

VOLATILE ORGANIC COMPONENTS OF MUNICIPAL PRIMARY SEWAGE

EFFLUENT AFTER CHLORINATION AND DECHLORINATION

by

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ABSTRACT

The extraction, separation and identification of volatile organic components of primary effluent before and after chlorination was undertaken to ascertain whether the chlorination of treatment plant effluents results in the formation of new volatile chlorinated organics.

Extraction efficiencies of 70 to 90 percent of an aqueous solution of phenols were obtained by both continuous solvent extraction and sorption on a column of a macroreticular resin. Tests with primary effluent showed that the macroreticular resin recovered a slightly larger number of compounds than the solvent extractor which also suffered from emulsion problems. Since the resin was also expedient in handling replicate samples it was adopted and further studies indicated that it had a capacity of 1.7 mg TOC/cc of resin and recoveries of the phenols were unaffected by pH or detergents.

Preliminary separation of the components on the basis of acidity with .05 M NaOH and diethyl ether and by thin layer chromatography on silica gel with pet ether and methanol proved to be useful. Gas chromatographic (GC) studies with various silicone liquid phases demonstrated that OV-101, OV-17, and OV-225 all provide good separation after optimization of temperature programs.

Primary effluent samples taken from Lion's Gate Treatment Plant in North Vancouver on Monday mornings proved to be remarkably consistent in their GC traces as monitored by ^{63}Ni electron capture (EC) and flame ionization (FID) detectors. A series of spectacular new peaks was consistently observed by EC as a result of chlorination, but the FID showed only minor changes. Dosage levels of up to 120 mg/l Cl_2 (NaOCl) produced similar chromatograms while a dosage of 200 mg/l produced a new set of changes not found at the dosage levels used in treatment plants. Gas chromatographic studies with a micro-

electrolytic conductivity detector showed that 10 or 11 new halogenated peaks in the neutral and basic fraction and 6 or 7 new halogenated peaks in the acidic fraction result from chlorination. These compounds all of which are in ng/l concentrations account for only 0.01 percent of the applied chlorine dosage but make up about 40 percent of the more volatile organically bound halogen present in chlorinated primary effluent.

After a series of partially successful attempts by retention time, GC-MS and GC effluent trapping, a number of components were positively identified by a computerized GC-MS. Thirty-one compounds were positively identified by mass spectra and GC retention times, another 24 were tentatively identified by mass spectra and an additional seven were very tentatively identified by GC retention times. Only three of the compounds resulting from chlorination were positively identified. All compounds identified by mass spectra are present in $\mu\text{g/l}$ concentrations in primary effluent. The implications of this study and suggestions for further investigations are also discussed.

Research Supervisor.

TABLE OF CONTENTS

	Page
Abstract	i
Table of Contents	iii
List of Tables	v
List of Figures	vii
Acknowledgments	ix
Symbols and Abbreviations	x
CHAPTER I INTRODUCTION, PURPOSE AND SCOPE	1
Definitions	1
Introduction	1
Purpose and Scope of This Research	2
CHAPTER II LITERATURE REVIEW	4
A. Preface	4
B. Composition of Domestic Sewage and Effluents	4
1. Organics	4
2. Inorganics	20
C. A Simplified Model of the Chlorination Process	20
D. Reactions of Chlorine with Organics in Aqueous Media	24
1. Reactions with Nitrogenous Compounds	24
2. Reactions of Chlorine with Other Organics	27
3. Reactions of N-Chloro Compounds with Organics	30
E. The Effects of Chlorine on Sewage Effluents	31
1. Practices in Treatment Plants	31
2. Biological Effects of Residual Chlorine	31
3. Toxic Effects of Chlorinated Organics	34
4. Chemical Effects of Chlorinations	36
F. Analytical Methods	41
1. Sampling and Preservation	41
2. Extraction and Concentration	42
3. Separation	45
4. Chemical Analysis	50
CHAPTER III EXPERIMENTAL	54
A. Outline of the Problems	54
B. Apparatus and Techniques	54
1. General Methodology	54
2. Sampling and Preservation	56
3. Design and Test of Extraction Methods	57
a. Solvent Extractor	57
b. Extraction with XAD-2 Resin	59
c. Comparison of XAD-2 and Solvent Extractor	62
d. Extraction of Particulates	62

4. Separation Experiments	63
a. Preliminary Separation	63
b. GC Optimization	64
c. TLC of Acidity Separated Fractions	64
5. Effects of Chlorination	65
a. Changes in Soluble TOC upon Chlorination	65
b. Effects Detectable by GC with EC and FID Detectors ..	65
c. Effects Monitored by MEC Detector and GC Correlations	65
d. GC-MS Studies on the MS-12	66
e. Tentative Identification by Retention Time	66
f. Trapping of GC Peaks	66
g. GC-MS-Computer	67
CHAPTER IV RESULTS AND DISCUSSION	69
A. Extraction Experiments	69
1. Solvent Extractor	69
2. Extraction with XAD-2 Resin	72
B. Separation Experiments	82
1. Preliminary Separation	82
2. GC Optimization	85
3. TLC of Acidity Fractions	87
C. Effects of Chlorination on Primary Effluent	92
1. Soluble TOC	92
2. Effects Monitored by EC and FI Detectors	92
3. GC with MEC Detector	111
4. GC-MS Studies on the MS-12	121
5. Tentative Identification by Retention Time	124
6. GC-MS-Computer Studies	130
7. Correlations Among GC Chromatograms	146
CHAPTER V SUMMARY, IMPLICATIONS AND SUGGESTIONS FOR FURTHER STUDIES	153
Summary	153
Implications	154
Recommendations for Further Studies	158
BIBLIOGRAPHY	160
APPENDIX I REFINEMENTS TO THE AQUEOUS CHLORINE-AMMONIA MODEL	179
1. Reactions of Chlorine with Water	179
2. Decompositions of HOCl and OCl ⁻	180
3. Reactions of HOCl and OCl ⁻ with Ammonia	181
4. Thermodynamic Properties of Chloramines	185
APPENDIX II SUMMARY OF CHROMATOGRAMS OF EFFLUENT SAMPLES	186
APPENDIX III GC CONDITIONS FOR FIGURES	188
APPENDIX IV MASS SPECTRA OF COMPOUNDS POSITIVELY IDENTIFIED IN CHLORINATED PRIMARY EFFLUENT	190
APPENDIX V MASS SPECTRA OF UNIDENTIFIED COMPONENTS OF CHLORINATED PRIMARY EFFLUENT	196

LIST OF TABLES

Table		Page
2.1	Major Inputs to Domestic Sewage	5
2.2	Typical Strength Distributions in Raw Sewages	7
2.3	General Composition of an American Domestic Sewage	9
2.4	General Composition of an English Domestic Sewage	10
2.5	Amino Acid Content of Raw Sewage	11
2.6	Organic Components of Primary Effluent	13
2.7	Volatile Components of Human Urine	16
2.8	General Composition of Secondary Effluent	18
2.9	Organic Components of Secondary Effluents	19
2.10	Inorganic Composition of Lion's Gate Effluent	21
2.11	Summary of Reaction Conditions for Organics in Sewage	28
2.12	Toxicity of Selected Compounds to Aquatic Life	35
2.13	Chlorinated Compounds Formed by Chlorination of Primary Effluent	39
4.1	Recoveries of Phenols by Solvent Extractor	70
4.2	Solvent Loss Due to Entrainment	71
4.3	Recoveries of Phenols from Distilled Water by XAD-2	74
4.4	Effects of LAS on Recoveries of Phenols by XAD-2	75
4.5	Breakdown of Losses for XAD-2 System	76
4.6	Breakthrough Study for Sewage on XAD-2	77
4.7	Effect of Chlorination on Soluble TOC	96
4.8	Effects of Chlorination by GC Analysis with FID and EC Detectors	98
4.9	Concentrations of Halogen as Chlorine in Primary Effluent ...	116
4.10	Chlorine Uptake by Volatiles	118
4.11	Retention Times of Test Compounds	125
4.12	Compounds Identified by GC Retention Time	128
4.13	Performance Check of Finnigan 3000	131
4.14	File Names for GC-MS-Comp Studies	132
4.15	Summary of RGC Data	134
4.16	Phthalates and Septum Bleed by LMRGC	140
4.17	Results of Spectral Searches and Retention Time Checks for CL1202	142
4.18	Results of Spectral Searches and Retention Time Checks for C-HALL	143
4.19	Compounds Positively Identified by Mass Spectrum and Retention Times	145

Table		Page
4.20	Compounds Tentatively Identified by MS	147
4.21	Spectrum Numbers of Halogenated Neutral and Basic Organics	149
4.22	Spectrum Numbers of Halogenated Acidic Organics	150
5.1	Guide to Environmental Effects of Identified Compounds	155

LIST OF FIGURES

Figure		Page
3.1	Flowchart of the Project	55
3.2	Continuous Solvent Extractor	58
3.3	Macroreticular Resin Extraction Apparatus	61
4.1	Recovery of Organics from Primary Effluent by XAD-2 Resin	79
4.2	Continuous Solvent and XAD-2 Resin Extraction of Organics from Primary Effluent Monitored by GC	81
4.3	Soxhlet Extracts of Particulates Analyzed by GC	83
4.4	Silica Gel Column Fractionation of Primary Effluent Extracts Analyzed by GC	84
4.5	Acidity Separation of Primary Effluent Extracts Analyzed by GC	86
4.6	GC Optimization - N + B by EC	88
4.7	GC Optimization - WA by EC	89
4.8	GCC Optimization - N + B by FID	90
4.9	GC Optimization - WA by FID	91
4.10	TLC of N + B Fraction; Silica Gel, Pet Ether	93
4.11	TLC of N + B/TLC Fraction; Silica Gel, Methanol	94
4.12	Flowchart of Separation Procedure	95
4.13	Effects of Chlorination by GC - N + B by EC-1	99
4.14	Effects of Chlorination by GC - N + B by FID-1	100
4.15	Effects of Chlorination by GC - WA by EC	101
4.16	Effects of Chlorination by GC - WA by FID	102
4.17	Effects of Chlorination by GC - SA by EC	103
4.18	Effects of Chlorination by GC - SS by FID	104
4.19	Effects of Chlorination by GC - N + B by EC-2	105
4.20	Effects of Chlorination by GC - N + B by FID-2	106
4.21	Effects of Chlorination by GC - A by EC	107
4.22	Effects of Chlorination by GC - A by FID	108
4.23	Effects of Chlorination by GC - A by MEC	112
4.24	Effects of Chlorination by GC - N + B by MEC-1	113
4.25E	Effects of Chlorination by GC - N + B by MEC-2	114
4.26	Calibration Curve of FID Detector	115
4.27	Total Ion Current Plot for N + B Fraction by MS-12	122
4.28	Mass Spectra from MS-12	123

Figure	Page
4.29 GC Retention Times of Test Compounds	126
4.30 RGC's of Acid Fractions	135
4.31 RGC's of Neutral and Basic Fractions	136
4.32 RGC's of TLC Fractions	137
4.33 RGC's and LMRGC's of Blanks	138
4.34 MEC - GC-MS Correlations	148

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SYMBOLS AND ABBREVIATIONS

A	Acidic Fraction
BOD	Biochemical Oxygen Demand
CIMS	Chemical Ionization Mass Spectroscopy
COD	Chemical Oxygen Demand
CRT	Cathode Ray Tube
DO	Dissolved Oxygen
EC	Electron Capture
EIMS	Electron Impact Mass Spectroscopy
EMW	Estimated Molecular Weight
FID	Flame Ionization Detector
GC/IR	Gas Chromatography Infrared
GC-MS-(Com)	Gas Chromatography Mass Spectrometer-(Computer)
GLC	Gas-Liquid Chromatography
GPC	Gel Permeation Chromatography
GSC	Gas-Solid Chromatography
GVRD	Greater Vancouver Regional District
IR	Infrared
LC _n	Lethal Concentration for n Percent of Population
LC	Liquid Chromatography
LLC	Liquid-Liquid Chromatography
LSC	Liquid-Solid Chromatography
MEC	Microelectrolytic Conductivity (Detector)
MLD	Minimum Lethal Dose For Death of One or More Members of the Group
N + B	Neutral and Basic Fraction
NMR	Nuclear Magnetic Resonance
S/N	Signal to Noise
SS	Suspended Solids
TL _m	Tolerance Limit (Median) for 50 Percent of the Population
TLC	Thin Layer Chromatography
TOC	Total Organic Carbon
TS	Total Solids
USEPA	United States Environmental Protection Agency
UV	Ultra Violet
VS	Volatile Solids

CHAPTER I

INTRODUCTION, PURPOSE AND SCOPE

Definitions

The terminology used in this thesis is that commonly used by those involved with environmental sciences and technologies. To avoid any misunderstandings however, some definitions will be stated. Sewage is defined as untreated wastewater. The standard definitions of domestic, storm, combined and industrial sewages are adhered to. Municipal sewage is that sewage in the municipal sewage system. The terms primary, secondary, and tertiary effluents are used to describe the effluents from the various types of municipal as opposed to industrial sewage treatment plants unless otherwise indicated. Standard abbreviations are used throughout this thesis and a list of abbreviations is provided on page x.

Introduction

In the United States, domestic sewage constitutes about a quarter of the total aqueous organic wastes. (ACS Subcommittee 1969). The amount of organic material in terms of BOD present in domestic sewage in 1963 was 7.3×10^9 lb, compared to BOD values of 9.7×10^9 lb for chemical industries, 5.9×10^9 lb for pulp and paper industries, 4.3×10^9 lb for food processing industries, and 0.5×10^9 lb for the petroleum and coal industry. It should be emphasized that these are wastewaters and not effluents. Values for effluents should be 0.3 to 2 orders of magnitude lower.

The response of an ecosystem to the discharge of organics in wastewaters will naturally depend upon the type of compound and the type of ecosystem. Vallentyne (1957), and Croll (1972), have reviewed the types of organics found in natural waters. Little (1970) and Ongerth et al. (1973) report that

only 66 of a suspected 456 organic chemicals in water have been positively identified. Most organics from domestic sewage are rapidly degraded by microorganisms, so rapidly in fact that depletion of dissolved oxygen in the receiving water often results from the discharge of untreated sewage. However, some compounds may be recalcitrant, metabolized to toxic material, or toxic. If a compound is recalcitrant concentration in the food chain of the ecosystem can occur as with DDT, (Woodwell et al., 1967), or it may even become ubiquitous. For example, carbon tetrachloride is now a normal constituent of the atmosphere (Iliff, 1972) and some drinking waters (Dowty et al., 1975a).

Dugan (1972) suggested that chlorination of domestic sewage may result in the formation of toxic and or recalcitrant chlorinated organic compounds. Zillich (1972), Brungs (1973), and Servizi and Martens (1974) have demonstrated or reviewed the toxicities of chlorinated effluents to aquatic ecosystems. There is little doubt that most of this toxicity is due to Cl^+ species. Current investigations by Jolley (1973), Glaze et al. (1973), Rook (1974) and Bellar et al. (1974) however, show that chlorinated organics are definitely formed during the chlorination of sewage or natural waters. These results have recently been sensationalized by the lay and scientific press (Time, 1974; Vancouver Sun, 1974; Marx, 1974). In order to maintain a proper perspective, calculations based on the data presented by Lillian et al. (1975), Jolley (1973) and JWPCF (1974) shows that well over 99.99 percent of chlorinated organics produced by man are intentionally produced industrially. Some organisms also produce and metabolize chlorinated organics (Doonan 1973). Moreover the fact that an organic compound contains chlorine does not necessarily mean that it is harmful or even recalcitrant.

Purpose and Scope of This Research

This present investigation will focus on the organics in primary effluents which are relatively volatile. The objectives will be to:

- 1.) develop an efficient method for the recovery and concentration of these materials,
- 2.) determine whether changes in the composition profile of the volatile organics in primary effluent occur as a result of chlorination,
- 3.) separate and identify the products and precursors of the reaction of chlorine with primary effluent.

CHAPTER II

LITERATURE REVIEW

A. Preface

This chapter will be divided into five sections. The first three sections will be devoted to predictions of the types of chlorination reactions which will occur during the chlorination of sewage. In order to accomplish this the composition of sewage and primary effluent will be reviewed, a simplified chemical model of the chlorination process will be presented, and the known reactions of chlorine with organics will be briefly reviewed. The final two sections will be devoted to a review of the known effects of the chlorination of sewage and of the analytical methods relevant to this and other similar investigations.

B. Composition of Domestic Sewage and Effluents

1. Organics

Sources The composition of sewage will naturally depend upon which industries are discharging into the collection system. Among the sewages from households, it has been found that although relative amounts vary, the major types of organic material present in domestic sewage are similar in the United States and England. The major inputs to domestic sewage are presented in Table 2.1. Excreta account for practically all of the organic-nitrogen but only 80 percent of the organic-carbon.

Physical Forms Raw sewage is a heterogeneous mixture of floating, suspended, emulsified and dissolved inorganic and organic matter in water. The composition equilibrium is affected by evaporation, solubility equilibria, sorption processes, precipitation, and biological metabolism. Due to the wide variation in physical forms of organic material in sewage and the corresponding variation

Table 2.1 Major Inputs to Domestic Sewage^a

Component	Organic Carbon	Organic Nitrogen	NH ₃ + Urea as N
Faeces*	17	1.5	
Urine*	5	1.7	10.5
Dishwashing and Food Preparation**	8	0.2	0
Personal and Clothes Washing**	7	3.4	10.5

* Units are g/adult/day.

**Units are g/person/day.

a) Painter and Viney (1959)

of degradation efficiency in sewage treatment plants or in natural waters, chemical analysis of sewage is more meaningful after segregation of organics by physical means. A disadvantage of mechanical separation of organics is that sorbed volatile materials (Fishbein, 1972b, Khan, 1972), and metal complexed organics (Chau, 1973) may not be included in the soluble fraction. While no standard segregation method has been adopted, sewages are generally classified as to settleable, colloidal, supracolloidal and soluble fractions. The soluble material has a particle size less than 0.2 to 1.0 microns. A description of the size fractions of raw sewage in terms of engineering parameters is presented in Table 2.2. From this table it can be seen that about one third of the organic carbon in sewage is dissolved, while the organic nitrogen is equally distributed amongst the four fractions.

Molecular Size Distribution Several gel permeation chromatographic (GPC) studies have been conducted to determine the molecular size of the organic compounds in raw sewage. Zuckermann and Molof (1970) found only two fractions, one with an Estimated Molecular Weight (EMW) of 400 and another of EMW 1200⁺. Hardt et al., (1971), and Robertson (1972), and Clesceri (1973) all found more complex molecular weight profiles. Robertson also found evidence of solute - gel interaction, thus some inaccuracies are inherent in the assignment of EMW values. The profiles are so different that as Robertson points out, no generalizations should be made. It can be said however that 20-60 percent of the dissolved organic carbon has an EMW of less than 350 and may thus be amenable to separation by gas chromatography. The upper limits of the material amenable to GC separation.

General Chemical Classes Two major studies have been undertaken to classify the organic material in sewage by chemical groupings. Both studies, one in England (Painter et al. 1959, 1961, Painter 1971), and the other in the eastern United States (Hunter and Heukelekian, 1965; Heukelekian and

Table 2.2 Typical Distributions in Raw Sewages

Fraction	Particle Size			TS		VS		TOC				Organic-N					
	a	b	c	b		d		b		a		c		b		c	
	μ	m μ	μ	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%
Soluble	<0.2	<1	<1.0	284	65	827*	63	88	42	46	42	90	29	2.0	27	10	37
Colloidal		1-10 ³		31	7			20	10	12	11	40	15	1.1	11	5.4	20
Supra colloidal		10 ³ -10 ⁵		44	10	482*	37	36	17	22	20	68	22	3.1	34	5.4	20
Settleable		> 10 ⁵		79	18			64	31	29	27	105	34	3.7	23	6.2	23

* Only values for soluble versus suspended were given.

a Rickert and Hunter (1971)

b Hunter and Heukelekian (1965), Rudolfs and Balmat (1952), Heukelekian and Balmat (1959)

c Painter and Viney (1959)

d Painter, Viney and Bywaters (1961)

Balmat, 1959; Rickert and Hunter, 1971; Hunter, 1971) employed classical solvent and TLC separation procedures followed by wet chemical quantification techniques. The results of the studies are presented in Tables 2.3 and 2.4. Direct comparison of these studies is difficult since the data is expressed in different units. It is noteworthy that the carbohydrates, proteins, volatile acids, and anionic surfactants account for most of the soluble carbon.

The amount of soluble organics recoverable by solvent extraction or sorption and sufficiently volatile for gas chromatographic analysis is of particular interest. In the American study it was found that 80 mg/l or 85 per cent of the dissolved organics were ether soluble. Volatile acids accounted for 30 mg/l, but any compounds volatile at 103°C were lost during analysis since VS was used to measure organic matter. In the English study, non-volatiles and volatile acids accounted for about 80 percent of the dissolved carbon. The remaining 20 percent of the carbon was unclassified rather than volatile enough to be lost during the concentration procedures. Thus one can conclude that the volatiles, exclusive of the volatile acids constitute only a very small portion of the soluble organic material.

Specific Compounds Prior to 1972, very few specific compounds had been identified in sewage. Most of the work was limited to amino acids (Painter and Viney, 1959; Hunter and Heukelekian, 1965) and to volatile acids (Viswanathan et al. 1962; Murtaugh and Bunch, 1965; Loehr and Kukar, 1965). The results of the amino acid studies are presented in Table 2.5. The volatile acid analyses generally show the presence of all acids from formic through pentanoic with acetic acid accounting for around 80 percent of the total weight of these compounds.

The only attempt to comprehensively survey the individual components of sewage was conducted in the Southeastern United States by Katz et al. (1972) and Jolley (1973). These investigators used liquid chromatography for initial separation followed by derivitization and GC and MS analysis.

Table 2.3 General Composition of an American Domestic Sewage

Constituent	Settleable		Supra Colloidal		Colloidal		Soluble
	a	b	a	b	a	b	a
Total Grease	11.70*	15.27	9.57	17.25	3.55	12.82	
Free Fatty Acids	0.89	0.46	1.70	0.78	1.48	0.66	22.56
Unsaturated	0.18	0.08	0.24	0.12	0.20	0.12	
Saturated	0.71	0.38	1.46	0.56	1.28	0.54	
Phenols	0.004		0.002		0.002		0.12
Detergents	0.08		0.14		0.10		3.94
Glyceride Fatty Acids	6.46	10.43	4.48	12.76	1.72	8.42	
Unsaturated	1.13	2.49	0.88	1.56	0.24	1.68	
Saturated	5.33	7.94	3.60	11.20	1.48	6.74	
Phospholipids	0.00	0.00	0.02	0.10	0.04	0.08	
Unsaponifiabiles	2.99	2.22	2.16	2.30	1.86	2.42	
Aliphatic	1.92		1.41		1.09		
Aromatic	0.74		0.38		0.26		
Oxygenated	0.34		0.37		0.51		
Total Carbohydrates and Lignin	18.05	19.6	10.60	6.25	6.09	6.57	
Pectin	1.48	0.13	2.16	0.13	1.35	0.57	
Hemicellulose	3.53	2.60	4.32	0.74	1.33	1.40	
Cellulose	11.50	11.8	3.15	0.68	2.43	1.32	
Lignin	1.54	5.12	0.97	0.86	0.98	3.28	
Hexose	0.26		0.13		0.10		9.77
Pentose							0.77
Amino Acids	8.59	15.44	12.84	6.44	5.37	19.52	9.05
Bases							3.24
Amphoterics							4.80
Neutrals	9.45		6.64		3.58		13.59
Cholesterol	0.04		0.02		0.03		0.03
Uric Acid							0.33
Creatine - Creatinine							0.20
Percent Volatile Solids Accounted for	72.5	94.1	77.8	94.5	81.9	95.5	88.2

* All concentrations are in mg/l

a Hunter and Heukelekian (1965)

b Heukelekian (1959)

Table 2.4 General Composition of an English Domestic Sewage^{a,b}

Constituent	Settleable	Supracolloidal	Colloidal	Soluble
Carbohydrates	9.3*	2.5	2.7	28.2
Amino Acids				
Combined	10.0	6.8	8.0	6.9
Free				2.8
Acids Soluble	2.1	2.2	0.8	23.9
Insoluble	26.8	21.8	15.7	
Volatile/non-volatile				10.2/13.7
Esters	16.6	9.1	4.5	0
Anionic Surfactants	1.4	1.0	1.5	10.1
Amino Sugars	0.3	0.1	0.6	0
Urea (as N)				12
Ammonia (as N)				31
Creatinine				2.7
Total Carbon	105	68.2	46.3	90
% Total Carbon				
Accounted For	63.3	63.7	72.2	82.1

* All concentrations are in mg/l carbon, unless otherwise stated.

a Painter and Viney (1959)

b Painter (1971)

Table 2.5 Amino Acid Content of Raw Sewage^a

Amino Acid	Concentration (mg/l)		
	Free	Total	Particulate
Cystine	0-trace	1.4-5.7	1.90
Lystine & Histidine	trace	5.1-9.7	(3.51)
Histidine	present	present	2.03
Lysine	absent/ present	absent present	1.48
Arginine	trace	4.6-11.0	
Serine, Glycine and Aspartic Acid	0.02-0.13	9.4-19.4	1.83/3.39/4.29 (9.51)
Threonine and Glutamic Acid	0.01 -0.18	4.5-24.8	1.85/5.18 (7.03)
Alanine	0.02-0.09	5.1-11.9	4.42
Proline	0	0	
Tyrosine	0.06-0.09	1.7-6.4	1.87
Methionine and Valine	0.05-0.024	0.09-15.7	4.21
Phenylalanine	0.02-0.33	4.7-16.8	5.42
Leucine	0.06-0.28	4.2-13.1	
Tryptophane	present	present	

^a Hunter (1971)

The compounds identified are relatively non-volatile and present in $\mu\text{g/l}$ concentrations. Other studies of more limited scope have been undertaken by Rudolfs and Heinemann (1939), Smith and Gourdon (1969), Bennett et al. (1973), Buehler et al. (1973), Farrington and Quinn (1973), Kolattukudy and Purdy (1973), and Singley et al. (1974). The results of these studies are summarized in Table 2.6.

Spector (1956) and Katz et al. (1968) have compiled a list of the relatively non-volatile compounds in urine and feces along with their excretion rates. This data can be used to estimate the concentrations of these components assuming no loss due to biological activity or physical processes. With the assumptions of an average body weight of forty-five kilograms and an average sewage flow of four hundred litres per capita per day, the concentration in sewage of each component can be estimated by the following formula.

$$\left[\right]_{\text{sewage}} = \frac{\text{Excretion rate (mg/kg)} \times 45 \text{ kg}}{400 \text{ l}}$$

$$\approx \text{Excretion rate (mg/kg)} \times 0.1 \text{ kg/l}$$

eg. cholesterol estimated 0.7 mg/l found 0.3 mg/l

Some idea of which volatile compounds one may expect to find in sewage can be garnered from the studies on urine. Zlatkis et al. (1973a, b, c) used headspace extraction followed by GC - MS analysis and identified about 50 volatile urine components which are listed in Table 2.7. Most of these compounds are present in mg/l to $\mu\text{g/l}$ concentrations in urine (Zlatkis, 1975) and one might expect to find them in $\mu\text{g/l}$ to ng/l concentrations in sewage.

The organic compounds identified in secondary effluents along with their concentrations are summarized in Tables 2.8 and 2.9. A comparison of these concentration values with those for primary effluents will yield some information on removal and/or biodegradability of the constituents. It is interesting to note that removal may be a function of concentration in that volatile acids are 99% removed while some of the trace constituents such as p-cresol and

Table 2.6 Organic Components of Primary Effluent^a

Compound	Concentration $\mu\text{g/l}$	Reference ^d
Aromatics (Benzenoid)		
Phenol	6	2
p-Cresol	20	2
Pentachlorophenol	4	1
2-Hydroxybenzoic Acid	7	2
3-Hydroxybenzoic Acid	40	2
4-Hydroxybenzoic Acid	-	2
4-Hydroxyphenylacetic Acid	190	2
3-Hydroxyphenyl- propionic Acid	20	2
3-Hydroxyphenylhydra- crylic Acid	6	2
Lignins	1500	7
Folic Acid	-	7
Benzoic Acid	-	2
Phenylacetic Acid	10	2
Hippuric Acid	-	5
Hexachlorophene	30	1
Aromatics (Heterocyclic)		
N-Methyl-2-pyridone 5-carboxamide	10	3
N-Methyl-4-pyridone- 3-carboxamide	10	2
Niacin	14	7
Uracil	13	3
5-Acetyl-6-amino- 3-methyl uracil	30	3
Thymine	7	2
Thiamine	29	7
Inosine	50	2
Orotic Acid	5	2
T Theobromine		3
q Caffeine	10	2
Xanthine	70	2
Hypoxanthine	25	2
1-Methylxanthine	17	2
3-Methylxanthine	-	3
7-Methylxanthine	-	3
1,7-Dimethylxanthine	-	3

Table 2.6 cont'd.

Compound	Concentration	Reference
Uric Acid	20	2
Guanosine	50	2
Adenosine	--	2
Riboflavin	22	7
Urocanic Acid	--	2
Indican	2	2
Cobalamin	0.8	7
Unsaturates		
Oleic Acid	17000 ^b	7
Linoleic Acid	10000 ^b	7
Biotin	3	7
Pantothenic Acid	--	7
Ascorbic Acid	--	7
Cholesterol	300	7
Saturates		
Formic Acid	--	5
Acetic Acid	10000	5
Propionic Acid	2600	5
Butyric Acid	1000	5
Pentanoic Acid	400	5
Lauric Acid	120 ^b	7
Myristic Acid	240 ^b	7
Palmitic Acid	11700 ^b	7
Stearic Acid	4600 ^b	7
Lactic Acid	--	5
Pyruvic Acid	--	7
Glycollic Acid	--	5
Oxalic Acid	--	7
Glutaric Acid	--	5
Citric Acid	--	5
Succinic Acid	--	2
Cutin	-- ^c	4
Glycerine	--	2
Corprostanol	100	7
5 β -Cholestan-3 β -ol	--	6
Allulose	--	3
Glucose	--	2
Galactose	--	2
Mannose	--	3
Fructose	--	3
Rhamnose	--	3
Sorbose and/or xylose	--	3
Arabinose	--	3
Ribose	--	3

Table 2.6 cont'd.

Compound	Concentration	Reference
Sucrose	--	3
Maltose	--	2
Lactose	--	3
Muramic Acid	--	2

a. See also Table 2.5.

b. Concentration found in whole sewage, concentration in effluent is unknown but probably 1-3 orders of magnitude lower.

c. Identified in sludge only.

d. References

1. Buehler et al. (1973)
2. Katz et al. (1972)
3. Jolley (1973)
4. Kolattukudy and Purdy (1973)
5. Painter and Viney (1959), Painter et al. (1961)
6. Smith and Gourdon (1969)
7. Hunter (1971)

Table 2.7 Volatile Components of Normal Human Urine^a

Component

Chloroform
 Ethanol
 1-Butanol
 Propionaldehyde
 Furfural
 Acetone
 2-Butanone
 3-Methyl-2-butanone
 2,3-Butanedione
 2-Pentanone
 3-Methyl-2-pentanone
 4-Methyl-2-pentanone
 3-Methylcyclopentanone
 3-Hexanone
 5-Methyl-3-hexanone
 2-Heptanone
 4-Heptanone
 6-Methyl-3-heptanone
 3-Octanone
 2-Nonanone
 Piperitone
 Carvone
 3-Penten-2-one
 4-Methyl-3-penten-2-one^b
 Thiolan-2-one^b
 Toluene
 p-Methyl propenylbenzene^b
 Benzaldehyde
 p-Cresol
 2,3-Dimethylfuran
 2,4-Dimethylfuran
 2-Methyl-5-Ethylfuran
 2,3,5-Trimethylfuran
 C₄-Furan
 2-n-Pentylfuran
 Acetylfuran
 Pyrrole
 1-Methylpyrrole
 2-Methylpyrrole
 Dimethylpyrrole
 1-Butylpyrrole^b
 Methylpyrazine
 2,3-Dimethylpyrazine
 2,5 or 2,6-Dimethylpyrazine
 2,3,5-Trimethylpyrazine
 2-Methyl-6-ethylpyrazine
 Vinylpyrazine
 2-Methyl-6-vinylpyrazine
 β-Pinene
 Allylisothiocyanate

Table 2.7 cont'd.

Component

Dimethyldisulphide

a Zlatkis et al. (1973 b,c)

b Identification is tentative

Table 2.8 General Composition of Secondary Effluent^a

Component	Percent by Weight of Organic Matter
Humic Acids	40 - 50
Fulvic	23
Humic	11
Hymanthomelanic	8
Ether Extractables	8
Anionic Detergents	14
Carbohydrates	12
Proteins	22
Tannins	2

a Rebhum and Manka (1971); Manka et al. (1974)

Table 2.9 Organic Components of Secondary Effluents

Compound	Concentration $\mu\text{g/l}$	Reference
Carbohydrates	2-50	1
Glucose		
Fructose		
Sucrose		
Mannose		
Allulose		
Xylose		
Raffinose		
Glycerine		2
Formic Acid	10	1
Acetic Acid	20	1
Propionic Acid	5	1
Butyric Acid	10	1
Iso-butyric Acid	10	1
Iso-valeric Acid	50	1
Caproic Acid	10	1
Uric Acid	10	1
Polycyclic Aromatics		1
Pyrene		
Perylene	1	
Benzopyrenes		
DDT	0.1	1
BHC	0.1	1
Dieldrin	0.1	1
Uracil	30	2
5-Acetylamino-6-amino-3-Methyl uracil	30	2
Inosine	20	2
1-Methyl Inosine	80	2
1-Methyl Xanthine	6	2
7-Methyl Xanthine	5	2
1,7-Dimethyl Xanthine	6	2
p-Cresol	90	2

1. Painter (1973)

2. Jolley (1973)

methyl xanthine are hardly removed at all.

2. Inorganics

The main purpose of reviewing the inorganic composition of sewage effluents is to assess their effects upon the aqueous chemistry of chlorine through various complexation reactions with both organics and species containing Cl^+ . In view of the voluminous amount of literature available and the complexity of primary effluent as a chemical system, this review will only attempt to estimate the amounts of inorganics available for such interactions.

The inorganic compositions of whole sewages were reviewed by Painter (1971). Tanner *et al.* (1973) and Koch *et al.* (1976) have surveyed the concentrations of some heavy metals in Vancouver sewages and treatment plant effluents. A sample of unchlorinated effluent from Lion's Gate Treatment Plant was surveyed in this study and the results are presented in Table 2.10 are similar to those of the other studies. In order to estimate the amount of each constituent actually available to influence the chlorination process, ratios of dissolved/total calculated from the data of Heukelekian and Balmat (1959) are also included in Table 2.10.

C. A Simplified Model of the Chlorination Process

The Process in the Sewage Treatment Plant

The mechanics of effluent chlorination have been discussed in detail by White (1971). The first step involves the preparation of a concentrated solution of chlorine from either chlorine gas or chlorinated lime. This concentrated solution is then added to the treatment plant effluent. In some plants the final effluent is dechlorinated with sulphur dioxide.

Chemical Model

The purpose of this model is to estimate the concentrations of species containing Cl^+ . The importance of these species lies in their ability to react with organics to form stable carbon - chlorine bonds. There are many

Table 2.10 Inorganic Composition of Lion's Gate Effluent

Component	Total Concentration mg/l	Fraction Dissolved/Total ^a
Al	0.095 ^c	0.12
As	<0.006	
B	<0.05	
Ba	<0.02 ^c	
Be	<0.05	
Ca	8.7 ^c	0.88
Cd	<0.001 ^c	
Cl	28	
Co	<0.005 ^c	
Cr	0.011 ^c	
Cu	0.10 ^c	0.92
F ⁻	0.07	
Fe	1.05 ^c	0.35
Hg	<0.002 ^c	
K	6.7 ^c	0.95
Mg	2.98 ^c	0.96
Mn	0.04 ^c	0.94
Mo	<0.02 ^c	
NH ₃ -N	15 ^b	
Ni	0.011 ^c	
Pb	0.013 ^c	0.0
Se	0.008 ^c	
Si	2.8	0.11
Ti	<0.2 ^c	
V	<0.07 ^c	
Zn	0.105 ^c	0.0

a For primary effluent as opposed to whole sewage as calculated from data of Heukelekian and Balmat (1959)

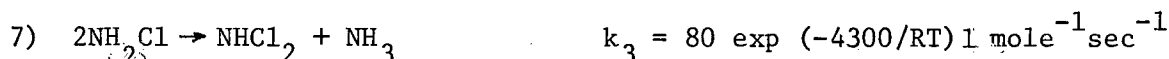
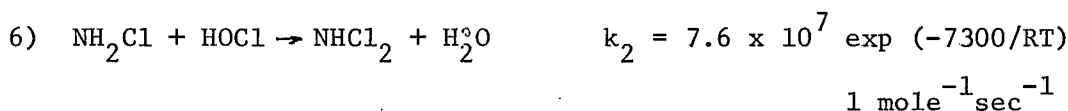
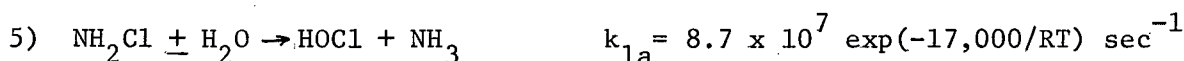
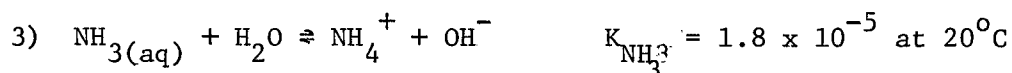
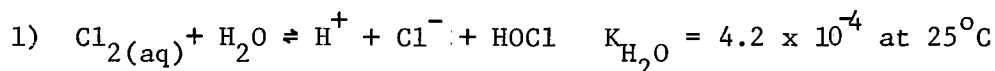
b GVRD data

c Total HCl - HNO₃ digestible

components and factors which should be included in the model. These include the sources of chlorine, the solvent, ammonia, other inorganics, particulates, organics, pH, reaction time, mixing, temperature and sunlight.

In order to keep the model simple only three factors will be considered.

- 1) the hydrolysis of chlorine, 2) the dissociation of hypochlorous acid, and
- 3) the reactions of chlorine and hypochlorous acid with ammonia to form chloramines. The following equilibria and reactions will be used.



