2C

PNL-4593

UC-11

Treatment of Biomass Gasification Wastewater Using a Combined Wet Air Oxidation/ Activated Sludge Process

C. J. English
S. E. Petty
D. S. Sklarew

February 1983

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

PNL-4593

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

PNL-4593
UC-11

TREATMENT OF BIOMASS GASIFICATION WASTEWATER USING A COMBINED WET AIR OXIDATION/ACTIVATED SLUDGE PROCESS

C. J. English
S. E. Petty
D. S. Sklarew

February 1983

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

PREFACE

This report is one of a series prepared by Pacific Northwest Laboratory for the U.S. Department of Energy on treatment of biomass gasification wastewaters. Other reports have dealt with biological treatment, carbon adsorption, chemical precipitation, reverse osmosis, solvent extraction, and wet air oxidation. All the reports include results of experimental work on a laboratory scale. Wastewater used in these studies came from the experimental Synthesis Gas From Manure (SGFM) biomass gasifier at Texas Tech University.

ACKNOWLEDGMENTS

The authors wish to acknowledge the efforts of the following PNL staff who assisted in performing the experiments described in this report:

- Marie Laegreid, who maintained the biological reactors and performed wet chemical analyses;
- Pete Swift, who operated the autoclave used to oxidize the wastewater; and
- Randy Pahl and Sylvia Downey, who performed GC and GC/MS analyses.

We also wish to acknowledge Dr. Steven Beck, of Texas Tech University, who furnished the wastewater samples used in this study.

Funding was provided by the U.S. Department of Energy through Argonne National Laboratory.

CONTENTS

FIGURES

TABLES

SUMMARY

This report describes a lab-scale treatability study for using thermal and biological oxidation to treat a biomass gasification wastewater (BGW) having a chemical oxygen demand (COD) of 46,000 mg/l. Wet air oxidation (WAO) at 300°C and 13.8 MPa (2000 psi) was used to initially treat the BGW and resulted in a COD reduction of 74%. This was followed by conventional activated sludge treatment using operating conditions typical of municipal sewage treatment plants. This resulted in an additional 95% COD removal. Overall COD reduction for the combined process was 99%.

A detailed chemical analysis of the raw BGW and thermal and biological effluents was performed using gas chromatography/mass spectrometry (GC/MS). These results showed a 97% decrease in total extractable organics with WAO and a 99.6% decrease for combined WAO and activated sludge treatment. Components of the treated waters tended to be fewer in number and more highly oxidized.

An experiment was conducted to determine the amount of COD reduction caused by volatilization during biological treatment. Unfortunately, this did not yield conclusive results.

Treatment of BGW using WAO followed by activated sludge appears to be very effective and investigations at a larger scale are recommended.

CONCLUSIONS

Treatment of BGW by WAO and activated sludge is highly effective for COD removal.

The thermal and biological oxidations greatly reduced the amount of organics in the water, but did not change the relative proportions of acid, neutral, and basic fractions.

The predominant reaction during WAO appeared to be oxidation of components in the acid fraction to form acids.

Both WAO and biological oxidation were more effective with the acidic and neutral fractions than with the basic fraction.

Activated sludge treatment of WAO treated BGW should be possible at higher organic loading rates than those used in this study.

Compared to previous studies with BGW, WAO appears to greatly increase the biological treatability of this wastewater.

RECOMMENDATIONS

Based on the results of this study, the WAO/activated sludge process should be investigated further for treatment of BGW. Specific objectives should be:

- study various reaction temperatures and times for WAO to define optimum conditions;
- conduct activated sludge treatment at higher organic loading rates;
- determine the sludge settling characteristics of the activated sludge;
- determine the kinetic coefficients for biological treatment so that the process can be optimized;
- demonstrate the technology at a larger scale.

In addition, lab scale treatment of BGW using WAO followed by anaerobic biological treatment should be investigated.

INTRODUCTION

Thermochemical conversion of biomass (animal manure, woodchips, straw, etc.) is being developed as a source of synthetic natural gas. In the process of gasification, water and some organic chemicals condense to form a wastewater having an organic strength ~100 times that of than domestic sewage. Several laboratory scale methods for treating these high strength wastewaters have been previously investigated at the U.S. Department of Energy's Pacific Northwest Laboratory (PNL) by Wakamiya, Maxham and Petty (1979); Maxham and Bell (1980); Maxham and Wakamiya (1980); Wakamiya and Maxham (1980); Bell (1981); English (1981); and Petty, Eliason and Laegreid (1981). These methods included aerobic and anaerobic biological treatment, activated carbon adsorption, coagulation/flocculation, reverse osmosis, solvent extraction, and wet air oxidation (WAO). The highest chemical oxygen demand (COD) removals were obtained with aerobic biological and WAO treatment. Results of these studies showed, however, that no one treatment method was suitable for treating this high strength wastewater to a level acceptable for discharge.

This study was undertaken to investigate a two-step treatment process consisting of wet air oxidation followed by aerobic biological treatment. Results of previous studies suggested that this combination should be capable of achieving a high level of treatment with biomass gasification wastewaters (BGW). Wastewater for this study was obtained from the Synthesis Gas From Manure (SGFM) gasifier at Texas Tech University in Lubbock, Texas. Characteristics of this wastewater are given in Table 1.

TABLE 1. Characteristics of Biomass Gasification Wastewater

Chemical Oxygen Demand (COD)	46,000 mg/l
Total Suspended Solids	1,100 mg/l
Volatile Suspended Solids	940 mg/l
pH	3.7

Specific objectives of this study were:

- to determine the feasibility of the WAO/activated sludge process for treating BGW at a small scale using typical operating conditions;
- to determine the chemical composition of raw BGW and WAO and activated sludge effluents; and
- to gain understanding of the processes and transformations that occur during the different treatment steps.

BACKGROUND

Several investigations of aerobic biological treatment of BGW have been made at PNL. Results of studies using the activated sludge process are summarized in Table 2. The high rate fixed film (HRFF) process is similar to conventional activated sludge except that inert, high density solids are placed in the aeration zone for microorganisms to attach to. This allows a much higher concentration of biomass in the aeration zone, and consequently, higher organic loading rates.

Wet air oxidation was also investigated at PNL as a means of treating full strength BGW (English 1981). The results of this study were encouraging with a maximum of 80% COD reduction occurring with treatment at 300°C and 13.8 MPa (2000 psi). This removal was obtained after 20 min of treatment and additional treatment, up to a maximum of 180 min, did not result in significantly greater removal.

TABLE 2. Results of BGW Treatment Studies at PNL Using Activated Sludge

Investigators	Treatment Type	Feed	Organic Loading Rate mg COD/1-day ($lb COD/1000 ft^3$-day)	COD Removal, %
Wakamiya, Maxham and Petty (1979)	Conventional AS	1% BGW in water	960 (60)	75
Wakamiya and Maxham (1980)	HRFF	10% BGW in water	880 (55)	65
		10% BGW in water	980 (61)	82
		10% BGW in water	1700 (110)	80
		10% BGW in water	3400 (220)	75
Maxham and Wakamiya (1980)	HRFF	100% BGW	2400 (150)	77
Maxham and Bell (1980)	HRFF	100% BGW	3500 (220)	70

Only limited data were available on the chemical composition of BGW. Kao (1980) reported that most COD was due to low molecular weight organics such as formic, acetic, and propionic acids, methanol, ethanol and acetone. The remainder was thought to consist mainly of larger volatile aromatic and aliphatic compounds.

The above chemical composition would help explain the limitations noted in both biological and WAO treatment. The low molecular weight acids and alcohols are readily degraded biologically, so that they would be removed easily at the high organic loading rates used with the HRFF process. The larger organics are more resistant to biologial degradation and would not be removed as readily at the high loading rates necessary for economical treatment of high strength wastes. Further COD reduction would probably require lower loading rates and longer retention times, resulting in much higher treatment costs.

Chemical composition has quite a different effect on WAO. Large organic compounds are readily broken down by WAO while low molecular weight compounds, particularly acids, are very resistant to further oxidation. This explains the rapid initial COD reduction seen with WAO and also explains why a maximum removal is reached. Based on results with BGW, additional COD removal beyond 80% would probably have required excessively high temperatures and pressures, leading to uneconomical treatment.

Based on the above considerations, a two-step treatment process consisting of WAO followed by activated sludge seemed very promising. The WAO should result in a rapid initial reduction of COD and destruction of large, poorly biodegradable organics. The WAO effluent should consist of primarily low molecular weight organics, which are readily removed by biological treatment.

The above treatment process also has advantages with respect to energy consumption. Most of the energy required for WAO is for heating the wastewater to treatment temperature. Since heat is generated during the oxidation of organic matter, energy use becomes less as waste strength increases. This would favor the use of WAO as the first treatment step. The opposite is true with activated sludge treatment. Most of the energy use is for aerating wastewater. For a given COD removal efficiency, energy use increases as waste strength increases. Activated sludge treatment would, therefore, be most efficient as the second treatment step.

Because of the apparent advantages to the wet air oxidation/activated sludge (WAO/AS) treatment process, it was decided to conduct a bench scale treatability study. The objective of this was to determine the effectiveness of the process under typical large scale operating conditions. In addition, since the effectiveness of the treatment method depends strongly on the composition of the wastewater, detailed chemical characterizations of the raw BGW and WAO and biologically treated effluents was planned. This would hopefully allow better understanding of the chemical transformations occuring during treatment. This would be helpful in designing future optimization studies if the method looked promising.

EXPERIMENTAL PROCEDURE

Experimental procedures are discussed in four major groups, corresponding to the major parts of the study. These are wet air oxidation of raw BGW, activated sludge treatment of wet oxidized BGW, determination of volatile COD losses during biological treatment, and chemical analysis of raw and treated BGW.

WET AIR OXIDATION OF BGW

Wet air oxidation was performed in a 3.78 (1 gal) Hastelloy C autoclave, as described previously by English (1981). A sketch of this equipment is given in Figure 1. Raw BGW was filtered through a Number 1 Whatman filter to remove char and refrigerated at 4°C until treatment. The treatment procedure consisted of loading the autoclave with sample, charging with air to the operating pressure, heating the autoclave and contents to operating temperature, stirring the autoclave contents vigorously for the desired reaction time, quenching the reaction, cooling and depressurizing the autoclave, and unloading the treated sample. Operating conditions are summarized in Table 3. These conditions were selected based on the results of English (1981) and on consideration of possible conditions that might be applied in larger scale treatment.

BIOLOGICAL TREATMENT

Biological treatment was done using the Davis-Swisher apparatus described previously by Maxham and Wakamiya (1980). A sketch of this apparatus is shown in Figure 2. These reactors have a volume of 290 ml in the aeration zone and 50 ml in the settling zone. Daily activities associated with reactor maintenance included measuring effluent volumes, preserving effluent samples for COD analysis, obtaining feed samples for COD analysis, measuring reactor pH, wasting activated sludge (when needed), preserving waste sludge samples for solids determination, and cleaning inside reactor walls by washing with clarified effluent. Sludge was wasted by pipetting from the aerated zone of the reactor and replacing the waste volume with distilled water. Reactor feed was prepared by filtering wet oxidized BGW through 0.45 μ filters, adding

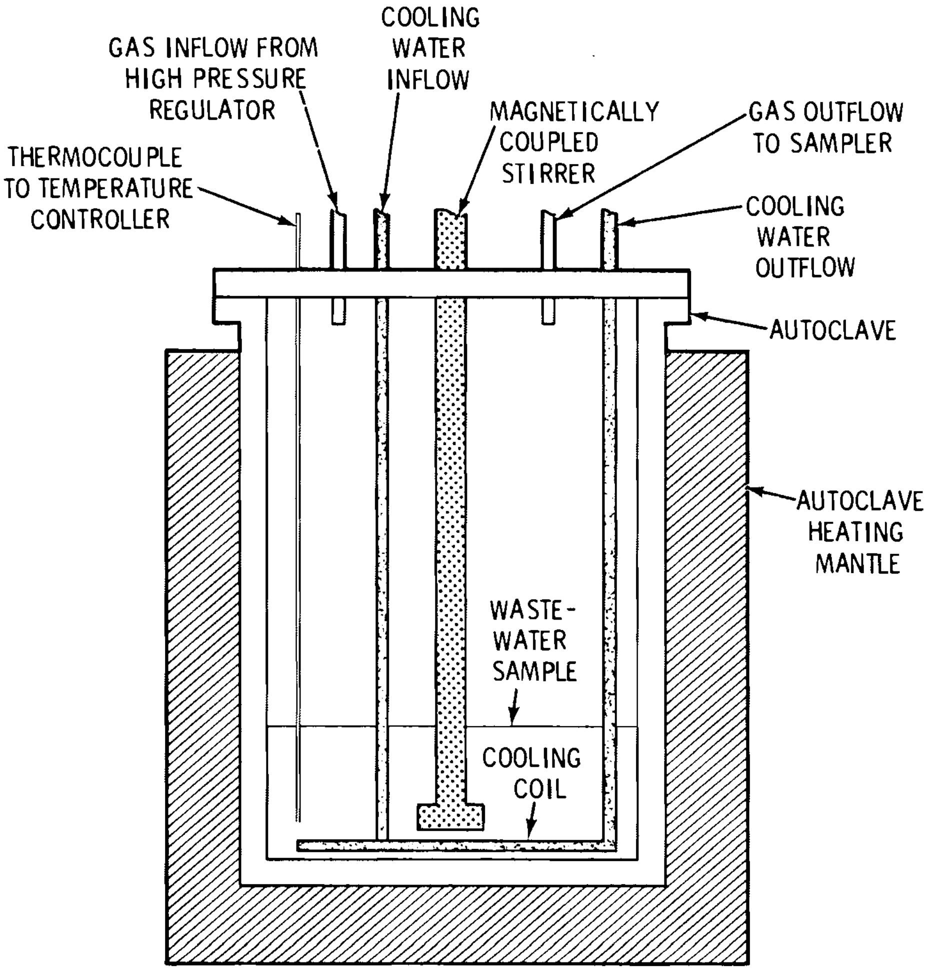


FIGURE 1. Laboratory Scale Wet Air Oxidation Apparatus

TABLE 3. Summary of Wet Air Oxidation Treatment Conditions

Temperature	300°C (572°F)
Pressure	13.8 MPa (2000 psi)
Reaction Time	20 min
Stirrer Speed	1000 rpm
Sample Volume	1130 ml

2 g/l ammonium phosphate for nutrients and adjusting the pH to 5.0 with 10 N NaOH. Reactors were fed using Masterflex pumps with 7013 pumpheads. An electronic timer controlled the pumps and provided feed every three hours. Air going to the reactors was first saturated by bubbling through a humidifier to prevent evaporative loss of reactor contents.

A summary of reactor feed and operating conditions is provided in Table 4. Reactors were initially started using 300 ml of activated sludge from the Union Oil Refinery near Rodeo, California. Reactors were then acclimated to an artificial feed consisting of 5 g/l acetate (from sodium acetate) and 2 g/l of dried milk solids. Acetate was selected as a major constituent of the artificial feed since acetic acid was expected to be the major component of the wet oxidized BGW. The reactors were operated on the artificial feed for two months. This was longer than initially intended because of delays in obtaining samples of raw BGW.

