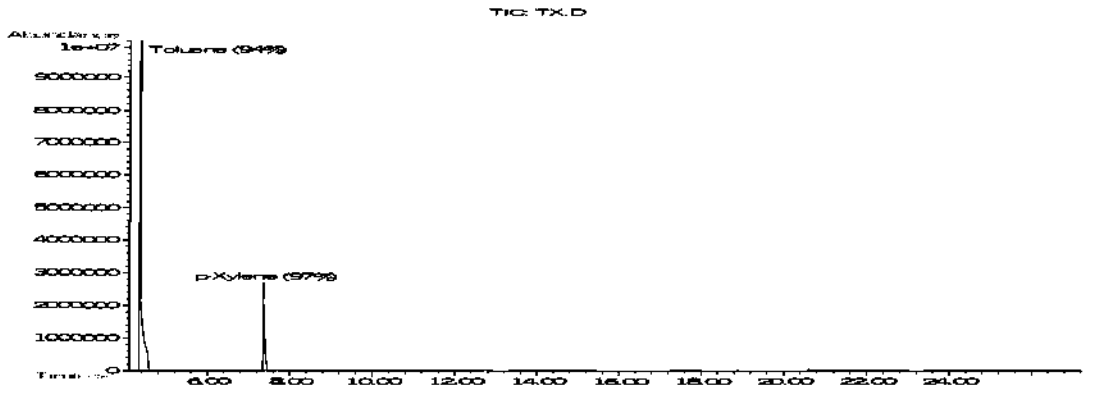

Figure 3. Chromatogram of toluene-xylenes mixture.