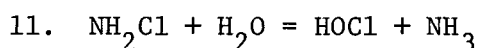
From $K_{\text{H}_2\text{O}}$ it can be seen that at pH 4 all of the chlorine is in the form of hypochlorous acid. Now if $A = [\text{HOCl}] + [\text{OCl}^-]$

$$B = [\text{NH}_3] + [\text{NH}_4^+]$$

$$\text{then } 8. \quad [\text{HOCl}] = A \left[\frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{HOCl}}} \right]$$

$$9. \quad [\text{NH}_3] = B \left[\frac{[\text{OH}^-]}{[\text{OH}^-] + K_{\text{NH}_3}} \right]$$

Since $k_1 \gg k_2, k_3$ the concentration of monochloramine is to a rough approximation independent of the concentration of dichloramine. From the equilibrium



it can be seen that

$$12. \quad [\text{NH}_2\text{Cl}] = \frac{k_1}{k_{1a}} [\text{HOCl}][\text{NH}_3]$$

From equations 6 and 7 it can be seen that

$$13. \quad [\text{NHCl}_2]_t = k_2 t [\text{NH}_2\text{Cl}][\text{HOCl}] + k_3 t^2 [\text{NH}_2\text{Cl}]^2.$$

The final concentrations of hypochlorous acid and hypochlorite ion can be calculated as follows:

$$14. \quad [\text{HOCl} + \text{OCl}^-]_{\text{final}} = [\text{HOCl} + \text{OCl}^-]_{\text{initial}} - [\text{NH}_2\text{Cl}] - [\text{NHCl}_2].$$

The individual concentrations of the acid and ion can be calculated from equation 8.

From these equations a solution of the initial composition: $[\text{NH}_3\text{-N}] = 1 \times 10^{-3}\text{M}$, $[\text{total Cl}^+] = 1 \times 10^{-3}\text{M}$; pH = 7.0; and reaction time = 10 minutes; will have the following final composition:

$$[\text{NH}_2\text{Cl}] \sim 10^{-3}\text{M}; [\text{HOCl}, \text{OCl}^-] \sim 1 \times 10^{-7}\text{M}; \text{ and } [\text{NHCl}_2] \sim 5 \times 10^{-5}\text{M}.$$

Limitations of the Model

There are many limitations to this model. The most important are that the reduction of Cl^+ to Cl^- through reaction with reducing agents and the decompositions of the chloramines to nitrogen gas and other products have not been included. Other less important factors not included are 1) formation of chlorine hydrate, 2) decomposition reactions of hypochlorous acid and hypochlorite ions, and 3) the formation of other N-chloro compounds. These factors are discussed in Appendix I.

Validity of the Model

Palin (1950) and Isomura (1967) have conducted studies on the compositions of dilute ammonia - chlorine solutions in distilled water. At ammonia/chlorine mole ratios of 1:1 both investigators found that the ammonia was almost totally converted to monochloramine. Unfortunately due to the detection

limits of the analytical methods no quantification of dichloramine and hypochlorous acid could be made.

A general feeling for the validity of the aqueous ammonia-chlorine system as a model of the primary effluent-chlorine system can be obtained from the plots of residual chlorine against added chlorine for the two systems. The plot for the aqueous ammonia-chlorine system was called the 'breakpoint curve' by Griffin and Chamberlain (1941a,b). An example of the plot for a primary effluent-chlorine system can be found in the study by McKee et al. (1960). The overall shapes of the two curves and the forms of the residuals are similar which indicates that the model is essentially valid. There are however, two differences between the curves in the region of the chlorine/ammonia ratio normally used in sewage treatment plants. Firstly, primary effluent instantaneously consumes $0.4 - 1.1 \times 10^{-3}$ moles/l of Cl_2 while the ammonia system has no instantaneous demand, and secondly, with primary effluent the slope of the line is between 0.82 and 0.92 rather than 1.0 as noted in the ammonia-chlorine system. In other words, primary effluent dosed with 28 mg/l of Cl_2 will consume 4.9 - 11.2 mg/l Cl_2 in fifteen minutes. The instantaneous consumption of 2.8 - 8.7 mg/l is probably due to oxidations of inorganics and/or some very rapid reactions with organics. The slower consumption of 2.1 - 3.5 mg/l as manifested in the differences in slopes tentatively suggests the occurrence of oxidation and substitution reactions with organics.

In summary, the form of the residual chlorine in a treatment plant is essentially mono and dichloramines as was predicted by the simple model. The value of a more refined model which includes minor interactions is tempered by the tremendous complexity of the chlorine-primary effluent system. There is some indication that reactions of Cl^+ sources with organics do occur.

D. Reactions of Chlorine With Organics in Aqueous Media

1. Reactions With Nitrogenous Compounds

Engineering Oriented Studies Taras (1950, 1953) conducted a comprehensive study of the chlorine demands and nitrogen losses of amino acids as well as some proteins and other compounds. Smaller studies were conducted by Wright (1926), Norman (1936), and Palin (1950). Strict comparison of the behaviour of these compounds to chlorine is not possible on the basis of these studies due to the differences in Cl/N ratios and analytical problems. From the results of Taras (1950, 1953) however some general trends can be observed with initial mole ratios of 4:1 (Cl/Albuminoid-N) and near neutral pH: a) primary α and β -amino groups, mercapto and thioethereal groups all consume two mole equivalents of Cl_2 in fifteen minutes, b) the δ and ϵ -amino groups and peptide linkage nitrogen atoms react very slowly with chlorine, c) aromatic substitution of chlorine probably occurs in tyrosine and tryptophane, and d) losses of nitrogen in a one hour occur only for α and β -amino acids and range from 25 to 50 percent. Zaloum (1973) investigated the reaction of varying dosages of chlorine on some amino acids and other compounds. At mole ratios of less than 2:1 (Cl/N) no loss of chlorine residual was observed except in the case of histidine. His result for histidine indicates that electrophilic addition or substitution to carbon probably occurs. He also demonstrated that with Cl/Glycine mole ratios greater than 21:1 oxidation of glycine with loss of carbon occurs.

Pure Chemistry Oriented Studies A concise picture of N-chlorination of amines was presented by Morris (1965) in the form of a Brønsted type plot of pK_b vs $\log k_u/k_r$, where k_u and k_r are the respective competitive molecular reaction rate constants of HOCl with the amine and ammonia. A good linear correlation with a slope of 0.5 was obtained. It should be noted however that ammonia itself showed a significant deviation of the type usually attributed to steric hindrance.

Investigations by Dakin (1916) among others indicated that the reaction of α -amino acids with NaOCl and other chlorinating agents results in deamination and/or decarboxylation to form the corresponding aldehyde or nitrile. A study

by van Tamelen et al. (1968) yielded the following: a) with dimethylglycine decarboxylation occurs most readily with a pH of 1.5 and a Cl/N mole ratio of 2:1, carbon dioxide, formaldehyde, and chlorodimethylamine were identified as products, b) decarboxylation most likely involves N-chlorination rather than formation of the acyl hypochlorite and definitely involves a trans, coplanar arrangement, and c) other complex reactions also occur with compounds such as tryptophan. Patton et al. (1972) present the following observations on the aqueous chlorination of cytosine: at a 1:1 mole ratio only 4,N-chlorination occurs, b) at a 2:1 mole ratio Cl/Cytosine the 4,N-chloro (I), 4,N-chloro, 5-chloro (II), 4,N-chloro, chlorohydrin (III), and 1,4N-dichloro-chlorohydrin (IV) were all formed, c) increasing the Cl/Cytosine mole ratio increased the yield of III and IV and at a 5:1 mole ratio a tetrachloro derivative was formed which decomposed on standing to I and II. Subsequent investigations by Pereira et al. (1973) at pH 4 and a 2:1 Cl/substrate mole ratio with some amino acids and dipeptides yielded the following: a) with tyrosine only the ring chlorinated aldehyde or nitrile rather than the ring chlorinated amino acids were observed which conflicts with the claims of Thompson (1954), b) with L-phenylalanine the nitrile/aldehyde ratio was 95/5, c) with glutamic acid only the carboxyl group alpha to the amino group was removed d) only terminal N-chlorination is observed with dipeptides with possible decomposition of the dichloramine to a chlorimine and e) no N-chlorination is observed with N-acetyl L-alanine; f) with cysteine only oxidation of the sulphur to cysteic acid and some dimerization to cystine was observed, cystine was oxidized to cysteic acid. Additional studies on the reaction of other organic sulphides with chlorine are discussed by Baker et al. (1946).

Hoyano et al. (1973) studied the reactions of some uracils and purines with aqueous hypochlorous acid at HOCl/substrate mole ratios of 2 and 4:1. With the uracils, N-chlorination preceded electrophilic substitution. The purines yielded 20-90 percent parabanic acids in seven days. Thus oxidative

degradation may be an important reaction with these compounds.

A somewhat special case is observed in the chlorination of cyanuric acid, (Brady et al., 1963; Sancier et al., 1964) where N-chlorination occurs only in the keto-tautomer. The stability of the N-chlorinated keto-tautomer combined with the facile release of chlorine from the enol and the fact that there are three tautomeric sites on the triazine ring has made cyanuric acid an important "chlorine stabilizer" in swimming pools (Gardiner, 1973; Canelli, 1974).

2. Reactions of Chlorine with Other Organics

Introduction The reactions of chlorine with organics can be classified into four groups: nucleophilic attack of Cl^- , electrophilic attack of Cl^+ , photochemical, and oxidation reactions. Excellent reviews of chlorination reactions in pure systems have been published by House (1965), Eisch (1966), Buehler and Pearson (1970) and Dorn (1972). In reading these reviews, it must be kept in mind that most of the yields quoted have been optimized. Furthermore, a yield of less than one percent is usually insignificant to a classical synthetic chemist whereas such a yield may be very important to an environmental chemist. Therefore a brief summary of conditions in a treatment plant is provided in Table 2.11 in order to obtain a feeling for the relative importance and possible magnitudes of these reaction groups in primary effluent. These groups will now be discussed in the most probable order of importance.

Oxidation Reactions These reactions have been reviewed by Barker (1964). The mechanisms are not completely understood. In most cases oxidation with HOCl is as rapid as with molecular Cl_2 however, factors such as acid and base catalysis, the greater propensity to oxidation of anions, e.g. formic acid, and hydrate formation e.g. aldehydes make generalization somewhat tenuous. It is well known that aldose sugars are oxidized to acids by hypochlorite. Several investigations of the oxidation of aromatic rings have been carried out. In acidic solutions, Van Buren and Dence (1967) working with lignin model compounds estimated that 20 - 80% of the products are oxidation rather than sub-

Table 2.11 Summary of Reaction Conditions for Organics in Sewage

a. Conditions in the Main Body of Water

Component	Remarks
Solvent	Water
Buffers	Acetic acid/Acetate Carbonate/Bicarbonate
pH	6.5 - 8.5
Temperature	2-12°C
Mixing	Variable
Cl ₂ /HOCl/OCl ⁻	Approximately 50/50 in HOCl/OCl ⁻ very little of each available
NH ₃	Partially converted to chloramines [Total Cl ⁺]* = 10 ⁻⁴ M
Cl ⁻	~10 ⁻³ M
Br ⁻	~10 ⁻⁴ M
Organic compounds	[Individual] ~10 ⁻⁶ - 10 ⁻⁴ M [Total] ~10 ⁻³ - 10 ⁻⁴ M
Bacteria	~10 mg/l
Heavy metals	0.001 - 10 mg/l
Reaction time	20 - 50 minutes

b. Conditions at the Surface

Component	Remarks
Solvent	Floating organics = 0.1 - 2.0% of the area Polywater?
Temperature (air)	2 - 37° C
Reaction time	15 - 30 minutes
UV light	Variable, direct sunlight sometimes variable
Cl ₂	Possibly present
Chloramines	Present
Organics	Abundance of some types is greater at the surface

* "Cl⁺" refers to all species containing chlorine in the +1 oxidation state as opposed to hydrated Cl⁺ ions. No Cl⁺(aq) is expected to be present (Swain and Crist 1972).

stitution or displacement products, while Vollbracht et al. (1968) determined that exhaustive chlorination of some other phenols yielded chlorinated cyclohexenones. In neutral solutions, EPA (1972) postulated ring cleavage of phenols. In basic solution, Moye and Sternhell (1966) state that phenol is converted to a chlorinated cyclopentane carboxylic acid probably by a Favorskii rearrangement and oxidation of the cyclopentenone intermediate.

Electrophilic Reactions Aromatic electrophilic substitutions of chlorine for hydrogen using sodium hypochlorite were reviewed by Hopkins and Chisholm (1946) and Soper and Smith (1926). The kinetics of the aqueous chlorination of phenol were investigated by Burttschell et al. (1959), and Leeland Morris (1962) among others. Eliasek and Jungwirth (1963) studied the exhaustive chlorination of phenol, ortho-cresol and pyrocatechol by sodium hypochlorite. They found that the completely o,p substituted phenol is initially formed followed by oxidation to a chloroquinone. The chloroquinone was then either further chlorinated, or in the presence of light, converted to a hydroxychloroquinone which polymerized at pH > 7 to humic acid type compounds. An unspecified type of oxidative decomposition was observed in the case of pyrocatechol to the extent of 60 percent. Van Buren and Dence (1967) observed the substitutive displacement of the propyl moiety from guaiacyl ethyl carbinol and veratryl ethyl carbinol.

Electrophilic addition is known to occur in aqueous solution or suspension, eg. Emerson (1945). Investigations by Gunstone and Pereira (1973) among others demonstrated that halogenation of unsaturated fatty acids and alcohols of the appropriate stereochemistry can respectively yield significant amounts of halogenated oxolanes and oxanes. Hawkins (1973) patented a process for the production of anone, NaOCl and an ammonium salt for the production of anone.

Photochemical Reactions Meiners and Morriss (1964) studied the effect of UV irradiation on the chlorine oxidation of starch in acidic aqueous solution. More recently Kobayashi and Okuda (1972) found significant photochemical up-

take of chlorine by a large number of compounds in dilute aqueous solution. Catalysis by Hg(II) and Pb(II) was also noted.

Nucleophilic Reactions Due to the competitive hydrolysis reactions, nucleophilic substitutions are unlikely to play an important role in sewage effluents. It should be noted however that halide exchanges involving the addition of chloride will make the compound more stable with respect to hydrolysis.

3. Reactions of N-Chloro Compounds with Organics

It has been noted by Burttschell et al. (1959) and others that the rate of chlorination of phenol in the presence of ammonia is very slow. Zaloum (1973) observed oxidative type chlorination reactions of amino acids by chloramines.

The classical mechanism of chlorination involves catalysis by acid and chloride with the limiting step being the dissociation of the chloramine to the amine and molecular chlorine, e.g. Hurst and Soper (1949). Some evidence has been presented for the direct chlorination (electrophilic substitution) by morpholinum ions (Carra and England (1958), dichloramine-T (Higuchi and Hussain, 1967)), and diethylchloramine (Brown and Soper (1953). An important facet of the investigation of Brown and Soper is that rate of chlorination of phenols with N-chlorodiethyl amine at neutral pH is 10^3 times greater than that of chlorination with HOCl probably due to the significant amounts of $\text{RR'NCI}^+\text{H}$ present. Onuska (1973) was unable to detect diethyl amine in sewage, although Rains et al. (1973) tentatively identified a series of alkyl amines in sludges. West and Barret (1954) observed the production of 5-chlorouracils from the reactions of some uracils with N-chlorosuccinimide in acetic acid. Chlorination of styrene by monochlorourea was discussed by Hanby and Rydon (1946). The alpha-chlorination of unsymmetrical benzylic sulphides with N-chlorosuccinimide in carbon tetrachloride was observed by Tuleen (1967). Substituted hydrazines have been prepared from chloramine and a substituted amine (Audrieth and Diamond, 1954; Diamond and Audrieth, 1955), or by other chlorinating agents

(Audrieth et al., 1956, Colton et al., 1954). Hawkins (1973) patented the use of cyclohexanone, NaOCl and an ammonium salt for the production of 1 - chloro-amino cyclohexanol. Other examples of the reactions of chloramines can be found in the reviews by Drago (1957) and Kovacic et al. (1970).

Free radical addition of chloramines to unsaturated compounds in $H_2SO_4/HOAc$ resulting in β -chloroamines has been noted (Kovacic et al., 1970). Gas phase reactions tend to yield only chlorinated products (Prakash and Sisler, 1970).

E970) The Effects of Chlorine on Sewage Effluents

1. Practices in Treatment Plants

The latest estimates of chlorine usages in the United States (JWPCF, 1974) are 1.87×10^5 tons/year for wastewater, 2.5×10^5 tons/year for water supplies and 2.1×10^4 tons/year for swimming pools. The composition of gaseous chlorine was discussed by Laubusch (1959). The purity is 99.5% or better with the major impurities being N_2 and CO_2 although some halogenated methane, ethane and benzene derivatives may be present in ppm quantities.

The uses of chlorine in wastewater treatment have been described by White (1972). The dosage applied varies according to the strength of the effluent. For example, during the night when the sewage is essentially infiltration, only 1 - 2 mg/l Cl_2 may be added while during peak loads and, especially during dumping of digestors, 30 mg/l Cl_2 may be added to the effluent. Contact times vary from 0.25 to 0.5 hr depending upon the flow and length of line between the plant and receiving water. The combined chlorine residuals in the effluents range from 0.0 to 5.0 mg/l depending on the time of year and whether or not dechlorination is practiced. Free residual chlorination is not the usual practice.

2. Biological Effects of Residual Chlorine

Disease Control The historical trends of water borne disease outbreaks have been reviewed by Craun (1972), Craun and McCabe (1973) and Kittrell and Furfai, (1963). There can be no doubt that chlorination of water supplies has

32
effected a significant decrease in diseases, however a total eradication has not occurred. The effect of waste-water chlorination on disease outbreaks has not been documented and is very difficult to establish. The effects of chlorination of effluents on coliform counts at a beach in the receiving water are ambiguous due to regrowth of coliforms and various environmental factors affecting dieoff (Kittrell and Furfai 1963). In addition, Silvey et al. (1974) found salmonellae bacteria in chlorinated effluents and receiving water.

Toxicities to Various Forms of Life The addition of material to an ecosystem can cause population changes due to specific or general toxicity, carcinogenicity, mutagenicity, teratogenicity, behavioural modification or its being a specific limiting nutrient. Toxicity of residual chlorine is a function of pH, temperature, form of the residual and other factors. In addition, toxic and other detrimental effects can be complicated due to synergistic and antagonistic effects (Longbottom, 1972; Ongerth, 1973). Studies or reviews of the toxicities of residual chlorine have been undertaken by Merckens (1958), Zillich (1972), White (1972) and Brungs (1973).

Microorganisms (Bacteria, Viruses and Algae). The effect of chlorine on sewage bacteria, especially coliforms has been discussed by Fair et al. (1948) and Heukelekian and Faust (1961) among others, and reviewed by White (1972). Although it is a function of pH, effective control (99.9% kill) of bacteria requires 0.1 to 5.0 mg/l combined residual for 10 minutes, while viruses require 0.2 - 0.5 mg/l free residual.

In receiving waters, regrowth is a function of many factors including temperature, pH, and nutrients. Kittrell and Furfai (1963) state that a regrowth of 4 to 8 times the original population of coliforms occurred in 0.5 days followed by a decline. Salmonellae, fecal coliforms, and fecal streptococci do not appear to exhibit this regrowth in surface waters (Silvey et al., 1974).

Inhibition of algal growth was effected by 0.15 - 3.0 mg/l (McKee and Wolf, 1971). Studies by Kott (Kott and Edlis, 1969; Betzer and Kott, 1969; Kott, 1969) showed that chlorine is algistatic to chlorella pyrenoidosa and C. sorokiniana at 0.4 mg/l and to cladophora sp. at about 1 mg/l. He also showed that 10 mg/l residuals of chlorine are necessary to kill these species while bromine or a mixture of chlorine and bromine killed chlorine resistant algae eg. Cosmarium and other algae at residuals of 0.4 to 2.0 mg/l total halogen. In addition he noted that the availability of light and the timing of dosages also affect the toxicity.

Invertebrates. Some values for toxic levels of residual chlorine taken from McKee and Wolf (1971) are chironomous (Blood worms) 15 - 50 mg/l, chironomous larvae 0.65 mg/l in 24 hrs., mussels, snails, sponges 2.5 mg/l, nematodes 95 - 100 mg/l, and shellfish pumping rates are reduced by 0.01 - 0.05 mg/l. Daphnia were killed in 48 hrs. by 4 mg/l of chlorine. Other studies have been conducted by McLean (1973) on the combined effects of chlorine and temperature and were inconclusive.

Fish. From the reviews by Brungs (1973), McKee and Wolf (1971) and Zillich (1972) it can be stated that toxic effects range from Brown trout exposure to 0.04 mg/l free Cl_2 for 2 minutes results in 100 % mortality in 24 hrs., to white suckers, 1.0 mg/l free Cl_2 is lethal in 0.5 to 1.0 hrs. White (1972) correlates this to scale size. Other effects such as "depressed activity" in brook trout are observed at concentrations as low as 0.005 mg/l free Cl . Servizi and Martens (1974) and Martens and Servizi (1974) working with various types of effluents found mortalities of salmon and rainbow trout at combined residuals of 0.02 mg/l which is the detection limit of the amperometric titrator. They also found evidence of gill damage after prolonged exposure to chlorine and that Coho salmon do not necessarily avoid areas containing lethal (1.3 mg/l) concentrations of chlorine.

Plant Life. The effect of chlorine on plant life in aquatic systems is essentially unknown. A study on kelp indicated 5 - 10 mg/l significantly reduces photosynthetic activity (McKee and Wolf, 1971).

Mammals. Muegge (1956) reports that humans have high tolerances for residual chlorine. Concentrations of 50 mg/l and higher in the form of free chlorine have no acute toxic effects. It should be noted however that allergic - type responses have been reported (Watson and Kibler, 1934), and that eye irritations have also been observed at concentrations of 0.5 mg/l (McKee and Wolf 1971).

3. Toxic Effects of Chlorinated Organics

A large volume of information is available on the toxic effects of industrially produced chlorinated organics. The acute toxic effects of these compounds have been reviewed by Fishbein and Flam (1972) and Gribble (1974). Their mutagenic effects were reviewed by Fishbein (1973b) while Miller (1974) discussed some teratogenic effects. A study by Das et al. (1969) showed that various chlorocatechols and chloro-o-benzo-quinones from bleached kraft chlorination effluent had 1-3 hr LC_{100} values of about 20 mg/l for young Salmo salar (Atlantic Salmon). Preliminary studies by Gehrs et al. (1974) on 4-chlororesorcinol and 5-chlorouracil indicated deleterious effects on hatching of carp eggs occur at concentrations of 0.1 and 5 mg/l respectively. While it is obvious that some chlorinated compounds are very toxic, the important question relating to the chlorination of sewage is whether halogenation or oxidation of an organic compound makes it more toxic to aquatic life. In considering this question it is useful to separate two facets of acute toxicity 1) the numerical values expressing the toxicity of a particular compound to an organism and 2) the structural features of a molecule which tend to make it toxic.

An example of the first facet is the comparison of the toxicities of a series of benzene derivatives to aquatic life Table 2.12. Two problems arise when attempting to compare the toxicities of different compounds by a liter-

Table 2.12 Toxicities of Selected Compounds to Aquatic Life^a

Compound	Organism	Toxicity	
		Criterion	Concentration ^b
Benzene	Sunfish	LC	46
"	Mosquito Fish	48 hr TLM	490
"	Rainbow Trout	LC ₁₀₀	13-26
o-Dichlorobenzene	Fish	LC ₅₀	2.2
p-Dichlorobenzene	Fish	LC ₁₀₀	34
Phenol	Goldfish	MTE ^c	1.00 ^c
2,4-Dichlorophenol	"	"	1.58 ^c
m-Chlorophenol	"	"	2.10 ^c
p-Chlorophenol	"	"	2.58 ^c
Phenol	Bluegill Sunfish	48 hr TLM	21
o-Chlorophenol	Bluegill Fingerlings	96 hr TLM	6.6
Pentachlorophenol	Various Fish	24 hr TLM	0.75-0.22
Benzoic Acid	Mosquito Fish	TLM	200
"	Goldfish	7-96 hr	
		LC ₁₀₀	160
2,3,5-Trichlorobenzoic Acid	Large Mouth Bass	24 hr TLM	67
2,3,6-Trichlorobenzoic Acid	Large Mouth Bass	24 hr TLM	670
Phenol	Daphnia	MLD	17
"	Scenedesmus (Alga)	"	43
"	Microregma		
"	(Protozoan)	"	32
"	E. Coli (Bacterium)	"	1100
Quinone	Daphnia	"	0.37
"	Scenedesmus	"	5.5
"	Microregma	"	0.18
"	E. Coli	"	46
Hydroquinone	Daphnia	"	16
"	Scenedesmus	"	7.3
"	Microregma	"	45
"	E. Coli	"	27
Toluene	Daphnia	"	6.5
Benzyl Alcohol	"	48 hr MLD	33
Benzoic Acid	"	prolonged	
		MLD	12

a. From McKee and Wolf (1971) unless otherwise indicated

b. Units are 10^5 times moles per litre unless otherwise indicated

c. Data from Gersdorff and Smith (1940); MTE = maximum toxic effect expressed in units of $1 \text{ mole}^{-1} \text{ min}^{-1}$ normalized to phenol; a larger number indicates a greater toxicity.

ature review. The first problem is that toxicities are reported in units of mg/l. While the numbers generated from the use of these units are indicative of the absolute toxicities of the compounds, they do not reflect the relative toxicities of a series of compounds on a molecule for molecule basis. Therefore for this review toxicity values have been converted to units of moles per litre. The second and more serious problem arises out of the non-standardized conditions used in the generation of toxicity data. As a result of this problem it is presumptuous to arbitrarily establish a minimum difference between the toxicity values for two compounds which must be considered significant.

A study of the second facet of toxicity is furnished by Table 2.12 as well as the reviews of the industrially produced chlorinated organics. From Table 2.12 it appears that chlorination or oxidation increase the toxicity of the compound only in certain cases and that toxicity is related to position of substitution and numbers of chlorine atoms present. From other studies it appears that although the toxicity cannot be easily predicted from structure the two are related. Important factors or coincidental properties appear to be:

- a) stability with respect to degradation, e.g. DDT, aldrin
- b) position of chlorine substitution, e.g. chlorinated dibenzodioxins;
- c) other forms of stereoisomerisms, e.g. BHC;
- and d) water solubility e.g. dichlorobenzenes

(McKee and Wolf, 1971).

Sublethal effects such as interference with or duplication of pheromones and alarm substances (Vallentyne, 1967) are probable but have not been investigated. These sublethal effects may be even more important than acute toxic effects due to the low concentrations of organics in primary effluents.

4. Chemical Effects of Chlorination

Engineering Studies The reactions with oxidizable inorganics have been previously discussed. Oliver et al. (1974) noted the solubilization of heavy metals from sewage sludges exhaustively chlorinated. This effect is probably

due to pH reduction rather than oxidation by chlorine.

Apart from the breakpoint curve, some investigators have noted a BOD reduction of the dechlorinated sewage. A recent investigation by Zaloum (1973) refutes these claims and postulates that the observed changes in BOD_5 were due to differences in initial microbial population during the BOD test. He did not observe any detectable reduction in TOC upon chlorination.

Chemical Studies The first major studies of the effects of chlorine on organics in wastes dealt with kraft mill bleaching wastes (Van Buren et al., 1969; Das et al., 1969; Rogers and Keith, 1974). Chlorinated quinones and phenols were found in these effluents.

A major investigation of the effects of chlorination on municipal treatment plant effluents was undertaken by Jolley (1973). He limited his investigation to the relatively non-volatile compounds and investigated the following areas:

1) primary effluent -

- a) the effects of various dosages of non-radioactive chlorine
- b) the magnitude of the uptake of radioactive chlorine by organics at a dosage of 26 mg/l Cl_2
- c) the separation and identification of the chlorinated compounds formed during chlorination.

2) secondary effluent

- a) the magnitude of the uptake of radioactive chlorine by organics and inorganics
- b) the effects of dechlorination upon chlorine uptake
- c) an evaluation of the effects of using NaOCl instead of Cl_2 (g) upon chlorine uptake
- d) the identification of chlorinated compounds formed during chlorination.

His concentration procedure involved rotary evaporation followed by lyophilization. Separation was accomplished by anion exchange liquid chromatography with a UV detector and continuous fraction collector for the radioactivity counts and cation exchange LC. Identification was based on chromatographic retention time. The most striking result of Jolley's experiments with non-radioactive chlorine and primary effluent was the disappearance of UV absorbing compounds with increasing dosages of chlorine. Several new peaks were also observed in the chlorinated samples. Some important results of his radioactivity work are as follows. Forty-nine of the sixty-two radioactive compounds appeared at similar concentrations in both primary and secondary effluents. Between 44 and 52 radioactive peaks were observed in the individual chromatograms, at a detection limit of about $50 \text{ ng/l } ^{36}\text{Cl}$ in unconcentrated sewage. The concentrations of the individual compounds ranged from 0.1 to $15 \mu\text{g/l}$ as chlorine in sewage. He found that reaction time only slightly affects the yields of chlorinated compounds while the form of the applied chlorine affects the formation of at most six compounds. Dechlorination had no significant effect upon the number of stable organo-chlorine compounds formed. A very important calculation showed that about 0.6 percent of the applied chlorine eluted in peaks other than chloride while another 0.4 percent remained in the resin. This means that about 1 percent of the chlorine applied to primary and secondary effluent at dosages of 6.0 and 2.6 mg/l Cl_2 respectively ends up in stable organo-chlorine compounds. This value may be even higher since the losses due to volatilization (Pitt and Scott, 1973) and insolubility during the concentration procedure were not further investigated.

A list of the compounds identified by Jolley appears in Table 2.13. Most of the products are those expected from direct electrophilic substitution, although the meta-substituted phenol, 5-chlorosalicylic acid, and 6-chloroguanine are obvious exceptions. Somewhat surprising is the 1:4 ortho-para

Table 2.13 Chlorinated Compounds Formed by Chlorination of Primary Effluent^a

Compound	Concentration in Primary Effluent		Concentration of Probable Precursor	
	$\mu\text{g/l}$	$\text{Mx}10^8$	$(\mu\text{g/l})$	$\text{Mx}10^8$
2-Chlorophenol	7.6	6.0	10.6	11.3
3-Chlorophenol ^{b,d}	(0.51)	(0.40)		
4-Chlorophenol ^d	(0.69)	(0.54)		
4-Chloro-3-methyl-phenol ^d	(1.5)	(1.1)		
3-Chloro-4-hydroxy-benzoic Acid ^d	(1.3)	0.80	--	
5-Chlorosalicylic acid	0.74	0.51	7	5.5
4-Chlororesorcinol ^d	(1.2)	(0.83)		
5-Chlorouracil	26.2	17.6	40	35
5-Chlorouridine	20.4	8.2		
8-Chloroxanthine	4.5	2.4	70	45
8-Chlorocaffeine	6.7	3.1	10	5.5
6-Chloroguanine ^d	(0.9)	(0.48)		
2-Chlorobenzoic acid	0.38	0.26	--	
3-Chlorobenzoic acid ^{b,d}	(0.62)	(0.42)	--	
4-Chlorobenzoic acid ^d	(1.1)	(0.75)	--	
4-Chlorophenylacetic acid	11.1	7.0	17 ^c	13.6
4-Chloromandelic acid	1.9	1.1		

a. Jolley (1973)

b. Identified as either or both of these compounds.

c. From total of compounds in chlorinated effluent, converted to equivalent concentration of unchlorinated species.

d. Not found in primary effluent, concentrations in parentheses refer to secondary effluent.

substitution ratio of the benzoic acid (Smith 1934). The yields of chlorinated compounds range from 5 to 50 mole percent based on the organic precursor. The high yield of 2-chlorophenol conflicts with the observations of Burttschell et al. (1959) although it should be pointed out that Burttschell's group worked with pure solutions rather than sewage.

Another study on sewage has been undertaken by Glaze et al. (1973) using XAD resin extraction. He found that volatile chlorinated compounds were formed at 10-100 mg/l Cl_2 , thus Jolley's estimate of the amount of chlorine in new stable organochlorine compounds may be low. Glaze doubly filtered his sewage before chlorination; thus the uptake of chlorine by bacteria and other solids was eliminated and, in addition, some loss of ammonia may have occurred. He also acidified his effluent to pH 2 - 3 which may have resulted in premature saturation of the resin with volatile acids. The only compound he has identified to date is chloroform.

Adams and Middlebrook (1973) studied closed loop hypochlorite systems such as those used in recreational boats and vehicles. Their analytical technique of extraction of flash evaporated or unconcentrated effluents with ether or chloroform followed by evaporative concentration and direct NMR and IR analysis is of limited value. The presence of halogen in the ether extract was detected by AgNO_3 . They postulated the presence of chlorinated fatty acids.

Rook (1974) established that haloform reactions occur with colored matter in natural water. This work was directed to drinking water and thus is not directly comparable.

A group in Minnesota, Carlson (1973) and Carlson et al. (1975), is investigating the chlorination reactions of a number of model organic compounds in dilute aqueous solution at different pH. These studies are not yet complete, however, as an example of his results, the chlorination of α -terpinol yielded a mixture of eight products. The composition of the product mixture was pH dependent.

Toxicity tests showed that all the products except the dichloride have about the same toxicity as α -terpinol to Daphnia magna, i.e.: LC_{50} 48 hrs \approx 120 mg/l whereas the dichloride had an LC_{50} 48 hrs of about 15 mg/l (Carlson and Capple, 1974). These workers are also involved in developing methods for relating the physical properties of a molecule to its ability to bioaccumulate and to exhibit toxicity.

F. Analytical Methods

The analysis of environmental samples is an especially difficult problem due to the complex nature of the samples and the very small concentrations of materials to be analyzed. Two general approaches to the problem are used:

- a) the complete physical separation of components followed by analysis and
- b) the quantitative determination of specific compounds in the presence of others through the use of specific detection methods.

In this study, the first approach will ultimately be used although the second will be a valuable aid in the development of the techniques to be used. The overall approach to the problem will involve techniques of sampling and preservation, concentration, separation and chemical analysis. These techniques will be briefly reviewed in the following sections.

1. Sampling and Preservation

Hunter and Heukelekian (1965) used 24-hour composite samples in their analysis of sewage to allow for the diurnal fluctuations in composition. This approach has several drawbacks. The concentration of slugs of compounds will be underestimated, automatic samplers which sample at a specific depth will miss floating material and finally, the storage time of the first sample is a minimum of 24 hours. Grab samples on the other hand, will overemphasize or entirely miss slug loads. In addition, when samples are taken by hand there is the psychological tendency to either catch or miss obviously rich portions or areas.

Various methods have been evaluated for preservation of sewage samples for specific analyses. The losses of materials are attributed to two main causes, biological decomposition and physical losses due to evaporation, precipitation and sorption on the sampling vessel and particulates. Loehr and Bergeron (1967) and Hellwig (1967) have reviewed the chemical preservatives used for sewage. Loehr and Bergeron (1967) found that storage at 1°C alone is satisfactory for preventing changes of COD, BOD, pH, DO and SS for six days. Lichtenberg (1973) found that storage in a cold, dark environment did not prevent loss of PCB's and recommended the addition of 15 mg/l of formaldehyde.

Desbaumes and Imhoff (1972) in their study of hydrocarbons stated that only glass or stainless steel containers are suitable because of sorption. They also indicated that substantial losses occur if storage time exceeds 10 hours although no details as to the mechanism of the loss are given. Adsorption on glass may also be a problem as Leithe (1973) states that glass containers should be extracted for 1 hour with pet ether for pesticide samples. Ahnoff and Josefsson (1974) found that 5% of the DDT in an 8 µg/l aqueous solution was adsorbed on the glass container. Desbaumes and Imhoff (1972) also identified some substituted benzenes leached by water from plastic bottles. The type of plastic was not identified. Phthalate esters and other plasticizers are also leached by water from plastics and some steel containers (Mathur, 1974).

2. Extraction and Concentration

Four general methods, namely, solvent extraction, adsorption, freeze concentration and gas stripping have been used for the concentration of organics from water.

Solvent Extraction Hunter and Heukelekian (1965) and Hites and Biemann (1972) used the separatory funnel technique. Methylene chloride, Freons, and a mixture of methylene chloride and diethyl ether are favourite solvents for

this technique. Continuous extractions, both with solvent distillation (Goldberg et al., 1973) and without solvent distillation (Ahnoff and Josefsson, 1974) have been used. Two or three of these extractors are usually set up in a series and total recoveries of 70 to 110% are reported by Goldberg et al. (1973) at flow rates of 8 l/hr.

Adsorption The optimum procedures for carbon adsorption of organics from wastewaters have been discussed by Buelow et al. (1973a, b). Studies on desorption have been conducted by Hoak (1964) and Allen et al. (1971), and the desorption of phenols from activated charcoal for example, ranges from 22 to 70 percent.

Cookson et al. (1972) have noted the oxidation of n-butylmercaptan to n-butyldisulphide during adsorption on charcoal, presumably due to the presence of molecular oxygen and quinone. Lee et al. (1965) used carbon adsorption to extract organics from Lake Mendota. Generally speaking carbon adsorption is not used for trace analysis of unknowns due to the activity of the carbon surface and the difficulty in eluting some material from carbon.

Kennedy (1973) and Gustafson and Paleos (1971) have reviewed the kinetics and applications of macroreticular resins for adsorption of organics from water, while Kim et al. (1974) discussed the engineering uses of synthetic resins for water treatment. Junk et al. (1974) have determined and optimized recoveries and concentration procedures for 99 different compounds using XAD-2 or XAD-4 resin. Recoveries vary from 80 to 100% except for short chain aliphatic alcohols, acids and some phenols whose recoveries are affected by pH and salt concentrations. Webb (1973) found these resins ineffective for aliphatic hydrocarbons. Pitt and Scott (1973) report poor recoveries of non-volatiles from domestic effluent. These resins can be selectively and/or completely regenerated depending upon choice of solvent. XAD-2 has been used in LSC of phenols (Grieser and Pietryzk, 1973). Examples of applications of macroreticular resins to environmental work are the studies by Burnham et al. (1972),

Harvey (1973), Glaze et al. (1973), Vinson et al. (1973) and Rogers and Mahood (1974).