Once wet oxidized BGW was obtained, reactors were gradually adapted to this feed. Initially, they were fed a mixture of 25% wet oxidized effluent and 75% artificial feed. This was gradually increased over three weeks to 100% wet oxidized BGW.

After six weeks of operation with full strength wet oxidized feed the autoclave developed difficulties. The supply of wet oxidized feed was interrupted and the reactors were fed effluent from earlier biological treatment of artificial feed for one week. Because of a faulty autoclave seal and heating mantle, the next treatment was limited to 209°C. This water was stronger than the 300°C water and appeared much darker in color so it was diluted 25% with WAO/AS effluent. The reactors were fed this mixture for two and one-half weeks.

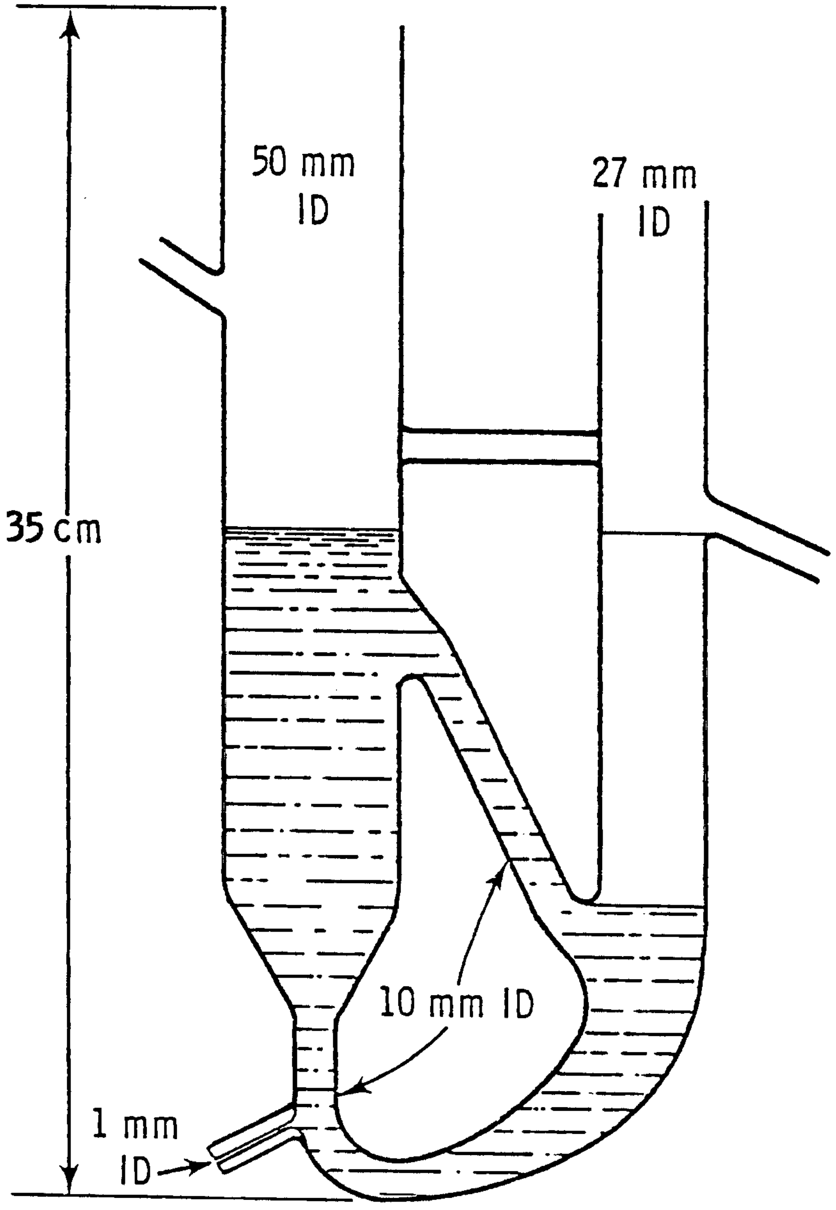


FIGURE 2. Davis-Swisher Biological Treatment Reactors

TABLE 4. Summary of Biological Reactor Operating Conditions

Time, wks	Reactor Feed		Average Organic Loading Rate, mg COD/l-day (lb COD/1000 ft^3-day)	Reactor Volatile Suspended Solids, mg/l	Average Solids Retention Time, days	Average Hydraulic Retention Time, days
1-9	Artificial Feed 5 g/l Acetate 2 g/l Milk Solids COD = 5400 mg/ℓ	Reactor 1	1900 (130)	6900	120	4.3
		Reactor 2	1700 (110)	7800	83	4.0
10-12	75-25% Artificial 25-75% WAO (300°C) COD = 7600 mg/ℓ	Reactor 1	2300 (140)	5900	240	3.4
		Reactor 2	2100 (130)	4800	210	3.7
12-18	100% WAO (300°C) COD = 13,400 mg/ℓ	Reactor 1	1900 (130)	6100	48	7.9
		Reactor 2	1900 (130)	5600	120	8.0
19	Biological Effluent COD = 15,759 mgℓ	Reactor 1	1000 (65)	4900	510	26
		Reactor 2	1200 (72)	4800	510	24
20-22	25% Biological Eff. 75% WAO (209°C) COD = 14,500 mg/ℓ	Reactor 1	840 (52)	4300	70	19
		Reactor 2	720 (45)	4500	70	19
22-25	100% WAO (260°C) COD = 14,000 mg/ℓ	Reactor 1	970 (60)	3100	27	11
		Reactor 2	1100 (66)	3800	28	9.6
25-30	100% WAO (300°C) COD = 12,300 mg/ℓ	Reactor 1	860 (54)	2600	19	10
		Reactor 2	1500 (94)	3700	20	6.7

The next treatment reached a temperature of 260°C. Since this water was approximately the same strength as the 300°C water, it was fed full strength. After three and one-half weeks with this feed, the autoclave was completely repaired and feeding with full strength 300°C water resumed. This continued for the remaining six weeks of reactor operation.

DETERMINATION OF VOLATILE COD LOSSES

Since the wet air oxidized BGW was expected to contain a high concentration of volatile acids, it was felt that volatilization during aeration might be a mechanism for COD reduction during biological treatment. A blank Davis-Swisher reactor was set up in an attempt to determine the extent of such volatile losses. Initially, this unit was filled with WAO/AS effluent which had been filtered through a 0.45 µ filter. The blank received the same feed and aeration rate as the biological reactors. After one week of operation, significant biological growth was noted and the unit was stopped. Contents were again filtered and mercuric chloride added at a rate of 0.2 mg/l to suppress biological growth. Feed was added to replace the contents lost during filtration. The blank unit was then restarted and run for two weeks.

CHEMICAL ANALYSES

Chemical oxygen demand and volatile suspended solids were determined using the procedures given in Standard Methods (APHA 1980).

The composition of the raw BGW and treated effluents was determined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Prior to analysis the raw wastewater and wet oxidation treated waters were filtered through a 4 to 8 µ glass fritted filter. The biological effluent water had previously been filtered through a 50 µ Whatman filter. Organics were extracted from the wastewaters using an acid-base procedure. Each type of wastewater was extracted in duplicate or triplicate. In each case 100 ml of water was acidified to pH 1 with 6 M H_2SO_4 and extracted three times with methylene chloride (DCM). The water was adjusted to pH 12 with 6 M NaOH and extracted three times with DCM to give the basic fraction. The first DCM fraction was extracted three times with 5% NaOH to yield the neutral fraction in DCM and acids in the aqueous portion. The acids were extracted into DCM after adjusting the aqueous phase to pH 1 with 6 M H_2SO_4.

All fractions were analyzed by fused silica capillary gas chromatography on two different columns: a moderately polar SE-52 and a polar Carbowax column. Duplicate (or in some cases, triplicate) samples showed similar chromatograms and were combined for GC/MS analysis. The wet oxidation samples were very similar and were also combined for GC/MS analysis. Chromatograms of procedural blanks showed only a very few weak peaks and did not appear to contribute to the peaks of interest. For GC/MS analysis, either an SE-54 (similar to SE-52) or Carbowax column was used, depending on the GC results. The basic fractions chromatographed better on SE-54, whereas the acid and neutral fractions gave better results on the Carbowax column. The temperature program for SE-54 started at 20°C, then programmed at 5°/min to 320°C and held isothermal for 10 min. For the Carbowax column the initial temperature was 20°C and the column was programmed at 10°/min to 220°C, where it was held isothermal for 10 min. The mass spectrometer was used in EI mode at 70 eV. Both computerized and manual literature searches were accomplished with the EPA-NIH data base.

RESULTS

WET AIR OXIDATION

Wet air oxidation of the raw BGW at 300°C for 20 min resulted in an average COD reduction of 74%. Results from run to run were very consistent, ranging only from 73 to 75%. One run made at 260°C for 20 min resulted in 68% COD removal. One run made at 209°C for 20 min resulted in ~60% COD removal.

BIOLOGICAL TREATMENT

Biological treatment of the wet oxidized BGW resulted in an average COD reduction of 95% over the period the reactors were fed full strength wet oxidized BGW. Combined with the COD removal during wet oxidation, the overall COD removal efficiency was 99%. Effluent CODs for the biological treatment units are shown in Figure 3. Week 12 corresponds to the start of full strength wet oxidized feed. The COD removal efficiency, solids retention time (SRT), hydraulic retention time (HRT), and mixed liquor volatile suspended solids (MLVSS) for the two reactors over the same period of time are shown in Figures 4 through 6, respectively. It should be noted that Figure 5 shows the average weekly SRT calculated as the quotient of the average MLVSS concentration and the average wasting rate. The large SRTs observed in some weeks reflect low wasting rates and have little meaning over short periods.

VOLATILE COD LOSSES

Results of the experiment to determine the volatile COD losses resulting from aeration are shown in Figure 7. These results include the actual effluent COD from the reactor, the expected COD if no volatile losses were occurring, and reactor pH. These results are shown for the three week period of the experiment.

CHEMICAL ANALYSES

The amounts of the acid, base, and neutral fractions for each water, expressed as a percentage of the extracted organics, are shown in Table 5.