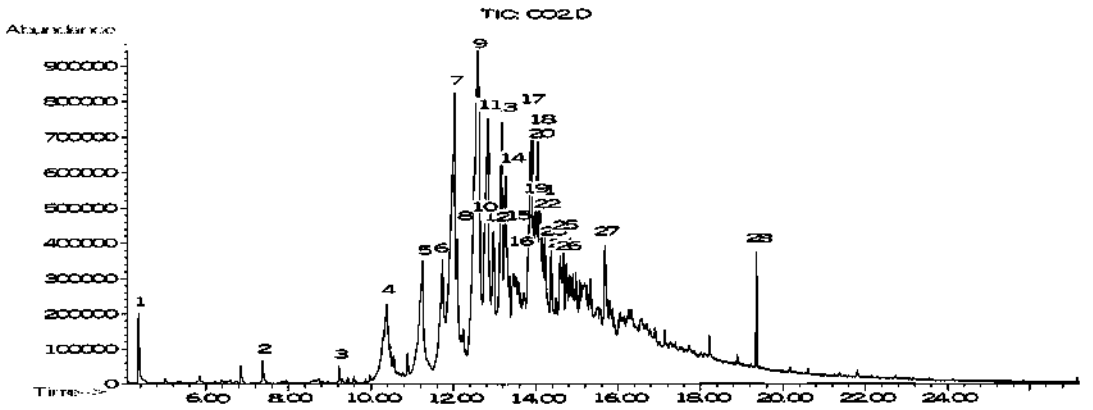

Figure 4. Chromatogram of non-ozonated Company-A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	90
2	7.38	*p*-Xylene	C_8H_{10}	95
3	9.23	Phenol	C_6H_6O	97
4	10.39	Cyclopentanecarboxylic acid	$C_6H_{10}O_2$	74
5	11.26	Cyclobutanecarboxylic acid, 2,2-dimethyl	$C_7H_{12}O_2$	17
6	11.75	Cyclopentaneacetic acid	$C_7H_{12}O_2$	53
7	12.04	Cyclohexanecarboxylic acid	$C_7H_{12}O_2$	76
8	12.09	2(3H)-Furanone, dihydro-4,5-dimethyl	$C_6H_{10}O_2$	38
9	12.59	Cyclohexanemethanol	$C_7H_{14}O$	43
10	12.65	Cyclopentane, 1-methyl-3-(1-methylethyl)	C_9H_{18}	49
11	12.85	2-Octenal, (E)-	$C_8H_{14}O$	46
12	12.97	Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-	C_9H_{16}	43
13	13.17	1,10-Dicyanodecane	$C_{12}H_{20}N_2$	35
14	13.27	Cyclohexane, 1-pentyl-	$C_{11}H_{20}$	35
15	13.33	1,4-Hexadiene, 2-methyl-	C_7H_{12}	38
16	13.47	Undecylenic acid	$C_{11}H_{20}O_2$	52
17	13.87	Cyclopentaneundecanoic acid	$C_{16}H_{30}O_2$	38
18	13.92	Cyclohexanemethanol, 4-methyl-,trans-	$C_8H_{16}O$	38
19	13.96	Cyclohexane, 1-ethyl-4-methyl-,cis-	C_9H_{18}	35
20	14.05	Cyclohexanemethanol, 2-methyl-	$C_8H_{16}O$	47
21	14.11	Cyclopropanemethanol,2,2,3,3-tetramethyl-	$C_8H_{16}O$	38
22	14.23	Cyclohexane, methylene	C_7H_{12}	30
23	14.38	Cyclohexane, ethylidene-	C_8H_{14}	50
24	14.60	1-Methyl-2-methylenecyclohexane	C_8H_{14}	45
25	14.67	Cyclohexanemethanol, 4-methyl-,cis	$C_8H_{16}O$	47
26	14.75	1-Hexadecyne	$C_{16}H_{30}$	53
27	15.69	1-Methyl-3-(1'methylcyclopropyl)cyclopentene	$C_{10}H_{16}$	38
28	19.36	Cyclopentane, 1,1'-ethylidenebis	$C_{12}H_{22}$	50

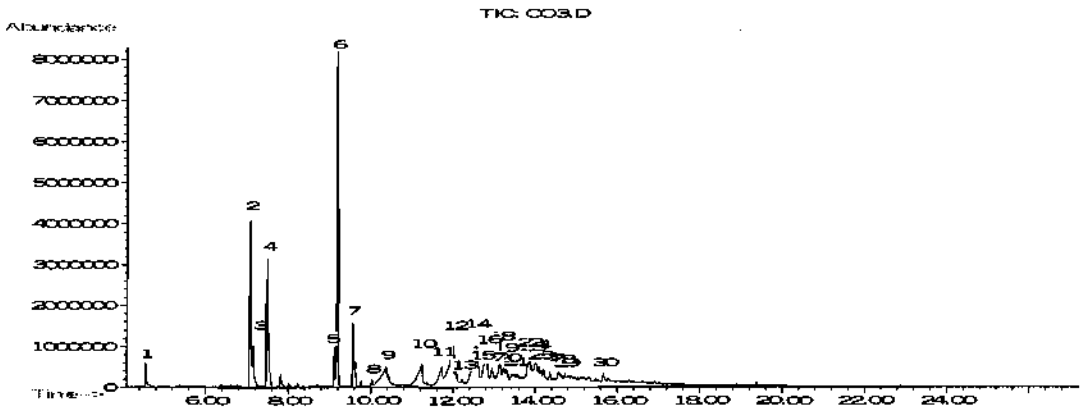

Figure 5. Chromatogram of partially oxidized Company-A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	7.08	Butanamide	C_4H_9NO	45
3	7.16	Methane, Tribromo-	$CHBr_3$	97
4	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25
5	9.12	1,3-Dioxolane, 2-ethyl-4-methyl-	$C_6H_{12}O_2$	59
6	9.19	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	43
7	9.57	2-Butene,1-bromo-3-methyl	C_5H_9Br	32
8	10.02	2-Butenoic acid, 4-nitrophenyl ester	$C_{10}H_9NO_4$	37
9	10.38	Cyclopentanecarboxylic acid	$C_6H_{10}O_2$	83
10	11.24	Cyclobutanecarboxylic acid, 2,2-dimethyl	$C_7H_{12}O_2$	35
11	11.73	Cyclopentaneacetic acid	$C_7H_{12}O_2$	59
12	12.02	Cyclohexanecarboxylic acid	$C_7H_{12}O_2$	93
13	12.08	Pentanal, 3-(hydroxymethyl)-4,4-dimethyl	$C_8H_{16}O_2$	32
14	12.57	Cyclohexanemethanol	$C_7H_{14}O$	47
15	12.63	Cyclopentane, 1-methyl-3-(1-methylethyl)	C_9H_{18}	46
16	12.84	3-Octyne, 2-methyl-	C_9H_{16}	30
17	12.96	Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-	C_9H_{16}	43
18	13.16	1,10-Dicyanodecane	$C_{12}H_{20}N_2$	35
19	13.25	Cyclohexene, 1-pentyl-	$C_{11}H_{20}$	43
20	13.31	Benzocyclodecene, tetradecahydro-	$C_{14}H_{26}$	43
21	13.45	1-Heptadecyne	C_7H_{32}	43
22	13.49	5-Eicosyne	$C_{20}H_{32}$	38
23	13.86	Cyclopentane, 1,1'-ethylidenebis	$C_{12}H_{22}$	43
24	13.89	Cyclohexane, 1-(cyclohexylmethyl)	$C_{13}H_{24}$	50
25	14.03	m-Menthane, (1S,3R) - (+) -	$C_{10}H_{20}$	43
26	14.09	Cyclohexane, 1-ethyl-4-methyl-,cis-	C_9H_{18}	43
27	14.21	Cyclohexane, methylene	C_7H_{12}	43
28	14.37	Cyclohexane, ethylidene-	C_8H_{14}	46
29	14.58	Methylenecyclooctane	C_9H_{16}	55
30	14.73	Cyclohexanol, 5-methyl-2-(1-methylethenyl)-	$C_{10}H_{18}O$	78
31	15.66	1-Methyl-3-(1'methylcyclopropyl)cyclopentene	$C_{19}H_{16}$	38