Columns of polyurethane foam plugs with acetone and hexane elution have been used by Chow et al. (1971) to recover 20 ppb of PCB's with 91-98% efficiency. In a study on pesticide recoveries, however, Uthe et al. (1972) found it necessary to coat the plugs with selective adsorbents. Webb (1973) found both coated and uncoated plugs ineffective for most other organics. Aue et al. (1972) used surface bonded silicones on 40 - 60 mesh Chromosorb G with methanol/benzene cleanup and pentane elution to recover ppt. levels of pesticides and PCB's. Recoveries varied from about 30% for lindane to 100% for aldrin in column tests. Ion exchange resins (Burnison, 1972) and chelotropic resins (Siegl and Degens, 1966; Webb and Wood, 1966) have been used for the recovery of amino acids from natural water.

Freeze Concentration and Lyophilization Freeze concentration (Baker, 1965; Kobayashi and Lee, 1964) involves slowly freezing the solution from bottom to top from the outside inwards and then separating the pure ice from the concentrate. Lyophilization involves freezing the sample and subliming the water. It has the advantage of leaving the non-volatile material as an anhydrous powder. Both these techniques involve removing the water from the organic material and are quite slow. Samples of more than two litres are difficult to handle. Hunter and Heukelekian (1965), Painter (1971), Katz et al. (1972) and Jolley (1973) have all used one or both of these techniques for studies on sewage.

Air Stripping and Headspace Analysis Novak et al. (1973) originally applied this technique to the analysis of drinking water. They used He as a stripping gas and a liquid nitrogen trap for collection. Kaiser (1973, 1974) used tubes packed with GC column material followed by elution by N₂ and got recoveries of 25 percent. Zlatkis et al. (1973a) tested Poropak P, Carbosieve and Tenax GC as trapping materials. They also heated the aqueous solution

to 100°C for better recoveries. Bellar and Lichtenberg (1974) tested the use of a number of adsorbents and found Tenax GC and Chromosorb 103 useful. Grob and Grob (1974) analyzed concentrations as low as 1 ng/l of individual petroleum components in water using 1 mg of charcoal and five 1.5 μ l portions of CS₂ for elution. Bellar, Lichtenberg and Kroner (1974) also used N₂ stripping to analyze for chlorinated solvents in drinking water and report that for components with boiling points less than 150°C and 500 mg of sample, detection limits are \sim 1 μ g/l.

Concentration The recommended method for concentration of organics in organic solvents is the use of Kuderna - Danish (K-D) concentrator (Leithe, 1973). Webb (1973) reports 85% recovery of compounds concentrated from 100 to 1 ml in CHCl₃ in a rotary evaporator compared to 90% in a K-D concentrator. He also recommends the airstream method for volumes less than 0.25 ml.

When working with solvents such as chloroform or diethyl ether which dissolve in water, drying is necessary before concentration. Sodium sulphate is the usual drying agent. It should be heated to 600°C for 2 hr before use, to remove organic impurities (Garrison, 1972). Losses of about 6 percent of α -terpinol and 2-methyl naphthalene occurred from CHCl₃ solutions due to drying with sodium sulphate (Webb, 1973).

3. Separation

Two general problems of separation occur when working with natural waters. The first is the physical separation of the particulate matter from the soluble compounds and the second is the separation of the components of the organic extracts or residues.

The first problem is usually solved by filtration or centrifugation as exemplified by the studies of Hunter and Heukelekian (1965) and Painter (1971). The usual definition of dissolved organics is those of size less than 0.1 - 1.0 μ . Typical glass fibre filters have pore sizes of 0.3 - 1.0 μ . The

cellulose acetate membrane filters are available from 0.2 μ pore size. Filtration times of 24 hr/l for moderately polluted waters are common for 0.45 μ filters (Andelman and Caruso, 1971).

The separation of organic extracts and residues is generally accomplished by chromatographic methods. Acid-base separations using the $\text{H}_2\text{SO}_4/\text{HCO}_3^-/\text{NaOH}$ system are commonly used prior to chromatographic separation.

Chromatography For a comprehensive treatment of the subject of chromatography, the reader is referred to the volume by Heftmann (1967). This discussion will be limited to some examples of applications of, or new developments in, the various types of chromatography used in the environmental field. For a review of the chromatographic separations of some environmentally important chemicals, the volumes by Fishbein (1972a, 1973a) are recommended.

Thin Layer Thin layer chromatography has been used as a cleanup procedure in pesticide analysis before quantification by GLC (EPA, 1971). This type of application typifies the use of TLC in environmental work.

In a number of cases, however, TLC has advantages over GLC and LC and is in some instances, the optimum separation method. The determination of the optimum conditions for resolution of a mixture of unknowns can be accomplished in a much shorter time for TLC than for GC and LC. The results of TLC separations can be used as a guide for the application of other chromatographic methods, especially LSC (Hurtubise et al., 1973). In air pollution work, arenes have been separated, identified, and quantified by TLC in combination with direct spectrofluorimetry, UV absorption spectrophotometry, and colour reactions on the TLC plate (Sawicki and Sawicki, 1972). Detection limits are about 1 μ g by UV and 1 to 10 ng by fluorescence. Majer et al. (1970) describes the use of TLC - Mass Spectrophotometry for arene analysis and reports detection limits of 1×10^{-11} g for anthracene and 1×10^{-14} g for benzopyrene. When working with mixtures rendered less complex by prior separation and chemical workup, characterization of the components by infrared or NMR methods is

much more expedient following separation by TLC than GLC or LC. An example of this is the work by Hall (1970) on the determination of some of the alkaline CuO and Na/Hg degradation products of naturally occurring coloured organics. Some of the problems with these techniques such as photo-oxidation, wet spots and charge transfer spectra among others are discussed in Sawicki's review. The problem of reproducibility of R_f values has been reviewed by de Zeeuw (1972), while the impurities in silica gel have been discussed by Spitz (1969) and Amos (1970).

Liquid Chromatography: Although florisil column clean-up techniques are routinely employed in pesticide analysis, high speed and high pressure LC methods will be emphasized in this review. An excellent summary of the principles, techniques, instrumentation and applications of LC is provided in the volume edited by Kirkland (1971). To date silica is a favourite material for LSC although other materials such alumina, charcoal and florisil are also used. Florisil has a tendency to irreversibly bond even some non-polar compounds and thus is not usually used for the analysis of a mixture of unknowns. Good reproducibility can be obtained through the use of commercially prepared supports and a solvent of non-varying composition but gradient elution is hampered by the problems associated with maintaining a constant or reproducible level of deactivating water on the support. Some applications of LSC in the environmental field include the work on organophosphate larvicides (Henry et al., 1971), nitrotoluenes in munition wastes (Walsh et al., 1973), phenols (Bhatia, 1973), aromatic hydrocarbons (Zsolnay, 1973), total hydrocarbons (Zsolnay, 1974) and non-ionic alkylphenol surfactants (Krejci et al., 1974).

High pressure IEC still suffers from retention times as long as 40 hr for the analysis of unknowns. Examples of the use of high pressure IEC include the separation of 100 - 120 UV absorbing peaks in human urine (Scott et al.,

1970) and 77 absorbing peaks in municipal wastewater after 500 fold concentration by vacuum distillation and freeze drying (Katz et al., 1972). Jolley (1973) used essentially the same system as Scott et al. (1970) and Katz et al. (1972) in his study on the effects of chlorination on sewage.

Detection limits by UV require concentrations in the range of 40 mg/l for unsaturated non-aromatics and 20 μ g/l for aromatics. Thus 40 μ g/l of non-aromatic and 20 ng/l of aromatic unsaturated hydrocarbons can be detected through concentration techniques. Refractive Index detectors are usually one or two orders of magnitude less sensitive. A fluorescence detector based upon the uncatalyzed reduction of Ce (IV) to Ce (III) was developed and tested by Katz and Pitt (1972). Detection limits for organic acids and other reducing compounds range from 0.1 μ g to 0.5 μ g using this technique.

Gel Permeation Chromatography~Although the development of semi-rigid polystyrene and polyvinylacetate gels has made high speed GPC possible, environmental application of GPC has been limited to the soft and, in most cases, dextran gels. The use of Sephadex gels for the molecular size fractionation of organics, mainly humic acids, in natural waters has been reviewed by Hall (1970) and Christman and Minear (1971). The GPC studies of sewage and treatment plant effluents has been previously discussed.

Gas Chromatography~This discussion will be limited to a few applications of GLC separation of organics in environmental samples. Direct coupling to a mass spectrometer will be discussed in a separate section.

The selection of a stationary phase and packing is a problem encountered by everyone working with GLC. A wide variety of stationary phases has been used in environmental work Fishbein (1972a, 1973a). The trend in pesticide analysis today is toward the use of the OV or SP series of silicones as the variation in composition between different lots of these phases is smaller

than the older silicone phases (Trash, 1973; Coleman, 1973). The favourite support in environmental analysis is silanized Chromosorb W. The graphitized carbons (Carbopak) deactivated by hydrogen treatment and coating with around 0.3% of a liquid phase show promise in the direct analysis of aqueous solutions (Supina, 1974). Both polar and non-polar phases have been used in the analysis of volatile organics in sewage. Dowty and Laseter (1975b) used a mixture of 10% GE SF - 96 and 1% Igepal CO whereas Glaze et al. (1973) used 5% Carbowax 20 M/TPA.

Open tubular columns are finding increasing utilization in environmental work (Grob and Grob, 1974; Rogers and Mahood, 1974; Lao et al., 1973). The use of SCOT and WCOT columns is discussed by Ettre (1973). The traditional open tubular columns were made of stainless steel due to the difficulty of evenly coating glass. This difficulty was overcome by German and Horning (1973) and the less active glass columns are now in common use. Theoretically, one expects better resolution in a shorter time with a SCOT column as compared to a packed column (Ettre, 1973), however in the study by Lao et al., (1973) fewer peaks were observed with the SCOT column than with the packed column, especially when materials with high retention times are separated. The reasons for this difference have not been determined. One disadvantage of the SCOT column is that only a few tenths of a microlitre of sample may be injected. This means that greater concentration of samples may be required.

The most common detectors used for environmental samples are the FID, EC and specific element detectors. The FID is sensitive to most organics and roughly speaking traces of FID response are similar to those of the total ion current produced by coupled GC/EIMS units in terms of sensitivity. The electron captive detector is used for organochlorine pesticide and PCB analysis due to its high sensitivity for electron capturing elements. Karasek et al. (1973) have conducted some studies on the mechanism of electron capture by a

series of chlorinated benzenes and biphenyls. They demonstrated that both associative and dissociative electron capture occur. The ^{63}Ni foil detector is favoured for environmental samples due to its high temperature stability. The problem of the narrow, one decade, linear range of the detector has been overcome through the use of constant current, variable pulsing rate electronics. Linearity over four decades has been obtained (Aue and Kapila, 1973). Their publication also discussed some aspects of temperature programmed GC with an EC detector. Essentially quantitation is difficult unless the detector is operated under conditions where only the mass of the compound is important as opposed to the concentration ratio of electrons to compound.

Among the specific element detectors, thermoelectrolytic conductivity (MEC) type is the most generally used for halogen detection. The original MEC detector was developed by Coulson (1965). Recent developments by Hall (1974) afford 20 to 50 times greater sensitivity for chlorine due to changes in reaction tube and cell geometry, use of isopropanol/water rather than water as the circulating solvent and use of an AC rather than DC bridge circuit for measurement of conductivity. Detection limits of 0.05 - 0.1 ng are reported for organochloride pesticides. Tests by Wilson and Cochrane (1975) revealed only a 4 to 7 fold increase in sensitivity to nitrogen over the Coulson detector. The recently developed multi-element helium plasma/atomic emission detector offers interesting possibilities and has detection limits of 0.08 ng/sec for carbon, 0.03 ng/sec for hydrogen and 0.06 ng/sec for chlorine (McLean *et al.*, 1973).

4. Chemical Analysis

This discussion will be limited to a review of the instrumental techniques of analysis which can be used either after trapping of the separated components from a chromatograph or in some cases by direct coupling or interfacing to the chromatograph.

Trapping Techniques Trapping LC effluents is rather facile and will not be discussed. The trapping of GLC effluents is much more complex. Howlett and Welti (1966), Föwli and Welti (1967), Milazzo et al. (1968), Armitage (1969) and Oertel and Myhre (1972) describe cryogenic trapping techniques for IR, NMR and Raman analysis. Losses due to mist or aerosol formation are common. Copier and Van der Mass (1967) and Block and Griffiths (1973) used KBr as an absorbent for IR analysis. The GC-trapping-IR methodology has been reviewed by McNiven (1965) and Leathard and Shurlock (1970). It should be kept in mind that one requires 10 - 100 μ g of sample for ordinate expanded IR and capillary tube-time averaged or Fourier Transform NMR.

Tandem GC-MS A general overview of GC/MS/computer systems is presented by Karasek (1972) and the available instrumentation and some applications are reviewed by Junk (1972). Identification limits with these instruments vary from 20 - 100 ng. To date, all of the work in the environmental field has been carried out on electron impact sources although preliminary GC-CIMS and GC-FIMS work is reported (Junk, 1972; Blum and Richter, 1974).

Environmental samples of organics usually contain a large number of volatile compounds. In the case of incomplete separation of these components or when one is interested in identifying more than one or two of the components, computerized data handling facilities are essential. Data handling is a technology in its own right and magnetic discs offer a considerable time saving over the tape units during data manipulation (Ward 1972). Hites and Biemann in a series of papers discussed the algorithms and mechanics for the production of reconstructed gas chromatograms (1968a), mass chromatograms or limited mass searches (1970), and background subtraction (1968b). The US EPA has a battery of 23 GC/MS units each equipped with a mini-computer, disk or tape unit, slow printer and keyboard, slow plotter, CRT with keyboard, CRT hard-copy unit and telephone connection to large computer (Heller, McGuire and

Budde, 1975).

The identification of an unknown from its mass spectrum is not always a simple task. Various file searching routines have been developed. These can be classified into two groups: a) those programs developed for the interpretation of the mass spectrum of a new or non-filed compound and b) the identification of an unknown by searching a file for its mass spectrum fingerprint. The first group of programs was reviewed by Kwok et al., (1973). These are designed primarily for complex polyfunctional compounds of molecular weight greater than 150. While the complete determination of structure by these programs is far from unequivocal, they do provide valuable information as to what functional groupings are present. Work with high resolution spectra, e.g. Venkataraghavan et al., (1969) will not be discussed as one does not generally obtain high resolution spectra by GC - MS due to limitations of computer storage space.

The programs used to identify an unknown by searching a fingerprint file have been discussed by Hertz, Hites and Biemann (1971). An international mass spectral search system (MSSS) is available and is being constantly upgraded. The unknown spectrum is abbreviated by choosing the two most intense peaks in each 14 m/e region beginning from m/e 6 since abbreviation to the five or eight most intense peaks will in many cases result in the loss of too much information. The output consists of a list of best fit compounds and similarity indices. Filed spectra may also be retrieved by molecular weight or formula, (Heller, 1972). A full list of the options currently available is included in the article by Heller, McGuire and Budde (1975). Although small computer banks have been developed (Wangen et al., 1971) their use is limited. When the spectrum of the unknown contains the spectra of more than one compound, difficulties arise. Abrahamson (1975) has developed a reverse search program where each spectrum in the reference file is compared to the un-

known's spectrum. The use of this technique with large libraries will obviously require some prescreening.

In summary GC-MS-Computer instrumentation has become very sophisticated. It must be noted however, that the identification afforded by the MS-Computer is only tentative especially when the molecule is complex and/or has stereoisomers. The possibility of alteration in the GC or interface is always present. Since one may not be able to employ IR and NMR methods due to sample size, chemical workup and subsequent further analysis by GC-MS-Computer, or GC retention time, may be necessary to afford positive identification.

Numerous examples of the use of GC/MS/Computer techniques for environmental samples have already been mentioned. Other studies include those of Hites and Biemann (1972), Hites (1973), Keith (1969, 1972), Harris Budde and Eichelberger (1974) and McGuire et al. (1973).

CHAPTER III - EXPERIMENTAL

A. Outline of the Problems

A flow chart of the project is shown in Figure 3.1 and its major facets are summarized below.

Extraction - The first problem was to devise an expedient method of recovering trace organics from water. Two systems, a continuous solvent extractor and an adsorption method were developed and tested.

Separation - Various methods for the separation of organics were tried. These included filtration, solubility, and liquid, thin layer, and gas chromatographic techniques.

Effects of Chlorination on Sewage - These effects were ultimately analyzed by gas chromatography, utilizing electron capture, flame ionization, microelectrolytic conductivity and mass spectrometric detectors.

Identification of Compounds in Sewage - This portion of the work was essentially coincidental with the study of the effects of chlorination.

B. Apparatus and Techniques1. General Procedures

Those techniques which were routinely used in all facets of this project are described below, while the others will be presented in the appropriate subsequent sections. All organic solvents were of analytical reagent (AR) grade and were glass distilled with at least a 1:1 reflux ratio. Sodium sulphate (AR) and sodium chloride (AR) were heated to 600°C for four hours to remove organics while aqueous reagents were extracted with three twenty ml portions of diethyl ether. Plastic and porcelain vessels and the five gallon glass carboys were cleaned by a detergent wash followed by rinses with distilled water and the aqueous sample. All other glassware was cleaned by a detergent wash followed by chromic acid treatment and rinses with distilled water, methanol, acetone and diethyl ether.

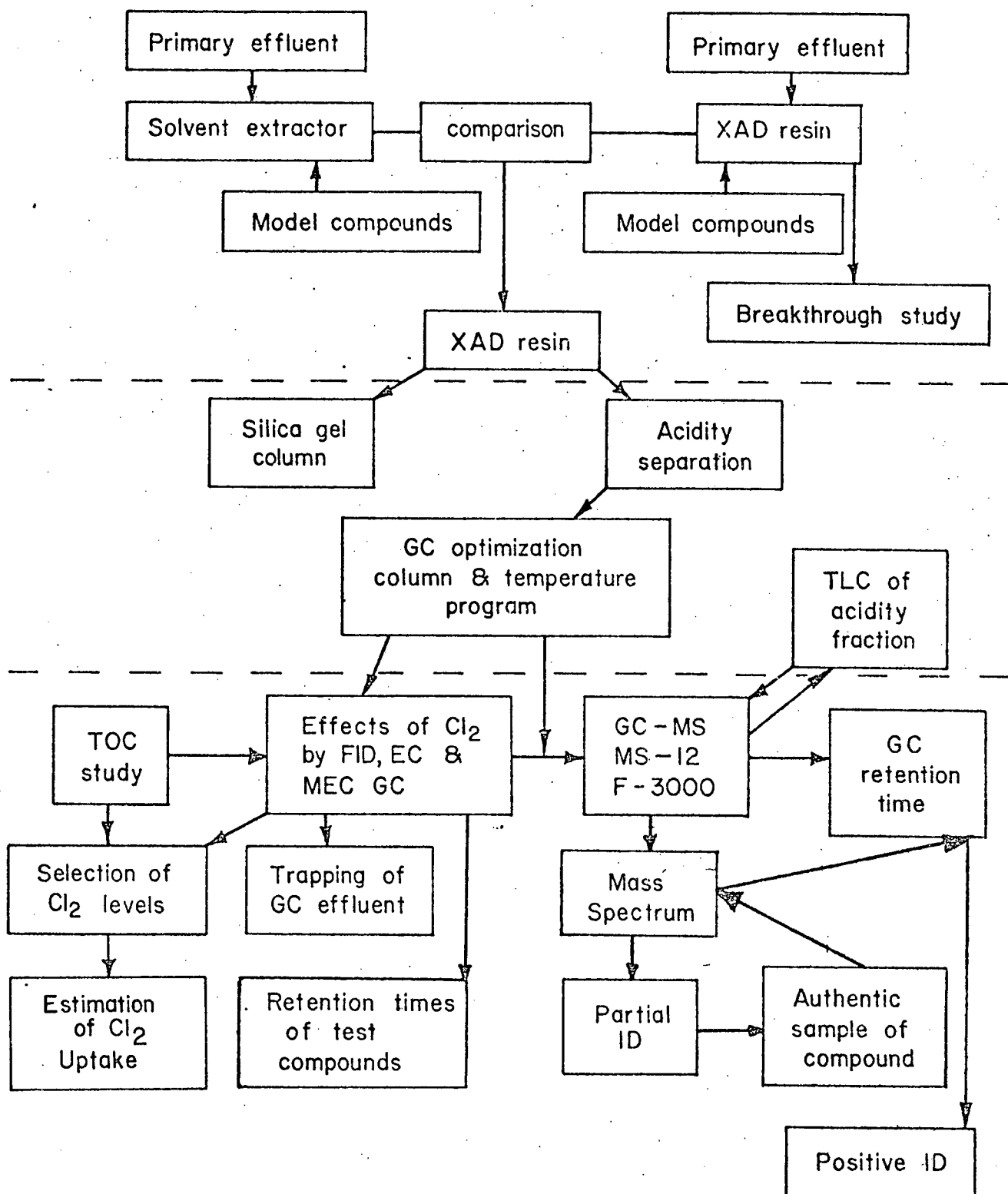


Figure 3.1. Flowchart of the Project.

Prior to extraction, primary effluent samples were filtered with the apparatus shown in Figure 3.3a. Filters of paper (Whatman 541) and glass fibre (Reeve Angel 934) were layered three of each deep in the 11.5 cm I.D. porcelain crucible and sealed by distilled water. They were sequentially removed when the filtration rate dropped below 300 ml/min during vacuum filtration at 10 inches water gauge into the five gallon glass carboys. All organic extracts were dried with sodium sulphate and concentrated to 0.5-2.0 ml in a rotary evaporator (Buehler) at 20°C. The concentrated extracts were analyzed on a Hewlett-Packard 5750 GC with a ^{63}Ni EC or H_2 /air FI detector. The detector temperature was 320°C and injector temperature was 260-280°C. Carrier gases were 95/5 Argon/methane for EC and helium for FID. Detector responses of 50 percent of full scale were produced by 1×10^{-10} g of dieldrin with the EC (50 μs pulse interval) and 5×10^{-8} g of "isô-octane" with the FID at attenuations of 32×10 . All columns were $4' \times \frac{1}{8}"$ glass fitted with silicone rubber, Supeltex M-1, or lead O-rings and ferrules (Suprelco). The 5 and 10 μl GC syringes (Hamilton) were cleaned by aspiration of 5 ml of acetone through the barrel and wiping of the plunger.

Chlorination of primary effluent samples involved the use of NaOCl solution (Fisher) which was analyzed prior to use by iodometric titration (APHA, 1971). Residual chlorine was determined by the Phenylarsine oxide-Iodine method (APHA, 1971) and a 5 percent excess of solid $\text{Na}_2\text{S}_2\text{O}_3$ (Fisher) was added to dechlorinate the sample and control reaction time. All primary effluent samples were stirred with a plastic overhead drive propellor to ensure complete mixing in the glass carboy.

2. Sampling and Preservation

Sampling Location

Lion's Gate Sewage Treatment Plant in North Vancouver was selected as a source of effluent. The plant serves a population (1973) of 108,000 with an

average flow of 11.0 MGD of mainly domestic sewage. It provides treatment via primary sedimentation, anaerobic sludge digestion, and effluent chlorination. Supernatant from the digestors is intermittently recycled through the plant. Prechlorination was not practiced during the period of this study. The average composition of the effluent is BOD_5 - 100 mg/l, $\text{NH}_3\text{-N}$ - 15 mg/l, TK-N - 30 mg/l and pH 7.2. The average daily chlorine dosage varies seasonally from 7 to 15 mg/l with a residual of between 2.0 and 5.0 mg/l as measured by amperometric titration.

Sampling and Pretreatment

Unchlorinated effluent samples were obtained from the outfall weir of the primary settling tanks. On one occasion a sample of chlorinated effluent was taken from the outfall of the chlorination chamber. Single grab samples were taken between 1000 hr and 1200 hr on Mondays. They were collected in five gallon Nalgene carboys. Work with these samples was commenced within one hour in most cases. Therefore the initial practice of adding 30 mg/l of sodium azide was discontinued after the second set of samples and subsequently no preservative was added.

3.2 Design and Test of Extraction Methods

a. Solvent Extractor

Apparatus - During preliminary tests of the initial extractor with sewage it was noted that some water overflowed into the solvent chamber, thus the design was modified. The modifications essentially made the flow of water through the extractor unrestricted in a direction opposite to the flow of the solvent.

The final extraction system is illustrated in Figure 3.2. It was designed for use with a lighter than water solvent. The solvent, petroleum ether bp 37-47° C is continuously distilled and channeled to the bottom of the extractor flasks. There it is finely dispersed with a Teflon coated magnetic stirring bar. The solvent then rises and overflows back to the distillation chamber. The rate

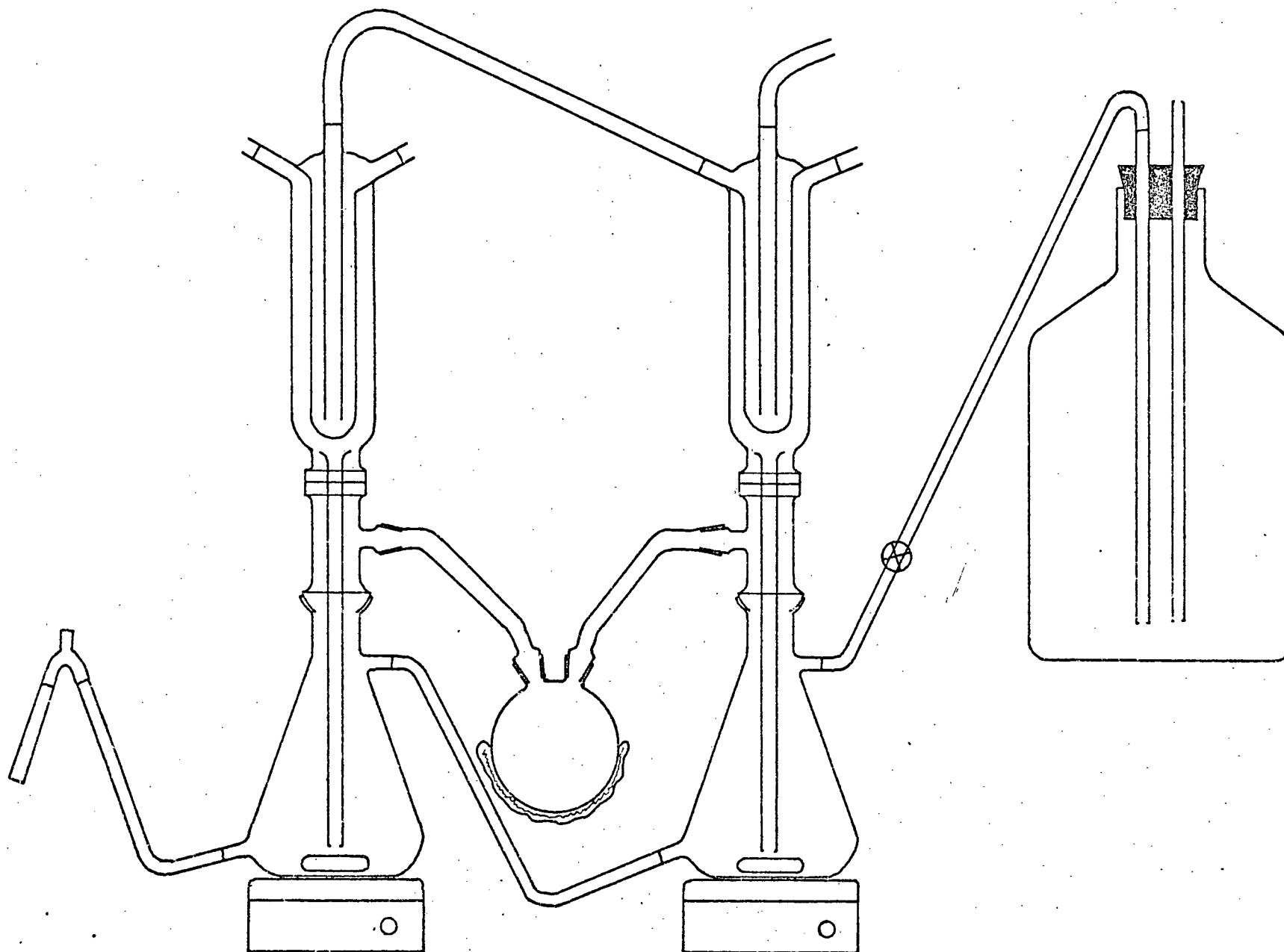


Figure 3.2 Continuous Solvent Extractor

of flow of the water sample was controlled by the Teflon valve.

Solvent Extraction of Model Compounds (Exp E-1) - In order to test the extractor under ideal conditions, two model compounds, 2,4-Dichlorophenol (DCP) and 2,4,6-Trichlorophenol (TCP) (Eastman) were selected. Aqueous solutions of these compounds were prepared by dissolving them in two millilitres of acetone and one litre of distilled water with magnetic stirring overnight, followed by final dilution, to eighteen litres. The solutions were passed through the extractor at flow rates of ten and one hundred ml/min with high and low stirrer speeds. At high stirrer speed the organic solvent was completely emulsified and at low stirrer speed the solvent was dispersed in discrete droplets. The organic extracts were divided in half, concentrated, diluted to the linear range and analyzed by GC (Hewlett Packard 5750) on 5% DC-11 on Chromosorb W (HP), with an EC detector. Peak areas were measured with a Disc Integrator. Distilled water was run through the extractor between tests without cleaning the tygon tubing and an estimate of memory effects made. After cleanup of the Tygon tubing with detergent and water another blank was run.

Solvent Extraction of Primary Effluent (Exp E-2) - In order to further test the performance of the extractor, tests were run with filtered and unfiltered sewage at a flow rate of 100 ml/min and low stirrer speed. Filtered sewage was also extracted at low stirrer speed and 10 ml/min flow rate. Extracts were concentrated to 2 ml and analyzed by GC on 5% DC-11 on Chromosorb W (HP) with an electron capture detector.

b. Extraction with XAD-2 Resin

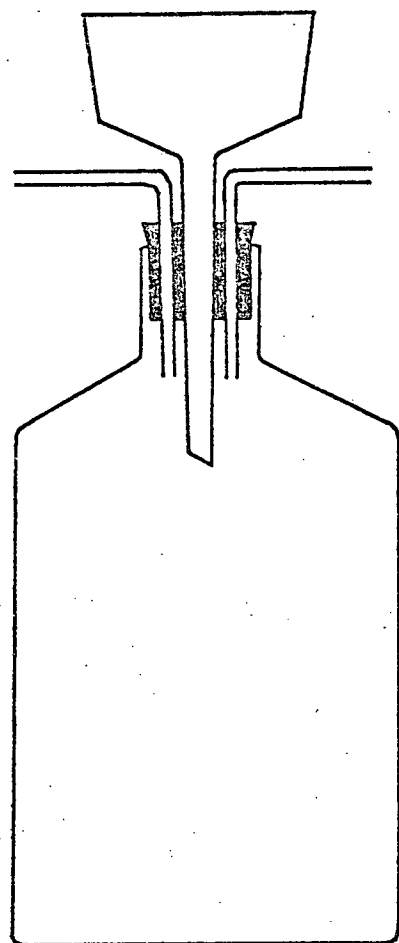
Apparatus - Due to problems with the solvent extractor a new method of extraction was necessary. A styrene-divinylbenzene macroreticular resin, Amberlite XAD-2 (Rohm and Haas) was tested. Resin cleanup was accomplished

by three washings with distilled water and decanting of the fines, followed by successive Soxhlet extractions with methanol for ten hours, acetone for twenty-four hours, and diethyl-ether for twenty-four hours. The clean resin was then stored as a methanol slurry until it was used. The extraction apparatus is illustrated in Figure 3.3. The resin, as a methanol slurry, was packed into eighteen by one inch glass columns or one hundred millilitre burets to a volume of 80 ml. Before extraction of a sample the column was washed with five litres of distilled water to remove the methanol. Desorption was originally accomplished by elution with 200 ml of acetone and drying of the acetone water eluant mixture with sodium sulphate. Extractions of the eluant mixture with petroleum ether and diethyl ether were also tried. The method finally adopted was elution with 200 mls of diethyl ether. The ether was allowed to run through the column until two layers were observed in the receiving flask. The flow was stopped for fifteen minutes to allow for complete permeation and then allowed to proceed at 3 - 4 ml/minute. The eluant was dried with sodium sulphate and concentrated. The columns were then washed with 200 ml of acetone and 100 ml of methanol for complete cleanup.

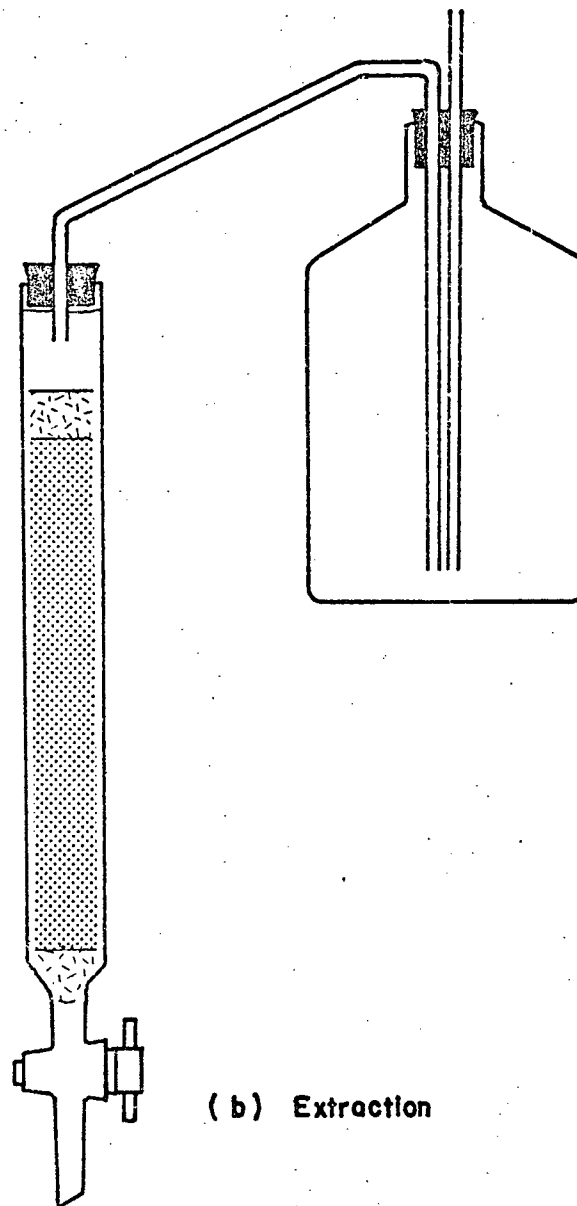
XAD-2 Extraction of Model Compounds (Exp. E-3) - This experiment was run in four parts in order to measure recoveries and determine the sources of losses in the system. The phenols were analyzed by GC-EC detector. The recovery of DCP and TCP from distilled water solutions was tested at neutral pH (Exp. E3a)3a).

The effect of detergent on recovery was determined by adding 4.9 mg/l of LAS standard solution (R. A. Taft, Cincinnati, Ohio) to the aqueous phenol solutions (Exp. E-3b). One fraction was acidified with H_2SO_4 to pH 1.8 and two litre portions of both fractions were extracted. LAS was analyzed by the Methylene Blue method (APHA 1971).

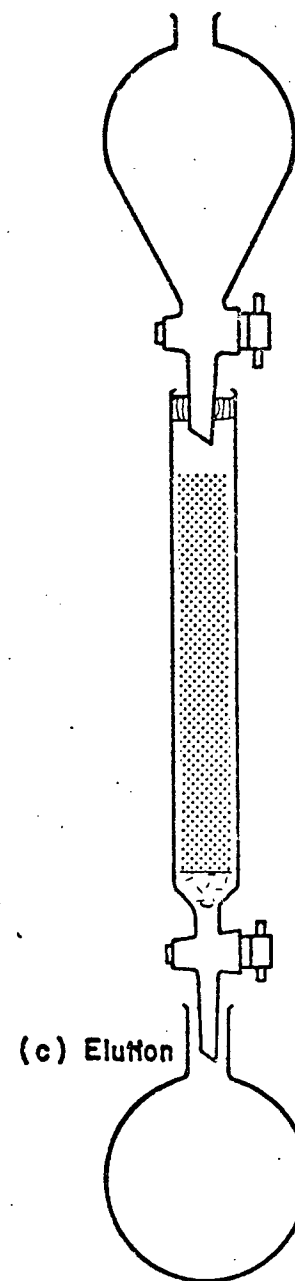
A detailed breakdown of losses in the system was made using distilled



(a) Filtration



(b) Extraction



(c) Elution

Figure 3.3 Macroreticular Resin Extraction Apparatus

water and the chlorophenols (Exp. E3-c). Recoveries and losses at various stages were determined by solvent extraction or sorption. Solvent extraction entailed three ten ml extractions with pet ether after acidification to pH 2 and addition of 20 g/l of NaCl.

Experiment E-3-d was identical to E-3-c except that raw sewage was used in place of distilled water. The solution of DCP was prepared by dissolving the phenol in acetone and water as before. This solution was then added to three or four litres of sewage.

Breakthrough Study (Exp E-4). To determine the capacities of the columns eighteen litre portions of filtered primary effluent, at both neutral and acid pH's, were extracted at a flow through rate of 100 ml/min. Column effluent samples were filtered (0.45 μ membranes) and analyzed for soluble TOC (Beckman 915 carbon analyzer).

c. Comparison of XAD-2 and Solvent Extractor - (Exp E-5.)

In order to compare the extraction efficiencies of the XAD columns and the solvent extractor, three five gallon aliquots of primary effluent were obtained. One aliquot was dosed with 106 mg/l Cl_2 for one hour. All three aliquots were filtered and the filters from each aliquot were collected damp but without free moisture. One aliquot of the unchlorinated effluent was extracted in the solvent extractor at 100 ml/minute and low stirrer speed. The other aliquots of filtered chlorinated and unchlorinated effluent were extracted by columns of XAD-2 resin. All three organic extracts were concentrated to 5 mls and analyzed by GC.

d. Extraction of Particulates - (Exp E-6) - The filter pads were cut up into 1" x 2" strips and placed in pre-extracted cellulose Soxhlet Thimbles. Filters from the chlorinated sample were extracted with a 1:1:3 mixture of methanol, acetone and n-hexane. Filters from the unchlorinated samples were extracted with methanol and a 1:1 mixture of chloroform and methanol to determine whether or not free chlorine in chloroform is a significant interference. Three

porcelain boiling chips (Hengar) were added to the distillation chamber and the extractors were operated at 20 - 25 minutes per cycle for 26 hours. All extracts were dried and concentrated to 5 ml. The pure methanol and chloroform/methanol extracts were further concentrated to 0.5 ml and rediluted to 5 ml with acetone. The extracts were then analyzed by GC.