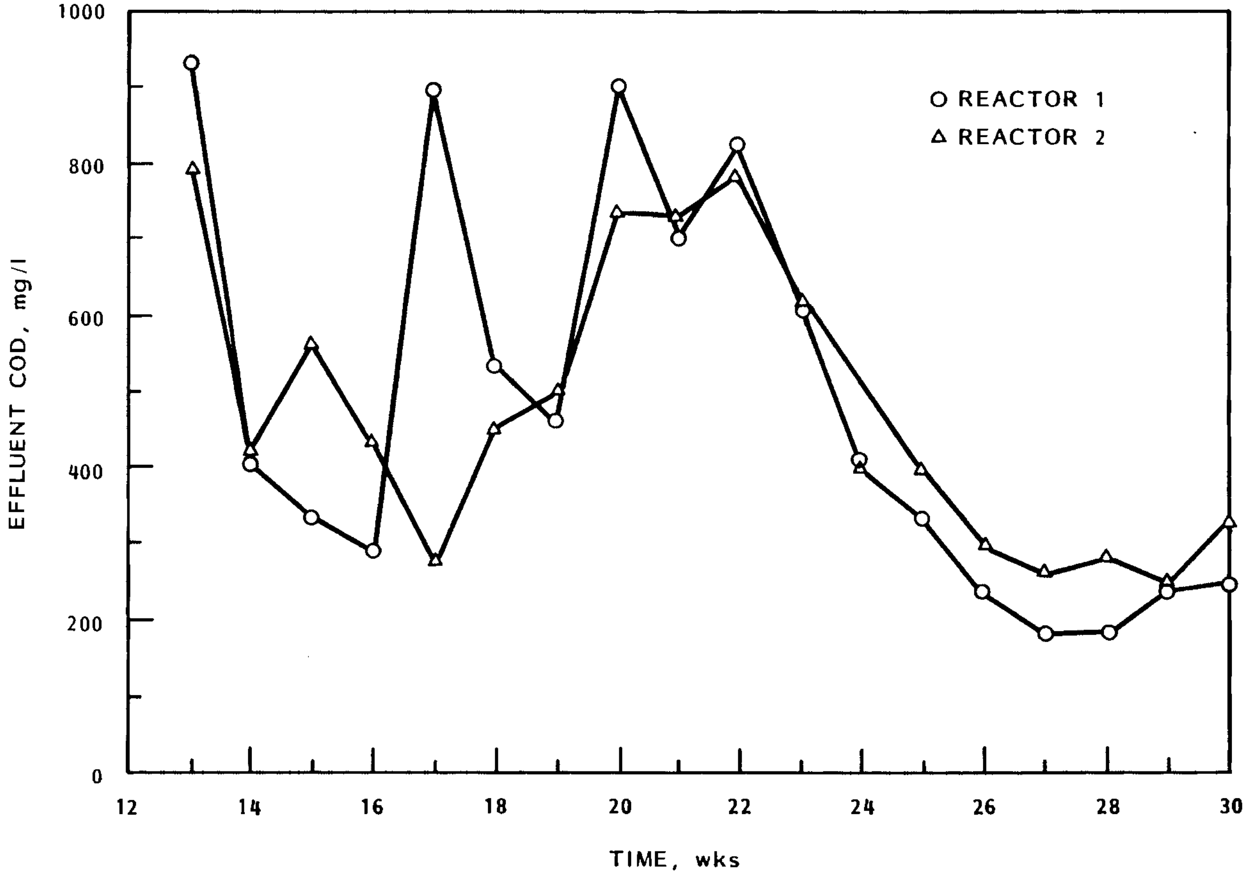


FIGURE 3. Effluent Chemical Oxygen Demand Versus Time for Biological Reactors

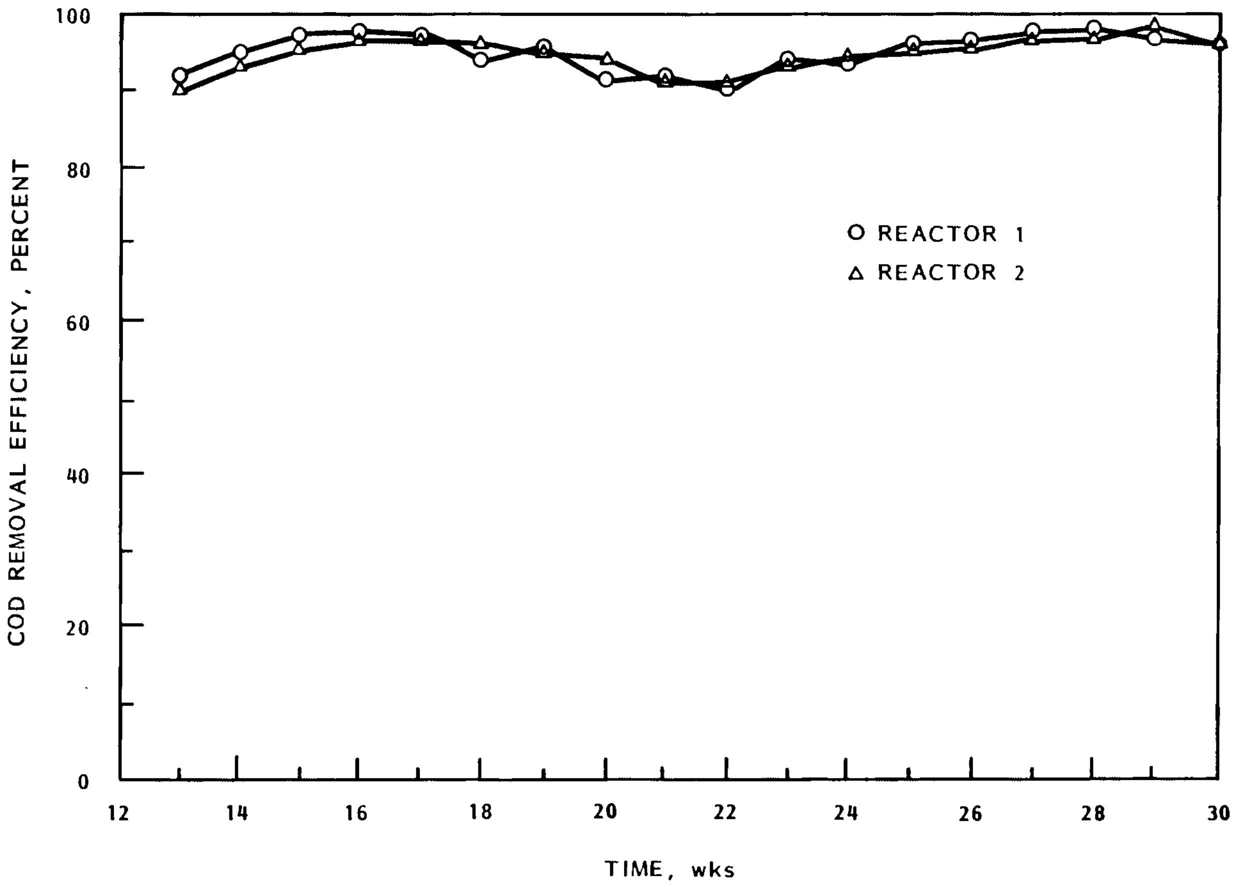


FIGURE 4. Chemical Oxygen Demand Removal Efficiency Versus Time for Biological Reactors

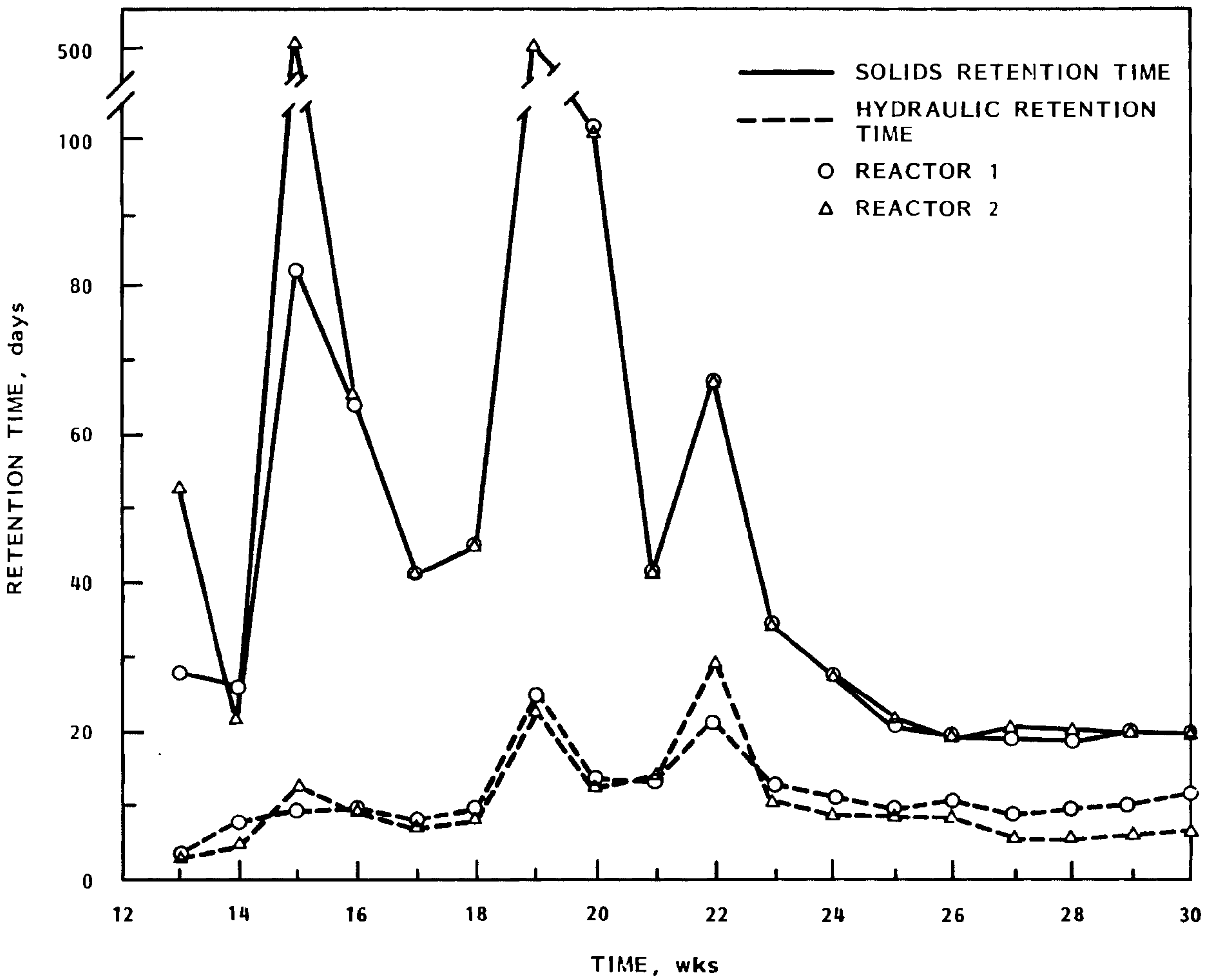


FIGURE 5. Solids and Hydraulic Retention Times Versus Time for Biological Reactors

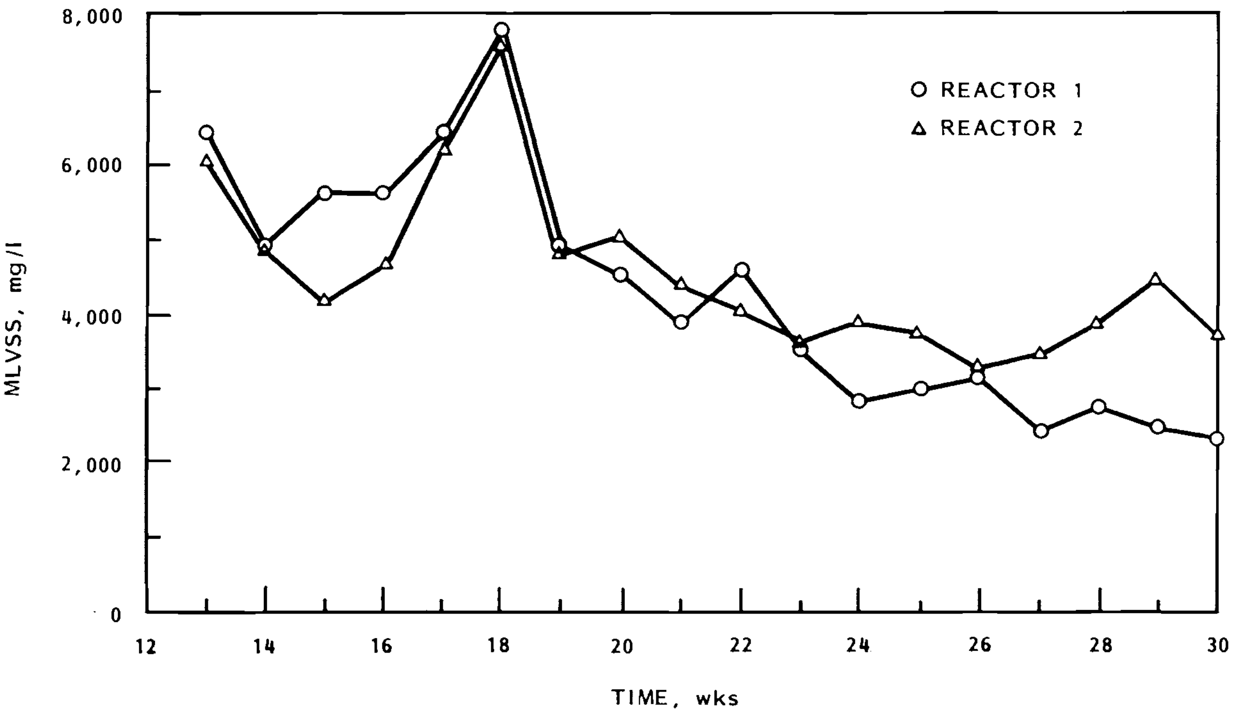


FIGURE 6. Mixed Liquor Volatile Suspended Solids Versus Time for Biological Reactors

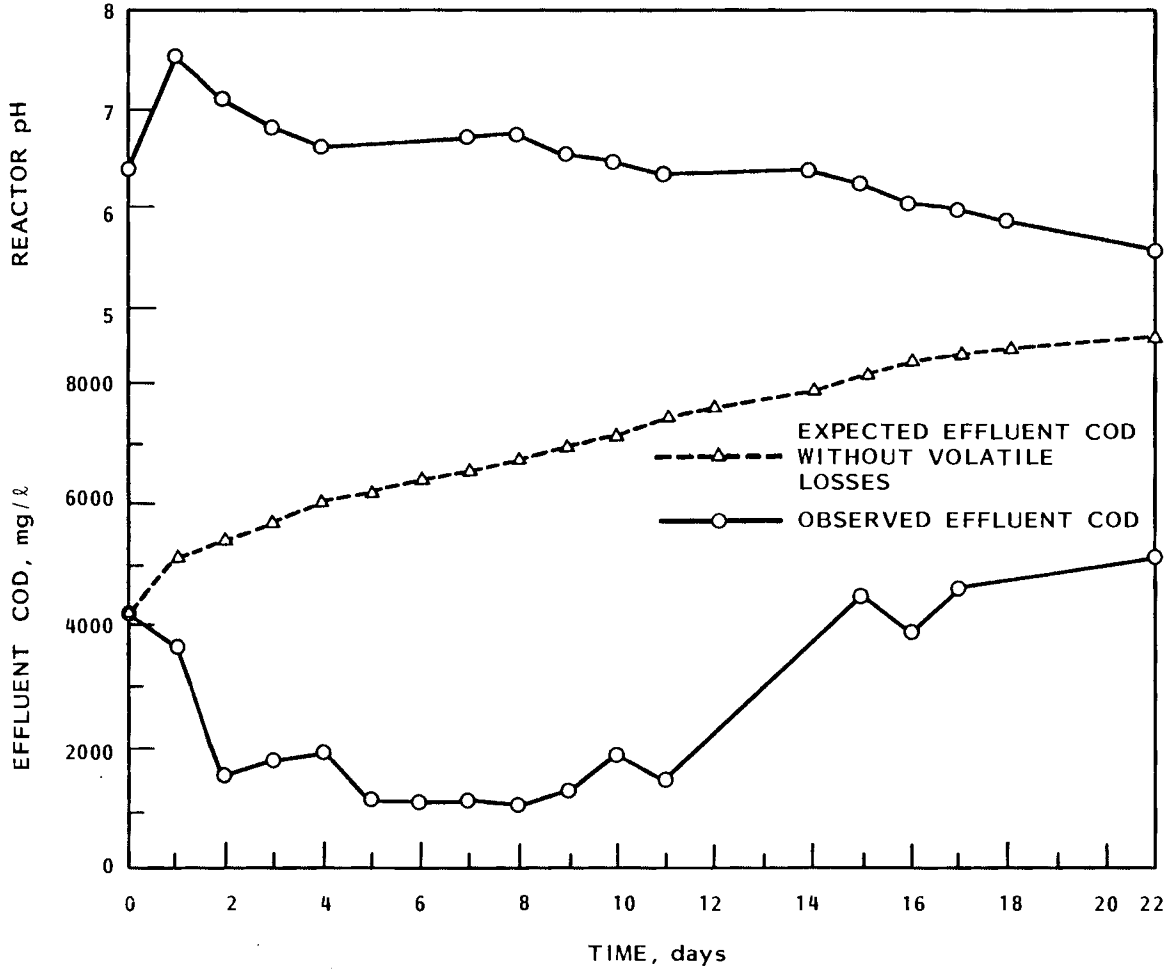


FIGURE 7. Effluent Chemical Oxygen Demand and pH Versus Time for Blank Reactor

TABLE 5. Mass Balance for the Wastewater Fractionation Procedure

	Total Weight Extracted (g)(a)	Acid Fraction (%)	Neutral Fraction (%)	Basic Fraction (%)
Raw	0.25	74	24	2
Wet Oxidation	0.007	70	26	4-6(b)
Biological Effluent	0.001	62	29	9(b)

(a) Sum of the weights of the three fractions extracted from 100 ml.

(b) These numbers were higher (~20%) and the acid fractions correspondingly lower in one set of experiments. The discrepancy may have been due to emulsion problems.

Compounds identified in the various fractions of the waters are shown in Tables 6 through 14, along with the correspondingly labeled total ion chromatograms (Figures 8 through 16). GC retention data were available for a number of the compounds, notably most of the phenols and methoxy phenols in the acid fractions. All other identifications are based on mass spectral fragmentation patterns and must be considered tentative. The agreement between the sample and data base spectra is indicated in the tables. Distinction among isomers was not possible.

TABLE 6. Components Identified in Acid Fraction of Raw BGW(a)

1. dihydrofuranone
2. methylbutenal
3. C_8 - cyclic ketone(b)
4. methyl butenoic acid
5. hydroxy methyl cyclopentenone
6. guaiacol
7. C_8-cyclic ketone
8. dimethylphenol
9. C_9-singly unsaturated cyclic ketone.
10. phenol
11. methylphenols
12. ethylmethoxyphenol
13. ethylphenols
14. C_2-phenol
15. Unknown, M^+=166
16. trimethylphenol
17. ethylmethylphenol
18. C_3-phenol
19. dimethylphenol
20. dimethoxyphenol
21. propenylphenol
22. dimethoxymethylphenol
23. ethylenyloxybenzene
24. dimethoxyethylphenol
25. ethylbenzaldehydes
26. C_3-singly unsaturated phenol
27. dimethoxypropenylphenol
28. hydroxymethoxybenzaldehyde (vanillin)
29. methylbenzofuran(c)
30. hydroxymethoxyphenylethanone (acetovanillin)
31. hydroxyphenylethanone
32. methoxybenzaldehyde
33. hydroxydimethoxybenzaldehyde

(a) Numbers correspond to those in Figure 8.
(b) Very uncertain.
(c) Uncertain, but reasonably good mass spectral fit.