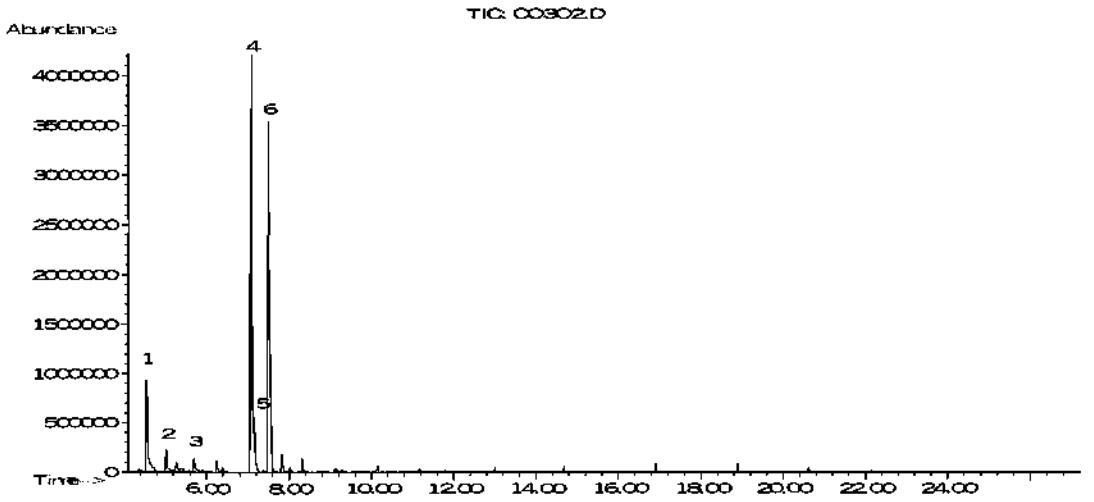

Figure 6. Chromatogram of completely oxidized Company-A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	5.03	Methane, dibromochloro	$CHBr_2Cl$	97
3	5.70	Butane, 2,3-dichloro-2-methyl-	$C_5H_{10}Cl_2$	90
4	7.08	Butanamide	C_4H_9NO	45
5	7.16	Methane, Tribromo-	$CHBr_3$	95
6	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25