4. Separation Experiments

a. Preliminary Separation (Exp S-1)

Preliminary separation of the organics by silica gel chromatography and acid-base solubility was attempted prior to gas chromatography.

Silica Gel Chromatography (Exp S-1a) - Silica gel (Fisher Grade 923, 100-200 mesh) was heated at 260°C for five hours and then 5% by weight of water was added in a glass stoppered round bottom flask. The silica gel was gently tumbled until free flowing and allowed to further equilibrate overnight. Glass columns (0.3 by 40 cm) were prepared from soft glass tubing. The columns were constricted near the bottom and a 2 cm plug of glass wool inserted. The columns were rinsed with methanol, benzene, and pet ether and then filled with pet ether. The silica gel was slurried in pet ether and the flask containing the slurry was partially evacuated to remove air bubbles. The slurry was then added to the column to a depth of 15 cm. A 0.5 ml aliquot of sample from Exp. E-5 was placed on the column and eluted with 8 ml of pet ether, 8 ml of benzene and 8 ml of 1:1 methanol/benzene (v/v).

Acidity Separations (Exp S-1-b) - Four five gallon aliquots of effluent were obtained and chlorinated at levels of 0.0, 15, 100 and 200 mg/l Cl_2 for one hour. They were extracted by XAD-2. The diethyl ether eluant was successively extracted with 3 x 10 ml of 0.1 M NaHCO_3 , and 3 x 10 ml of 0.01 M NaOH to separate strong acids, weak acids and neutral compounds. The aqueous solutions were acidified to pH 2 with aqueous H_2SO_4 and re-extracted with diethyl ether after the addition of NaCl. A total operations blank consisting of distilled water and sodium thiosulphate, and a sample of $\text{NaOCl}/\text{Na}_2\text{S}_2\text{O}_3$

were also analyzed. After concentration to 1 ml, the extracts were stored at -10°C in 2 ml glass stoppered volumetric flasks (Kimax). Subsequently, the bicarbonate extraction step was omitted and 0.05 M NaOH was used.

b. GC Optimization (Exp. S-2)

An attempt was made to determine the optimum packing and conditions for GC separation. The GC work was performed on a Hewlett Packard 5750 instrument with EC and FID detectors. Four column packings were tested. Packings of 3% OV-1 and of 3% OV-225 on Chromosorb W (HP) were obtained from Pierce Chemicals. Packings of 3% OV-101 and of 3% OV-17 on Chromosorb W(HP) 80-100 mesh (Chromatographic Specialities) were prepared by the solution-filtration method (Supina, 1974). The packings were dried at 50°C for twenty minutes before filling the columns with 7.0-7.5 g of material. Packed columns were conditioned by a temperature program of 30° for 20 minutes, a 1° /minute increase, followed by an isothermal period of two days at the maximum temperature. Helium gas and lead ferrules were used during conditioning.

Samples from Exp. S-1-b were analyzed on all four columns using both FID and EC detectors under various temperature programs. The detector responses were optimized for the initial or final conditions of the temperature program.

c. TLC of Acidity Separated Fractions (Exp S-3)

In an attempt to accomplish more complete preliminary separation of the effluent samples, the neutral and basic fractions of the samples chlorinated at 0 and 120 mg/l Cl from Exp. Cl-7 were separated by TLC. A preliminary test of the developers was made on commercially prepared plates (Eastman) while final separation was made on plates prepared as follows. Silica gel (Kieselgel) was extracted for 24 hours in a Soxhlet extractor with methanol. It was oven dried until free flowing and 5% by weight CaSO_4 (Fisher AR) was added. Glass TLC plates were washed with detergent and rinsed with water and acetone. Silica gel was applied as an aqueous slurry and the coated plates

were oven dried at 103°C for 24 hours and stored over CaSO_4 in a dessicator prior to use. Samples were applied as a streak. The plates were developed with pet ether and arbitrarily divided into four or eight fractions. Recovery of the material from the plates was accomplished by the technique devised by Hall (1970) except that the asbestos was omitted. The recovered material was monitored by EC-GC. The fractions showing EC responses were recombined and re-separated by TLC using methanol as a developer. After division of the plate and recovery of the material, the fraction showing EC response was then concentrated to 0.1 ml and analyzed by GC-MS. A worst possible blank was obtained from non-soxhlet extracted silica gel and the "clean" areas of the second TLC plate which corresponded to the same R_f values as the fraction analyzed by GC-MS.

5. Effects of Chlorination

a. Changes in Soluble TOC Upon Chlorination -- (Exp C1-1)

Three fresh effluent samples were chlorinated at levels of 0, 12 and 103 mg/l Cl_2 . The samples were filtered (0.45 μ membrane) and the TOC of the samples determined on a Beckmann 915 TOC analyzer.

b. Effects Detectable by GC with EC and FI Detectors (Exp C1-2)

Extracts were analyzed by GC with EC and FID detectors to determine if changes occur as a result of chlorination and to determine whether changes occurring at high levels of chlorination also occurred at the levels of chlorination used in the treatment plants. Experimental conditions used in these experiments were identical to those in Experiment S-2.

c. Effects Monitored by MEC Detector and GC Correlations (Exp. C1-3)

Samples were analyzed on a Micro-Tek (Tracor 222) GC equipped with a Tracor 310 detector operating on the C1 mode at 815°C and a 6' x 1/8" glass column containing the packing as used with the GC-MS (Exp C1-7). The response of the detector was calibrated with a standard mixture of pesticides.

An attempt was made to correlate the GC chromatograms from the GC-MS, Microtek GC, and Hewlett-Packard GC. Samples were analyzed on the Hewlett Packard with a 4' x $\frac{1}{4}$ " glass column of the packing used with the other instruments. The individual optimum temperature programs were retained for each GC. Three compounds, o-chlorophenol, p-chlorophenol and o,p' - DDT were used as markers.

d. GC-MS Studies on the MS 12 (Exp C1-4)

The extracts from experiment C1-2 were initially used in this experiment. A second set of samples was prepared by extracting, acidity separating and concentrating effluent chlorinated at 0 and 25 mg/l Cl_2 . In this second experiment ten gallon aliquots of effluent samples were analyzed by combining the extracts of two XAD-2 columns.

The GC-MS is a combination of a Pye 104 GC and a Micromass 12 single focussing mass spectrometer interfaced by a differentially pumped porous frit-type separator. Glass columns (1 m x 2 mm OD) with stainless steel Swagelock fittings were packed with the OV-101 and OV-225 packings previously described. Electron energies of 70 and 25 eV were used. They were scanned at a rate of 3 sec/400 amu and recorded on UV chart paper. Low boiling perfluorokerosene was used as a calibrant. Mass spectra were taken at the beginning, maximum and tail of each peak which appeared on the GC.

e. Tentative Identification by Retention Time (Exp C1-5)

To tentatively identify some of the organic compounds formed as a result of chlorination, the GC retention times of a number of recrystallized chlorinated compounds were determined under conditions used to analyze the samples of chlorinated effluent. Retention times of composite solutions and individual components were determined at 120 and 160°C and with the temperature programs used for the primary extracts.

f. Trapping of GC Peaks (Exp. C1-6)

An attempt was made to trap a specific peak and analyze it by direct probe MS. A new set of samples was chlorinated at 0, 12 and 100 mg/l of Cl_2 . A 30:1 stainless steel effluent splitter was installed in the Hewlett Packard GC operating on the EC detector mode. Capillary glass tubes were rinsed with methylene chloride and dried. Attempts were made to trap one specific peak with an air cooled tube, a tube packed with one cm of Tenax GC, and a tube packed with one cm of the OV-225 material. Eight $3\ \mu\text{l}$ injections of the neutral and basic fraction of the sample chlorinated at 100 mg/l were made with each trapping system. The tubes were handled only with forceps and eluted with $100\ \mu\text{l}$ of diethyl ether which was allowed to evaporate in the atmosphere down to a volume of $2\ \mu\text{l}$. No peak was discernable upon reinjecting this $2\ \mu\text{l}$ aliquot into the GC.

g. GC-MS-Computer (Exp C1-7)

A new set of samples was chlorinated at 0, 12 and 120 mg/l Cl_2 , and a sample of plant chlorinated effluent was obtained. A blank of 35 l of distilled water and thiosulphate was run through the collection and extraction systems. The concentrated extracts were analyzed on the Hewlett Packard 5750 by EC and FID on OV-101 and OV-225. The samples were cooled with dry ice and transported by car to the USEPA lab in Seattle where they were stored in a freezer.

The GC-MS-Computer was a Finnigan 3000 consisting of a Finnigan 9500 GC and a Finnigan 3100 D MS interfaced by a jet separator. Auxiliary equipment included a Systems Industry PDP8 computer with magnetic disc and Dec Tape transfer unit, teleprinter and Houston Instruments slow plotter, Tektronix CRT display/control console with a hard copy unit, and a telephone hookup device. Samples were separated on a $4' \times 1/8''$ glass column containing 6% SE-30/4% OV-210 on Gas Chrom Q. Spectra were obtained at 70 eV ionizing voltage and scanned at 1 sample $1/100$ amu, integration time of 8, over the mass

range 34-450. Numerous limited mass searches were conducted to attempt to locate peaks of interest. Ultimately, each spectrum was manually inspected and appropriate background corrections made. The resultant spectra were compared with the MSSS files or the AWRE ~~at~~ Aldermaston (1974) and Cornu and Massot (1975) eight peak indices. In addition, spectra not matching those in the file were interpreted by the methods outlined by McLafferty (1973). The tentatively identified spectra were then compared with those collected by Stenhagen et al. (1974). Authentic samples of the compounds whose spectra passed these tests were obtained when possible and their GC retention times and mass spectra were obtained on the Finnigan 3000 GC-MS.

CHAPTER IV RESULTS AND DISCUSSION

In this chapter the results from each experiment described in Chapter III will be presented and discussed. In the interest of brevity all of the GC traces and mass spectra will not be reproduced. A selection of chromatograms and mass spectra chosen on the basis of positive importance will be presented while only the salient features of the others will be described. A summary of the chromatograms of effluent samples is presented in Appendix II. The GC conditions for the chromatograms presented in this chapter are described in detail in Appendix III.

A. Extraction Experiments

1. Solvent Extractor

The recoveries of DCP and TCP from distilled water by the solvent extractor (Exp. E-1) are presented in Table 4.1. A test for memory effects indicated residuals of 0.30 mg DCP and 0.35 mg TCP or about 4 percent of the total phenol passed through the Tygon tubing. No detectable memory effects persisted after cleaning the Tygon.

Loss of solvent proved to be somewhat of a problem, primarily due to the entrainment of solvent in the aqueous sample. In order to estimate the importance of this loss, measurements were made of the solvent needed to replenish the stock in the distillation flask and of the rate of solvent distillation into the extraction flasks. These results presented in Table 4.2 are accurate only to $\pm 10\%$ due to the difficulty of filling the distillation flask exactly to the calibration mark. From Tables 4.1 and 4.2 it appears that poor recoveries are coupled with large solvent losses.

In summary, slightly better recoveries are obtained at low flow rates. In view of the long extraction times required with low flow rates, the optimum operating conditions are a flow rate of 100 ml/minute and a low stirrer

Table 4.1 - Recoveries of Phenols by Solvent Extractor

Run No.	Compound	Concentration mg/l	Flow Rate mg/min	Stirrer Speed	mg Passed Through Extractor	Recovery mg	%
1	DCP	0.48	10	high	8.2	5.8	71
1	TCP	0.48	10	high	8.2	5.8	71
2	DCP	0.41	10	low	7.1	5.8	82
2	TCP	0.33	10	low	5.7	4.3	76
3	DCP	0.51	100	high	8.7	3.2	37
3	TCP	0.46	100	high	7.9	3.4	43
4	DCP	0.39	100	low	6.7	4.6	69
4	TCP	0.26	100	low	4.5	3.2	71
5	DCP	0.50	100	low	8.6	5.8	67
5	TCP	0.43	100	low	7.4	4.9	66

Table 4.2 - Solvent Loss Due to Entrainment

Run	Time of Run hrs	Stirrer Speed	Solvent Distilled ml	Solvent Lost	
				ml	% of Solvent Distilled
1	28.5	high	20,500	650	3.2
2	28.5	low	20,500	300	1.7
3	3.0	high	2,160	830	38
4	3.0	low	2,160	300	14
5	3.0	low	2,160	250	12

speed.

When filtered sewage effluent (Exp E-2) was extracted an emulsion problem developed. At a flow rate of 100 ml/minute and low stirrer speed an emulsion with entrained brownish scum formed at the top of the extractor flask and overflowed into the distillation chamber. The boiling in the distillation chamber then became bumpy. At a reduced flow rate (10 ml/minute) the emulsion and bumping were slower to develop. Discrete bubbles with a brownish scum quickly appeared at the top of the extraction flask and after 15 hours the emulsion in the distillation flask was similar in volume to that obtained in 1 hour with a high flow rate.

Examination of the gas chromatograms of the sewage extracts showed a total of 34 peaks detectable by EC. Three of these peaks appeared in the distilled water blank.

Although the extractor is reasonably efficient, it was decided to develop an adsorption method for extraction due to the emulsion problem. The alternative solutions of acidification of the sample to pH 1.8 and addition of 20 g/l NaCl would probably increase sorption losses. In addition, experience has shown that such practices do not eliminate emulsions with environmental samples.

2. Extraction with XAD-2 Resin

The first problems to be solved were the development of a cleanup method, and the development of an efficient method of elution. Since the resin contains inorganic as well as unknown organic impurities, the approach described in Chapter III was devised. The purpose of the methanol extraction was to remove the water and residual inorganics from the resin. Acetone and diethyl ether were chosen because they were the solvents used for elution of the sorbed organics. The methanol extract was yellow while all of the others were colourless. Since brittle plastics tend to crack upon drying the cleaned resin

was stored as a methanol slurry. The release of organics from cleaned resin which was allowed to dry has recently been confirmed by Junk et al. (1974).

The eluting solvent must satisfy three requirements. It must be a good general solvent, displace water from the column and be easily removed to allow concentration of the extract. The column contains about 8 ml of water as measured by elution of the column with hexane. When the acetone eluant was dried with Na_2SO_4 and concentrated, about 0.3 ml of water remained. The presence of such a large amount of water will cause large losses of volatile organics during the concentration step. To accomplish a 3 x 10 ml extraction of the acetone - water eluant approximately 120 ml of petroleum ether and 200 ml of diethyl ether were needed. Tests on the recoveries of DCP from a 200:10 mixture of acetone and water yielded recoveries of 77% with pet ether and 64% with diethyl ether. Due to these extraction difficulties the stopped flow method of elution with diethyl ether was adopted. Comparison of the elution efficiencies of acetone and diethyl ether showed recoveries of 93% for acetone and 89% by diethyl ether. Thus the solvents were identical within the 5% error limits and no residual water was noted after drying the diethyl ether.

A breakdown of the recoveries of DCP and TCP from the XAD-2 column according to eluant fraction (Exp. E-3) is shown in Table 4.3. The effect of LAS detergent on recoveries of phenols from acidified and non-acidified solutions is shown in Table 4.4. A detailed breakdown of losses is shown in Table 4.5.

From Table 4.3 it can be seen that the elution of sorbed phenol is essentially complete after about 1 bed volume of diethyl ether has passed through the column. Neither the pH of the solution nor the concentrations of the phenols appear to affect the recovery. These results concur with the recently published work of Vinson et al. (1973) and Junk et al. (1974). Detergents also had no effect upon the recoveries of the phenols. Adsorption of the LAS detergent

Table 4.3 Recoveries of Phenols from Distilled Water by XAD-2

Run No.	Sample Description	Initial Concentration		mg Through Column		Recovery mg		%	
		mg/l							
		DCP	TCP	DCP	TCP	DCP	TCP	DCP	TCP
1.	Original Solution	1.1	1.05	18.7	17.8				
1	1st 50 ml of Eluant					12.3	10.5	66	58
1	2nd 50 ml of Eluant					1.9	2.3	10	13
1	3rd 50 ml of Eluant					0.05	0.05	--	
1	4th 50 ml of Eluant					0	0	--	
2	Composite of Concentrates					15.0	13.4	80	75
2	Original Solution	0.133	0.189	2.3	3.2				
2	1st 50 ml of Eluant					1.6	2.6	70	81
2	2nd 50 ml of Eluant					0.1	0.15	4	5
2	3rd 50 ml of Eluant					<0.01	<0.01		
2	4th 50 ml of Eluant					<0.01	<0.01		
2	Composite of Concentrates					1.80	2.65	79	83

Table 4.4 Effect of LAS on Recoveries of Phenols
by XAD-2

Run	Volume of Sample Passed Through Column (l)	pH	Recovery Concentration (mg/l)			percent		
			LAS	DCP	TCP	LAS	DCP	TCP
1	Original Solution	1.8	4.5 ^a	0.55 ^a	1.25 ^a	---	---	---
	0.0 - 0.5		0.9			20		
	0.5 - 1.0		2.3			50		
	1.0 - 1.5		1.8			40		
	1.5 - 2.0		2.0			55		
	Total		1.8	0.45	1.05	40	82	84
2	Original Solution	7.1	4.5 ^a	0.90 ^a	1.35 ^a	---	---	---
	0.0 - 0.5		0.0			0		
	0.5 - 1.0		0.3			7		
	1.0 - 1.5		0.3			7		
	1.5 - 2.0		0.2			4		
	Total		0.4	0.70	1.10		78	82
3.	Original Solution	1.8	0.0 ^a	0.00 ^a	0.00 ^a	0.00	0.00	0.00

a - Original concentration of component as determined by analysis or from amount of material added and volume of solution.

Table 4.5 Breakdown of Losses for XAD-2 System

Run	Compoundration in Original Solution	Concentration in Original Solution		Loss Due to Filtration		Loss Due to Sorption on Tygon		Loss Due to Non- Adsorption on XAD Resin	
		by weight	by solvent extraction	mg/l	%	mg/l	%	mg/l	%
		mg/l	mg/l						
Distilled	DCP	0.55	0.52	0.0	0	0.071	14	0.00	0
Water-1	TCP	1.0	1.0	0.0	0	0.092	9	0.00	0
Distilled	DCP	0.25	0.24	0.0	0	0.032	13	0.0	0
Water-2									
Sewage-1	DCP	0.83	0.74	0.12	16	0.13	18	0.03	4
Sewage-2	DCP	0.76	0.66	0.08	12	0.14	21	0.03	5

occurred only when the sample was acidified. Similar results were obtained by Junk et al., (1974) with volatile acids. Detergents cannot be analyzed by GC-MS and volatile acids are of no interest in this study. From Table 2.3 it can be seen that these compounds are present in high concentrations in sewage. In order to prevent premature saturation of the resin with these compounds, it was decided to extract primary effluent samples at near neutral pH's.

From Tables 4.3 and 4.5 it can be seen that the major source of loss in this method is sorption on the Tygon tubing. The losses during concentration were 7 - 9 percent. From Table 4.5 it is also evident that the recoveries of DCP are significantly lower when sewage rather than distilled water is extracted. Therefore the recoveries of organics from sewage are affected by sorption and/or precipitation reactions even though LAS in distilled water had no effect. The significant sorption on particulates indicates that quantification will be more difficult by sorptive extraction which required pre-filtration, than by solvent extraction where removal of particulates is unnecessary.

In summary, the XAD-2 resin method appears to be slightly more efficient than the solvent extraction method for the recovery of DCP and TCP from neutral distilled water solutions. However the recoveries of DCP from sewage were about 25% lower than those from distilled water.

The results of the breakthrough studies of sewage (Exp. E-4) are listed in Table 4.6 and displayed in Figure 4.1. Deviations of up to 6 mg/l or 13 percent among the TOC values for samples which should have been identical were noted. The stated reproducibility of the instrument is about ± 1 percent while about 1 percent error is expected due to syringe measurements. The deviations are probably due to the solids in the samples. Because of these deviations no comparisons of the TOC of acidified and unacidified

Table 4.6 Breakthrough Study for Sewage on XAD-2

Volume Through Column (l)	Total Organic Carbon in Effluent			
	pH 2.0	(mg/l)	pH 7.2	
	Run 1	Run 2	Run 1	Run 2
Raw Sample	67	65	63	64
0.5		43	40	40
1.0	45	45	43	42
2.0	48	46	45	41
2.5	43	43	41	40
3.0	43	48	44	44
4.0	45	45	46	45
5.0	51	53	47	43
6.0		50	45	45
6.5	52			
7.0	67	62	56	50
8.0	62	64	55	50
9.0	68	66	54	58
10.0		66	63	60
10.3	69			
11.0	65	64	60	63
12.0		66		60
13.0	70	63	65	64
14.0	71	65	64	66
15.0	65	68	62	62
17.0	68	67	66	62
18.0		64	62	64
Composite	61	60	52	58

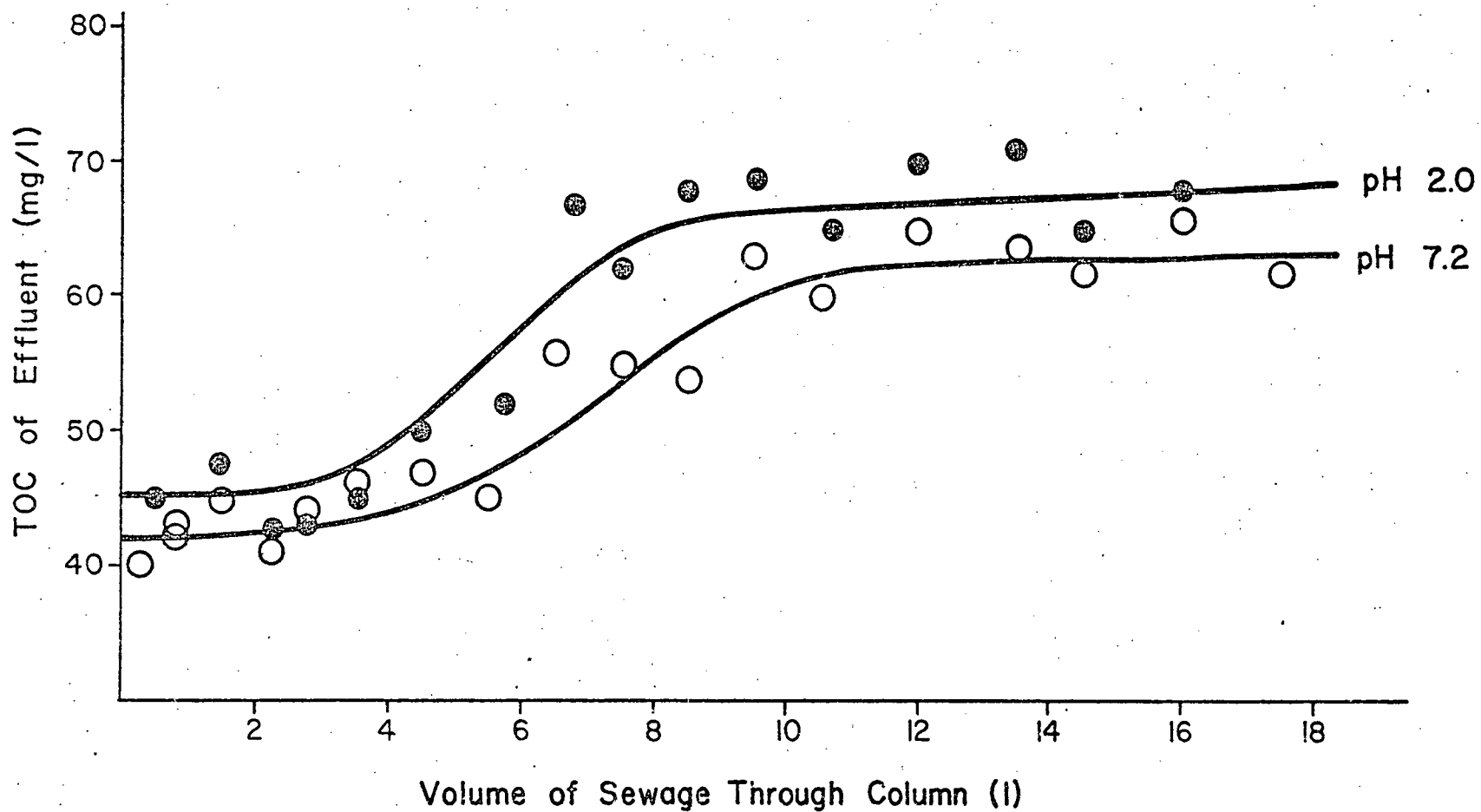


Figure 4.1 Recovery of Organics from Primary Effluent by XAD-2 Resin

effluent are justified. From the graphs in Figure 4.1 the capacity of the resin in terms of mg TOC/cc resin is 1.7 for both samples. This compares well with the results of Kennedy (1973) who showed that resin capacity can vary over an order of magnitude depending upon the polarity of the compound and quoted a capacity of 3.5-5.2 mg/cc for Vitamin B-12. There was no change in the turbidity of the samples after passage through the column. Turbidity values ranged from 20-25 JTU's as determined by the Jackson Candle (APHA 1971). The breakthrough point could be estimated visually by the movement of the yellowish brown colour down the resin column.

The breakthrough volume of the acidified sample appears to be smaller than that of the non-acidified sample. The breakthrough volumes are about 9 and 10 l or 120 and 133 column volumes respectively for acidified and non-acidified samples. The shift in breakthrough volumes corresponds to an increase in recovery of TOC upon acidification of about 4 mg/l. From Table 2.3, assuming the volatile acids are primarily acetic and the detergents dodécyl benzene sulphonates, the volatile acids and detergents contribute 12.1 mg/l of soluble TOC.

In summary, the XAD-2 resin extracts about 30% of the TOC from filtered primary effluent and has a saturation capacity of 130 column volumes. There is some evidence that acidification of samples results in premature saturation of the resin by volatile acids and detergents.

The extraction efficiencies of the solvent extractor and the XAD-2 resin for volatiles in primary effluent were compared by analyzing the concentrates. The GC traces are shown in Figure 4.2. The reasons for the poor quality of the chromatogram of the unchlorinated XAD-2 extract as compared to those of the solvent extract and chlorinated XAD-2 extract are not known. One likely explanation is the presence of sulphur compounds. Comparison of chromatograms (a) and (b) in Figure 4.2 indicates that the recoveries by the two techniques are very similar in terms of the concentrations of the

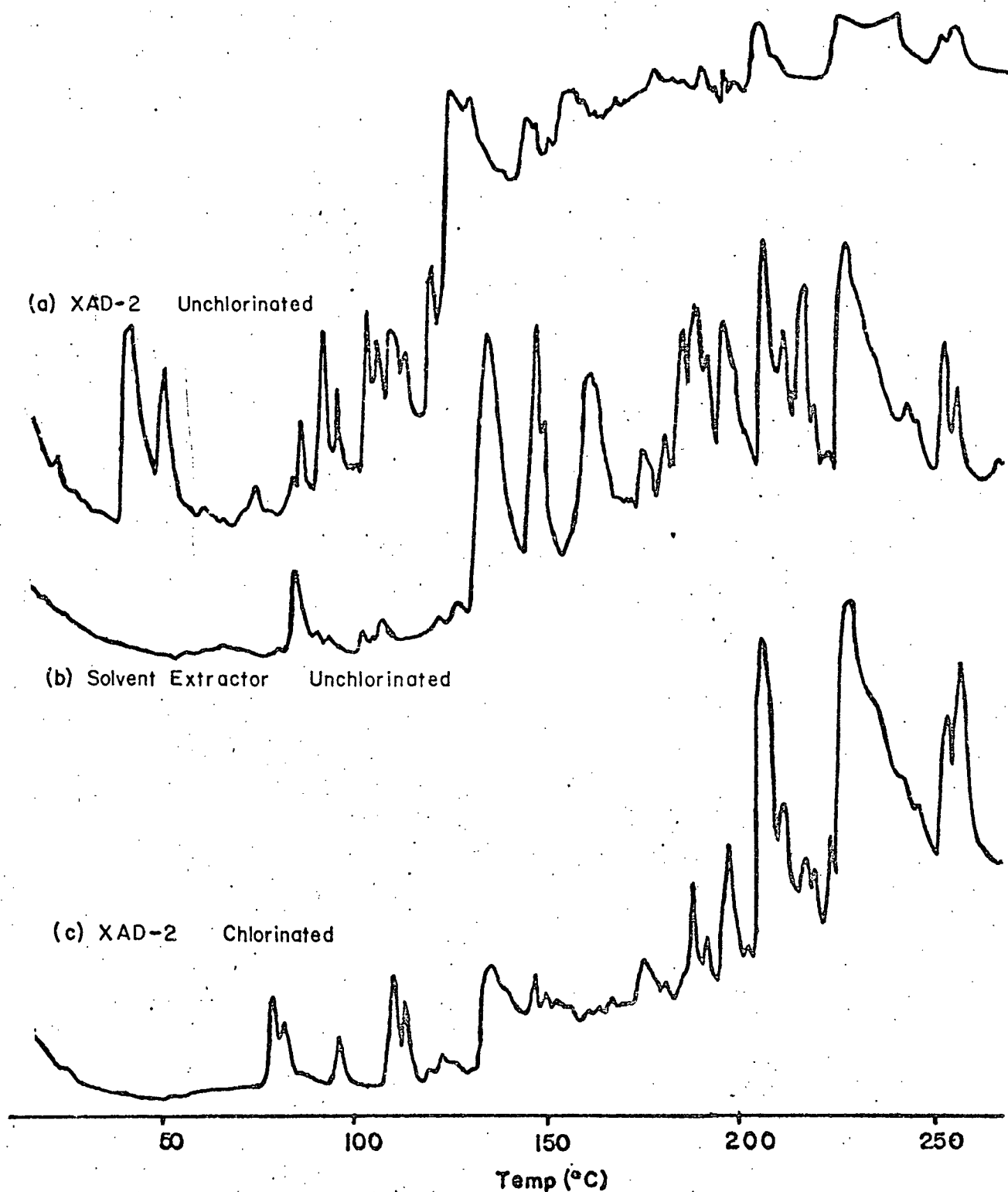


Figure 4.2 Continuous Solvent and XAD-2 Resin Extraction of Organics from Primary Effluent Monitored by GC. GC conditions in Appendix III.

individual components. The XAD-2 resin appears to be slightly better than solvent extraction with pet ether in terms of the number of compounds extracted.

A cursory examination of the volatiles extractable from the particulates was made to gain some idea as to their complexity. The results of the GC investigation of the extracts are shown in Figure 4.3. The extracts contain twelve to seventeen peaks, two or three of which are extremely large. There are fewer peaks in the chlorinated sample. It must be kept in mind that different solvents were used, however the solubilization of organics through oxidation is also possible. There are also some new peaks in the $\text{CHCl}_3/\text{MeOH}$ extract as compared to the MeOH extract. Although further investigation of these extracts is obviously warranted, due to limitations on time it was decided to concentrate on the soluble fraction.

B. Separation Experiments

1. Preliminary Separation

GC resolution was not sufficient to adequately separate all of the components of the primary effluent extract (Exp. E-5). It is further recognized that the sensitivity of the EC detector for chlorinated and oxygenated compounds is much greater than that of a GC-MS, thus it was decided to concentrate the extracts to 0.2-0.5 ml which would tend to increase the problems of resolution. Therefore it was decided to attempt preliminary separation of the extracts prior to GC analysis.

A representative set of results from the Silica Gel column experiments (Exp. S51a) are shown in Figure 4.4. Although the background is considerably reduced, upon close inspection of these GC traces, one finds them remarkably similar. It would appear that channeling occurred in the Silica Gel columns. Furthermore, changing of the eluting solvent resulted in a dramatic change in the consistency of the gel with the result that the flow rate through the

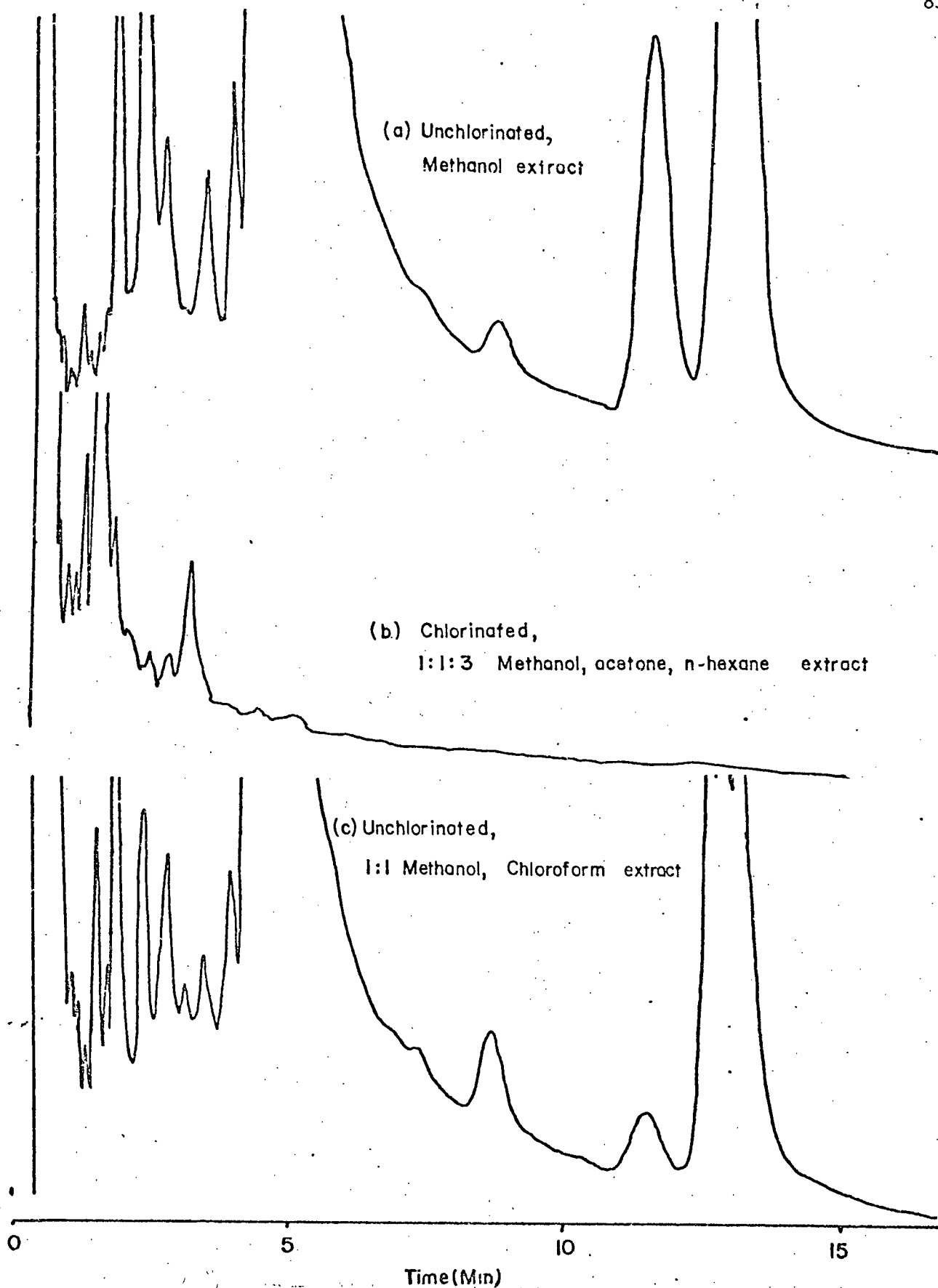


Figure 4.3 Soxhlet Extracts of Particulates Analyzed by GC. GC conditions in Appendix III.

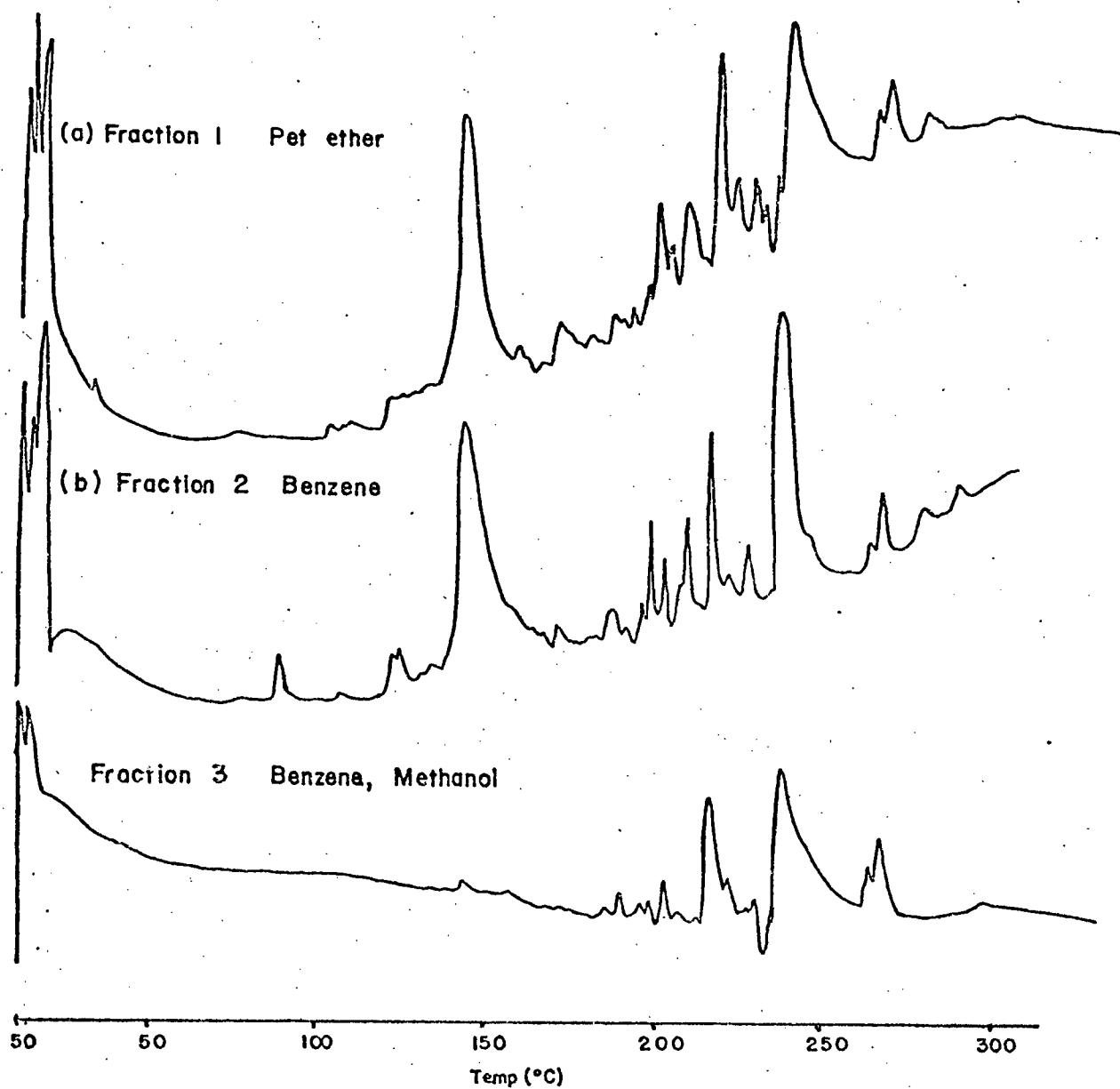


Figure 4.4 Silica Gel Column Fractionation of Primary Effluent Extracts Analyzed by GC. GC conditions in Appendix III.

column was considerably decreased. Flow rates with MeOH/Benzene were about 0.01 ml/min. In order to speed separation either wide columns with large volumes of eluant and decreases in resolution or some type of pressurization of the column were necessary. Only propipettes were available for the latter purpose and rather than risk the introduction of impurities, the silica gel column method was discontinued in favour of acidity separation.