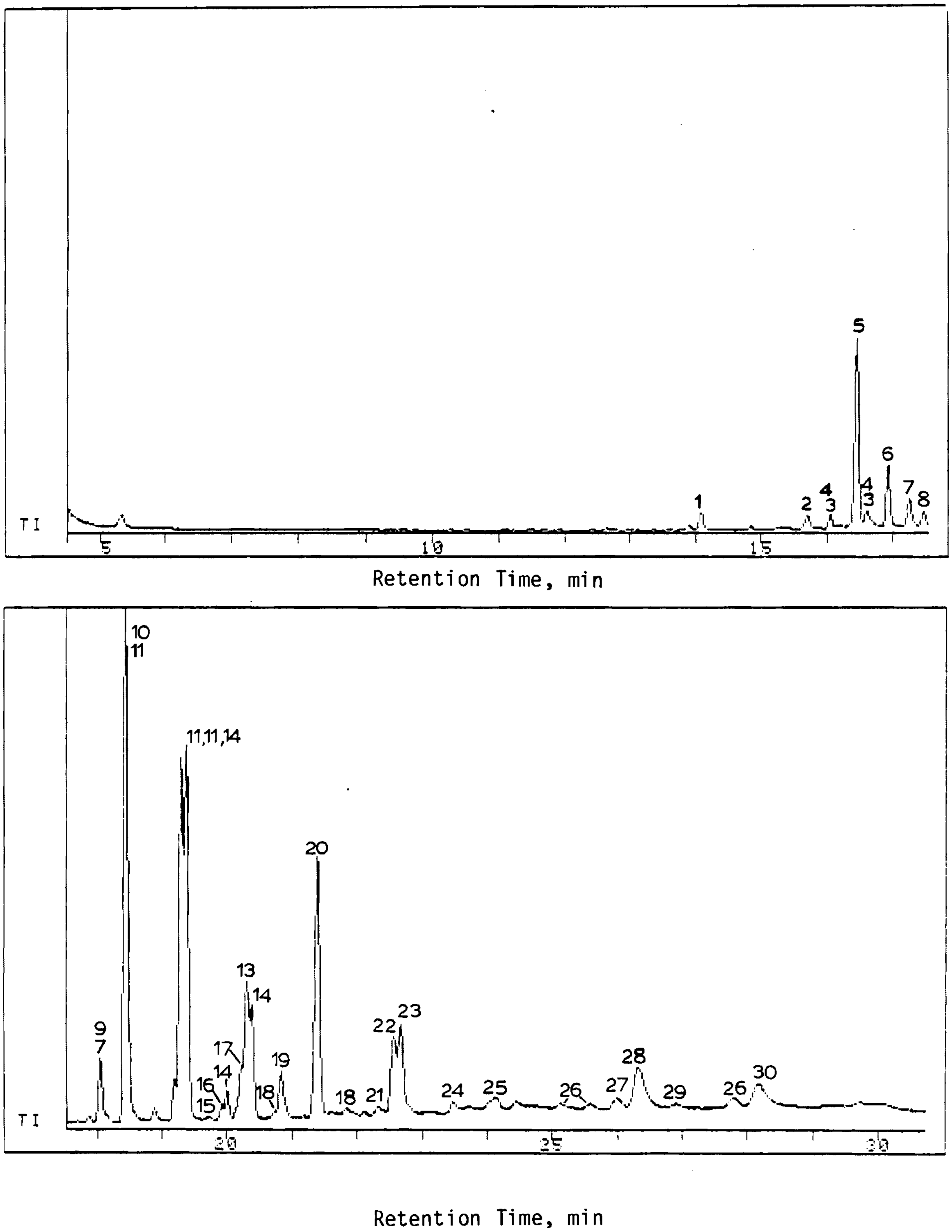
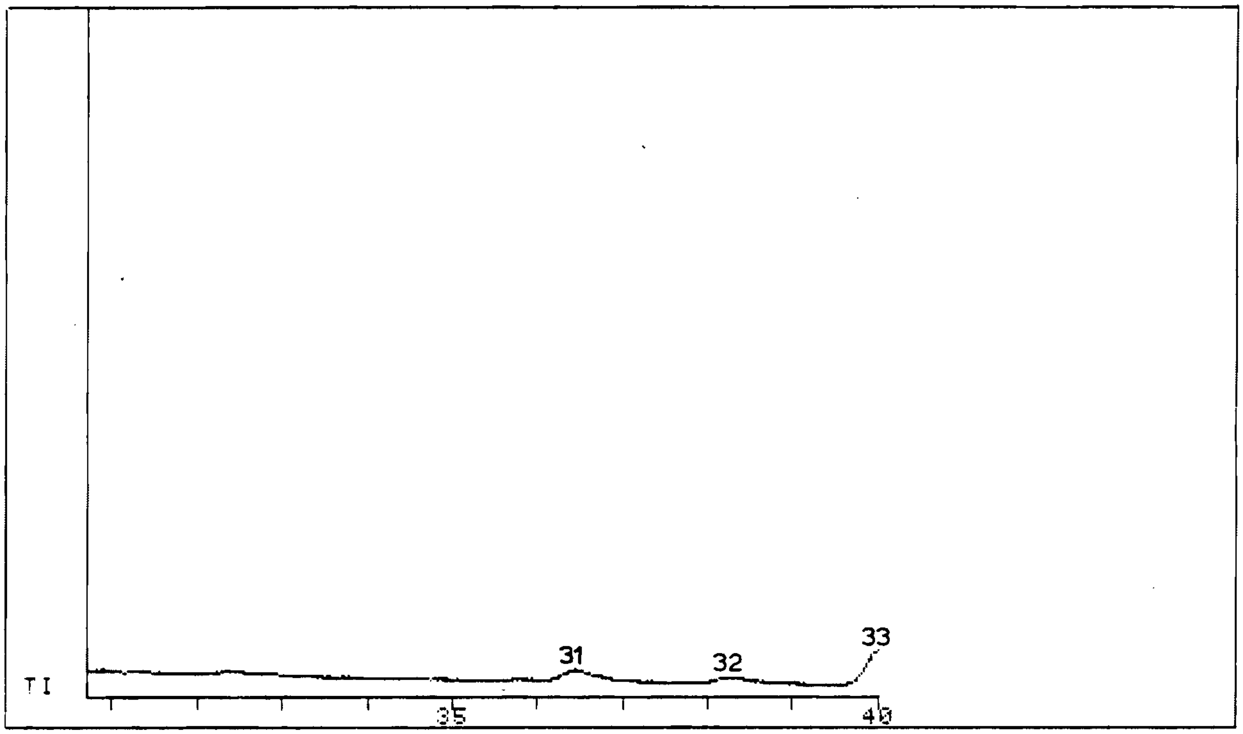


FIGURE 8. Total Ion Chromatogram for Acid Fraction of Raw BGW



Retention Time, min

FIGURE 8. (contd)

TABLE 7. Components Identified in Acid Fraction of WAO Treated BGW[a]

1. dihydrofuranone
2. methylpyrrolidinone[b]
3. pyridinylethanone
4. unknown, $M^+ = 99$
5. unknown, $M^+ = 99$
6. pyrrolidinone
7. methylpyrrolidinone
8. methyl-oxide-pyridine[b]
9. unknown, $M^+ = 163$
10. unknown, $M^+ = 148$
11. isobenzofuranone
12. unknown, $M^+ = 164$
13. benzoic acid
14. methylbenzoic acid
15. benzenepropanoic acid
16. benzamide
17. hydroxybenzaldehyde
18. unknown, $M^+ = 182$
19. hydroxyphenylethanone

(a) Numbers correspond to those in Figure 9.
(b) Uncertain, but reasonably good mass spectral fit.

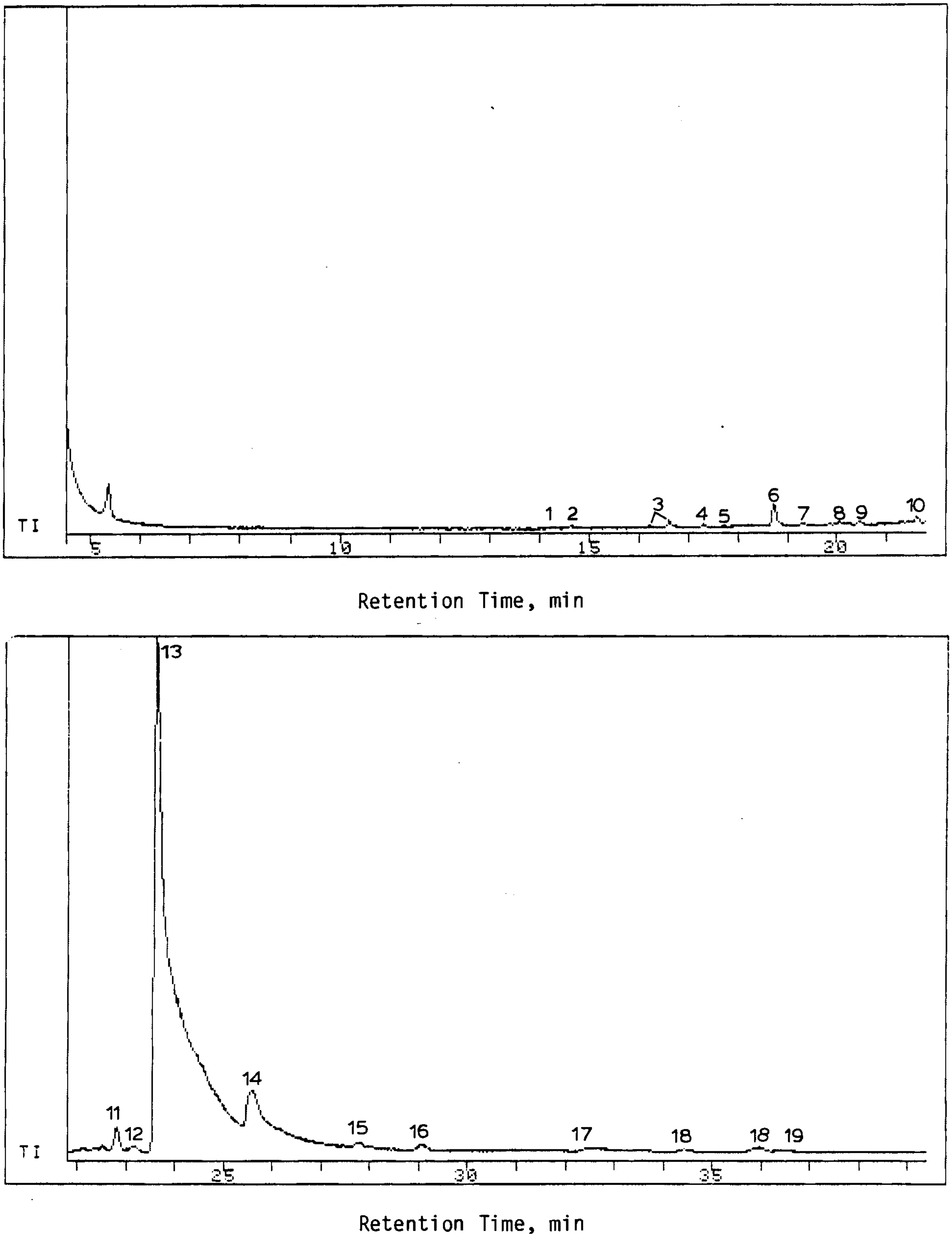
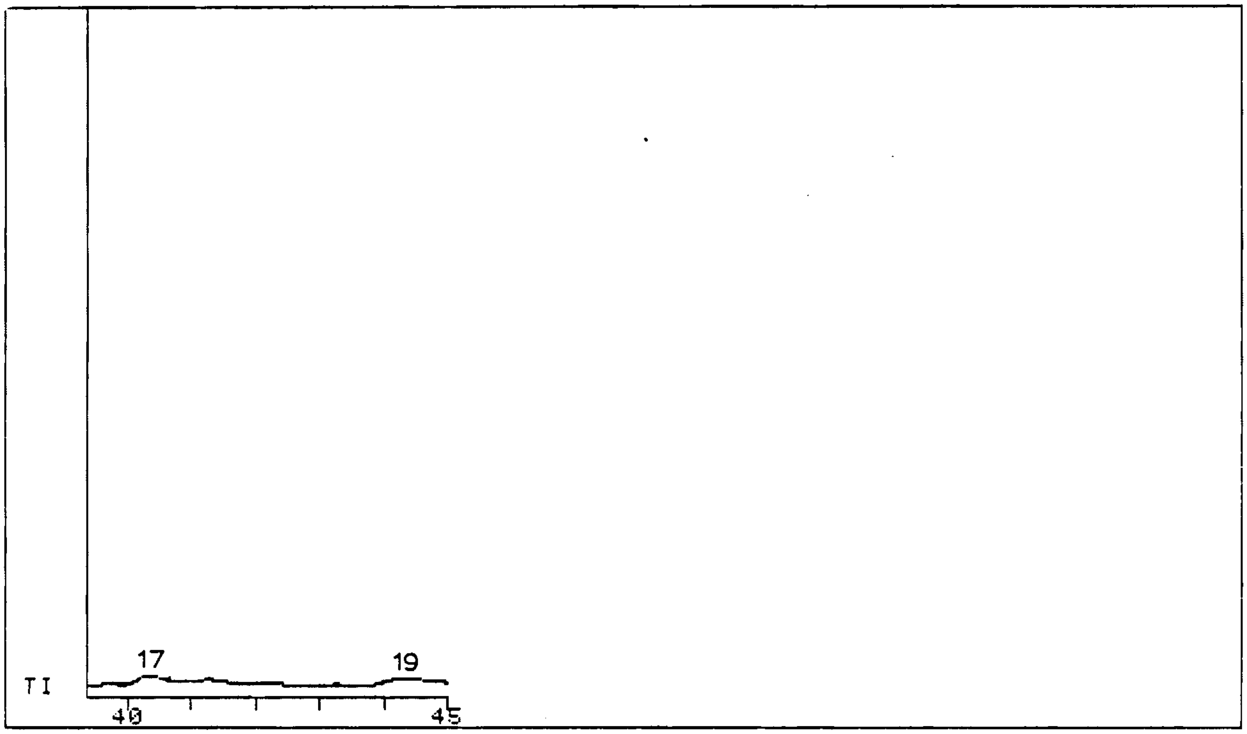


FIGURE 9. Total Ion Chromatogram for Acid Fraction of WAO Treated BGW



Retention Time, min

FIGURE 9. (contd)

TABLE 8. Components Identified in Acid Fraction of Biological Effluent[(a)]

1. acetonitrile
2. toluene
3. cyclohexanediol[(b)]
4. alkene or alcohol[(c)]
5. octanoic acid
6. methylpyridinone
7. unknown, $M^+ = 163$
8. tributyl phosphate (impurity)
9. nonanoic acid
10. unknown, $M^+ = 178$
11. unknown
12. decanoic acid
13. C_5-phenol
14. undecanoic acid
15. unknown
16. dodecanoic acid
17. methylbenzoic acid
18. unknown, $M^+ = 154$
19. phthalate (impurity)
20. unknown, $M^+ = 185$
21. aliphatic carboxylic acid
22. aliphatic carboxylic acid
23. aliphatic carboxylic acid
24. dimethylbenzebutanoic acid[(c)]
25. aliphatic carboxylic acid
26. unknown
27. unknown

(a) Number correspond to those in Figure 10.
(b) Very uncertain.
(c) Uncertain, but reasonably good mass spectral fit.