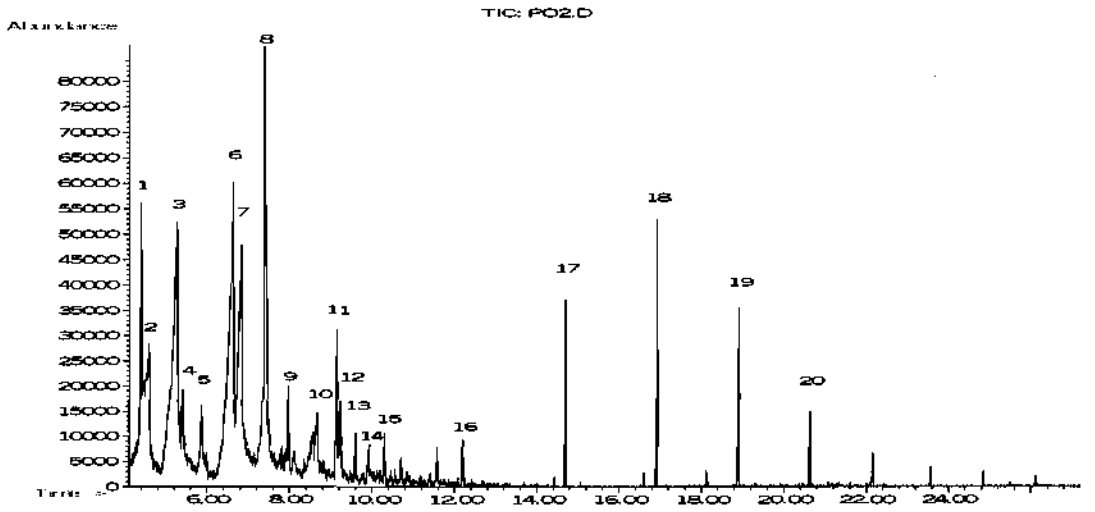

Figure 7. Chromatogram of non-ozonated Company-B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.38	Toluene	C_7H_8	58
2	4.56	Propanoic acid, 2-methyl-	$C_6H_{12}O_2$	53
3	5.25	Butanoic acid	$C_4H_8O_2$	86
4	5.39	Ethanol, 2-[(2-ethylhexyl)oxy]-	$C_{10}H_{22}O_2$	40
5	5.86	Cyclotrisiloxane, hexamethyl	$C_6H_{18}O_3Si_3$	78
6	6.62	Butanoic acid, 3-methyl-	$C_5H_{10}O_2$	39
7	6.82	Pentanoic acid, methyl ester	$C_6H_{12}O_2$	25
8	7.38	*p*-Xylene	C_8H_{10}	91
9	7.96	Bicyclo[2.2.2]octane, 1-bromo-4-methyl	$C_9H_{15}Br$	38
10	8.66	Pentanoic acid, 4-methyl-	$C_6H_{12}O_2$	9
11	9.13	1,4-Dioxane, dimethyl	$C_6H_{12}O_2$	59
12	9.23	Phenol	C_6H_6O	80
13	9.60	Cyclotetrasiloxane, octamethyl	$C_8H_{24}O_4Si_4$	56
14	9.94	Azetidine, 1-nitroso-	$C_3H_6N_2O$	7
15	10.29	Cycloheptene, methyl	C_8H_{14}	40
16	12.20	Cyclopentasiloxane, decamethyl-	$C_{12}H_{36}O_4Si_5$	56
17	14.68	Cyclohexansiloxane, dodecamethyl-	$C_{12}H_{32}O_6Si_6$	78
18	16.91	1,1,1,3,5,7,9,9,9-Nonamethylpentasiloxane	$C_9H_{30}O_4Si_5$	38
19	18.90	Silane, [[4-[1,2-bis[(trimethylsilyl)oxy]ethyl]-1,2-phenylene]bis(oxy)]bis[trimethyl-	$C_{20}H_{42}O_4Si_4$	37
20	20.62	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	$C_{13}H_{40}O_5Si_6$	59