A representative set of GC chromatograms of the acidity separated fractions of the XAD-2 extracts are presented in Figure 4.5 (Exp. S-1b). Comparison of the three traces shows that the EC detectable material is almost equally divided between the neutral + basic fraction (N + B) and the weak acid fraction (WA). There were few compounds in the strong acid fraction which is not surprising since no derivatization was carried out to make the acids volatile enough to be analyzed by GC.

There are an unexpectedly large number of peaks at the low temperature end of the WA fraction. The chromatograms on OV-17 and OV-225 also have this feature. This leads one to suspect incomplete separation probably due to the high solubility of diethyl ether in water. The peaks numbered 1 through 7 in Figure 4.5 are those suspected of being present in both the WA and N + B fractions and which rightly belong in the N + B fraction. The alternative of using pet ether is not attractive since many oxygenated or polar compounds are only sparingly soluble in this solvent. It was therefore decided to wash future aqueous extracts with 4 x 10 ml of diethyl ether rather than with just the one 10 ml portion employed in this separation. Since many phenols are not sufficiently acidic to be completely extracted by the bicarbonate, it was decided to discontinue the bicarbonate extraction and use only the sodium hydroxide extraction.

2. G.C. Optimization

The objective of this portion of the project is to determine the best

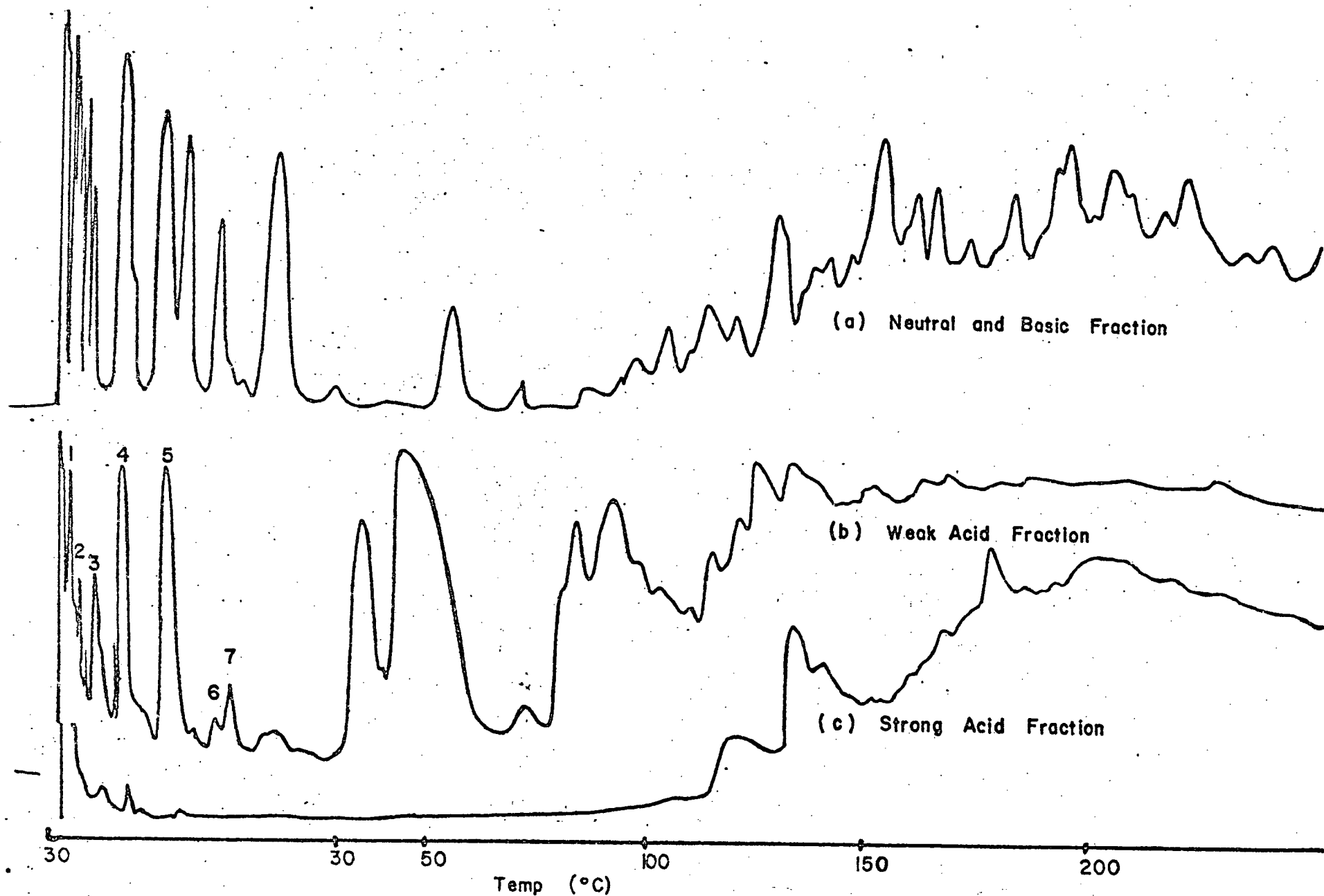


Figure 4.5 Acidity Separation of Primary Effluent Extracts Analyzed by GC. GC conditions in Appendix III.

GC phase and the optimum temperature program for separation of the volatiles in sewage (Exp. S-2). The OV series of silicones were chosen for reasons outlined in Chapter II. The basic criteria to be used for comparison of these phases and temperature programs are the elution of the maximum number of compounds in a reasonable time and the resolution of these compounds.

Representative chromatograms of the N + B and WA fractions of the sample chlorinated at 15 mg/l Cl_2 are shown in Figures 4.6 through 4.9. The SA fractions showed about a dozen fairly well resolved peaks by EC and FID (Figs. 4.17, 4.18). With the OV-101, OV-17 and OV-225 columns, the optimum temperature program was 30°/10 minutes, 6°/minute, and 200°C/20 minutes for both fractions. Due to the large number of low-boiling compounds in the extracts, OV-1 was of limited use because of its lower temperature limit of 100°C. The other phases provide good separation of the N + B fraction (Figures 4.6 and 4.8) at low temperatures, however all of them have some resolution problems above 100°C. Comparison of the WA fraction on the various phases (Figures 4.7 and 4.9) shows that fewer peaks are observed with the OV-225 phase than with OV-101 or OV-17. This is probably due to the high polarity of the OV-225 phase. No memory effects were observed during these analyses.

3. TLC Separation of Acidity Fractions

The main objective of this work was to further separate the acidity fractions so that each peak observable in the GC-MS consisted of only one compound.

A sample set of chromatograms as monitored by GC with an EC detector are presented in Figures 4.10 and 4.11. A "worst possible" blank and EC trace of the sample before TLC are included in these figures. It is evident that most of the more volatile compounds are lost during TLC manipulations. With pet ether as the developer one can see from Figure 4.10 that most of

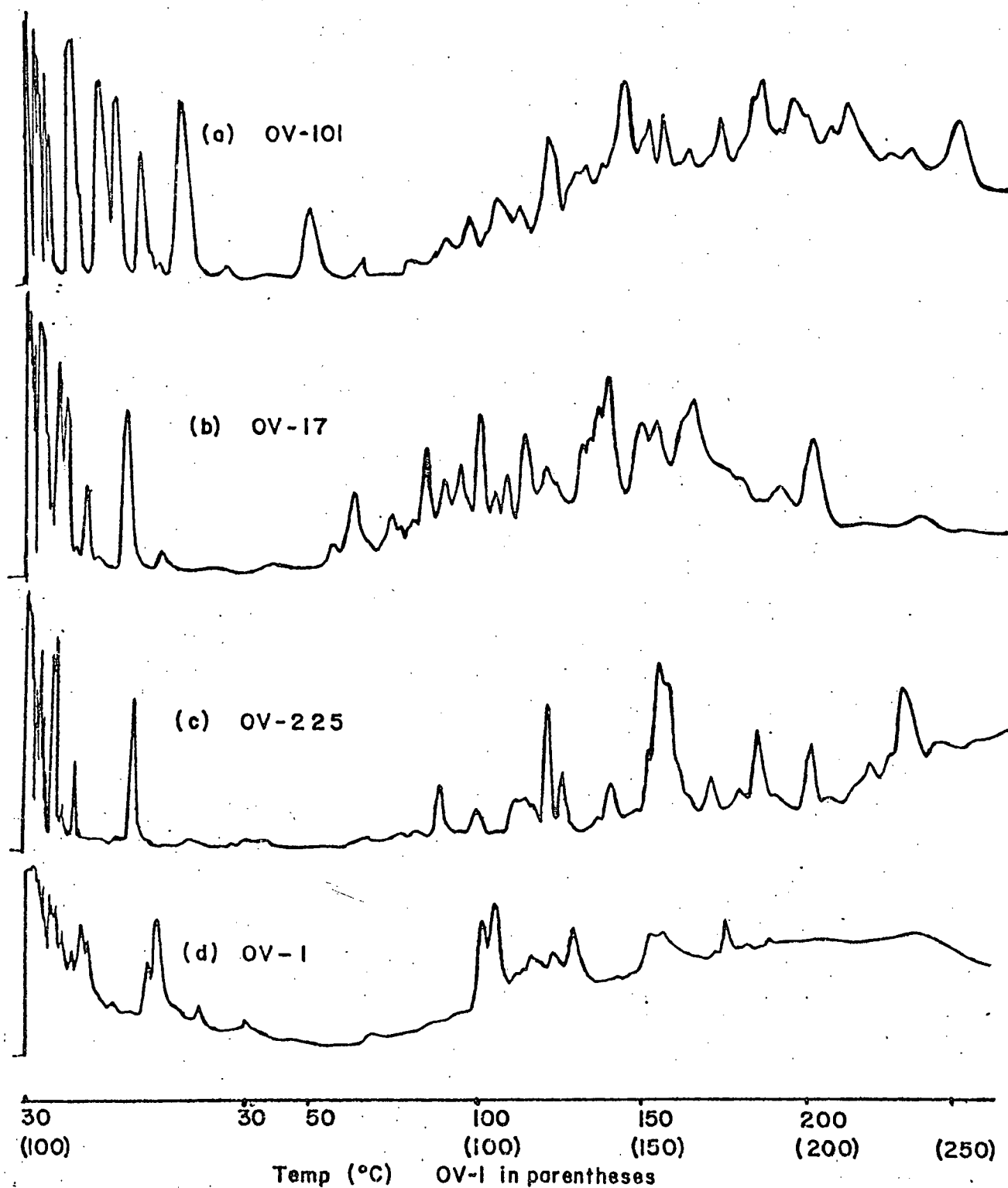


Figure 4.6 GC Optimization N + B by EC. GC conditions in Appendix III.

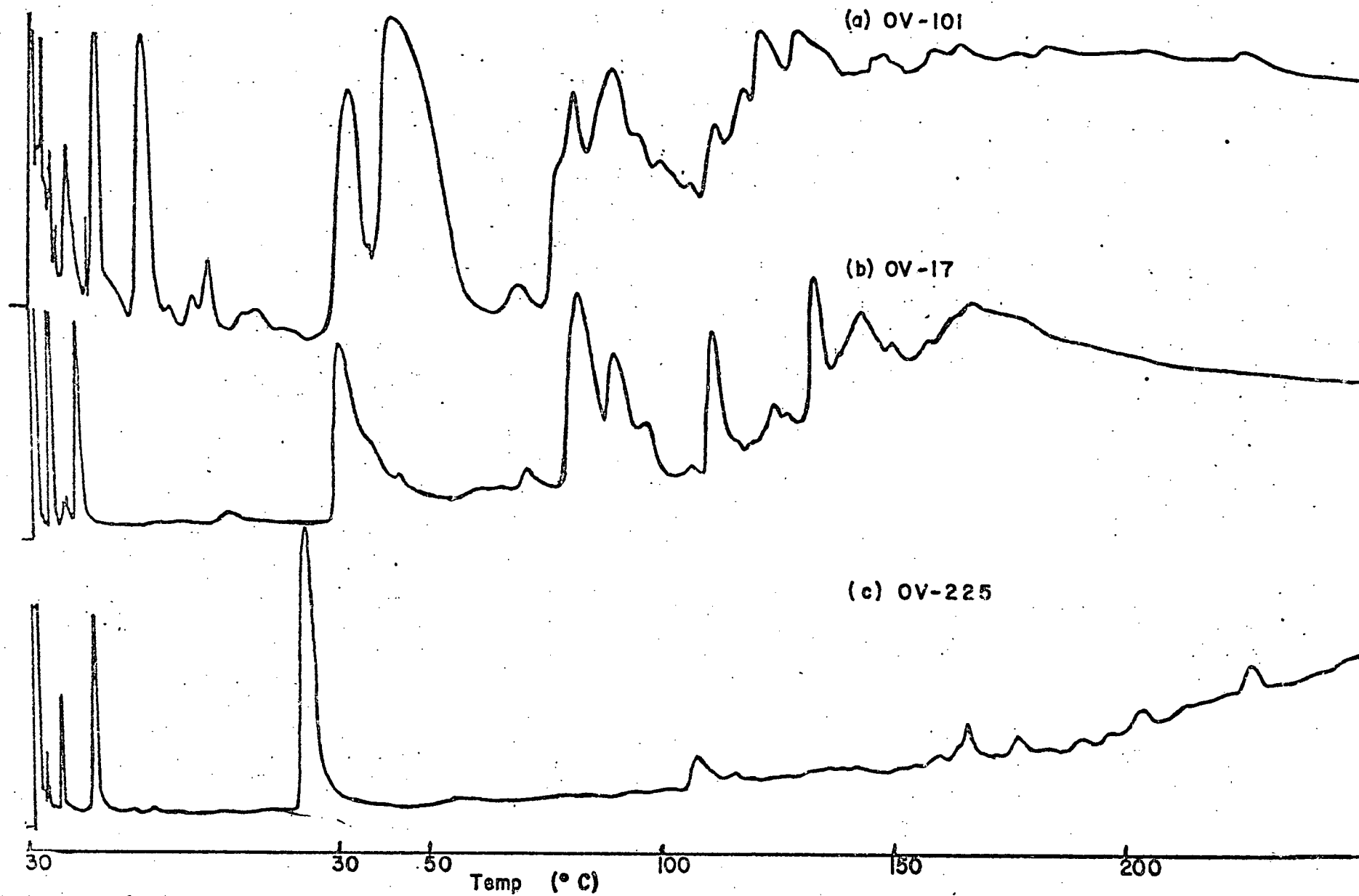


Figure 4.7 GC Optimization WA by EC. GC conditions in Appendix III.

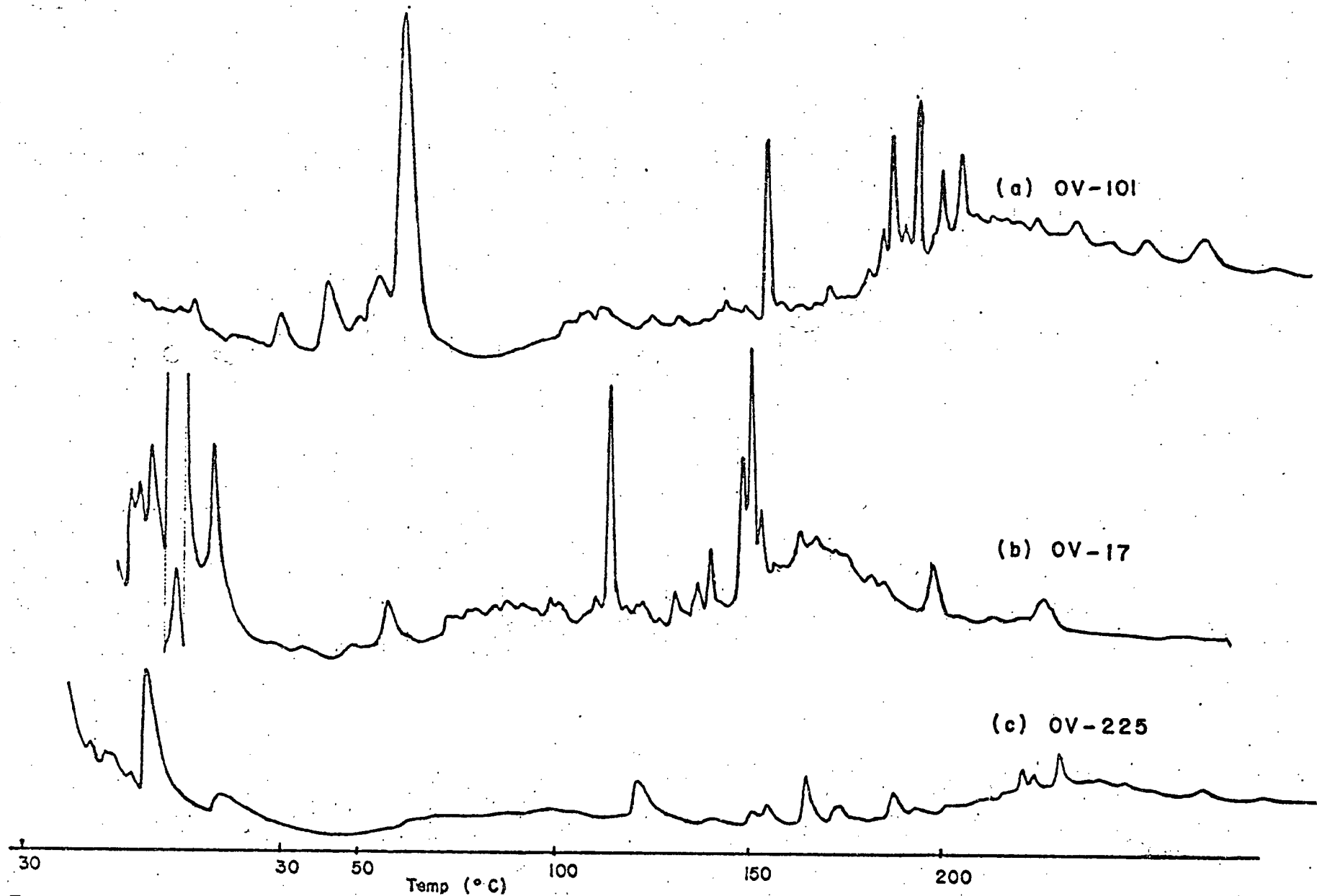


Figure 4.8 GC Optimization N + B by FID. GC conditions in Appendix III.

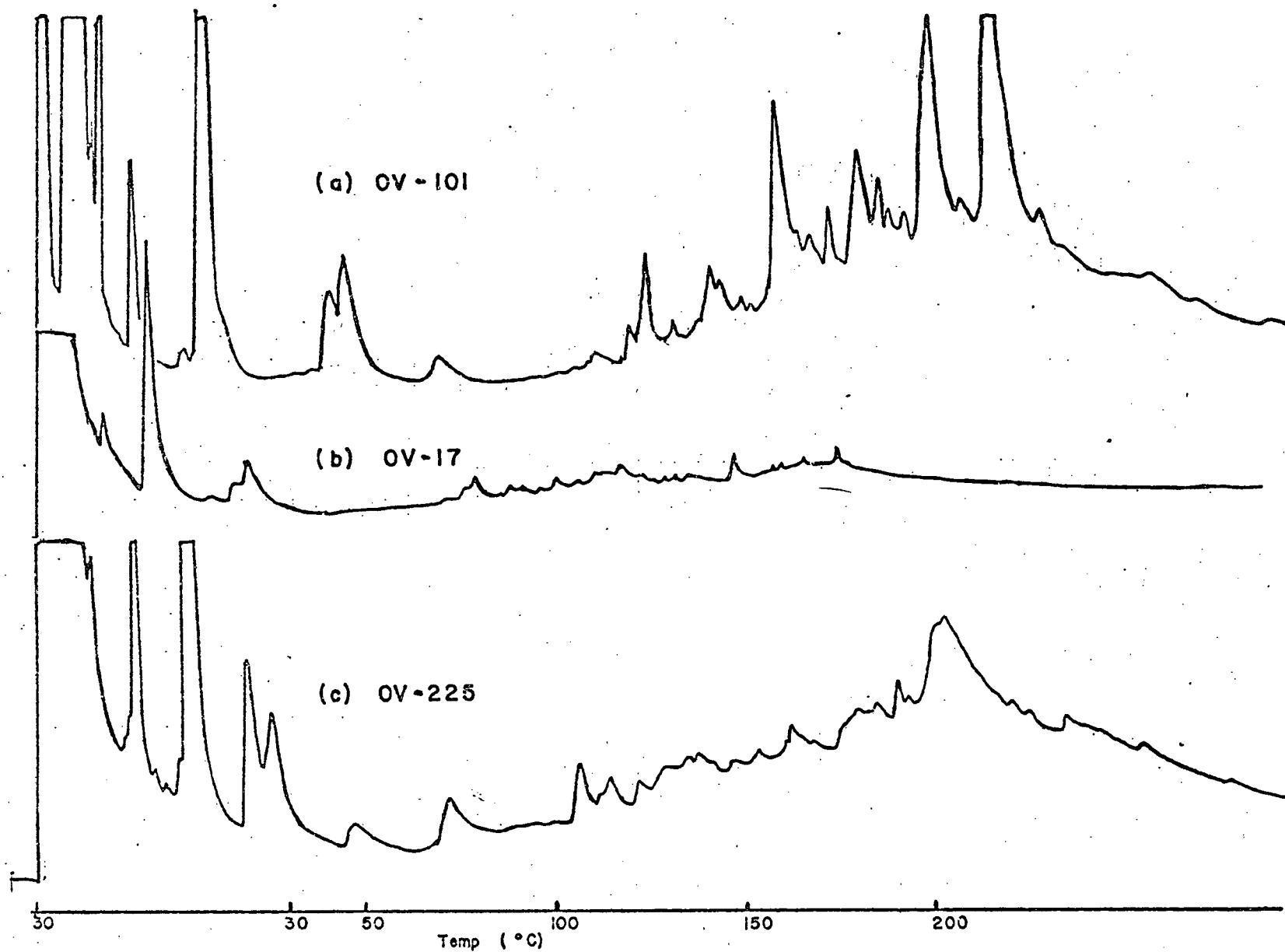


Figure 4.9 GC Optimization WA by FID. GC conditions in Appendix III.

the recoverable EC detectable material has an R_f of less than 0.25. This fraction was rechromatographed with methanol as a developer. In this second chromatogram (Figure 4.11) it is extremely surprising that most of the material has an R_f value of less than 0.5. Unfortunately the material from this chromatogram having R_f 0.0 to 0.25 was lost and only the material of R_f 0.25 to 0.50 was analyzed by GC-MS.

Figures 4.10 and 4.11 and subsequent GC-MS analysis showed that along with the loss of the more volatile components, there was also some removal of the less polar compounds. The data showed however that many of the peaks observable by GC-MS were probably still containing more than one component.

In summary, it is suggested that for preliminary separation high speed liquid chromatography rather than the combination of acidity and TLC techniques should be employed. This would allow a cleaner, less cumbersome separation of components without loss of the more volatile ones, and could be expediently complemented with ultimate separation by GC.

In any case an outline of the extraction and separation methods finally adopted for this project is shown in Figure 4.12.

C. Effects of Chlorination on Primary Effluent

1. Soluble TOC

The results presented in Table 4.7 indicate that there is very little change in the soluble organic carbon of sewage as a result of chlorination (Exp. C1-1).

It is also apparent from these results that the 0.45 μ membrane filters can remove 20 percent of the carbon from primary effluent which has been previously filtered through glass fiber filters of 1.0 μ pore size.

2. Effects Monitored by EC and FI Detectors

The chromatograms of the various extracts are shown in Figures 4.13 through 4.22 (Exp. C1-2). These chromatograms were chosen to illustrate

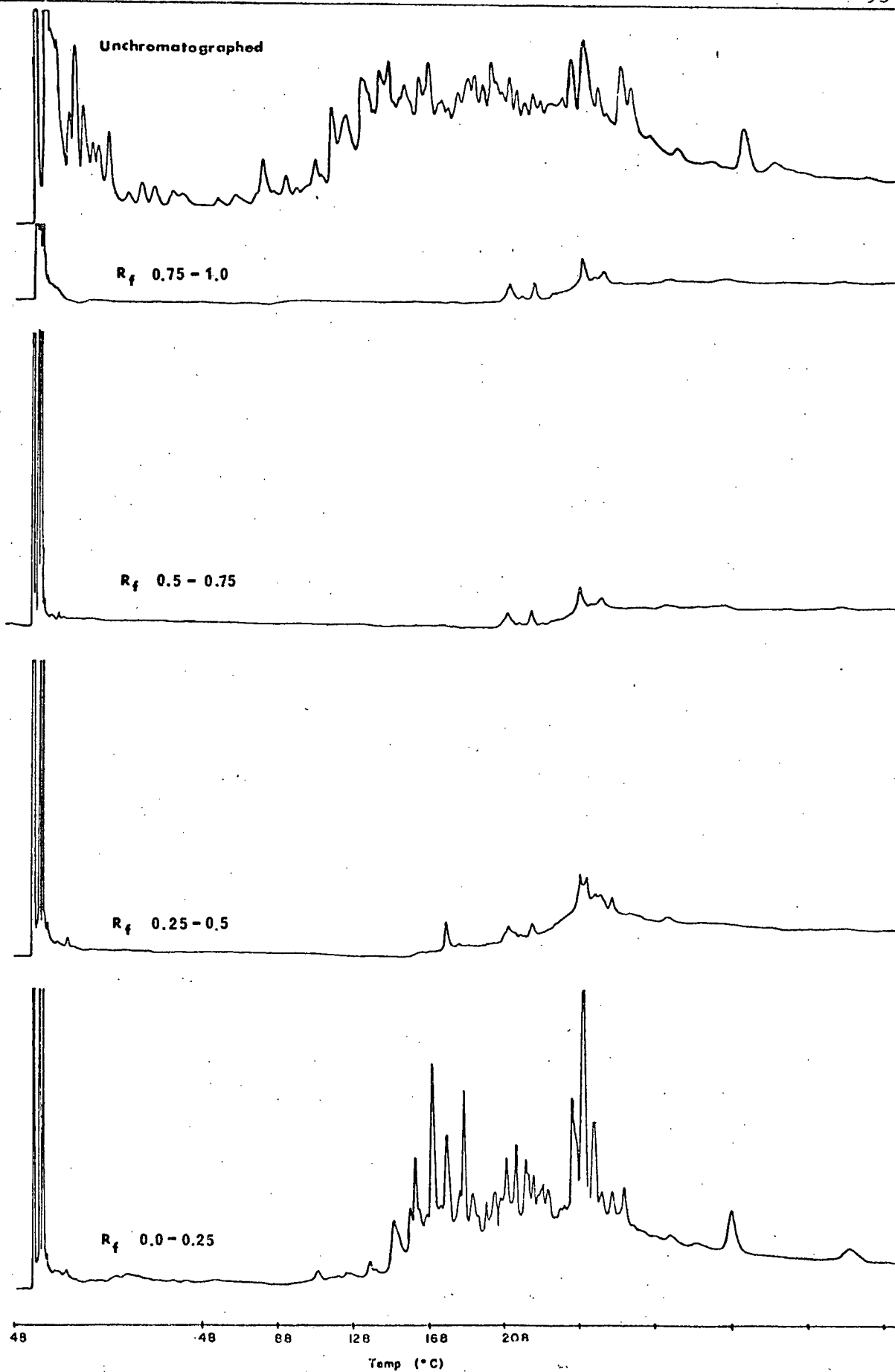


Figure 4.10 TLC of N + B Fraction; Silica Gel, Pet Ether. GC conditions in Appendix III.

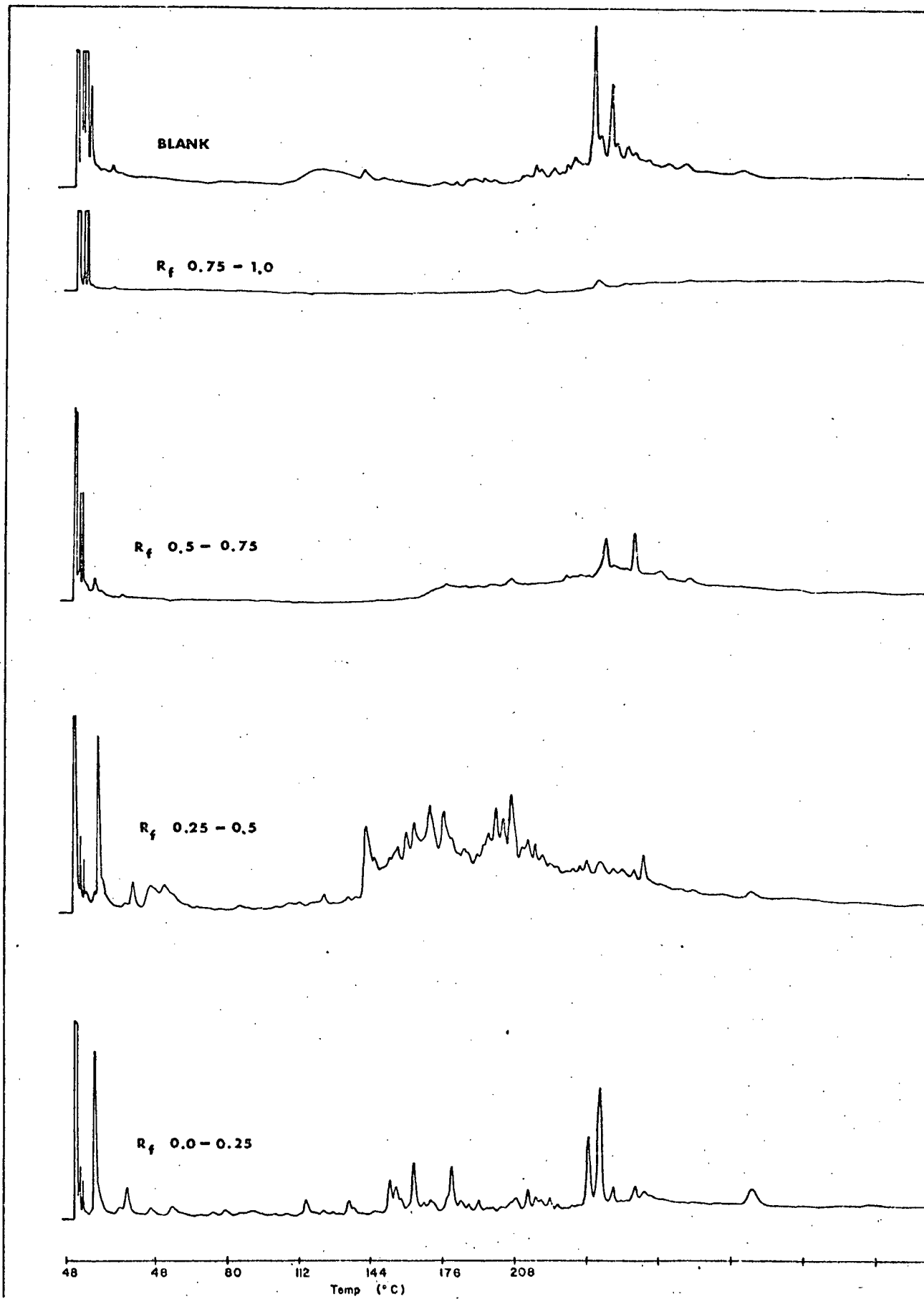


Figure 4.11 TLC of N + B/TLC Fraction; Silica Gel, Methanol. GC conditions in Appendix III.

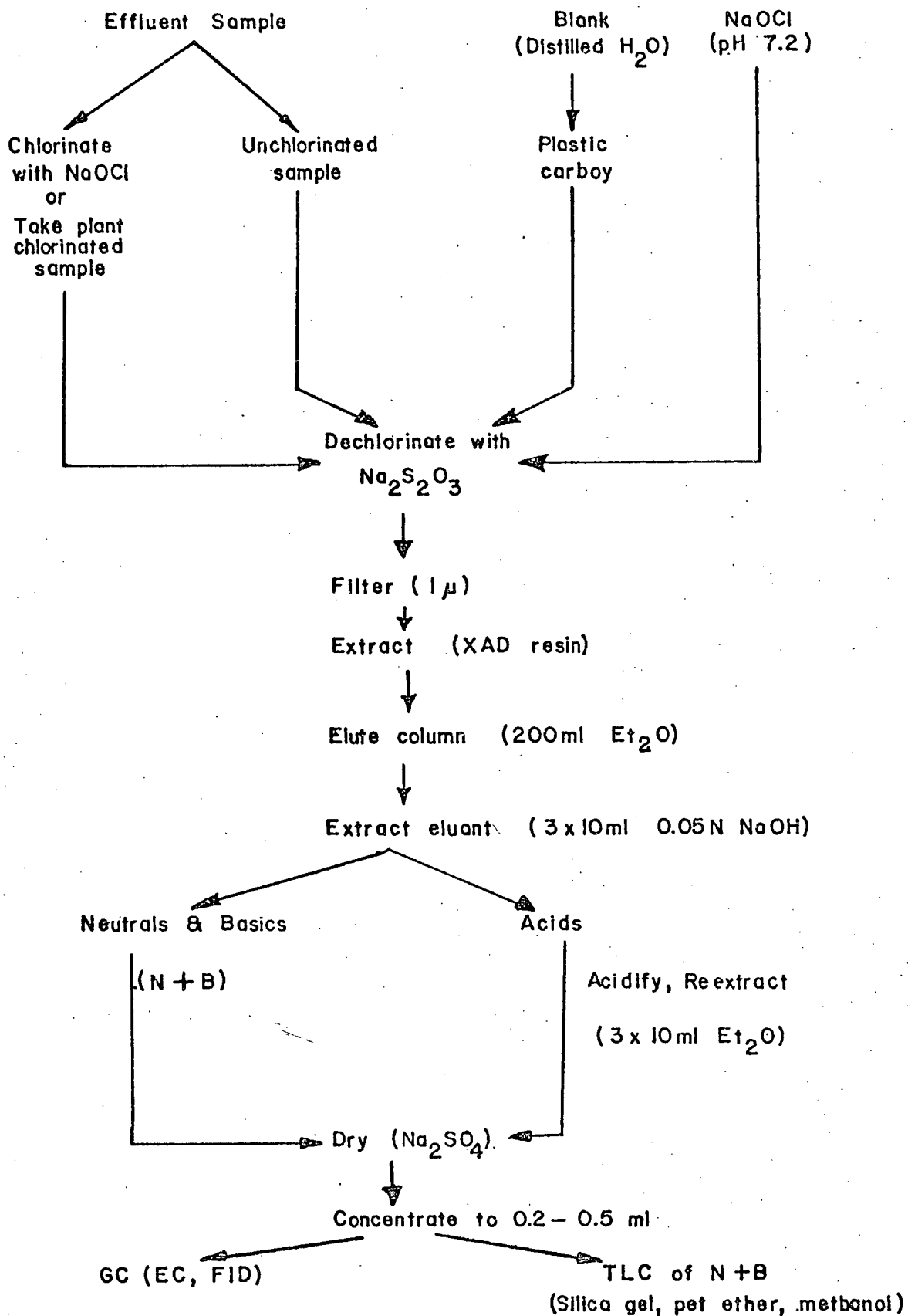


Figure 4.12 Flowchart of Separation Procedure

Table 4.7 Effect of Chlorination on Soluble TOC

Chlorine dose		TOC	TOC
mg/l Cl_2	mg/l Cl_2	(size $< 1\mu$)	(size $< 0.45\mu$)
		(mg/l)	(mg/l)
	0	50	37
	12	50	37
	103	48	39

the effect of various dosages of chlorine upon the acidity separated fractions of the extracts and the reproducibility of these effects between two different samples of primary effluent. Before discussing these chromatograms in detail some general points should be made. The reproducibility of the chromatograms is not good particularly in the low temperature region due to the long initial isothermal period at almost ambient temperature. Therefore only changes in patterns of peaks are taken as indications of changes due to chlorination although it is recognized that shifts in the retention time of a series of peaks may not always be an artifact of analysis. It is further noted that there may be differences in concentration among the various extracts. These differences which are most apparent in the FID traces, can be minimized by normalizing peak heights to those of the unchanged peaks. Finally, the carrier gas flow rate was significantly higher during the analysis of the sample dated March 8. The higher flow rate resulted from detector response optimization studies carried out on March 10. Since flow rates are never exactly reproducible and pattern recognition techniques could be employed during the comparisons, it was decided to sacrifice flow rate reproducibility in order to standardize the detector response.

The peaks whose magnitudes were increased due to chlorination are marked with an "I" and those whose magnitude was decreased are marked with a "D" in each figure. The total number of changes in each extract is summarized in Table 4.8. One of the most striking features of Table 4.8 is that with an EC detector the number of increases far outnumbers the number of decreases. This indicates that the yields of these products of chlorination are small, the products result from non-electron capturing precursors or the precursors are high molecular weight and/or non-solvated molecules.