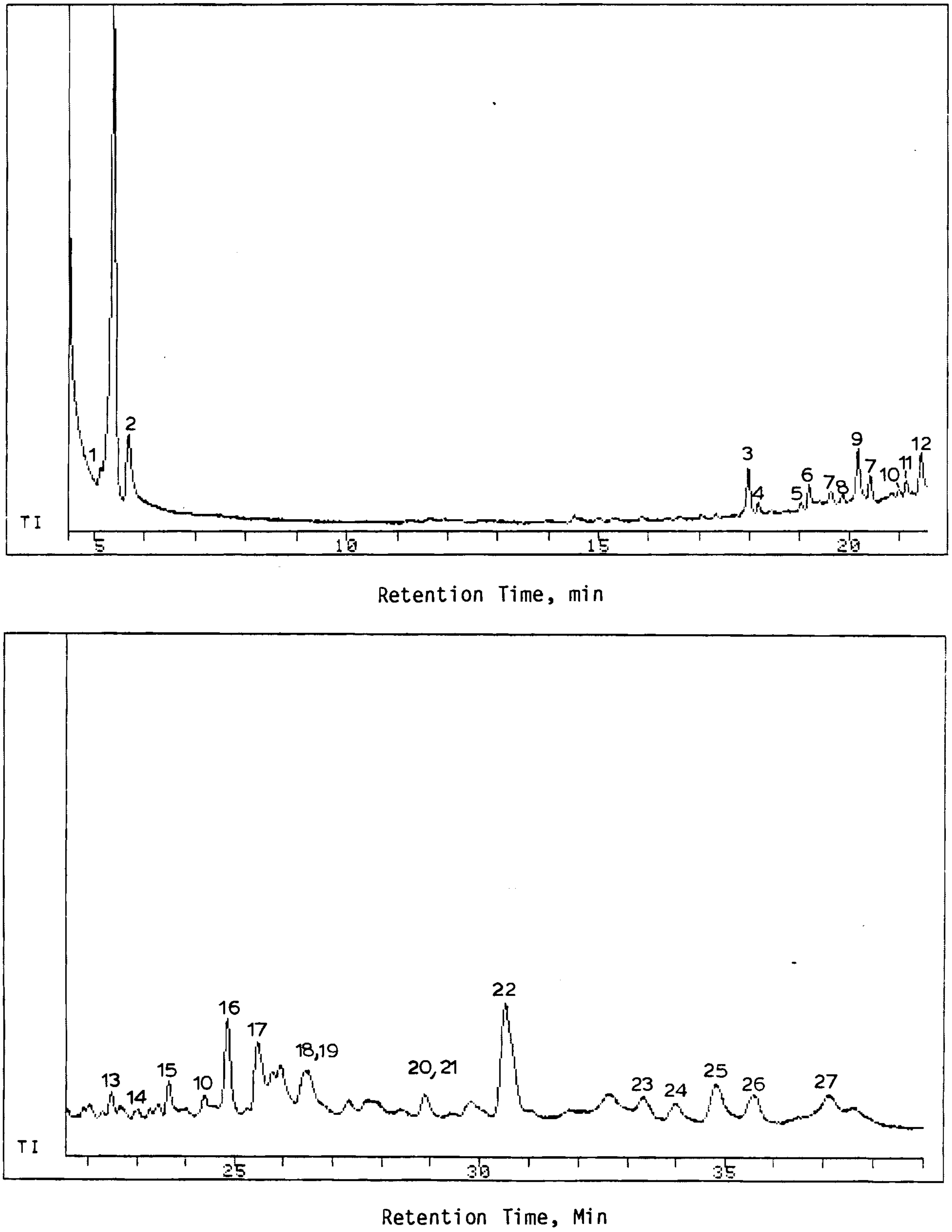
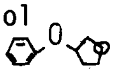


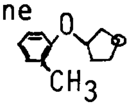
FIGURE 10. Total Ion Chromatogram for Acid Fraction of Biological Effluent

TABLE 9. Components Identified in Neutral Fraction of Raw BGW(a)

1. 2-furancarboxaldehyde
2. C_7 cyclic ketones (dimethylcyclopentenone)
3. C_6 cyclic ketones (methylcyclopentenone)
4. benzaldehyde
5. methylfurancarboxaldehyde(b)
6. acetophenone
7. methylfuranone
8. naphthalene
9. pyranone
10. unknown
11. benzene methanol
12. benzene ethanol
13. M^+ = 164(b)



14. C_3-phenols
15. unknown
16. unknown
17. dihydroindenone
18. M^+ = 178(b)



19. C_4-phenol
20. unknown
21. methoxy propenyl phenol(b)
22. unknown
23. dimethoxymethylphenol
24. isobenzofuranone
25. unknown
26. dimethoxyethylphenol
27. benzopyranone
28. unknown, M^+ = 178
29. dimethoxypropenylphenol
30. unknown, M^+ = 174
31. unknown, M^+ = 188

(a) Numbers correspond to those in Figure 11.
(b) Uncertain, but reasonably good mass spectral fit.

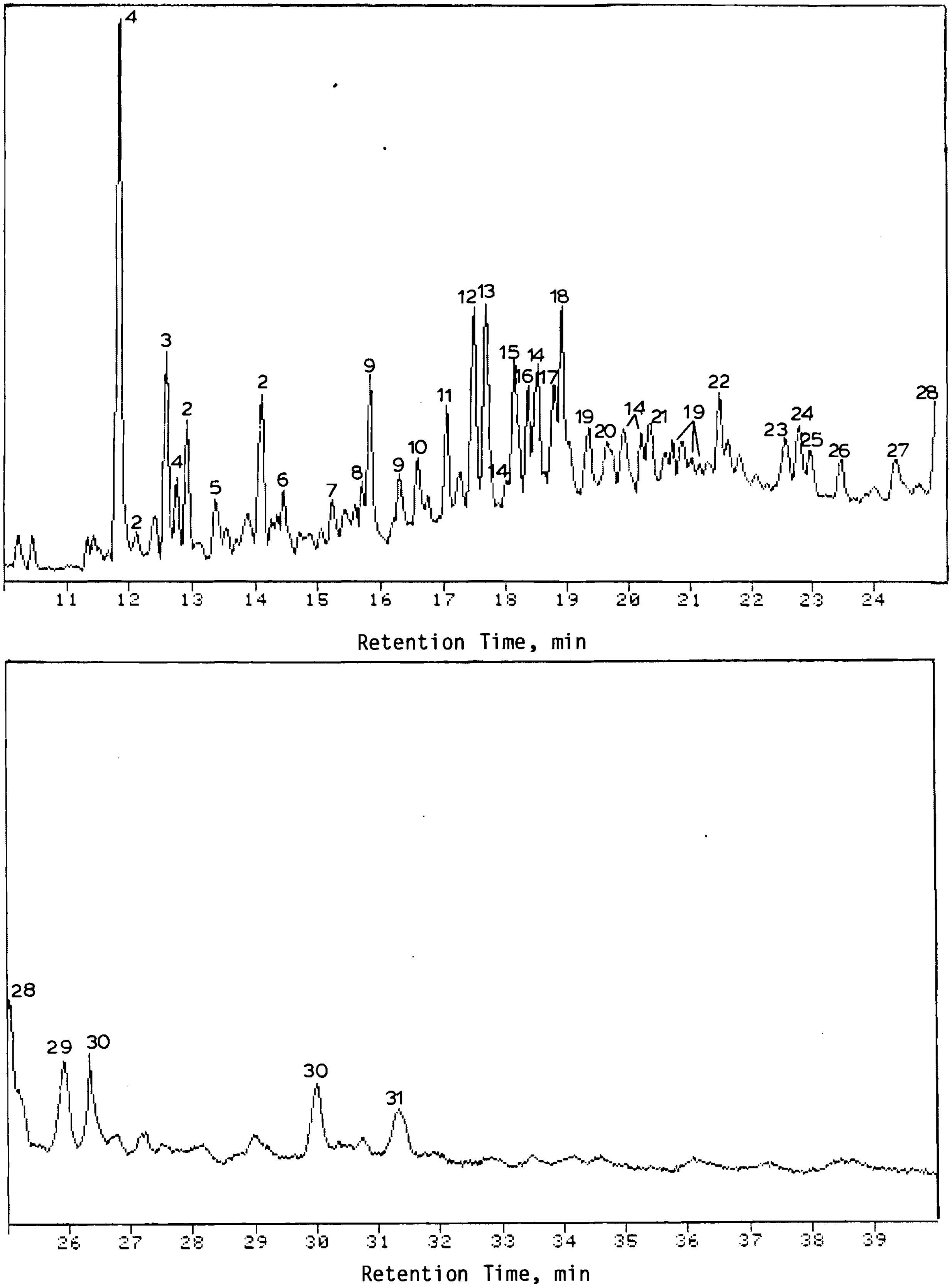


FIGURE 11. Total Ion Chromatogram for Neutral Fraction of Raw BGW

TABLE 10. Components Identified in Neutral Fraction of WAO Treated BGW(a)

1. hydroxy methylpentanone
2. C_6-cyclic ketone (cyclohexenone)
3. acetic acid
4. cyclohexenol(b)
5. benzaldehyde
6. acetopyridine
7. methylbenzaldehyde
8. acetophenone
9. pyridinecarboxaldehyde
10. methylphenylethanone
11. pyridinylethanones
12. methyl pyridinylethanone or amino phenylethanone(c)
13. unknown
14. pyrrolidinone
15. dihydroindenone
16. unknown, $M^+ = 163$
17. phenylbutenone(c)
18. benzenedicarboxaldehyde
19. unknown, $M^+ = 177$
20. methylethyl phenylethanone(b)
21. unknown, $M^+ = 160$
22. unknown, $M^+ = 148$
23. unknown
24. isobenzofurandione
25. unknown, $M^+ = 175$
26. isobenzofuranone
27. unknown, $M^+ = 162$
28. unknown
29. benzopyranone
30. unknown
31. methylisobenzofuranone
32. unknown, $M^+ = 148$
33. benzamide
34. phenylpyridinyl methanone
35. unknown, $M^+ = 175$
36. unknown, $M^+ = 181$
37 fluorenone
38. unknown
39. unknown, $M^+ = 182$
40. xanthenone
41. methylphenylpyridyl methanone
42. unknown

(a) Numbers correspond to those in Figure 12.
(b) Very uncertain.
(c) Uncertain, but reasonably good mass spectral fit.

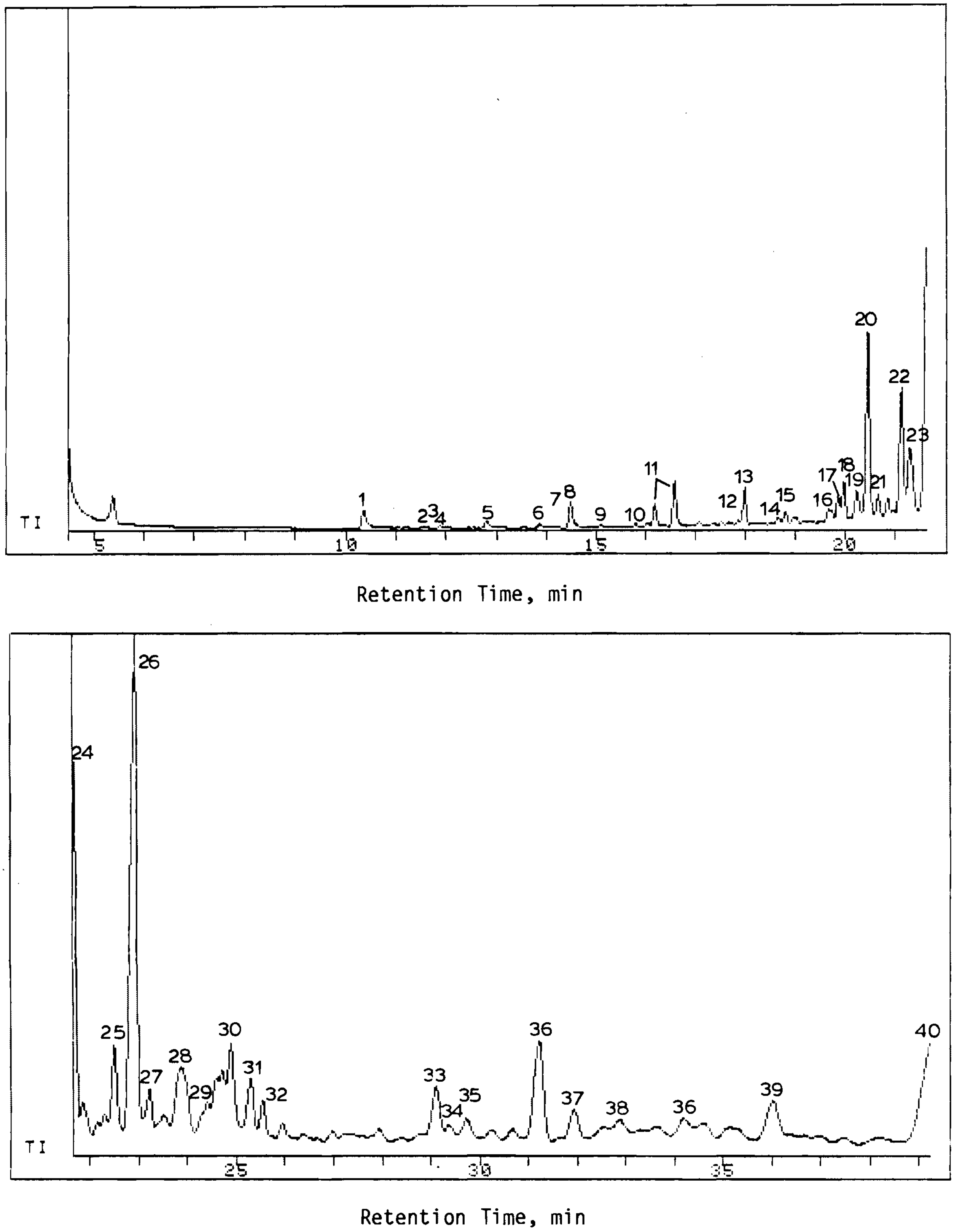
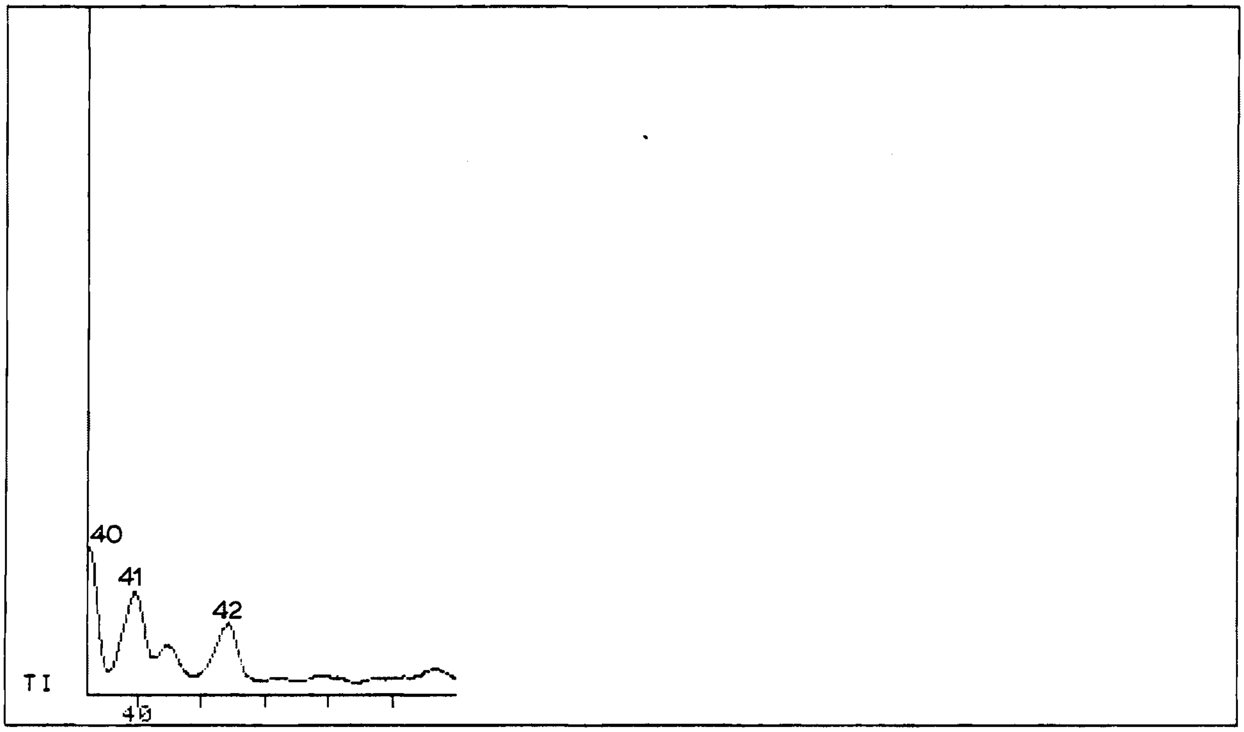