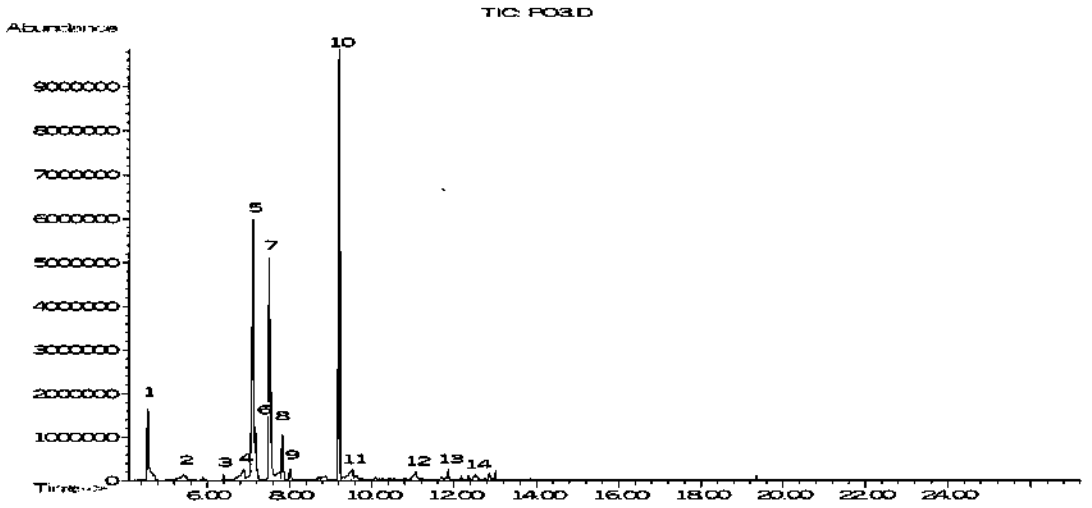

Figure 8. Chromatogram of partially oxidized Company-B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	5.42	Butanoic acid	$C_4H_8O_2$	58
3	6.39	2-Butene,1-bromo-3-methyl	C_5H_9Br	80
4	6.89	Butanoic acid, 3-methyl-	$C_5H_{10}O_2$	64
5	7.10	Butanamide	C_4H_9NO	45
6	7.16	Methane, Tribromo-	$CHBr_3$	96
7	7.50	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25
8	7.76	Pentanoic acid	$C_5H_{10}O_2$	78
9	8.01	Pentane,1,4-dibromo	$C_5H_{10}Br_2$	53
10	9.20	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	43
11	9.54	Hexanoic acid	$C_6H_{12}O_2$	83
12	11.08	Heptanoic acid	$C_7H_{14}O_2$	87
13	11.86	Bromisovalum	$C_9H_{18}O_3Br$	38
14	12.51	Octanoic acid	$C_8H_{16}O_2$	72

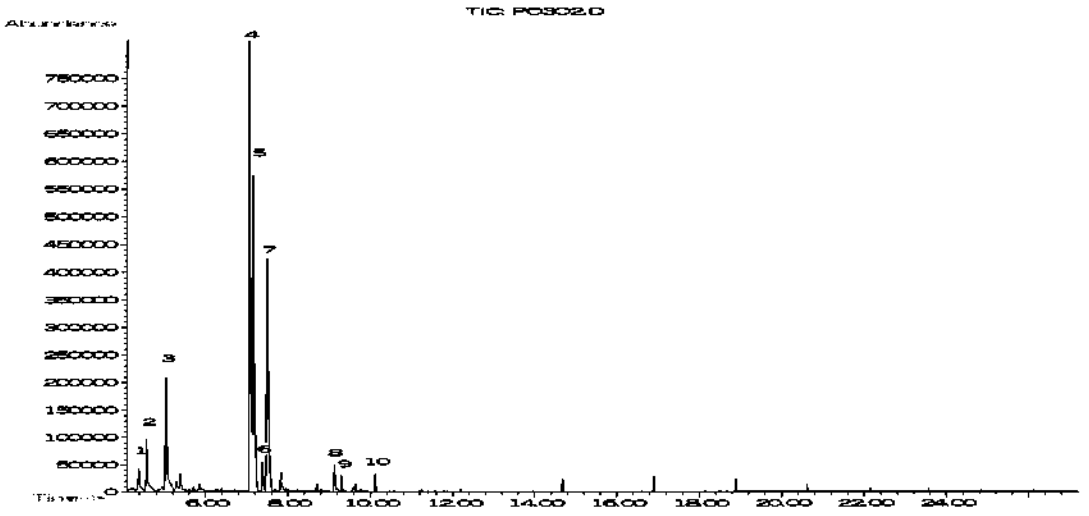

Figure 9. Chromatogram of completely oxidized Company-B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	70
2	4.57	2-Butene,1-bromo-3-methyl	C_5H_9Br	72
3	5.03	Methane, dibromochloro	$CHBr_2Cl$	97
4	7.06	Butanamide	C_4H_9NO	59
5	7.15	Methane, Tribromo-	$CHBr_3$	94
6	7.38	*p*-Xylene	C_8H_{10}	95
7	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	33
8	9.13	1,4-Dioxane, dimethyl	$C_6H_{12}O_2$	53
9	9.29	2-Piperidinone	C_5H_9NO	89
10	10.11	3-Hexen-2-one	$C_6H_{10}O$	50