Many more increases are detected by the EC than by the FID whereas the

Table 4.8 - Effects of Chlorination by GC Analysis

With FID and EC Detectors

Figure	Sample Date	Fraction	Detector	No. of Increases	No. of Decreases
4.13	18/12/74	N + B	EC	15	3
4.14	18/12/74	N + B	FID	4	2
4.15	18/12/74	WA	EC	12	5
4.16	18/12/74	WA	FID	4	2
4.17	18/12/74	SA	EC	1	0
4.18	18/12/74	SA	FID	0	0
4.19	8/03/75	N + B	EC	18	5
4.20	8/03/75	N + B	FID	5	1
4.21	8/03/75	A	EC	2	0
4.22	8/03/75	A	FID	0	0

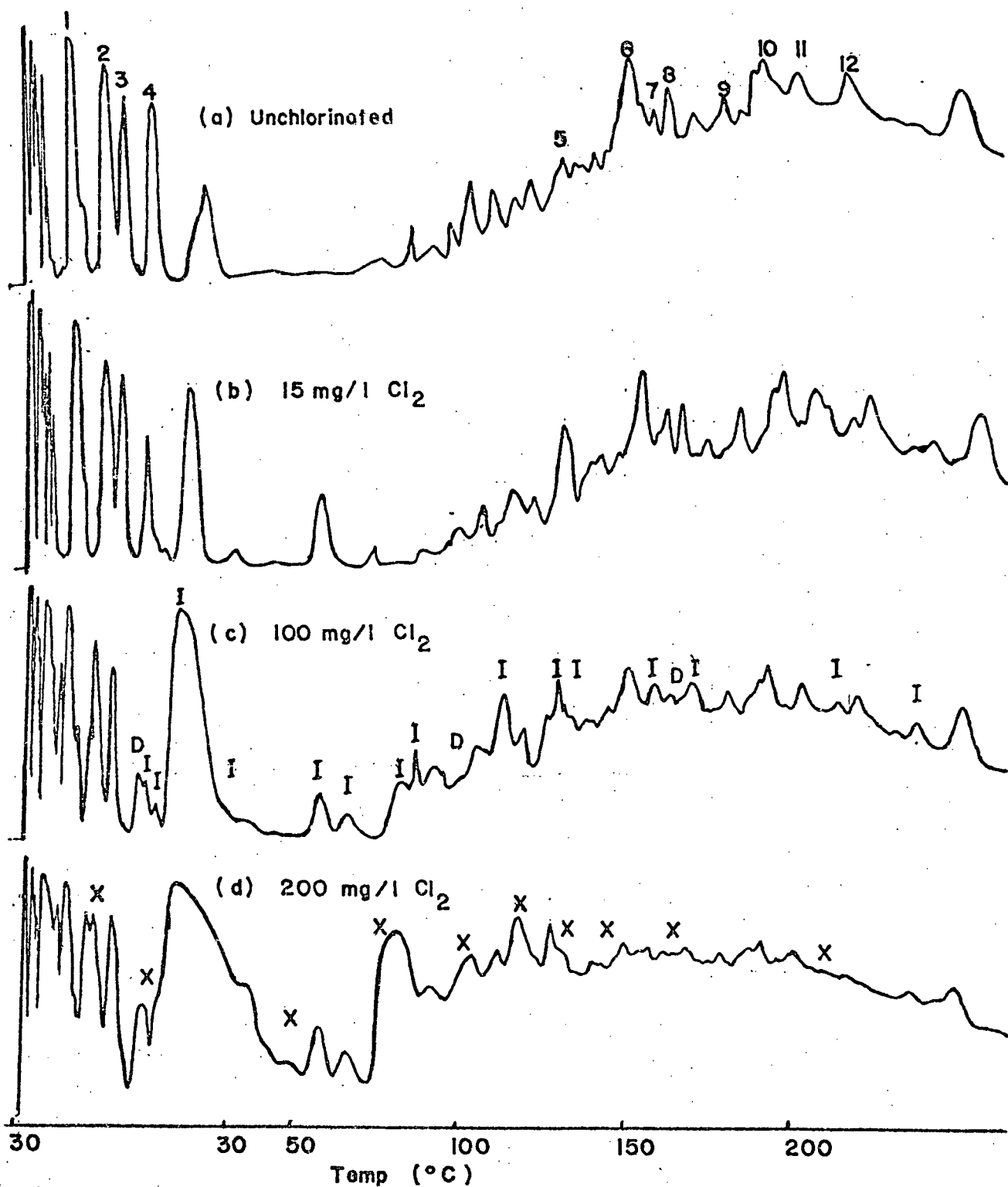


Figure 4.13 Effects of Chlorination by GC - N+B by EC-1. GC conditions in Appendix III. Explanation of Symbols in text.

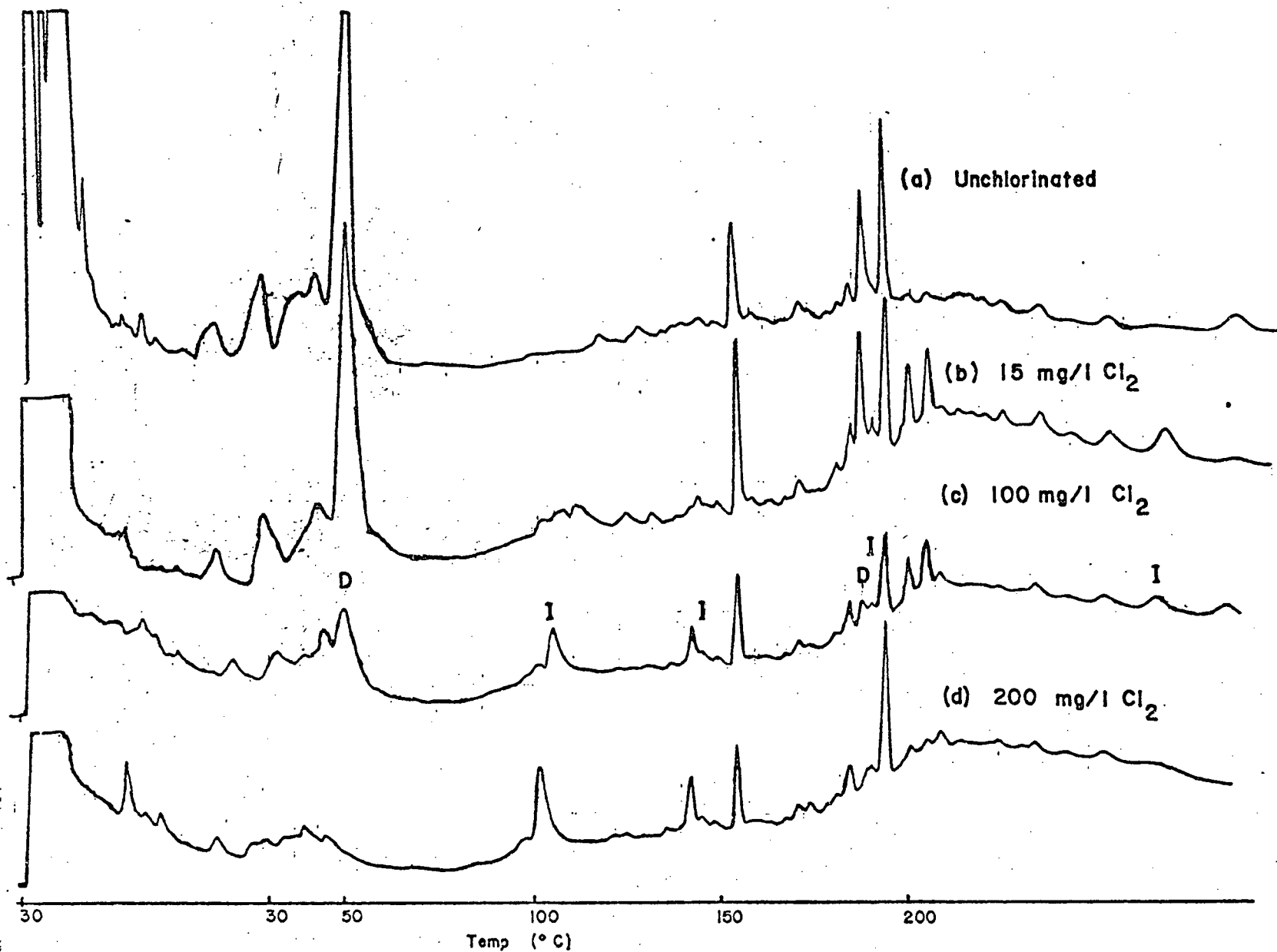


Figure 4.14 Effects of Chlorination by GC - N+B by FID-1. GC conditions in Appendix III. Explanation of Symbols in text.

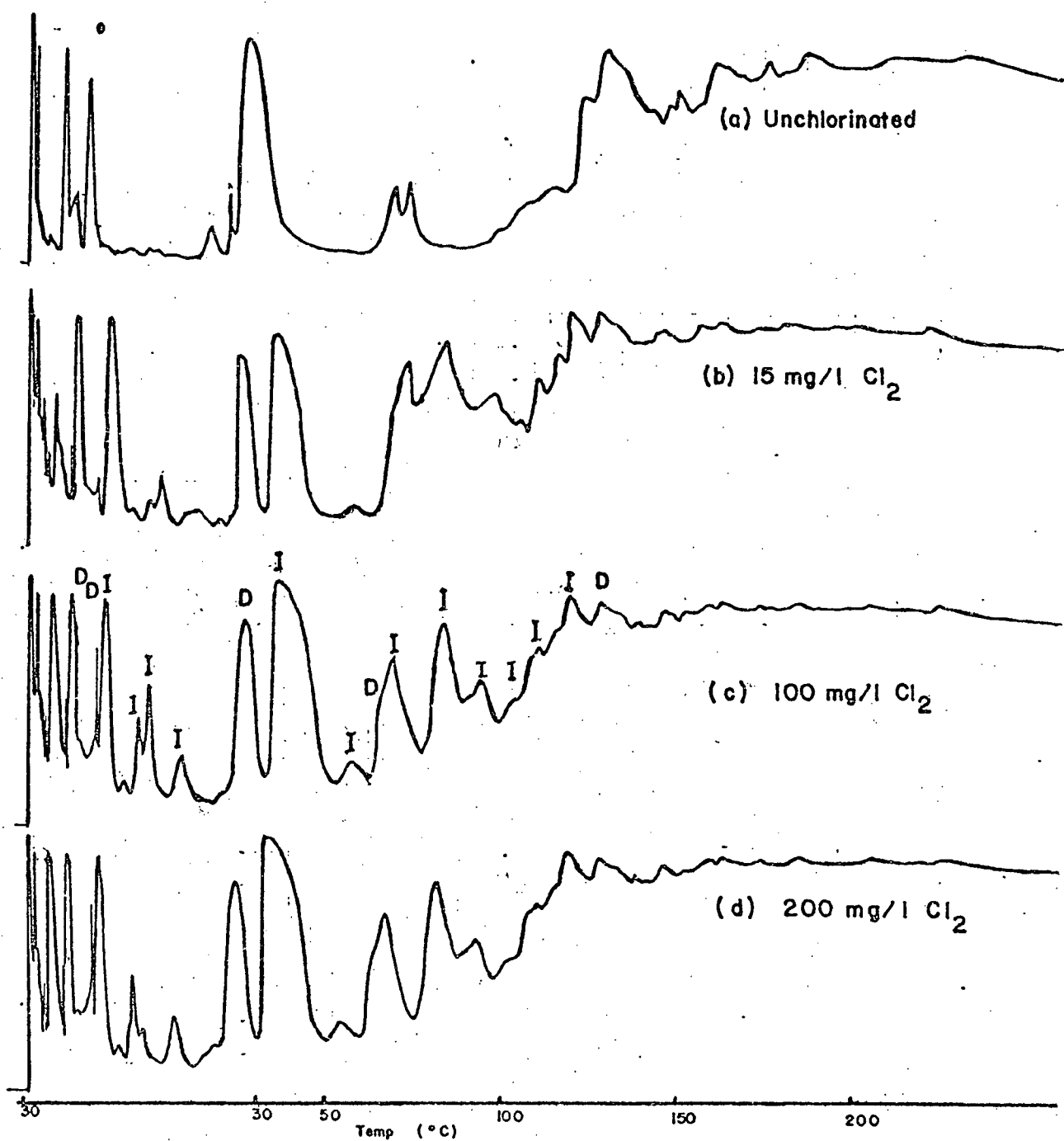


Figure 4.15 Effects of Chlorination by GC - WA by EC. GC conditions in Appendix III. Explanation of Symbols in text.

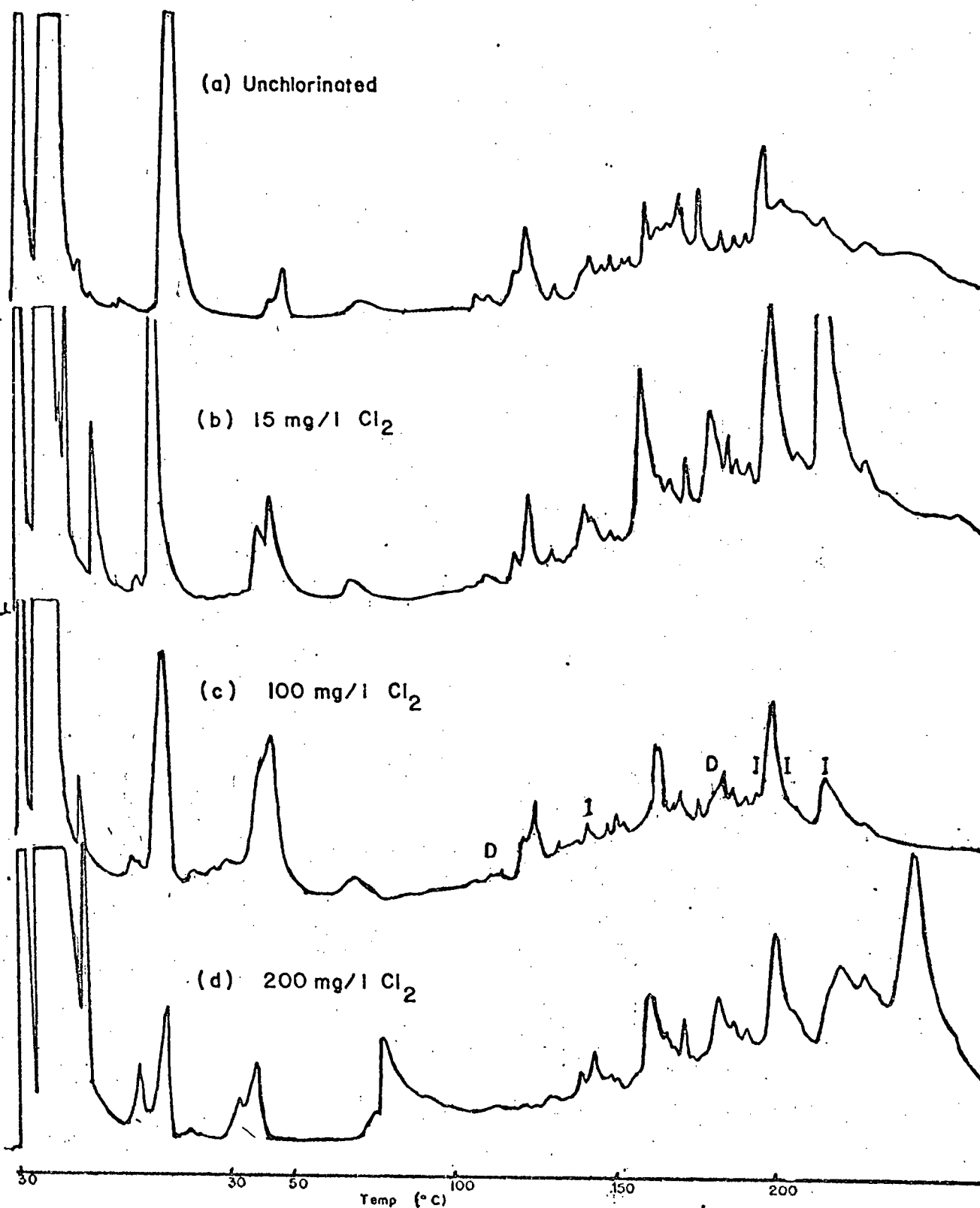


Figure 4.16 Effects of Chlorination by GC - WA by FID. GC conditions in Appendix III. Explanation of Symbols in text.

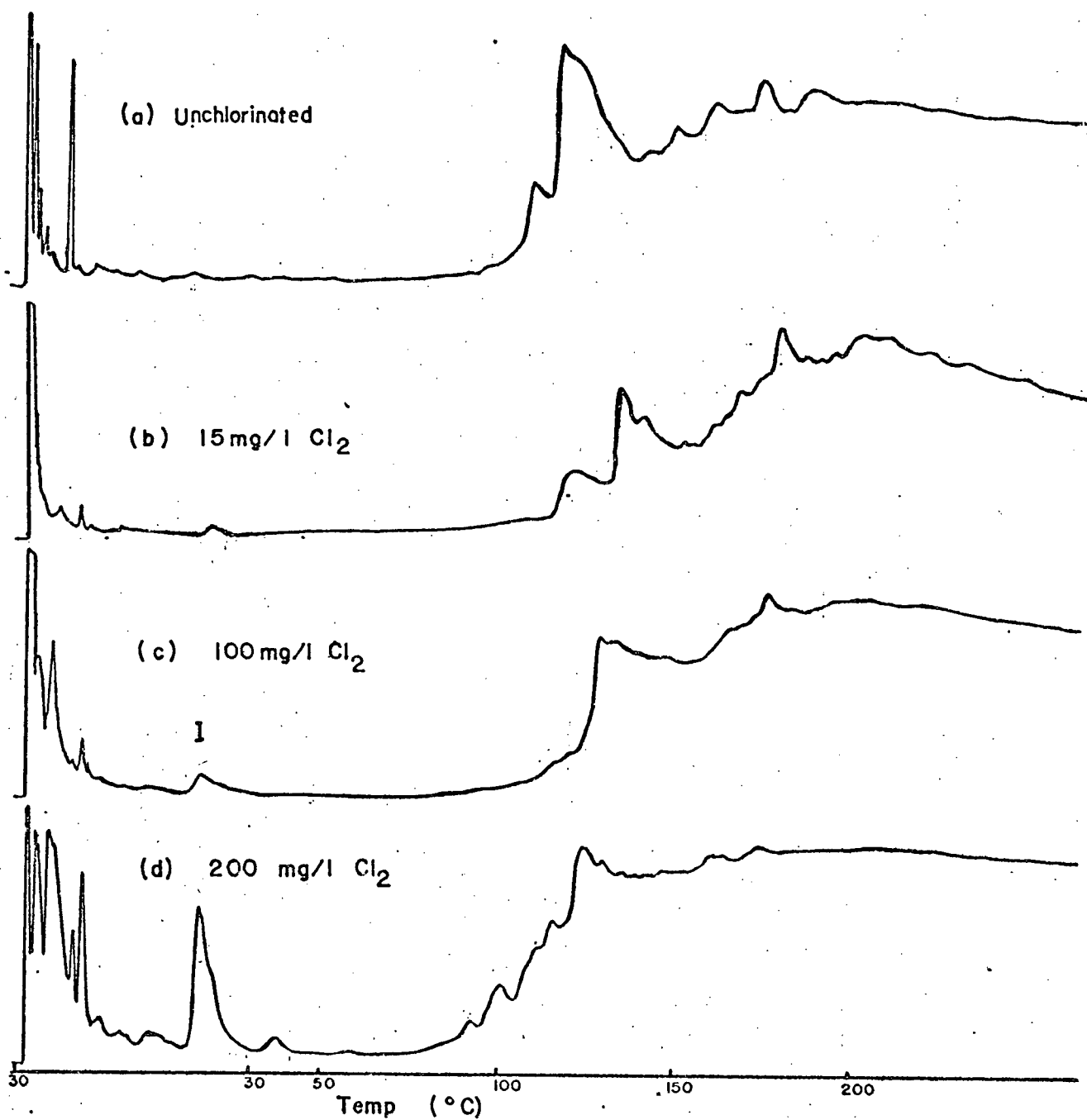


Figure 4.17 Effects of Chlorination by GC - SA by EC. GC conditions in Appendix III. Explanation of Symbols in text.

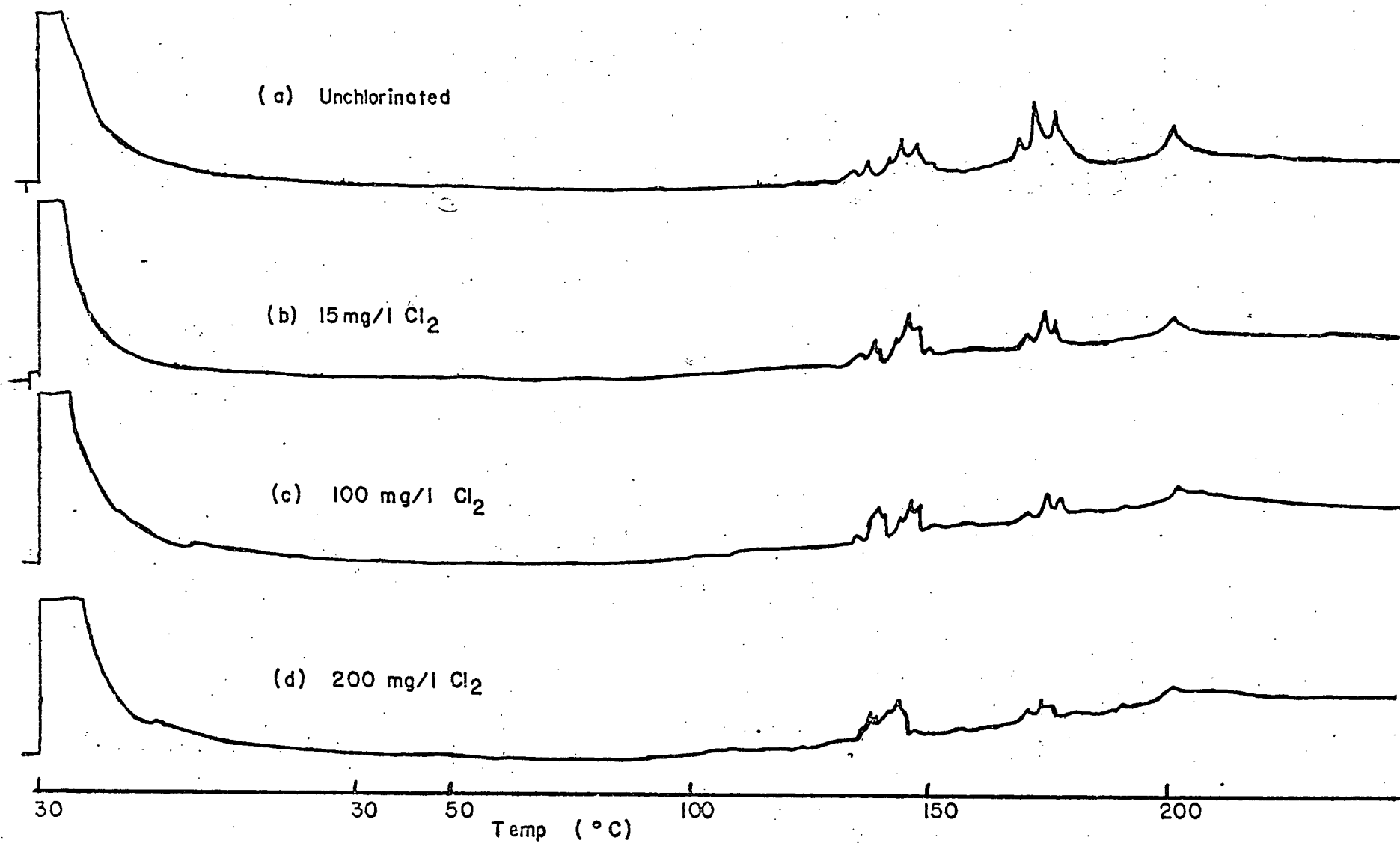


Figure 4.18 Effects of Chlorination by GC - SA by FID. GC conditions in Appendix III.

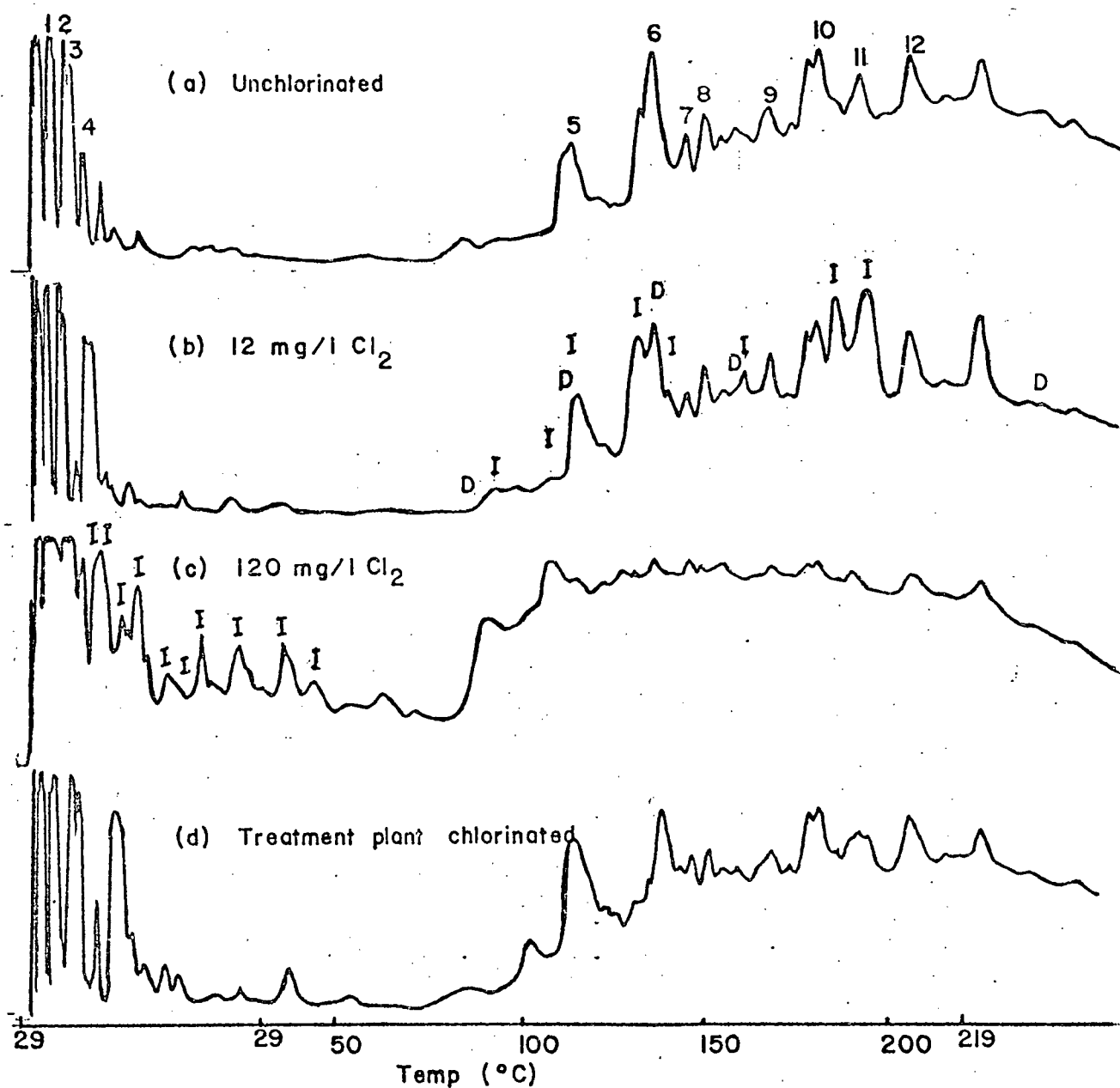


Figure 4.19 Effects of Chlorination by GC - N+B by EC-2. GC conditions in Appendix III. Explanation of Symbols in text.

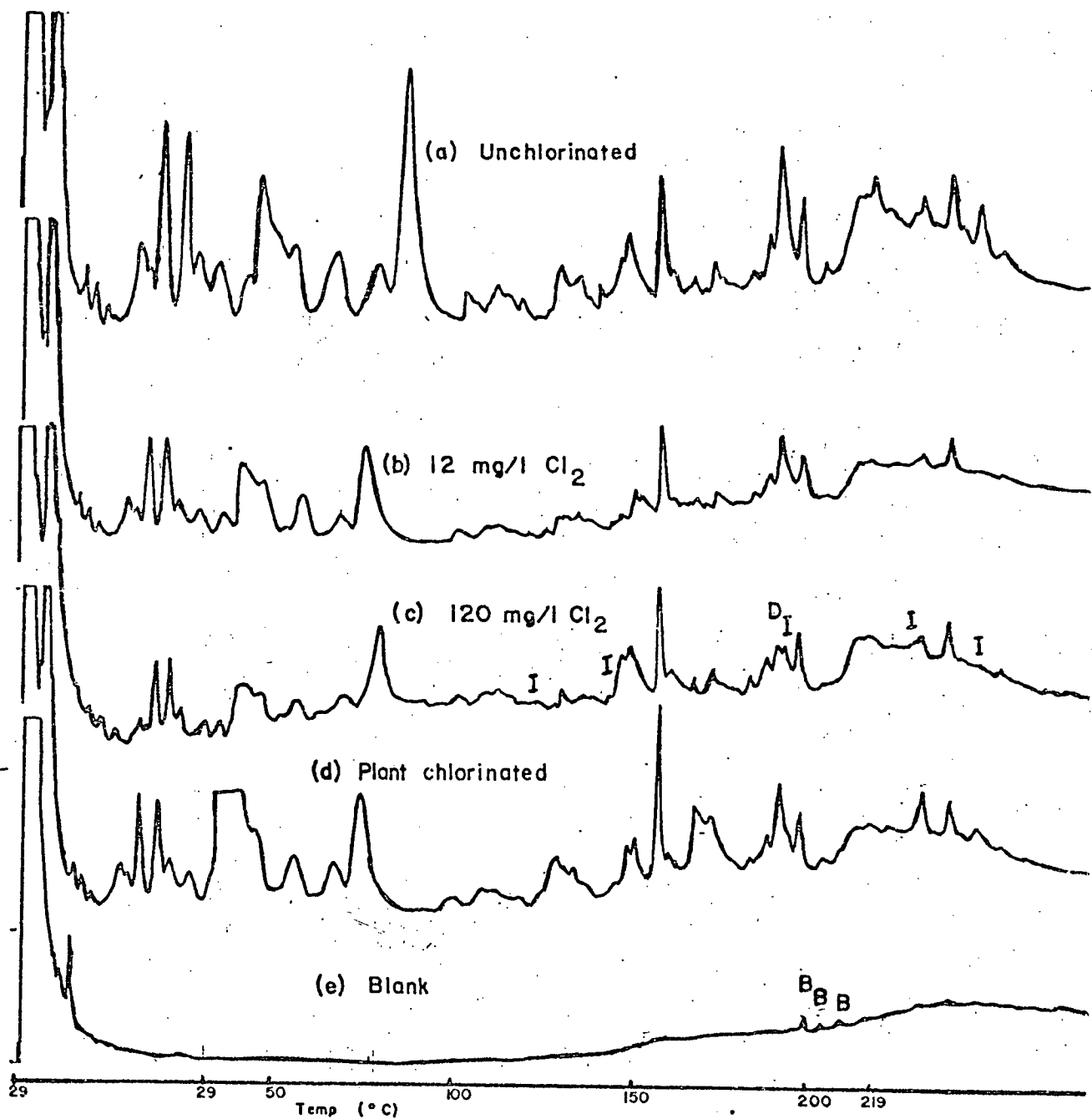


Figure 4.20 Effects of Chlorination by GC -N+B by FID-2. GC conditions in Appendix III. Explanation of Symbols in text.

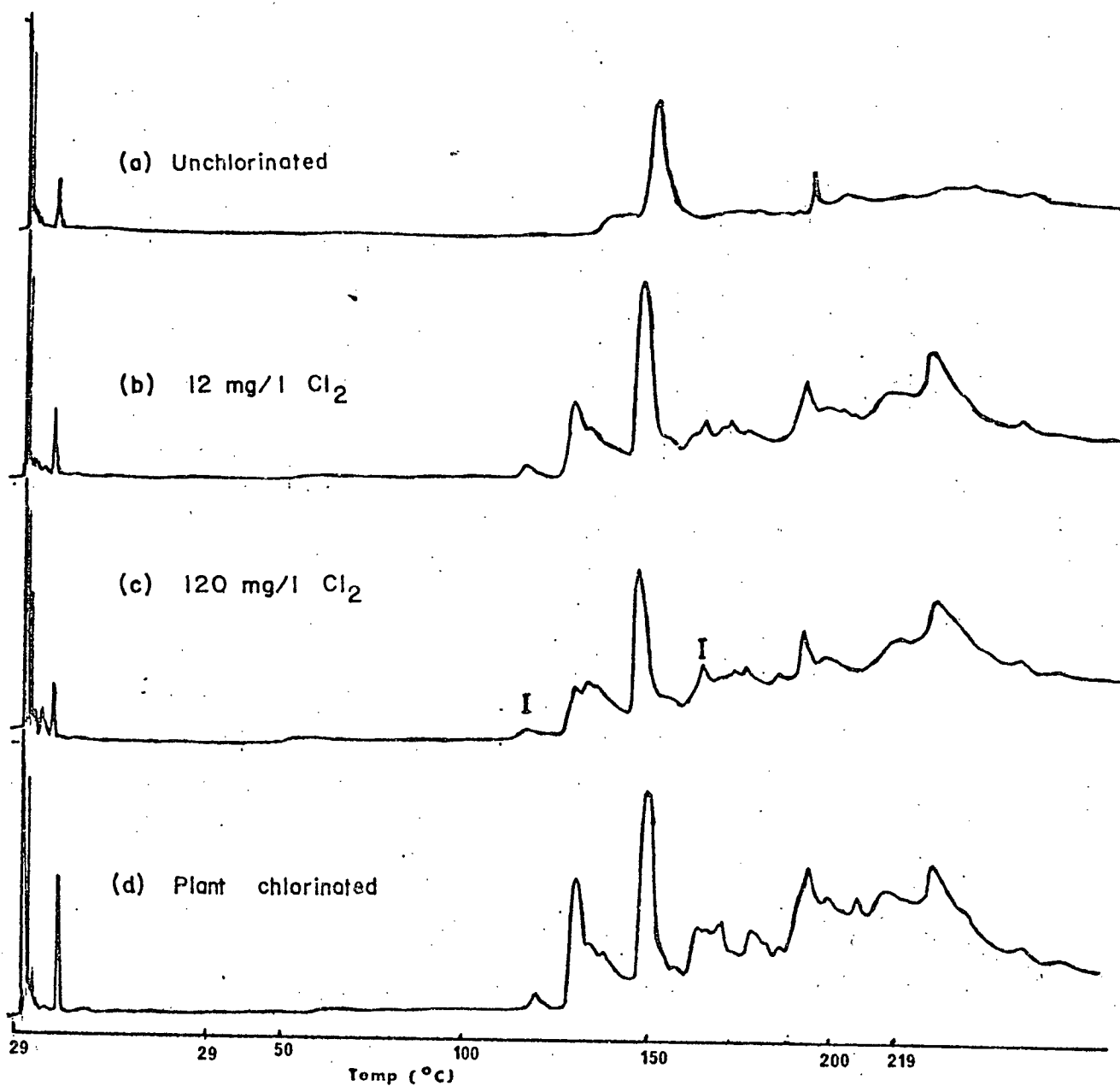


Figure 4.21 Effects of Chlorination by GC - A by EC. GC conditions in Appendix III. Explanation of Symbols in text.

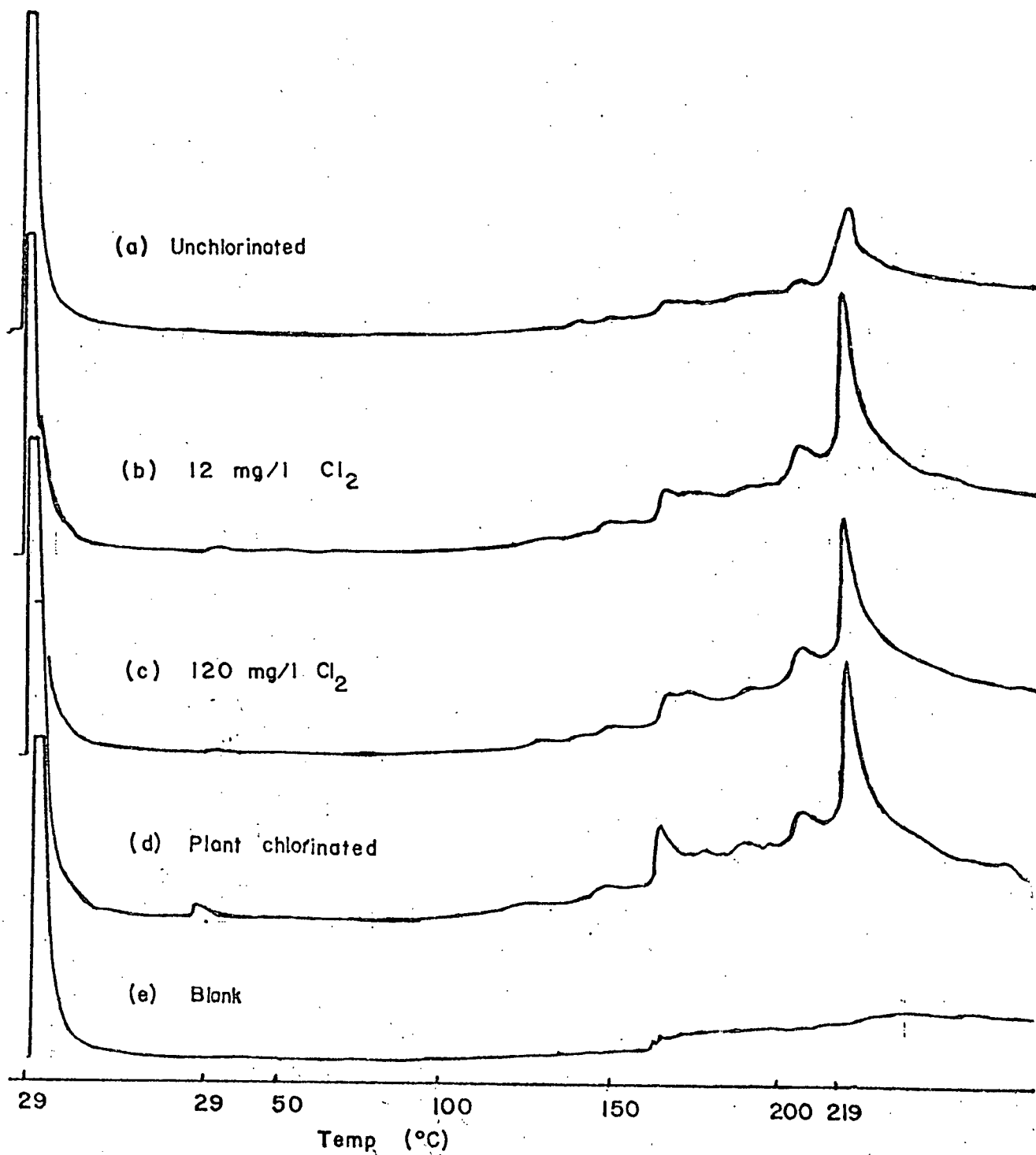


Figure 4.22 Effects of Chlorination by GC - A by FID. GC conditions in Appendix III.

number of decreases are more similar. This is not surprising since addition of oxygen or chlorine to a molecule can dramatically increase its response factor for an EC detector. Other aspects of Table 4.8 such as the difference between the two effluent samples can be more precisely discussed during a detailed analysis of the chromatograms.