FIGURE 12. Total Ion Chromatogram for Neutral Fraction of WAO Treated BGW



Retention Time, min

FIGURE 12. (contd)

TABLE 11. Components Identified in Neutral Fraction of Biological Effluent(a)

1.	alkanes	(impurities)
2.	aliphatic carboxylic acids	
3.	tributyl phosphate	(impurity)
4.	unknown, $M^+ = 148$	
5.	ethyl phthalate	(impurity)
6.	alkene or alcohol	(impurity)
7.	unknown, $M^+ = 160$	
8.	butyl phthalate	(impurity)
9.	phthalates	(impurity)
10.	unknown, $M^+ = 146$	(impurity)
11.	unknown, $M^+ = 181$	(impurity)
12.	unknown, $M^+ = 147$	(impurity)
13.	unknown, $M^+ = 182$	(impurity)

(a) Numbers correspond to those in Figure 13.

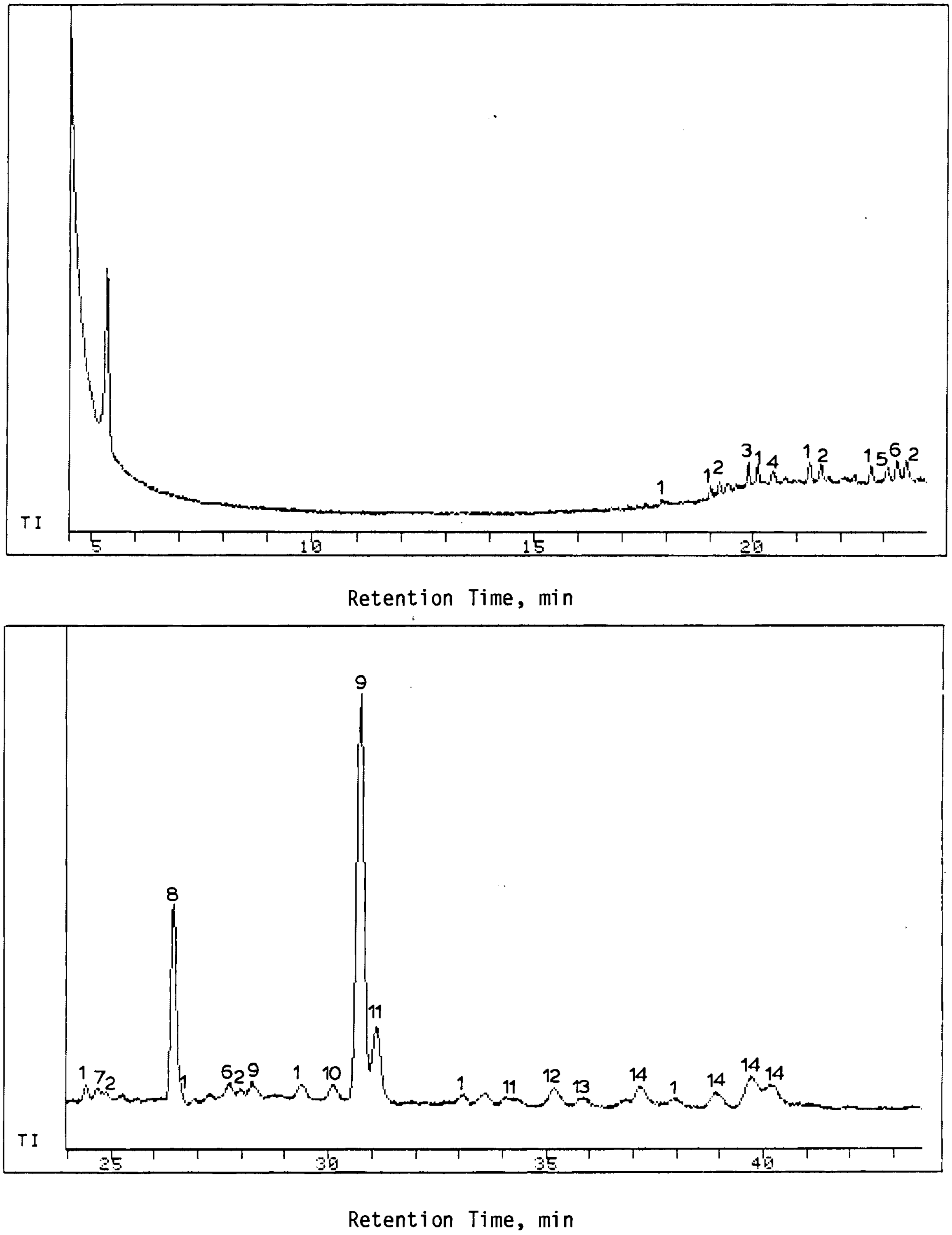
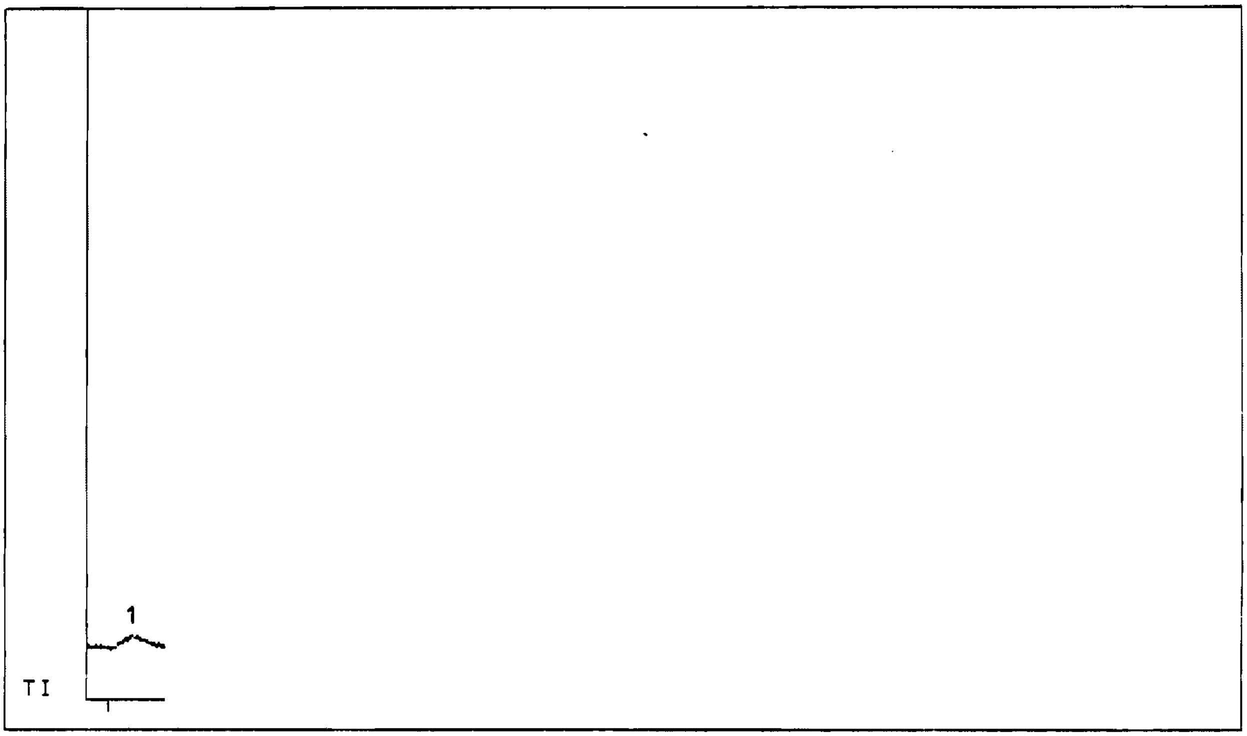


FIGURE 13. Total Ion Chromatogram for Neutral Fraction of Biological Effluent



Retention Time, min

FIGURE 13. (contd)

TABLE 12. Components Identified in Basic Fraction of Raw BGW(a)

1. pyridine
2. methylpyridine
3. furandione(b)
4. furaldehyde
5. ethylpyridine
6. pyranone
7. phenol
8. dihydroxymethylbenzene(c)
9. benzotriazole(c)
10. unknown
11. benzoxazole(b)
12. methylphenols
13. naphthalenol(b)
14. quinoline
15. iosquinoline
16. indazole(b)
17. methylquinolines
18. C_2-quinolines
19. C_2-singly unsaturated quinolines(b)
20. unknown
21. phthalate (impurity)
22. alkyl and phthalate impurities (impurity)

(a) Numbers correspond to those in Figure 14.
(b) Uncertain, but reasonably good mass spectral fit.
(c) Very uncertain.