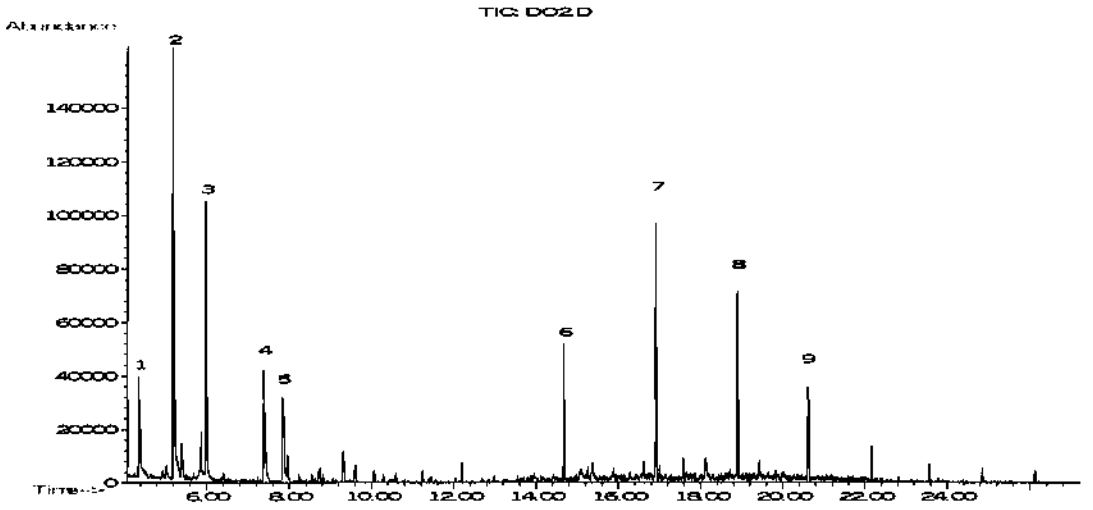

Figure 10. Chromatogram of non-ozonated Company-C sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.38	Toluene	C_7H_8	83
2	5.20	3-Buten-2-ol,2-methyl	C_5H_8O	43
3	5.99	3-Penten-2-ol	$C_5H_{10}O$	43
4	7.38	*p*-Xylene	C_8H_{10}	95
5	7.85	Ethane, 1,1,2,2-tetrachloro-	$C_2H_2Cl_4$	90
6	14.69	Cyclohexasiloxane, dodecamethyl-	$C_{12}H_{32}O_6Si_6$	83
7	16.91	1-(3-Hydroxy-4-methylphenyl)-1,3,3,6-tetramethylindan-5-ol	$C_{20}H_{24}O_2$	27
8	18.90	Silane, [[4-[1,2-bis[(trimethylsilyl)oxy]ethyl]-1,2-phenylene]bis(oxy)]bis[trimethyl-	$C_{20}H_{42}O_4Si_4$	47
9	20.62	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	$C_{13}H_{40}O_5Si_6$	25