The effects of chlorination upon the N + B fractions are illustrated in Figures 4.13 through 4.16 and 4.19 and 4.20. There are between 50 and 60 peaks present in each of the figures. With the EC detector (Figs. 4.13 and 4.19) one can see that the new peaks marked "I" which appear at a chlorine dosage of 100 mg/l or 120 mg/l also appear at a chlorine dosage of 15 mg/l or 12 mg/l. The effects of chlorination at the plant are generally intermediate between those of dosages of 12 and 120 mg/l. There is a one to one correspondence between the peaks of chromatograms (c) and (d) in Figure 4.19. In fact there are some areas where plant chlorination more closely resembles a dosage of 120 mg/l than 12 mg/l. There are some new peaks which appear near the solvent peak but these are not marked as they cannot be analyzed by GC-MS with the OV-101 column.

One can also see that many changes marked "X" appear in the sample dosed with 200 mg/l of chlorine which are different from those appearing at lower dosages of chlorine. These changes unique to high dosage levels are probably due to the presence of free residual chlorine since the "breakpoint" is expected to lie between 140 and 170 mg/l Cl_2 . In the interest of optimizing the yields of only those products of chlorination which result from treatment plant dosage levels, it was decided to only chlorinate samples at levels of 0, 12, and 120 mg/l Cl_2 .

It is evident from Figures 4.14 and 4.20 that most of the peaks in the N + B fraction are much smaller with the FID as compared to the EC detector. Since the changes due to chlorination also occur in areas of poor resolution

they are much less spectacular in these chromatograms. Because of the substantial differences in detector responses no unequivocal correlations can be made between the EC and FID chromatograms, however it does not appear as though any of the effects of chlorination are visible with both detectors. Judging from the FID one would expect to see about 60 peaks in the N + B fraction by GC-MS, however the effects of chlorination will probably not be very evident.

The chromatograms of the acidic fractions are displayed in Figures 4.15 through 4.18 and Figures 4.21 and 4.22. Comparison of Figures 4.17 and 4.21 shows that the NaOH extracts contain one new EC detectable peak resulting from chlorination. The appearance of effects of chlorination unique to high dosage levels is again evident in chromatogram '(d)' in Figure 4.17. The FID chromatograms in Figures 4.18 and 4.22 show the lack of any detectable effects of chlorination. Judging from these chromatograms there should be nine peaks visible in the acid fraction by GC-MS, none of which is due to chlorination.

The chromatographic profiles of the various samples of primary effluent collected throughout this study as well as the effects of chlorination appeared to be remarkably consistent. For example the peaks numbered 1 through 12 in chromatograms '(a)' in Figures 4.13 and 4.19 appear to be identical. A total of nine new peaks resulting from chlorination obviously present in Figures 4.13 and 4.19, and if for reasons previously discussed some of the peaks in Figure 4.15 are included in Figure 4.13 this number increases from nine to seventeen or eighteen. Only one or two peaks do not appear in both effluent samples. This combination of Figures 4.15 and 4.13 is further justified by the analysis of samples taken on July 8, 1974 and Nov. 19, 1974. These extracts (Appendix II), one with bicarbonate extraction and one without produced GC chromatograms similar to either the Dec. 18/74 or March 8/75

extracts on columns of OV-101, OV-17 and OV-225. Evidence for the consistency of the other chromatograms of the extracts is provided by comparison of the appropriate figures. It is noted that the consistency of the FID chromatograms is not as striking as that of the EC chromatograms because of factors previously mentioned.

In summary, two major points arise out of these studies. Firstly it was demonstrated that chlorine dosages as high as 120 mg/l but less than 200 mg/l can be used to increase the yields of chlorination products without forming products not produced in treatment plants. Secondly it was shown that new EC and FID detectable compounds are consistently produced as a result of chlorination at treatment plant dosage levels. A total of 16 to 18 new peaks were detected in the N + B fraction and 4-6 new peaks in the acidic fraction as a result of this chlorination.

3. MEC Detector

This detector was used to study the magnitude of chlorine uptake by the volatile organics (Exp. C1-3). The chromatograms are presented in Figures 4.23, 4.24, and 4.25 and the detector calibration curve is shown in Figure 4.26. The chlorine content of each peak was determined and the total chlorine content of each sample calculated assuming a sewage sample volume of 10 l (Exp. E-4). These results are summarized in Table 4.9. The chlorine uptake in each fraction was then expressed as a percentage of the dosage and the total organic chlorine present in the sample. These calculations are presented in Table 4.10.

Before discussing the significance of the chlorine uptake data, four points should be made. Firstly, the MEC detector is not specific for chlorine, although it is specific for halogens. Secondly, even assuming that all peaks were due to chlorine, the response per nanogram of chlorine is not constant for all types of compounds as can be seen from Figure 4.26. Thus

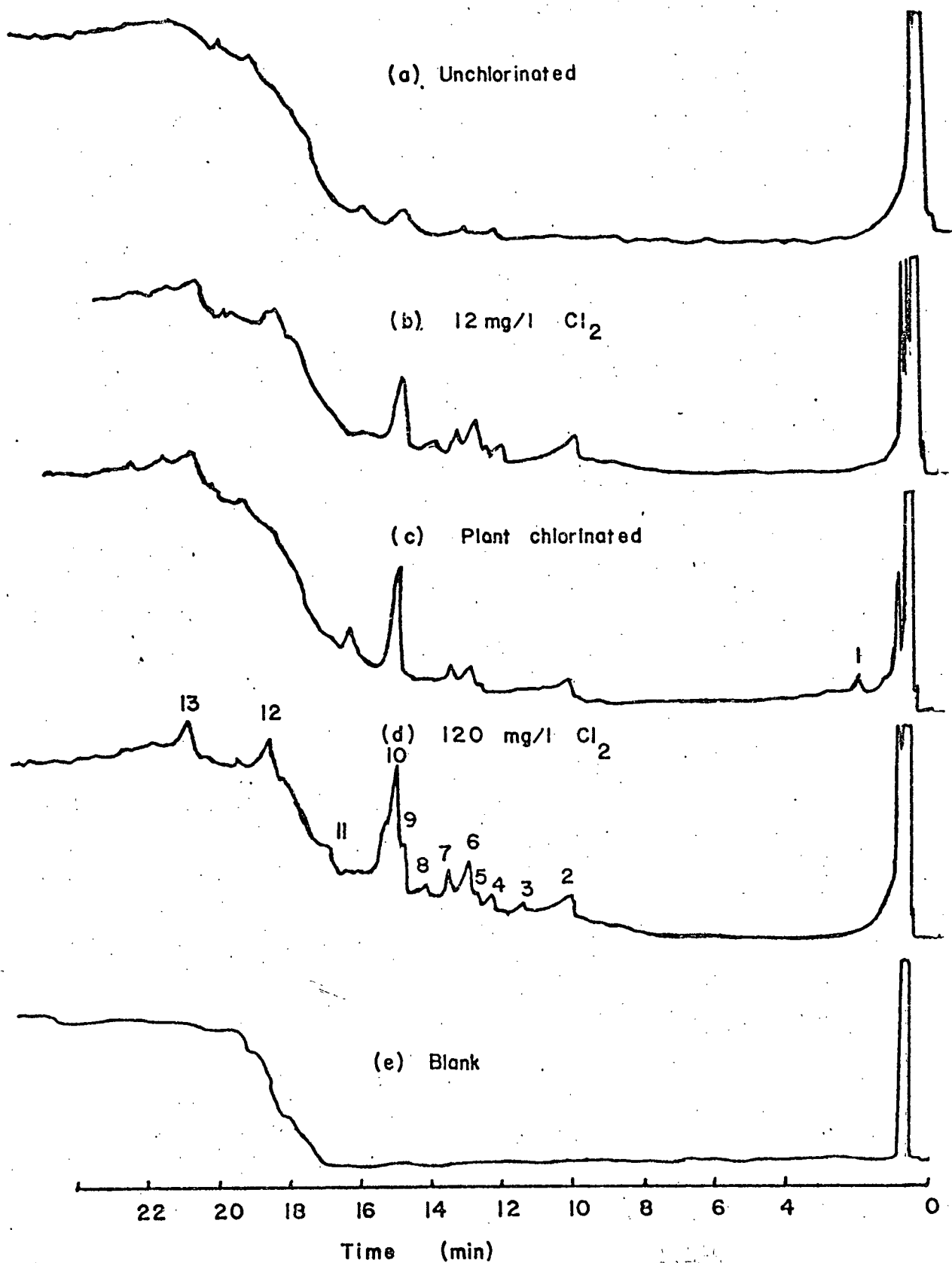


Figure 4.23 Effects of Chlorination by GC - A by MEC. GC conditions in Appendix III. Explanation of Symbols in text.

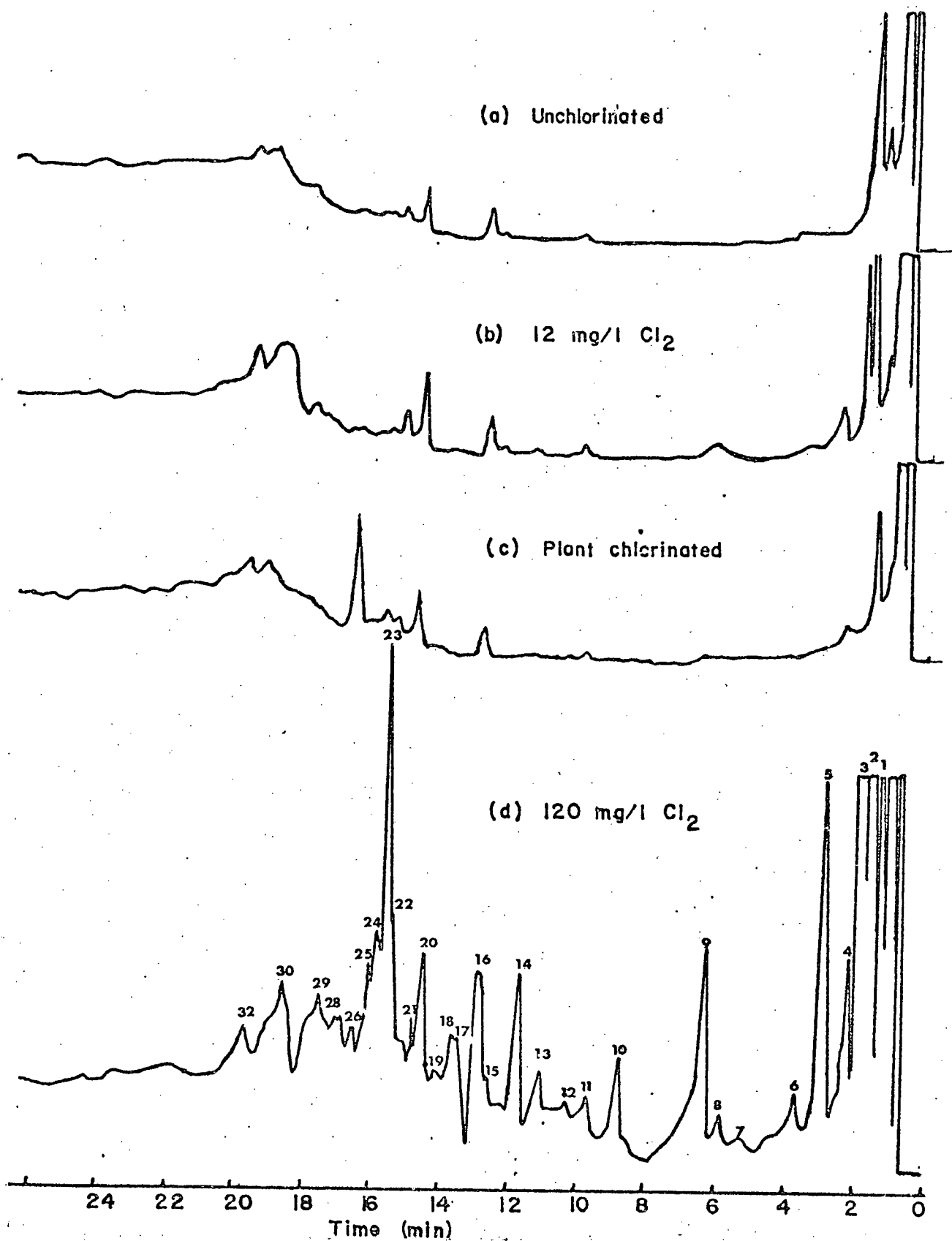


Figure 4.24 Effects of Chlorination by GC - N+B by MEC-1. GC conditions in Appendix III. Explanation of Symbols in text.

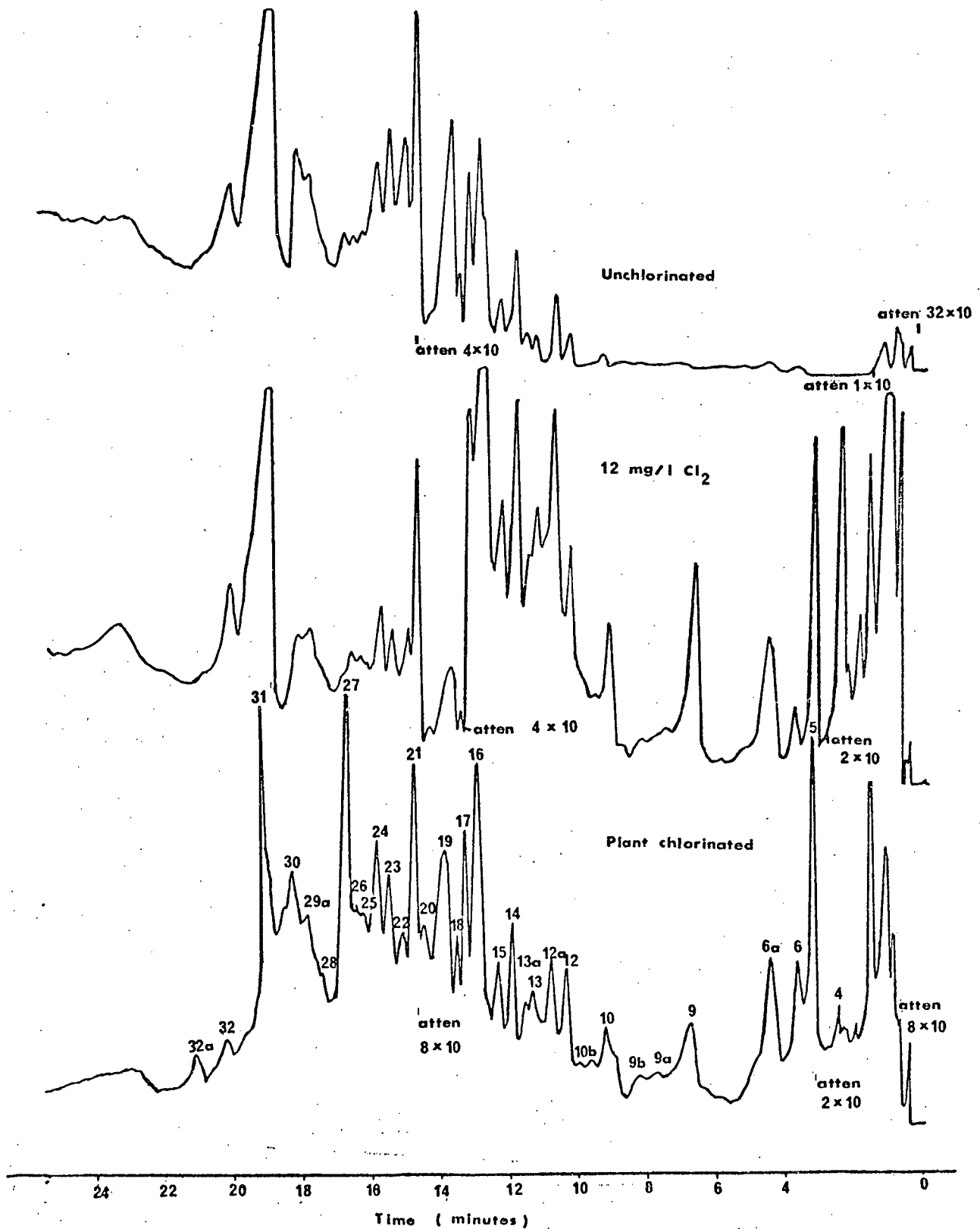


Figure 4.25 Effects of Chlorination by GC - N+B by MEC-2. GC conditions in Appendix III. Explanation of Symbols in text.

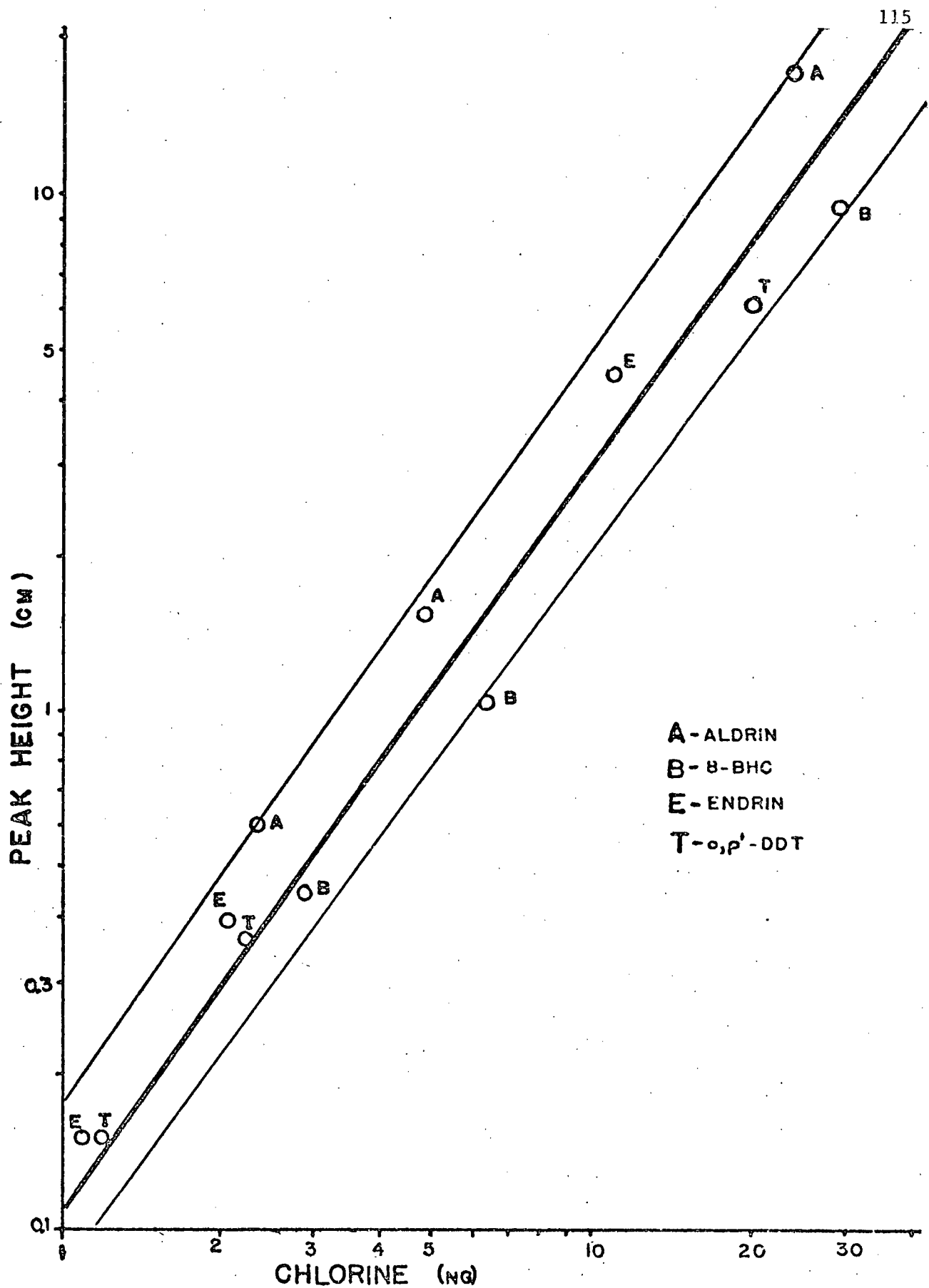


Figure 4.26 Calibration Curve for MEC Detector.

Table 4.9 - Concentrations of Halogen as Chlorine in Primary Effluent

a) Acid Fraction

Peak	Concentration of Chlorine (ng Cl/l)			
	Chlorine Dose (mg /Cl ₂ /l)			
	N(0)	12	P (12)	120
1			60	
2		80	70	80
3				40
4		60		60
5	40	40	40	40
6		100	70	100
7	40	60	60	80
8		60		60
9				140
10	100	180	240	260
11	70		90	30
12		60		120
13		40	40	100

b) Neutral and Basic Fraction

Concentration of Chlorine (ng Cl/1)							
Chlorine Dosage (mg Cl ₂ /1)							
N (0)	12		P (12)		120		
Concentration Factor							
10 ⁴	5 x 10 ⁴	10 ⁴	5 x 10 ⁴	10 ⁴	5 x 10 ⁴	10 ⁴	
1		OS		OS	30	OS	940
2	220	OS	260	OS	200	OS	OS
3	500	OS	1050	OS	360	OS	OS
4			100	90	60	50	450
5			160	110	50	100	850
6			50	40		25	150
6a				50		50	
7							90
8		10		10		10	180
9a		5	90	100		40	600
9b				10		10	0
9b				5		5	
10a				30		35	360
10a		10		10		10	
11				5		5	180
12a	60	15	60	60	60	45	50
12a		40		50		35	
13		15		15		20	200
13a		15		5		10	
14	30	45	60	50	50	50	500
15*		20		30		30	160
16*	140	95	160	OS	140	100	500
17		40		40		35	300
18		30		25		30	90
19		70		55		60	60
20*				15		15	440
21*	220	205	320	240	260	240	160
22*	90	70	140	60	120	60	420
23	50	80	50	85	90	130	1000
24		65		110		130	120
25*		20	50	40	90	60	120
26*							180
27*		20		20	420	280	180
28							50
29a							140
29a	90	100	40	100	60	140	
30		40		20		100	360
31	120	OS	120	OS	140	OS	
32a	50	50	120	90	80	50	160
32a						60	

OS - Off scale

Table 4.10 - Chlorine Uptake by Volatiles

a) Acid Fraction

Cl ₂ - Dosage mg/l	Total Chlorine ^b		Chlorine Uptake ^b	
	μg/l	μg/l	% Dose	% Total Cl
N (0)	0.25	---	---	---
12	0.68	0.40	0.0033	59
P (12)	0.67	0.24	0.0020	36
120	1.11	0.70	.0006	63

b) Neutral and Basic Fraction

Concen. Factor	Cl ₂ Dosage mg/l	Total Chlorine		Chlorine Uptake			
		μg/l		μg/l	% Dose	% Total Cl	
		a	b			a	b
10 ⁴	N (0)	1.57 ^a	.85	---	---	---	---
10 ⁴	12	2.83	1.52	0.40	0.0033	14	26
10 ⁴	P (12)	2.21	1.62	0.53	0.0044	24	33
10 ⁴	120	---	8.05	3.12	0.0026	--	39
5x10 ⁴	N (0)		1.18	---	---		--
5x10 ⁴	12		1.85	0.45	0.0038		24
5x10 ⁴	P (12)		2.16	0.59	0.0049		27

c) Totals Uptake

a Cl ₂ - Dosage b (mg/l)	Total Cl ^b		Cl-Uptake ^b	
	(μg/l)	(μg/l)	% Dose	% Total
N (0)	1.10	---	---	---
12	2.20	0.80	0.007	36
P (12)	2.29	0.87	0.006	38
120	9.16	3.82	0.005	42

a - excluding unnumbered peaks at beginning

b - excluding peaks 1, 2, 3

an error of plus or minus 25 percent or more is expected in the individual values. Also peak height was used as a response rather than peak area; it was felt that this was a valid substitution mainly because of the large number of shoulders on the peaks. Third, the variability of concentration factors among a set of identically handled extracts is expected to be about 10 percent. Finally, the detection limit for the less concentrated samples was 30 ng/l Cl while the detection limit of the more concentrated samples at lower attenuation was 3 ng/l Cl, assuming a minimum detectable peak of 0.2 cm.

From the chromatograms of the acid fraction, Figure 4.23, it is evident that there are six or seven peaks which appear as a result of chlorination. From Table 4.9 it can be seen that all of these peaks are present in concentrations below the detection limit of the mass spectrometer unless the compounds are less than twenty percent chlorine by weight.

Comparison of the chromatograms of the neutral plus basic fractions in Figures 4.24 and 4.25 shows that there is a one to one correspondence between peaks in identical samples run at different concentrations and attenuations. There are also 10 or 11 new peaks which appear as a result of chlorination as denoted in Table 4.9. Of these, only peaks 4, 5, 9, 10 and 20 will probably be detectable with a mass spectrometer. In addition to the 10 or 11 new peaks, there are several others in the sample dosed with 120 mg/l Cl₂ which appear to be enhanced as a result of chlorination. It is unlikely that the hypochlorite contained many chlorinated compounds since both the microelectrolytic conductivity and electron capture traces of an extract of 50 mls of hypochlorite solution showed no peaks except in the region of the unnumbered peaks at the start of the chromatograms. These unnumbered peaks are probably halogenated methane and ethanes.

The chlorine uptake summary in Table 4.10 shows that at dosage levels

commonly used in primary treatment plants about 0.01 percent of the applied chlorine ends up in the extractable volatile compounds, of this amount about two-thirds is somewhat surprisingly incorporated into neutral and basic compounds rather than acidic compounds. Furthermore, about 40 percent of the extracted organic chlorine found in primary chlorinated effluent, excluding methanes and ethanes, resulted from chlorination.

The use of the term 'extracted' in the preceding paragraph to describe the volatiles should be emphasized. It is well known that clays and natural organic matter sorbs organics from water (Weber 1972). On the other hand, dissolved organic matter can increase the solubility of other organic compounds (Wershaw et al., 1969), although the dissolved organic matter in sewage was shown to have no effect on the sorption of dieldrin by montmorillonite (Huang 1971). Since clays and organic particulates will be removed during the filtration of the samples between the chlorination and extraction steps, losses due to sorption may be significant. In Table 4.5, the loss of dichlorophenol due to sorption on particulates was 15 percent. This confirms that sorption is significant however the application of 15 percent as a general estimate is obviously not justifiable.

With these sorptive losses in mind it is possible to make a very rough comparison of the values for total chlorine in Lion's Gate Effluent with those for other sewages. Using unfiltered samples and solvent extraction, Dube et al. (1974) found about $0.2 \mu\text{g}/\text{l}$ PCB's in domestic sewage, while McDermott (1974) found about $0.5 \mu\text{g}/\text{l}$ total identifiable organochlorine pesticides in domestic sewage. Therefore the total dissolved and sorbed organic chlorine in these sewages was at least $0.4 \mu\text{g}/\text{l}$. No data is available for other volatile chlorinated compounds. Judging from the distribution of chlorine throughout the chromatogram it appears that the $1.4\text{--}2.0 \mu\text{g}/\text{l}$ of organic chlorine in the unchlorinated sample of Lion's Gate effluent is in the

same range of concentrations, although no PCB's or pesticides were identifiable by mass spectrometry. The individual concentrations of chlorine containing organics resulting from chlorination on a chlorine basis range from 0.02 to $0.15 \mu\text{g}/1$ while Jolley (1973) reported concentrations of 0.2 to $14 \mu\text{g}/1$. Differences in extraction and analytical procedures as well as the fact that Jolley measured mainly non-volatile compounds may account for these concentration differences.

4. GC-MS Studies on the MS-12

The initial experiments with the GC-MS showed some promise. The chromatograms of all N + B fractions of the extracts were identical. Figures 4.27 presents a typical chromatogram while some of the corresponding mass spectra are shown in Figure 4.28. Only two compounds, a phthalate (Spectrum 34) and caffeine (Spectrum 36) are identifiable. Peaks 9, 11, 14, 17 and 19 in Figure 4.27 have almost identical mass spectra with the major ion series being m/e 45, 59, 73... and 137, and thus appear to be alkyl silanes. There were some differences but background subtraction was very difficult. It proved difficult to trigger the MS at the precise times for the minor components of the extracts. Fluctuations in accelerating voltage and hysteresis problems were also noted during a GC run.

During the course of this project the performance of the MS-12 seriously deteriorated. Negative baseline drift occurred during temperature programming due to an increase in pressure drop across the column with increasing GC oven temperature. The sensitivity of the instrument decreased to the point where the identification limit of DCP was 1.2×10^{-6} g. The pressure in the analyzer chamber was about 5×10^{-4} Torr and the GC detector had to be set at 1×10^{-6} Amps full scale rather than the manufacturer's recommended 1×10^{-9} Amps. Only one or two rather broad peaks could be detected per run. An attempt to conduct a search for $^{35}\text{Cl}^+$, H^{35}Cl^+ , $^{37}\text{Cl}^+$, and H^{37}Cl^+ by a limited

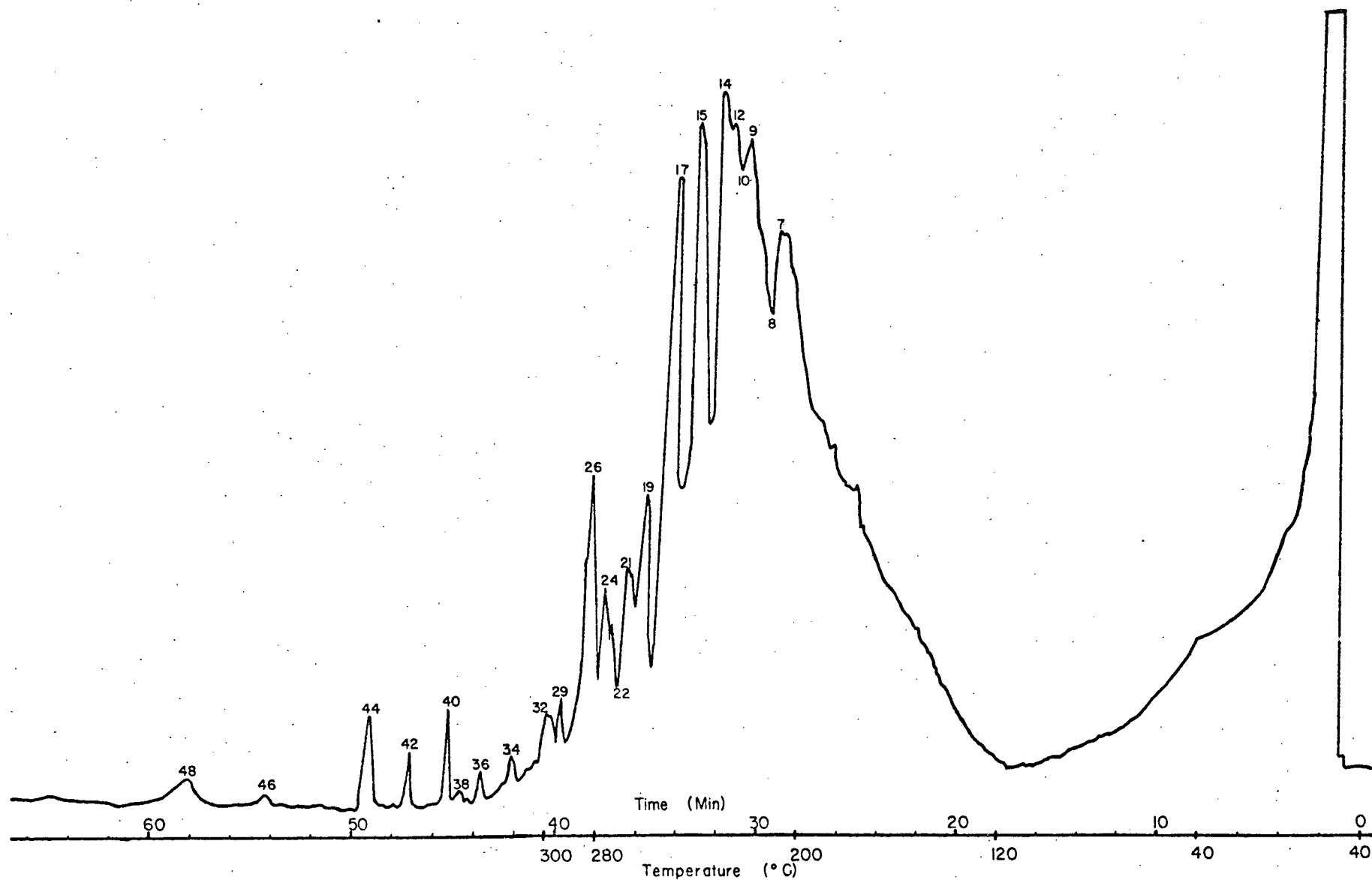
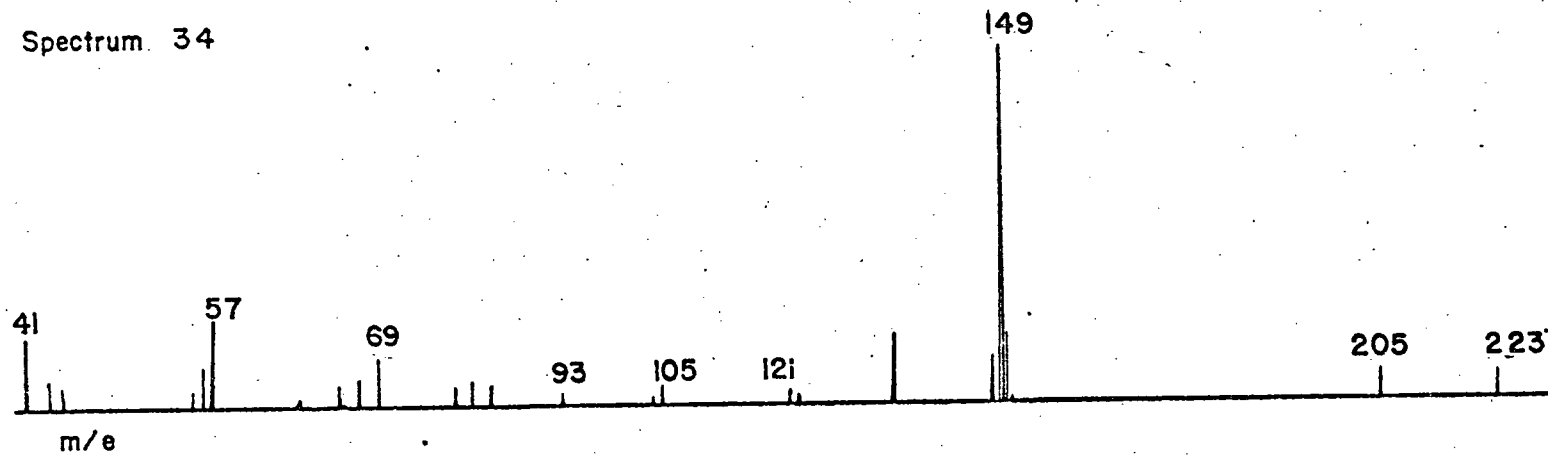


Figure 4.27 Total Ion Current Plot for N+B Fraction by MS-12. GC conditions in Appendix III. Numbers denote Spectrum.

Spectrum 34



Spectrum 36

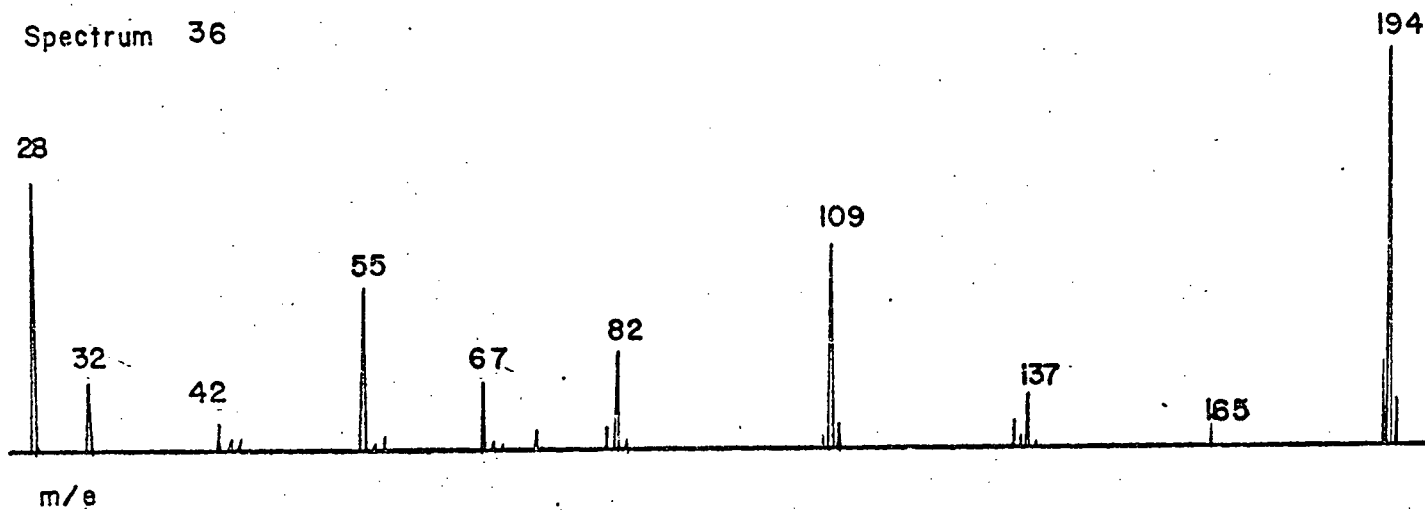


Figure 4.28 Mass Spectra from MS-12. Spectrum numbers correspond to peaks in Figure 4.27.

mass scan showed two peaks. However during this run the hysteresis problem was very evident.