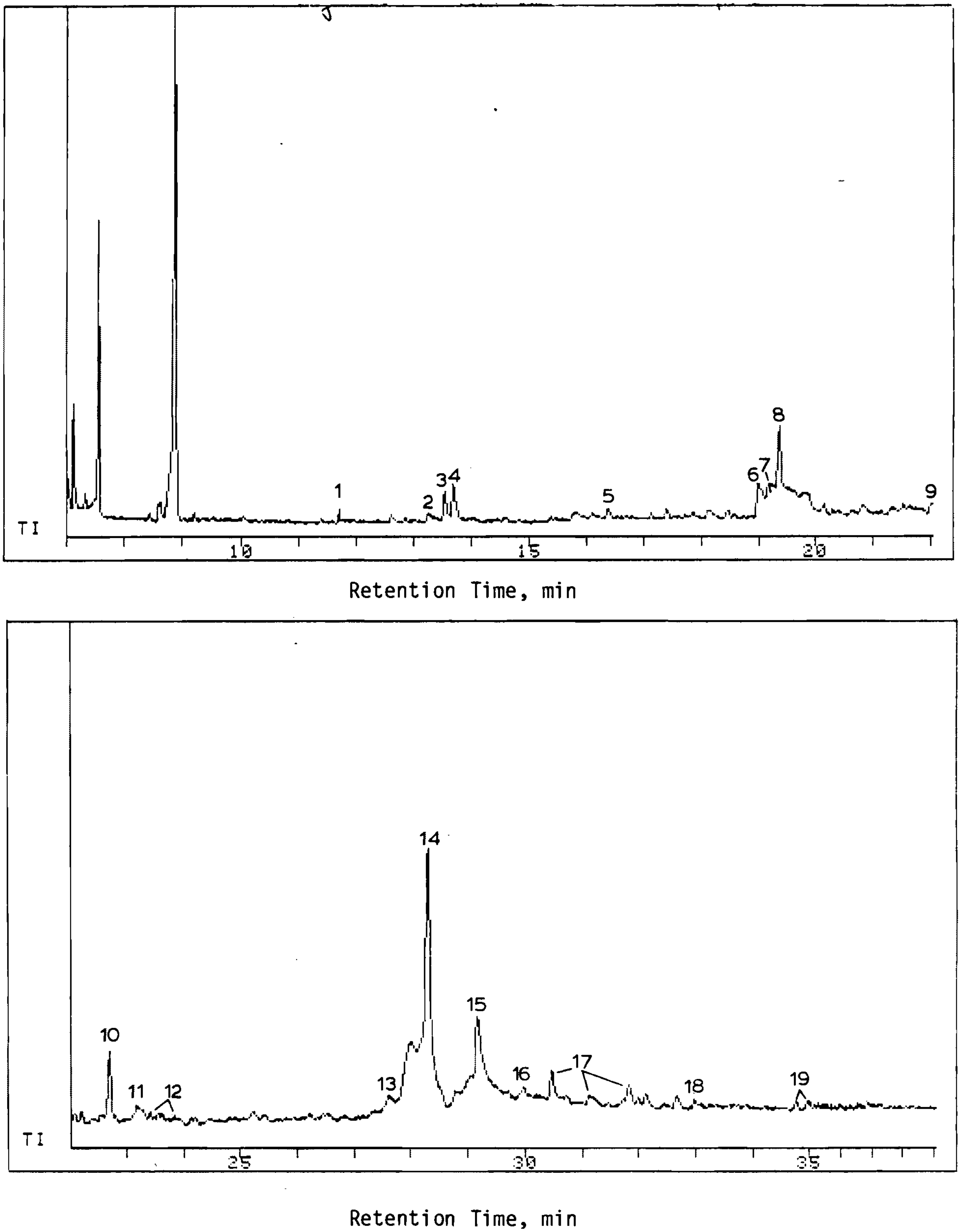
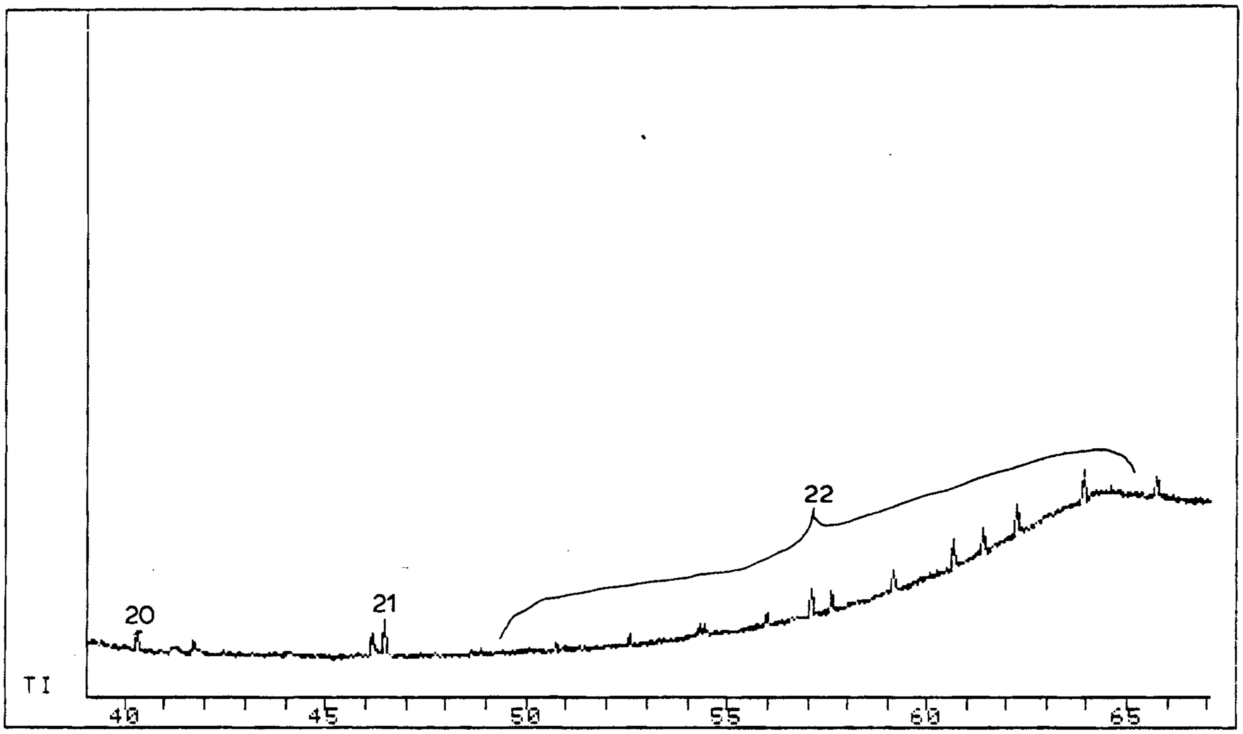


FIGURE 14. Total Ion Chromatogram for Basic Fraction of Raw BGW



Retention Time, min

FIGURE 14. (contd)

TABLE 13. Components Identified in Basic Fraction of WAO Treated BGW(a)

1. pyridine carboxylic acid(b)
2. benzaldehyde
3. pyridine carboxaldehydes
4. C_3-pyridine
5. pyrrolidinone(b)
6. pyridinylethanones
7. unknown, $M^+ = 132$
8. methylpyridinylethanones(b)
9. pyridinone(b)
10. oxide-methylpyridines(b)
11. quinoline
12. unknown, $M^+ = 122$
13. isoquinoline
14. naphthyridine
15. unknown, $M^+ = 122$
16. dihydroindolone(b)
17. methylquinolines
18. benzamide
19. methyltetrahydroquinolines(b)
20. methylnaphthyridines
21. pyridinecarboxamides(b)
22. C_2-tetrahydroquinoline(b)
23. bipyridines
24. ethenylquinolines(b)
25. methyldihydroindole(c)
26. C_3-singly unsaturated quinolines or dipyridopyrroles(b)
27. biphenylol(b)
28. methylbenzopyranone(b)
29. unknown, $M^+ = 170$
30. unknown, $M^+ = 172$
31. phenylpyridinyl methanone
32. unknown
33. dipyridylmethanones(b)
34. N-phenylmethylbenzenemethanamine (impurity)
35. N-phenylmethylenebenzenemethanamine (impurity)
36. unknown, $M^{+0} = 182$
37. unknown, $M^{+0} = 181$
38. unknown, $M^{+0} = 198$
39. methoxydibenzofuran(c)
40. pyranoisoquinolinone (or isomer)(b)
41. unknown, $M^+ = 225$
42. unknown, $M^+ = 211$
43. unknown, $M^+ = 210$
44. C_{16}-singly unsaturated hydrocarbon (impurity)

TABLE 13. (contd)

45.	unknown	
46.	phthalate	(impurity)
47.	alkyl and phthalate impurities	(impurity)

(a) Numbers correspond to those in Figure 15.
(b) Uncertain, but reasonably good mass spectral fit.
(c) Very uncertain.

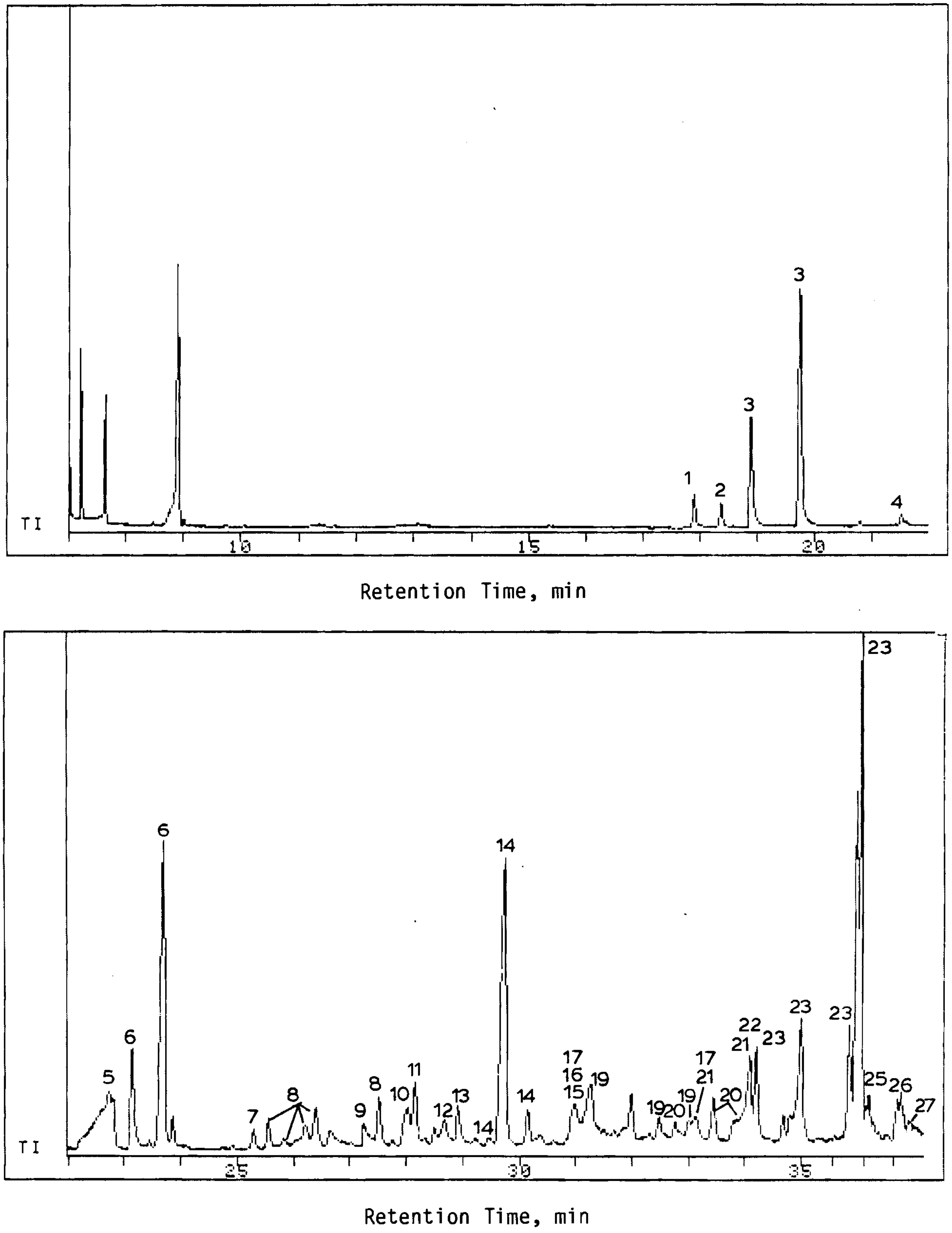
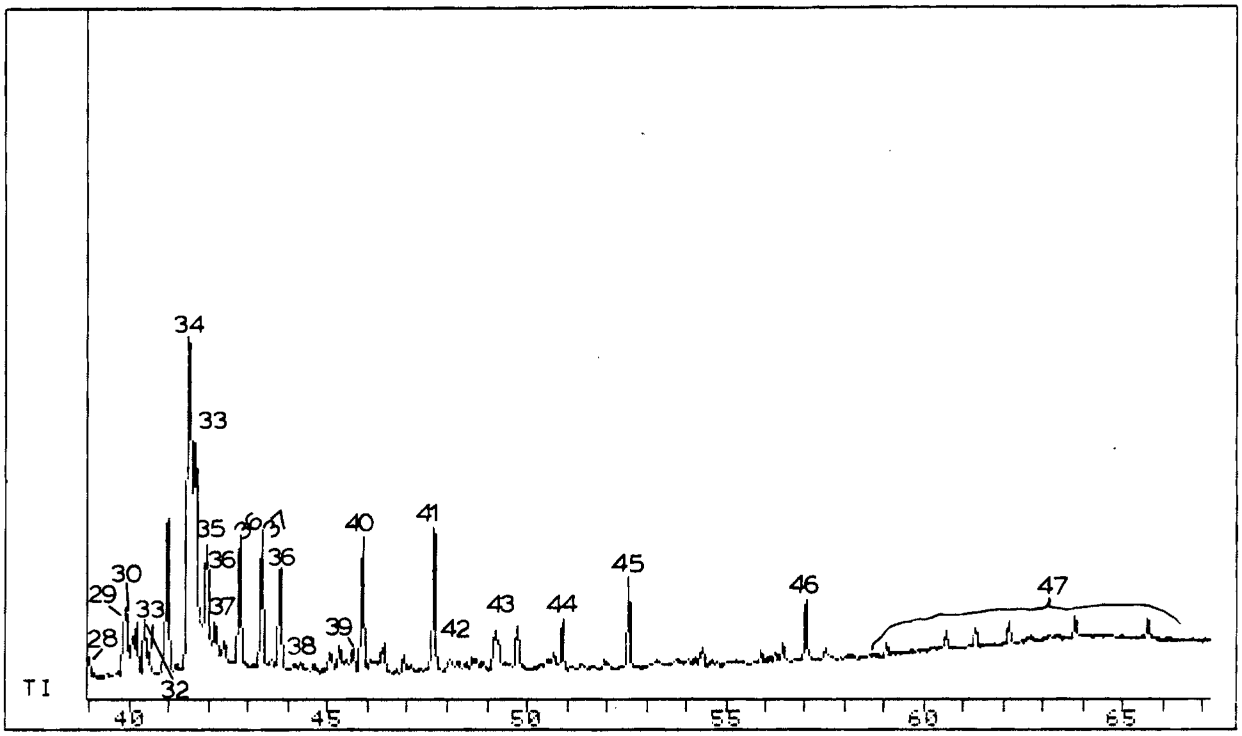


TABLE 15. Total Ion Chromatogram for Basic Fraction of WAO Treated BGW



Retention Time, min

TABLE 15. (contd)

TABLE 14. Components Identified in Basic Fraction of Biological Effluent(a)

1. unknown
2. benzaldehyde
3. pyridinylethanone(b)
4. benzothiazole(b)
5. carboxylic acid (impurity)
6. unknown, $M^+ = 140$
7. naphthyridines
8. methylpyrrolidinyl pyridine(b)
9. unknown, $M^+ = 149$
10. N-nmethylpyridine carboxamide(b)
11. bipyridines
12. C_3-singly unsaturated quinolines or dipyridopyrrole(b)
13. biphenylols(b)
14. unknown, $M^+ = 148$
15. unknown, $M^+ = 160$
16. phenylpyridinylmethanone
17. methylbenzopyranone
18. benzimidazole carboxaldehyde
19. N-phenylmethylbenzenemethanamine(c) (impurity)
20. unknown, $M^+ = 182$
21. unknown, $M^+ = 181$
22. pyraniosoquinolinones (or isomer)(b)
23. C_{16}-carboxylic acid (impurity)
24. phthalate (impurity)
25. unknown, $M^+ = 225$
26. unknown
27. C_{18}-carboxylic acid (impurity)
28. alkene (impurity)
29. unknown
30. unknown
31. alkene (impurity)
32. phthalate (impurity)
33. alkyl, phthalate impurities (impurity)

(a) Numbers correspond to those in Figure 16.
(b) Uncertain, but reasonably good mass spectral fit.
(c) Very uncertain.