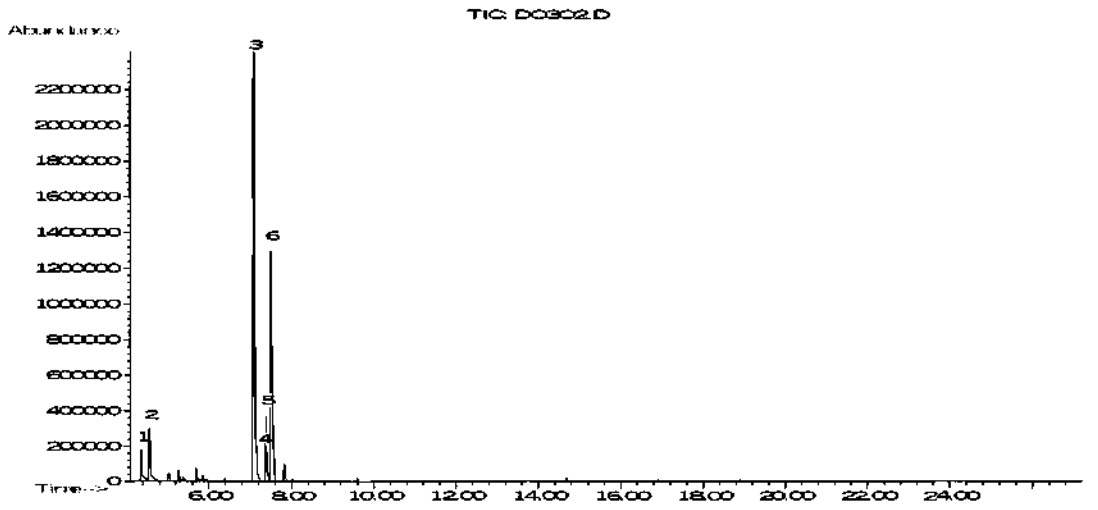

Figure 11. Chromatogram of completely oxidized Company-C sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	91
2	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	72
3	7.07	Butanamide	$C_5H_{10}Cl_2$	45
4	7.15	Methane, Tribromo-	$CHBr_3$	95
5	7.38	*p*-Xylene	C_8H_{10}	97
6	7.49	Pentane, 2,2-dichloro	$C_5H_{10}Cl_2$	25

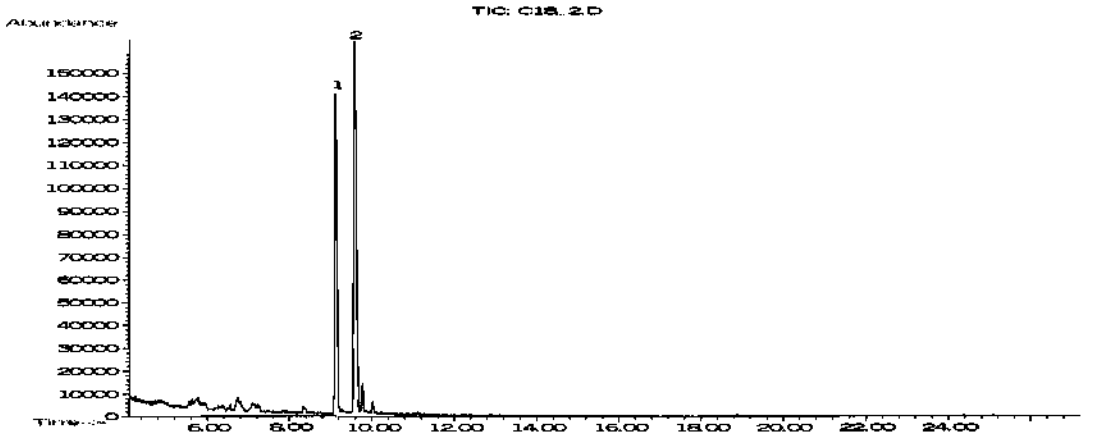

Figure 12. Chromatogram of Company-A 18-2 (A18-2) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	9.11	1,3-Dioxolane, 2-ethyl-4-methyl-	$C_6H_{12}O_2$	50
2	9.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	38

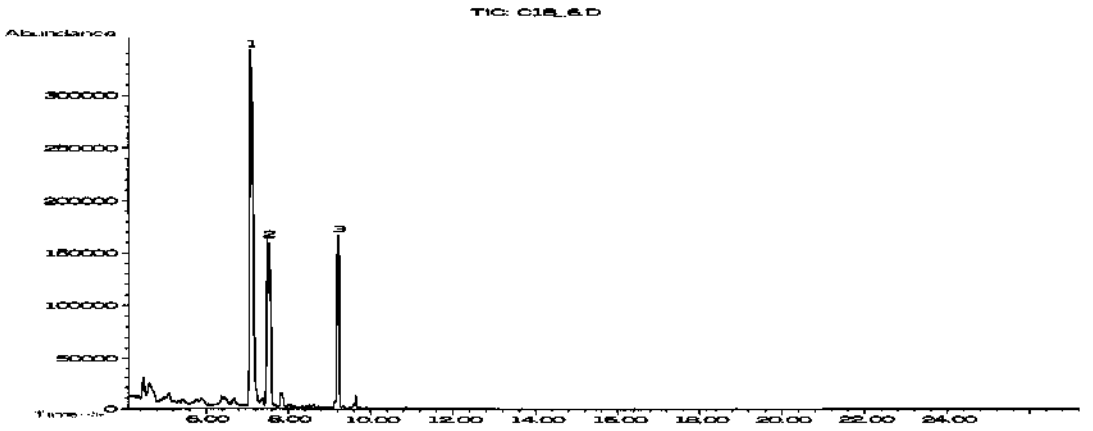

Figure 13. Chromatogram of Company-A 18-6 (A18-6) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	7.04	Butanamide	C_4H_9NO	45
2	7.47	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25
3	9.20	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	64