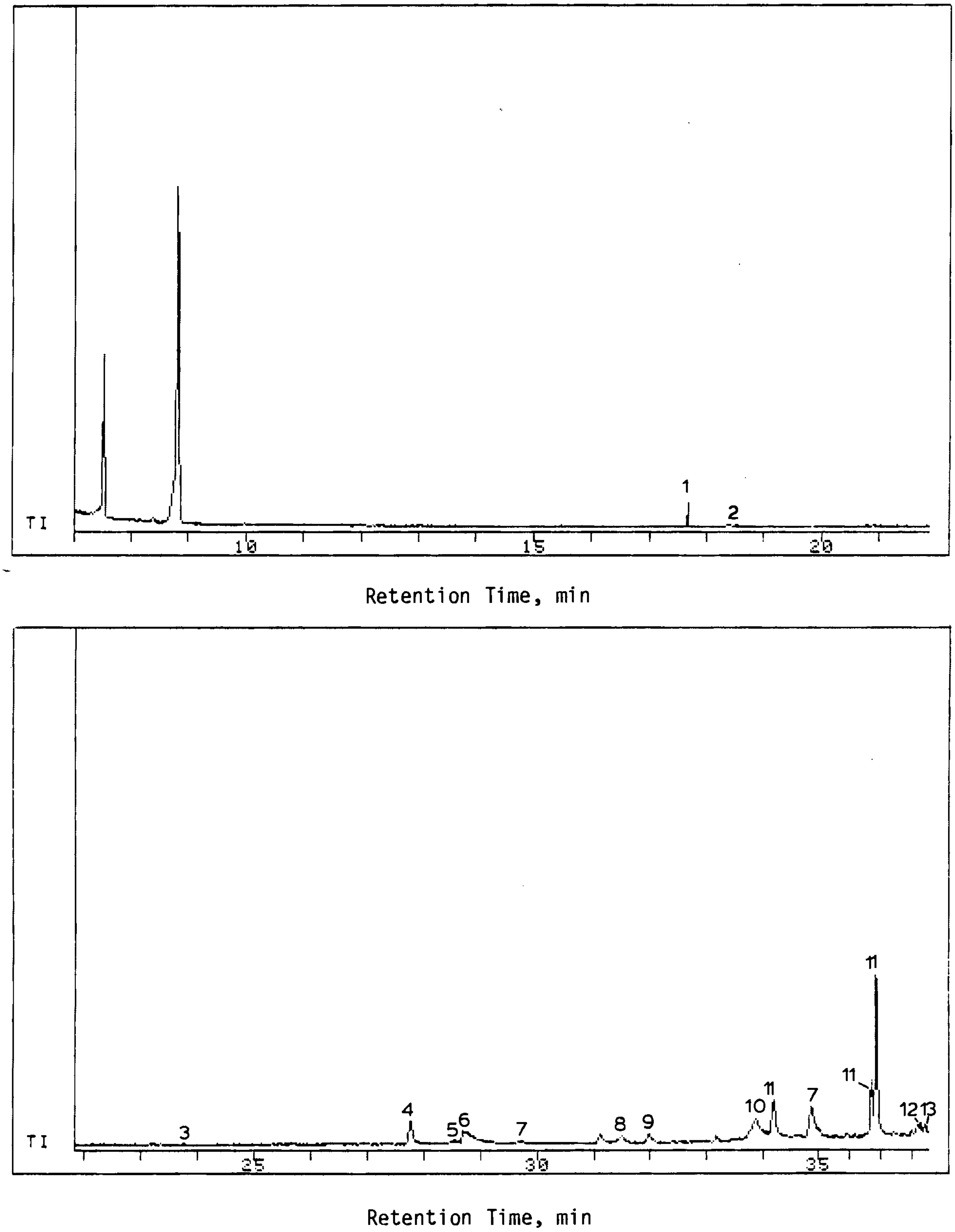
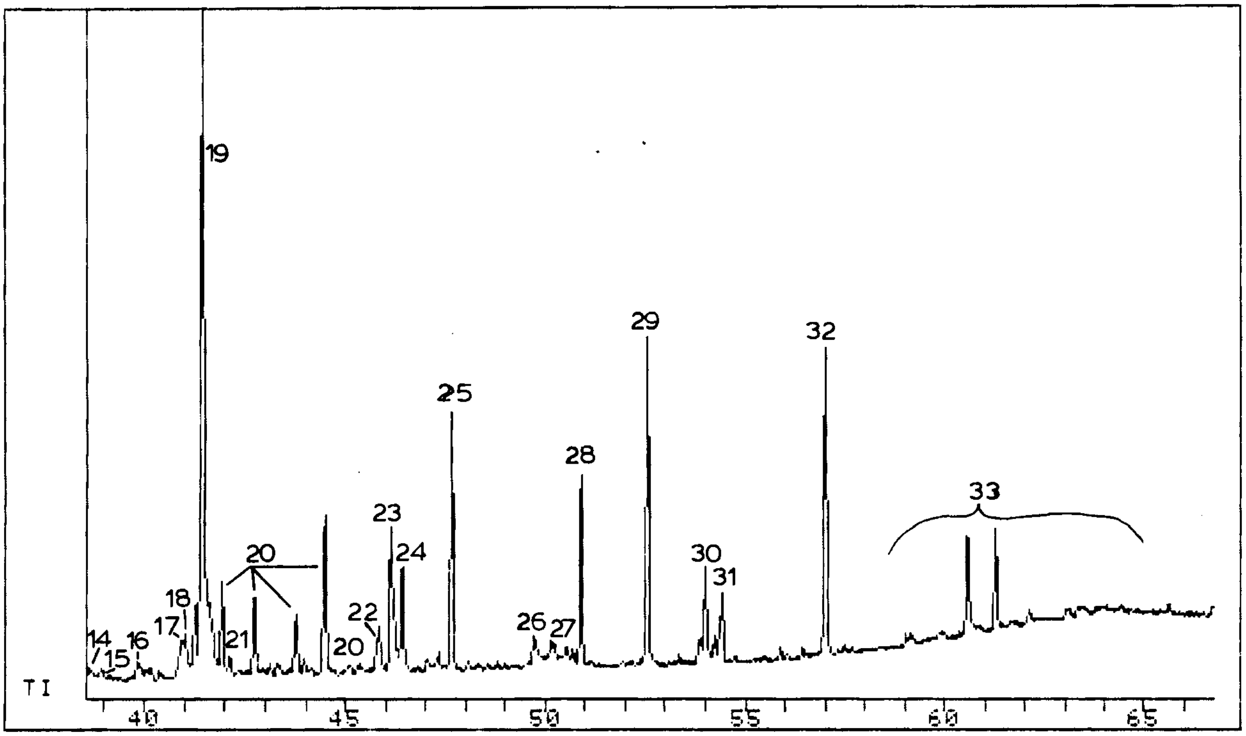


FIGURE 16. Total Ion Chromatogram for Basic Fraction of Biological Effluent



Retention Time, min

FIGURE 16. (contd)

DISCUSSION

CHEMICAL CHARACTERISTICS OF RAW BGW

The compounds identified by GC/MS in extract of the raw wastewater consisted of predominantly alkylphenols and methoxyphenols. Aromatic aldehydes, furans, aliphatic cyclic ketones and aromatic ketones were also present in (relatively) significant quantities in the acid and neutral fractions. The phenols and ketones are typical of biomass products and have frequently been seen in the biomass oils as well as in lignin degradation products. The furans are typical of cellulose (and biomass) degradation products.

The basic fraction of the raw BGW was relatively minor, being only 2% of the total extractable organics. This fraction is often important, however, since it contains many of the more toxic or inhibitory organics. The basic components identified in the raw wastewater consisted mainly of alkylquinolines and some pyridines. The presence of minor amounts of acidic components in the basic fraction indicating overlap in the procedure seems to be typical of acid-base extractions.

It should be noted that since all fractions were taken to dryness, volatile components were lost or depleted. Highly water soluble components (e.g., low molecular weight acids and dibasic acids) may not have been extracted by this procedure.

WET AIR OXIDATION

Wet oxidation treatment resulted in the virtual disappearance of the alkyl- and methoxyphenols from the extracted acid fractions. Benzoic acid is instead the overwhelmingly dominant peak in the chromatogram. Aromatic ketones, aldehydes, and their hydroxy derivations as well as their nitrogen-containing derivatives are present in minor amounts. Aromatic ketones and aldehydes, including the oxygen- and nitrogen-heterocyclic derivatives, predominate in the neutral fractions and do not appear to have been affected by the oxidation to the same extent as the phenols. (Since quantitative analysis was not attempted, it is not possible to determine relative amounts of the ketones and aldehydes in the raw and treated waters.)

The basic fraction of the wet oxidation treated waters contains predominantly oxidized nitrogen heterocyclics and condensed nitrogen heterocyclics. It is not known if the acid-base procedure catalyzed the condensation of the oxidized nitrogen heterocycles creating procedural artifacts or if these components were produced by the wet oxidation treatment.

The amount of organics extracted from the WAO treated water was only 3% of the amount extracted from the raw water. This 97% reduction is substantially greater than the 74% COD reduction achieved. This indicates a relatively greater proportion of non-extractable organics in the treated water. The distribution of fractions was approximately the same as for the raw water.

BIOLOGICAL TREATMENT

Composition of Effluent

Biological treatment resulted in the loss of many of the components in the acid and neutral fractions from the wet oxidation treatment. The resulting relatively weak chromatograms contain mainly aliphatic carboxylic acids, alkanes, and phthalates, many of which may be considered impurities. Biological treatment did not appear to be as effective with the basic components. Many of the nitrogen heterocyclic ketones and condensed nitrogen heterocycles remain, although their absolute amounts appear to have decreased.

The removal of COD during the biological treatment was slightly higher than the removal of extractable organics. This indicates a slightly lower proportion of nonextractables in the biological effluent. Again, the distribution of the fractions remained approximately the same as for the raw and WAO treated waters.

Performance of Reactors

In general, the biological reactors operated quite well, achieving excellent COD removals with a relatively high strength wastes. Periods of reactor upset, noted by rising effluent COD and falling MLVSS appear to be related to changes in feed. Very stable operation was observed during the final five weeks of operation when a steady supply of 300°C treated BGW was available and a constant SRT of 20 days was maintained. Earlier, higher SRTs had been used during times of suspected upset to maintain MLVSS levels.

The major difficulty encountered during operation was the formation of bulking sludge caused by filamentous bacteria. Sludge bulking would occasionally plug the reactors, stopping circulation of contents. Mechanical agitation was necessary to disperse the sludge. This problem seemed to alleviate itself as the SRT was lowered.

Final operating conditions for reactors 1 and 2, respectively, were organic loading rates of 860 and 1500 mg COD/ℓ-day (54 and 94 lb COD/1000 ft^3-day), MLVSS of 2600 and 3700 mg/ℓ, SRT of 19 and 20 days, and HRT of 10 and 6.7 days. Typical values for conventional activated sludge treatment of sewage are 460-920 mg COD/ℓ-day (30-60 lb COD/1000 ft^3-day), 2000-4000 mg/ℓ MLVSS, 5-15 days, and 4-8 hr, respectively (Metcalf and Eddy 1972). The high value of HRT in this study was necessitated by the high feed strength. Otherwise, it appears that wet oxidized BGW could be treatable by conventional activiated sludge technology. The effluent COD levels achieved in this study, 200-400 mg/ℓ, would probably be suitable for discharge to a municipal treatment plant. Quantitative chemical analysis would be necessary to assure that priority pollutants (e.g., phenol, toluene) were not present in levels above criteria (45 FR 231).

The results also indicate that aerobic treatment using even higher organic loading rates should be possible. This would mean that smaller, more economical aeration basins could be used. Possible limitations to higher loading rates are aeration capacity and sludge settling problems resulting from higher MLVSS levels.

An especially encouraging result of the study was the ease with which the biological reactors were acclimated to the full strength feed. This occurred much more easily than in previous studies with BGW that had not been pretreated. This seems to be due to the difference in chemical characteristics between the raw and treated waters. This might prove especially beneficial for anaerobic treatment. In previous studies, anaerobic systems could not be acclimated to full strength BGW because of apparent toxicity problems. Anaerobic treatment is well suited for lower molecular weight acids and would probably do quite well with wet oxidized BGW. An advantage is that is does not require energy for aeration and, in fact, results in a net production of energy from methane formation.

VOLATILE COD LOSSES

The results obtained from the blank reactor (Figure 7) are somewhat anomalous and no conclusions can be drawn from them. Initially, there was a sharp drop in effluent COD, indicating that volatilization was occurring. However, a sudden rise in COD was noted beginning midway through the experiment. This corresponds to approximately the time that feed was changed. Falling pH also indicates that volatilization of acidic components was not occurring. The rise in effluent COD between days 11 and 15 is greater than can be accounted for by the feed during this period. This suggests that there was problems with the COD analysis of the effluents. The mercuric chloride added to the reactor may have interfered with the analyses.

Because of the chemical nature of the wet oxidized BGW, some volatilization of organics was expected, especially with the high hydraulic retention times. Unfortunately, the results of this experiment do not allow this to be determined. Obviously, volatilization could not account for a major portion of the COD removal because of the growth of biological solids observed.

REFERENCES

APHA, Washington, DC. *Standard Methods for the Examination of Water and Wastewater*. APHA, Washington, DC.

Bell, N. E. 1981. *Treatment of Biomass Gasification Wastewaters Using Liquid-Liquid Extraction*,PNL-4016, Pacific Northwest Laboratory, Richland, WA.

English, C. J. 1981. *Treatment of Biomass Gasification Wastewaters Using Wet Air Oxidation*, PNL-4013, Pacific Northwest Laboratory, Richland, WA.

Koa, C. 1980. *Extraction of Wastewater from Biomass Gasification*. M.S. Thesis, Texas Tech University, Lubbock, TX.

Maxham, J. V., and N. E. Bell. 1980. *Treatment of Biomass Gasification Wastewater*. Presented at the 11th Biomass Thermochemical Conversion Contractors Meeting, September 23-24, Richland, WA.

Maxham, J. V., and W. Wakamiya. 1980. "Innovative Biological Wastewater Treatment Technologies Applied to the Treatment of Biomass Gasification Wastewater." Presented at the *35th Purdue Industrial Waste Conference*, May 13-15, West Lafayette, IN.

Metcalf and Eddy, Inc. 1972. *Wastewater Engineering*, McGraw-Hill, New York, NY.

Petty, S. E., S. D. Eliason and M. M. Laegreid. 1981. *Treatment of Biomass Gasification Wastewater Using Reverse Osmosis*, PNL-4018, Pacific Northwest Laboratory, Richland, WA.

Wakamiya, W., and J. V. Maxham. 1980. "Treatability of Biomass Gasification Wastewater." Presented at the *10th Biomass Thermochemical Conversion Contractors Meeting*, February 12-13, Berkeley, CA.

Wakamiya, W., J. V. Maxham and S. E. Petty. 1979. *Biomass Gasification Wastewater Treatment - Interim Report*, PNL-SA-8165, Pacific Northwest Laboratory, Richland, WA.

45 FR 231. 1980. "Water Quality Criteria Documents; Availability," *Federal Register*, 45, 231, Friday, November 28, 1980.

DISTRIBUTION

No. of Copies	
	OFFSITE
	Russ O'Connell Biomass Energy Systems Division U.S. Department of Energy 600 E Street, N.W. Mail Stop 404 Washington, DC 20545
5	Han Chang Argonne National Laboratory Building 362 9700 South Cass Avenue Argonne, IL 60439
27	DOE Technical
	J. V. Maxham Institute of Paper Chemistry Appleton, WI 54911
	Battelle Columbus Laboratories
	S. E. Petty (5)
	ONSITE
	Richland Operations Office
	H. E. Ransom
33	Pacific Northwest Laboratory
	D. B. Cearlock G. W. Dawson C. J. English (10) J. S. Fruchter M. M. Laegreid E. B. Schwenk D. S. Sklarew (5) J. A. Stottlemyre Publishing Coordination (2) Technical Information (5) Geosciences Research and Engineering Laboratory (5)