In summary, although the initial work with the MS-12 was promising, problems developed which forced the suspension of work with this instrument. Alternative methods of analysis were therefore needed.

5. Tentative Identification by Retention Time

The objective of this experiment was to tentatively identify some of the major peaks in the chromatograms of the sewage extracts by comparison of GC retention times. The test compounds, their recrystallization solvents and retention times are listed in Table 4.11. The composited GC traces of these compounds along with corresponding GC traces of some chlorinated sewage extracts are shown in Figure 4.29.

All of the test compounds, with the exceptions of peaks 3 and 4, have corresponding peaks in either of the sewage extracts. However only a few of them, listed in Table 4.12, correspond to major peaks in the sewage extracts.

It is also noted that some of the high boiling compounds were not eluted. For example the dihydroxybenzene and the dichloroquinone were not eluted within the temperature program. These negative results are useful in determining the limits in terms of volatility of compounds analyzed in this project.

Several factors mitigate against pursuing this experiment further by the use of other GC column packings. It is not possible to correlate the chromatograms of the sewage extracts run on different column packings due to the large number of peaks. Furthermore, since major peaks may contain several components, a change in column packings may cause major peaks to become minor ones while different major peaks may appear. The list of compounds chosen as test compounds is obviously far from comprehensive and one would expect to obtain a list of several possible compounds for each peak in the sewage sample.

Notwithstanding the aforementioned problems, it can be said that the

Table 4.11 Retention Times of Test Compounds

Compound	Recrystallization Solvent	Retention Time (min) (Temp. prog.)
o-Chlorobenzoic acid	Pet ether	29.6
m-Chlorobenzoic acid	"	N
p-Chlorobenzoic acid	"	N
2-Amino-5-Chlorobenzoic Acid		N
4-Chlorometanilic Acid		N
p-Chloro phenol		21.0
p-Bromo phenol		21.6
2,4-Dichlorophenol	Benzene	25.0
2,4,6-Trichlorophenol	H ₂ O/MeOH	26.8
Resorcinol	Benzene	N
p-Chloroaniline	Pet ether	26.4
2,4-Dichloroaniline	"	27.0
2,4,6 Trichloroaniline	"	32.9
4-Chloro-2,6-Dinitroaniline	Ethanol	34.2
4,5-Dichloro-2-Nitro Aniline	"	35.5
4-Chloro pyridine . HCl		N
3-Amino-2-Chloropyridine		17.2
2,4-Dichloropyrimidine		17.2
2-Amino-4,6Dichloropyrimidine	Pet ether	30.6
1-		
1-Chloro-2,4-Dinitrobenzene	MeOH	32.8
1-Chloromethyl-2 methyl napthalene		34.2
4-Chlorobenzaldehyde		9.5
2,5 Dichloro p-quinone		N
4,4'-Dichlorobenzophenone		38.6
1-Bromo-4-Chlorobenzene		9.0
Carbontetrachloride		0.8
Chloroform		0.8
Methylene Chloride		0.7
Solvent peak		0.7=

N - Compound did not elute

Figure 4.29 Identity of Numbered Peaks in Chromatogram (a)

- | | |
|-----------------------------|---------------------------------------|
| 1. 1-Bromo-4-chlorobenzene | 10. 2,4-Dichloroaniline |
| 2. 4-Chlorobenzaldehyde | 11. 2-Chlorobenzoic acid |
| 3. 3-Amino-2-chloropyridine | 12. 2-Amino-4,6-dichloropyrimidine |
| 4. 2,4-Dichloropyrimidine | 13. 1-Chloro-2,4-dinitrobenzene |
| 5. 3-Chlorophenol | 14. 2,4,6-Trichloroaniline |
| 6. 3-Bromophenol | 15. 1-Chloromethyl-2-methylnapthalene |
| 7. 2,4-Dichlorophenol | 16. 4-Chloro-2,4-dinitroaniline |
| 8. 2,4,6-Trichlorophenol | 17. 4,5-Dichloro-2-nitroaniline |
| 9. 3-Chloroaniline | 18. 4,4'-Dichlorobenzophenone |

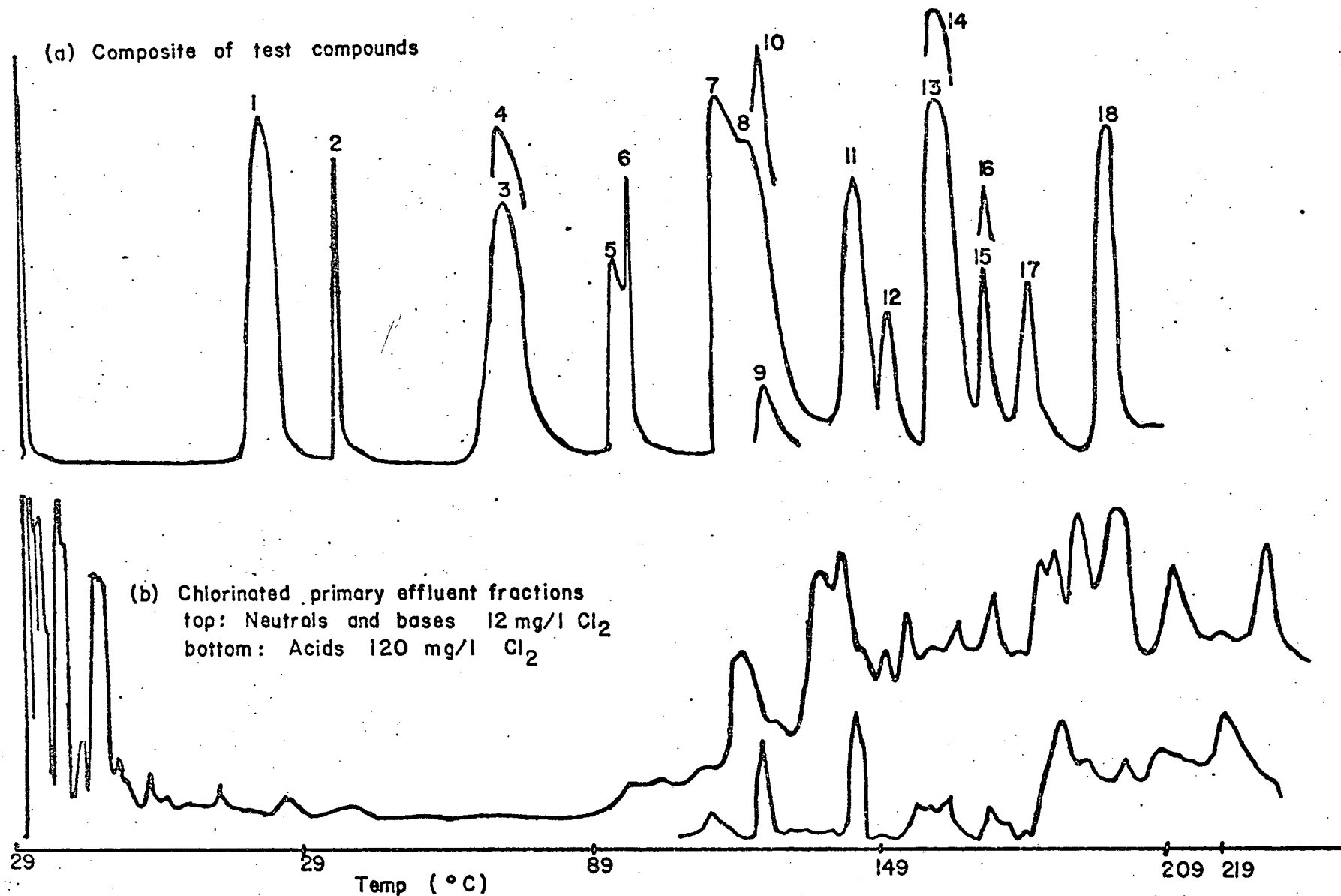


Figure 4.29 GC Retention Times of Test Compounds. Numbers in chromatogram (a) are explained on facing page. GC conditions in Appendix III.

Table 4.12 Compounds Identified by GC Retention Time

Compound	Detector	
	Authentic Compound	Primary Effluent
4-Chlorophenol ^a	MEC, MS	MEC
2,4-Dichlorophenol	EC, FID	EC
2,4,6-Trichlorophenol	EC, FID	EC
2-Chlorobenzoic Acid	EC, FID	EC
1-Chloromethyl-2-Methyl Napthalene	EC, FID	EC
or 4-Chloro-2,4-Dinitro-Aniline	EC, FID	EC
4,4'-Dichlorobenzophenone	EC, FID	EC

a - See Section 7 of this chapter.

identification of five or six chlorinated compounds in chlorinated sewage has been very tentatively established. Further investigations are obviously needed to confirm these identifications.

6. GC-MS-Computer Studies

The objective of this experiment was to identify as many components of the sewage extracts as possible on the basis of mass spectra and GC retention time. A typical set of instrument performance evaluation data is shown in Table 4.13 along with the criteria of Harris, Eichelberger and Budde (undated). The deviations at 365 and 442 are not considered to be serious.

A voluminous quantity of information was generated from the manipulation and reduction of data during the analysis of the various extracts and blanks. In the interests of brevity only some illustrative examples of the reconstructed gas chromatograms (RGC) and limited mass searches (LMRGC) will be presented. The mass spectra of the compounds positively identified will be presented graphically in Appendix IV, while the remaining mass spectra will be presented in Appendix V. For convenience, the chromatograms and associated spectra will be referenced by file name. An explanation of these file names is given in Table 4.14.

Since the RGC's have been normalized in some cases to the solvent peak, the peak heights do not reflect the relative concentrations of a particular component in the various fractions. However, a problem of loss of volatiles is evident upon comparison of ~~CL~~CL1202 and C-HALL with 120N1. One would expect to find peak heights in CL1202 to be fifteen times those in 120N1. In fact, below spectrum number 20 the ratio is only 2:1, while above spectrum number 150 the ratio is 10 or 12:1.

Various temperature programs were employed to optimize reproducibility, and resolution. Of the initial temperatures of 100, 75, 60 and 55°C, 60°C was chosen to be optimum. A deviation of ± 3 spectra or 12 seconds persisted

Table 4.13 Performance Check of Finnigan 3000

AMU	Rel. Int. (%)	Criterion	Meets Criterion
51	39.42	30-60 % of 198	Yes
68	0.62	<2 % of 69	Yes
69	41.04		
70	0.33	<2 % of 69	Yes
127	44.49	40-60 % of 198	Yes
197	0.24	<1 % of 198	Yes
198	100.00	100 %	Yes
199	6.68	5-9 % of 198	Yes
275	15.66	10-30 % of 198	Yes
365	1.08	≥2 % of 198	No*
441	3.32	< 443	Yes
442	22.43	40-60 % of 198	No*
443	4.48	19-21 % of 442	Yes

* Criteria are for Finnigan 1015 which has a mass range of 0 - 750 Amu; the Finnigan 3000 has a range of 0 - 500 Amu.

Table 4.14 - File Names for GC-MS-Comp. Studies

File Name	Extract Fraction	Chlorine Dose mg/l	Date of Run
ARAWS1	Acids	0	May 6-8/75
CL12A1	"	12	"
APLCL1	"	Plant	"
CL12DA	"	120	"
BLANKA	Blank-Acidic	0	"
NBRAW1	Neutrals + Bases	0	"
CL12N1	" "	12	"
NBPLCL	" "	Plant	"
12ONB1	" "	120	"
CL1202	" "	120 (30 μ l conc. to 2 μ l)	"
35LBK1	Blank-Neut. + Base	0	"
C-HALL	Neut. + Base /TLC	120	July /75
B-HALL	Blank for C-HALL	0	"
RAWNB1	Same Sample as NBRAW1	0	Dec. 18/75
MLXA2	Mix of Test Compounds	---	"
MLXB	Mix of Test Compounds	---	"

with this initial temperature. This may be due to slight differences in initial temperature or program rates. When samples were run on different days the reproducibility of retention times was much poorer. Deviations of six spectrum numbers (24 sec) were noted.

An unexpected development militated against allowing more than half an hour to cool the GC oven and allow for re-equilibration between runs. It was noted that even with no sample injection, two peaks appeared in the chromatogram. The mass spectra of these peaks (Appendix V) were identical but did not match those of the GC stationary phases. It was therefore concluded that these peaks were the result of condensation of septum bleed material onto the GC column and subsequent volatilization of this material at higher temperatures. This problem could be ameliorated but not eliminated by changing the septum daily. Although these peaks presented a problem, they also provided a set of reference points for comparison of the RGC's.

The RGC's of the acid, neutral plus basic, and TLC separated neutral plus basic fractions are presented in Figures 4.30, 4.31 and 4.32, while the blank is presented in Figure 4.33. Table 4.15 presents a summary of the total number of peaks in, and the effects of chlorination on each effluent extract. There does not appear to be any noticeable effect of chlorination upon the acidic fraction as predicted by FID studies, although phenolic compounds should appear in this fraction. The RGC's of the neutral plus basic fractions show some changes as a result of chlorination. Some new peaks are apparently produced, however they may have been due to changes in resolution since no different mass spectra could be obtained from these peaks.

The LMRGC's provided an invaluable aid in the data reduction process. Searches for septum bleed (m/e 293), o-phthalate esters (m/e 149), and chlorine (m/e 35, 36) were routinely made for each chromatogram. Chlorine searches yielded peaks in NBRAW1 at Spectra 7, 11, 62, 83, and 234. These peaks were

Table 4.15 Summary of RGC Data

File	Total Number of Peaks	Peaks Resulting from Chlorination (Spectrum Numbers)	Peaks Decreased by Chlorination (Spectrum No's)
ARAWS1	15	None	None
CL12A1	15	None	None
APLCL1	15	None	None
CL120A	15	None	None
BLANK A	4	None	None
NBRAW1	64	None	None
CL12N1	60	43, 145, 167, 257	None
NBPLCL	60	41, 146, 168, 192, 257	252, 272
120NB1	63	41, 144, 167, 183, 191	252, 257
CL1202	62	40, 82, 85, 145, 169, 183, 187, 193	282, 172
35LBK1	6	None	None
	49		
C-HALL	49	Not Determined	Not Determined
B-HALL	6	" "	" "

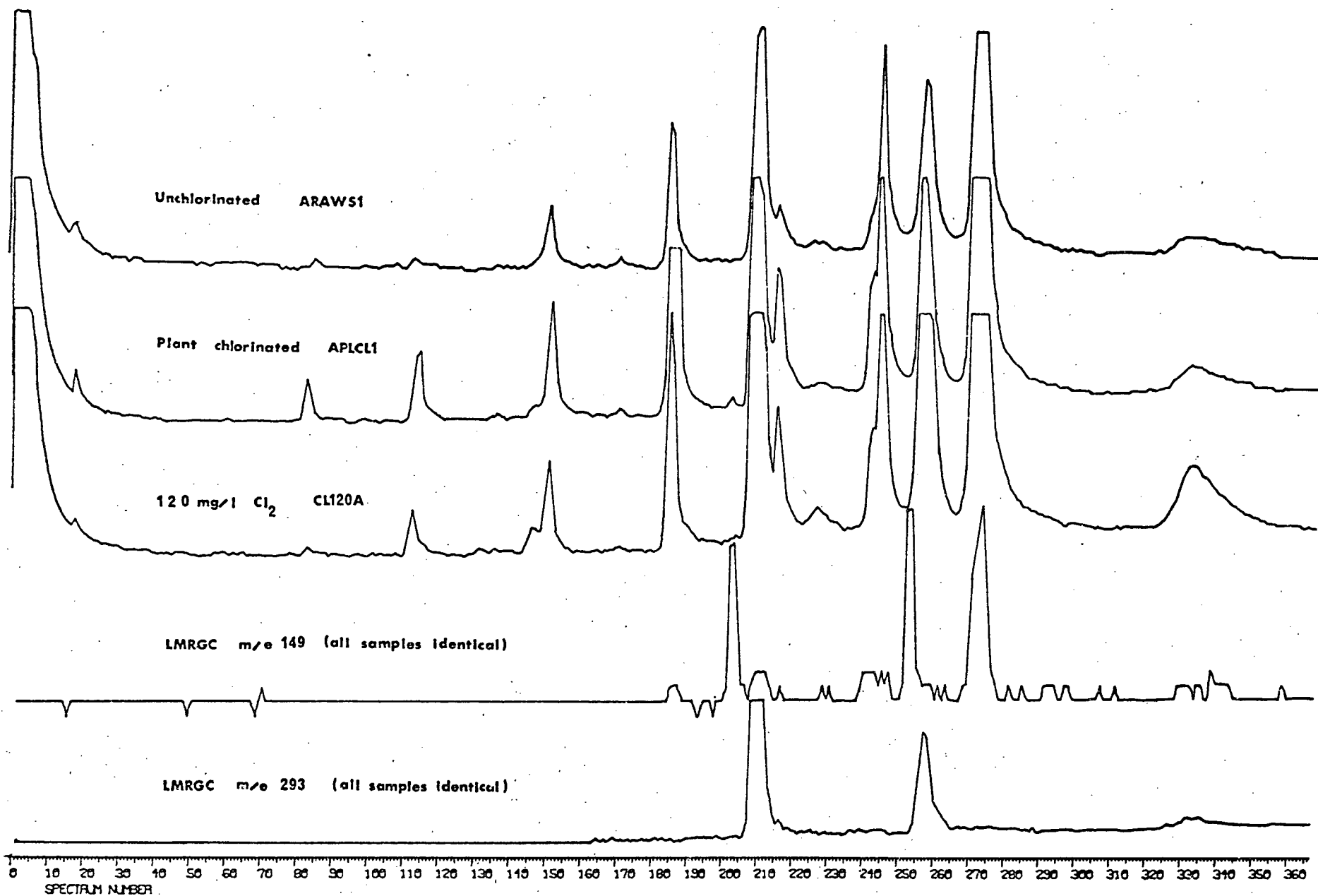


Figure 4.30 RGC's of Acid Fractions. GC conditions in Appendix III.

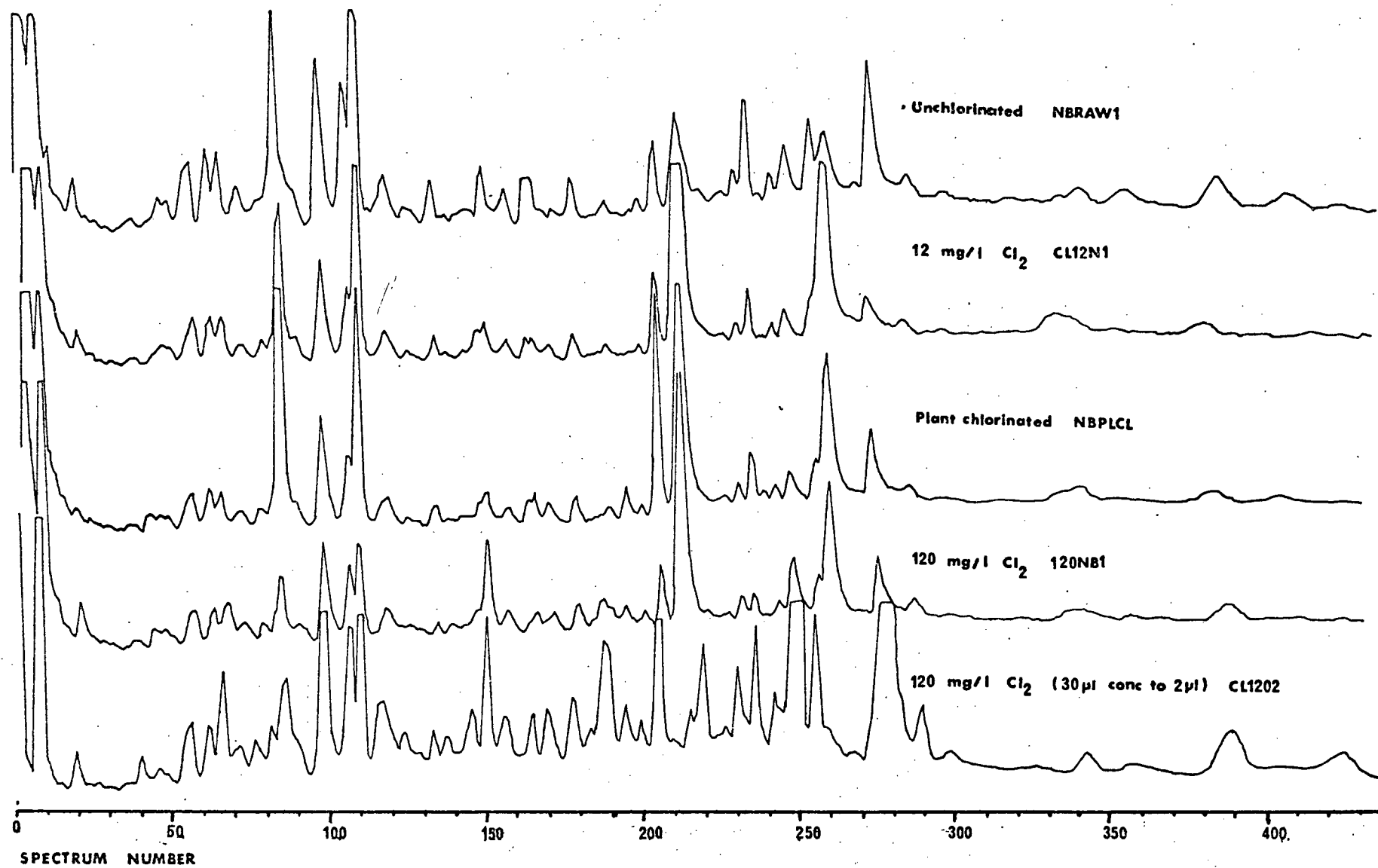


Figure 4.31 RGC's of Neutral and Basic Fractions. GC conditions in Appendix III.

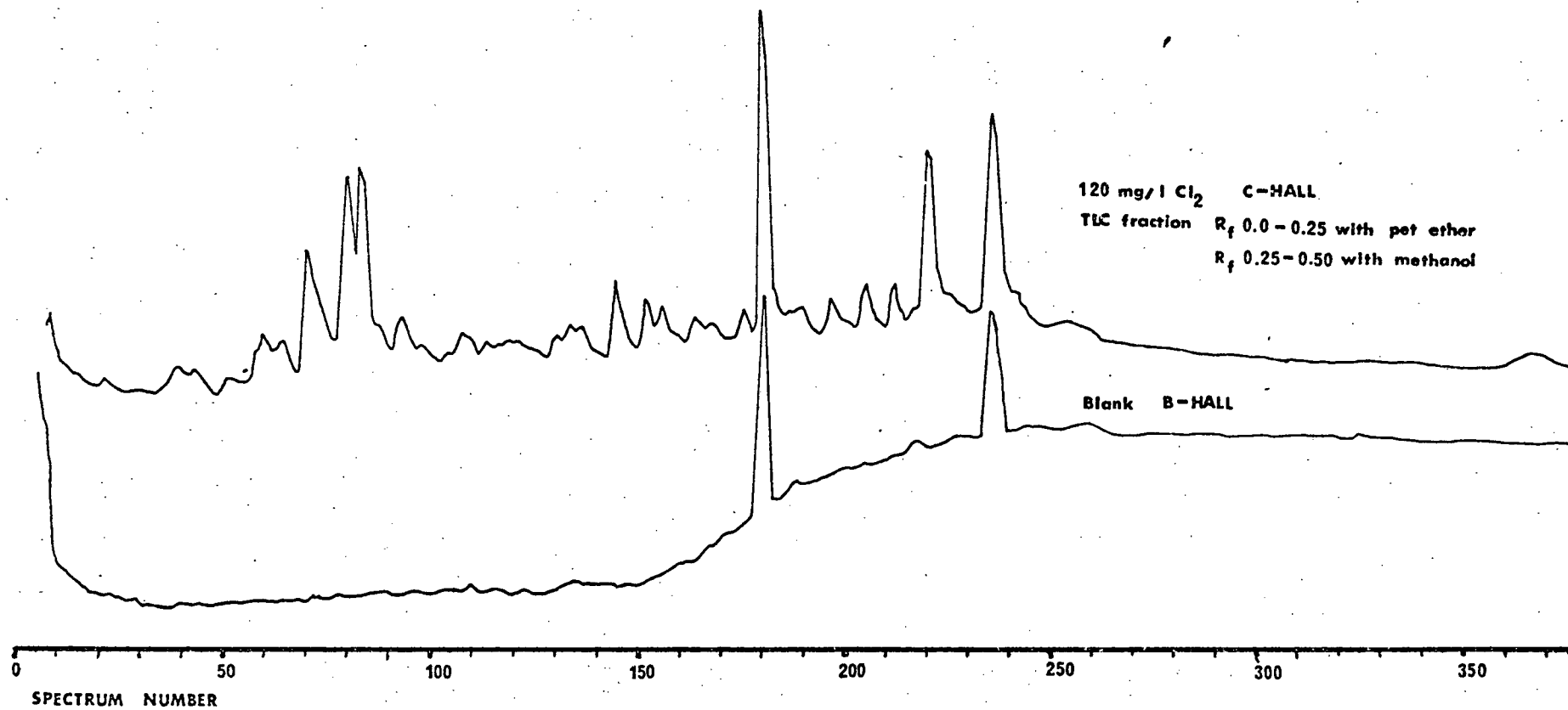


Figure 4.32 RGC's of TLC Fractions. GC conditions in Appendix III.

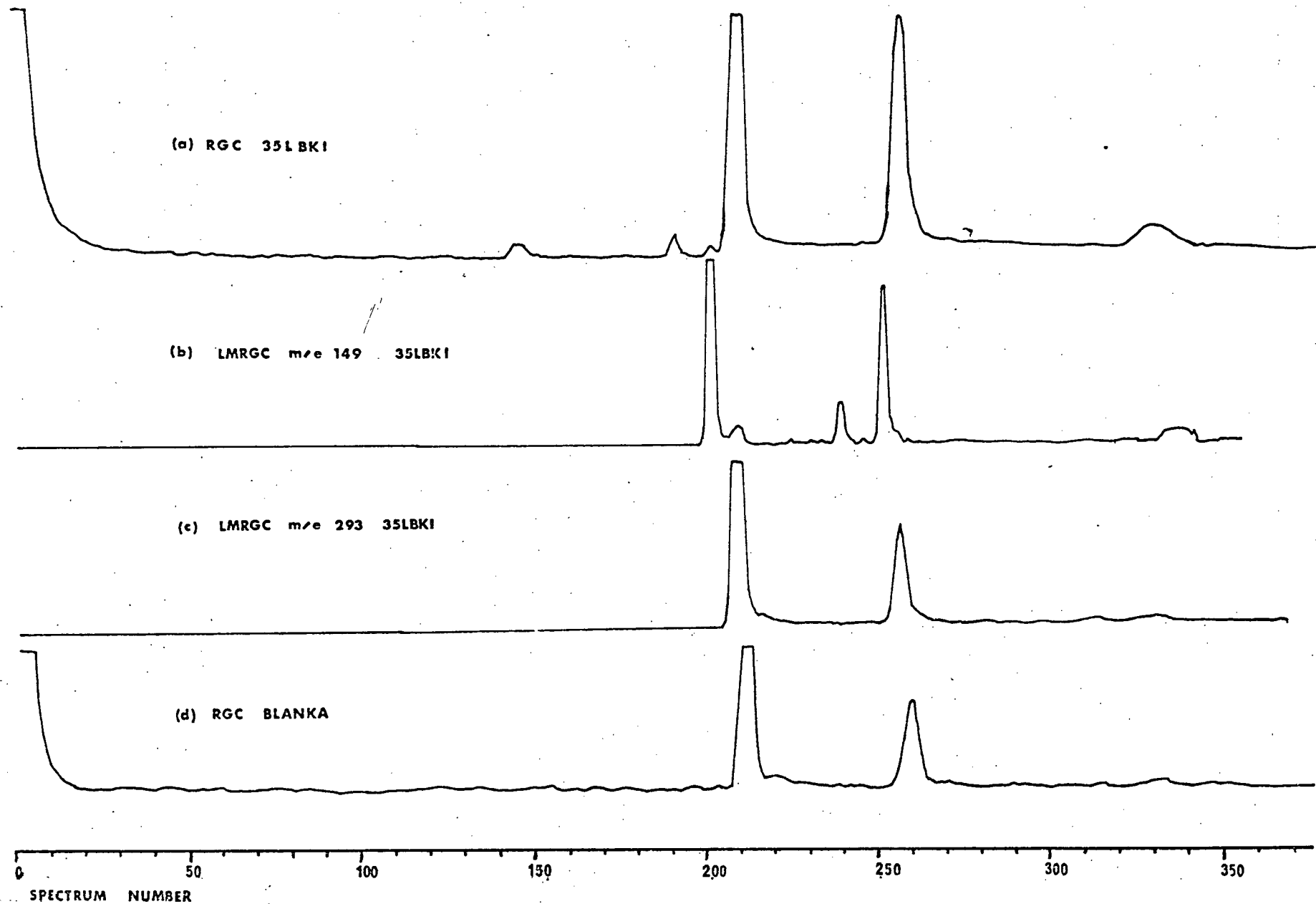


Figure 4.33 RGC's and LMRGC's of Blanks. GC conditions in Appendix III.

consistently and uniquely present at all chlorine dosages although the great difference in yields of these ions from aliphatic as opposed to aromatic chlorinated compounds tends to decrease the importance of this search. The septum bleed search showed that these peaks are in some cases most intense peaks in the chromatograms. The LMRGC of m/e 149 shows that the phthalate esters are found in both the neutral plus basic and acidic fractions although judging from the ratio of peak intensity to average baseline their concentrations in the neutral plus basic fraction is about 20 times those in the acid fraction. In addition, one additional phthalate appears in the acidic fraction at spectrum 274 APLCL1. This peak may be due to the saponification of a phthalate ester. A summary of the information contained in the LMRGC's of m/e 149 and 293 is presented in Table 4.161.

The other very important application of the LMRGC was to pinpoint the spectra of the components. For example in M1XA2 the phthalate appears at spectrum 214 while the septum bleed occurs at spectrum 213 although these components show up as a single peak in the RGC. The general method involved single or double display of consecutive spectra, selection of peaks for LMRGC's, construction of the LMRGC, pinpointing of the spectrum or spectra of interest and the 'background' spectra, background subtraction, and printing. The CRT console and magnetic disk were invaluable in performing these functions. One complete cycle could be carried out in 4 - 5 minutes.

Once a mass spectrum was chosen it was subtracted from the next higher number spectrum to ensure that major peaks found in the chosen spectrum did in fact belong in that spectrum. For example, if spectrum 11 - 9 was chosen, spectrum 12 - 11 was also retrieved to attempt to ensure that peaks from the compound(s) eluting at spectrum 12 or higher were not included in the spectrum of the compound whose maximum occurred at spectrum 11.

The matching of spectra to reference files led to the compilation of a

Table 4.16 Phthalates and Septum Bleed from LMRGC

File	Phthalates (m/e 149)	Septum Bleed (m/e 293)
	Spectrum Numbers	Spectrum Numbers
ARAWS1	204, 211, 253, 273	210, 257
CL12A1	203, 210, 252, 274	209, 257
APLCL1	203, 211, 253, 274	210, 257
CL120A	203, 210, 253, 274	209, 256
BLANK A	203, 210, 252, 338	210, 257
NBRAW1	203, 211, 241, 247, 254, 276, 341, 406	209, 257
CL12N1	202, 210, 240, 246, 252, 273, 336, 409	210, 258
NBPLCL	203, 211, 241, 247, 253, 339, 403	210, 258
12ONB1	203, 211, 241, 247, 253, 341, 423	209, 257
CL1202	195, 204, 211, 242, 248, 254, 277, 342, 425	210, 258
35LBK1	203, 211, 241, 253, 338, 401	210, 258
C-HALL	182, 209, 222, 229, 236, 269, 366, 508	187, 237
3B-HALL	181, 221, 229, 365, 508	187, 237
RAWNB1	211, 219, 251, 257, 265, 291, 369	217, 265
MLXA2*	209, 214, 235, 239, 262	213, 261
MLXB*	179, 201, 206, 226, 233	184, 234

* Spiked with phthalates

list of possible compounds for each spectrum. Analysis of a mixture of authentic samples of these compounds by GC-FID and GC-MS-Com provided spectra and retention times. The comparison of GC-retention times was based on relative retention times as follows:

$$R_1 = \frac{(R_{B1C} - R_C) - (R_{B1S} - R_S)}{R_{B1C} - R_{B1S}} = \frac{R_{B1C} - R_{B1S} + R_S - R_C}{R_{B1C} - R_{B1S}} \quad (4.1)$$

where R_C = Retention time of peak in CL1202 or C-HALL

R_S = Retention time of peak in M1XA2 or M1XB

R_{B1C} = Retention time of 1st Septum bleed in CL1202 or C-HALL

R_{B1S} = Retention time of 1st Septum bleed in M1XA2 or M1XB.

This method of correlation of the retention times was chosen for the following reasons. First, since relative retention times on a ratio basis are a function of temperature the error limits for these ratios will also be a function of temperature. This would necessitate a rather complex type of analysis to determine the retention time correlations. Second, the phthalate and septum bleed peaks appear to be linearly shifted when comparing C-HALL with M1XB or CL1202 with M1XA2. This implies that the differences in the chromatograms were due either to changes in flow or column deterioration over the four month period between the runs. In any case the linear shift provides a very simple method for correlation of retention times and thus equation 4.1 was adopted.

The use of spectrum numbers as a measure of retention time contributes an error of about 0.25 spectrum numbers. Since the maximum deviation in retention times of identical peaks among the runs on the same day was shown to be 2 of 3 spectrum numbers, the maximum allowable deviation in R_1 is $-1.00 < R_1 < +1.00$ for the retention time correlations. The results of the spectral file searches and retention time checks are summarized in Tables 4.17 and

Table 4.17 Results of Spectral Searches and Retention Time
Checks for CL1202

Spec. No (CL1202)	Possible Compd. from File Search	Spec No (M1XA2)	R _I	R _I within limits
11	C ₂ Cl ₄	16	-0.67	yes
19	Cl-Benzene	24	-0.67	yes
31	Et-Benzene	31	+1.00	yes
31	o-Me ₂ -Benzene	37	-1.00	yes
31	m-Me ₂ -Benzene	30	+1.33	(no)
23	p-Me ₂ -Benzene	28	-0.67	(no)
40	2-n-Butoxy ethanol	--		
44	iPr-Benzene	46	+0.33	yes
44	1,2,4-Me ₃ -Benzene	64	-5.67	no
56	1-Me-3-Et-Benzene	--		
56	1-Me,2-Et-Benzene	--		
61	p-Cl ₂ Benzene	70	-2.00	no
69	o-Cl ₂ Benzene	77	-1.67	no
69	p-Cl ₂ Benzene	70	+0.67	yes
62	n-Bu-Benzene	80	-5.00	no
62	t-Bu-Benzene	64	0.33	yes
66	Benzaldehyde	71	-0.67	yes
66	and α-chloro toluene	72	-1.00	yes
77	or o-chlorotoluene	53	+5.3	no
77	Benzyl alcohol	83	-1.00	yes
86	p-Cresol	92	-1.00	yes
98	2-phenyl ethanol	103	-0.67	yes
986	Dihydroheptafulvene	--		
106	Menthol	112	-1.00	yes
106	Isomenthol	--		
110117	Terpineol	115	-0.67	yes
117	Me-Salicylate	123	-1.00	yes
133	1-Me-Napthalene	139	-1.00	yes
137	2-Me-Napthalene	139	-1.00	yes
137145	Dichlorocresol	--		
145	Indazole	--		
194	Benzimidazole	--		
	Benzo-furan	--		
204	Diethyl phthalate	209	-0.67	yes
211	phthalate			
242	n-propyl phthalate	236	+3.00	no
248	n-Bu-phthalate	263	-4.00	no

Table 4.18 Results of Spectral Searches and Retention

Time Checks for C-HALL

Spec # C-HALL	Possible Compd. From File Search	Spec # MIXB	R ₁	R ₁ within limits?
39	Benzaldehyde			
51	Benzyl alcohol			
59	p-Cresol			
69	Methyl Benzoate	68	+0.67	yes
71	2-Phenyl ethanol			
81	Menthol			
	Isomenthol			
89	Camphor	87	+0.33	yes
99	Indazole			
121	2,4 or 2,5-Me ₂ Benzy-OH			
	3-Phenyl propylamine			
	Benzimidazole			
	Benzofuran			
111	1-Me Napthalene	110	+0.67	yes
	2-Me Napthalene			
114	Iso-borneol	72	-13.00	no
	Bornyl acetate	111	0.00	yes
136	1,3-Dimethylnapthalene			
	2,7-Dimethylnapthalene			
152	Glycerol triacetate	150	+0.33	yes
	Diacetin	125	-8.00	no
156	1,4,5 Trimethylnapthalene			
159	Dimethyl phthalate	1577	+0.33	yes
164	Coumarin	162	+0.33	yes
168	Cedrol			
176	α -Tetrahydrofuryl-OH			
178	Benzophenone	178	+1.00	yes
182	Diethylphthalate	178	0.00	yes
201	Anthracene	200	+0.67	yes
	Phenanthrene	200	+0.67	yes
	Diphenylacetylene	176	-7.33	no
209	Propyl phthalate	206	0.00	yes
211	p-t-Bu phenoxyethanol			
222	Phthalate			
229	Phthalate	226		
236	n-Bu phthalate	233	0.00	yes
260	Me-Stearate	254	-1.00	yes
269	Phthalate			
366	Benzyl Bu-phthalate			
508	Octyl phthalate			

4.18.

Most of the mass spectral and retention time correlations are straightforward however spectra 31, 61 and 69 in CL1202 present special problems. For spectrum 31 the correlation factor for o-xylene is -1.00 while those for ethyl benzene and the other xylenes range from +1.00 to +2.00. Since almost all of the other positively correlating matches have retention time correlation factors between +0.33 and -1.00 it was felt that the correlation factors for the meta and para xylenes was sufficiently large to warrant probable rejection. With respect to the dichlorobenzenes the expected order of elution is meta, para and ortho (ASTM 1967, Zweig and Sherma 1972). Since the ortho-dichlorobenzene shows a large deviation in relative retention times, it is most probable that the compounds present in CL1202 are the meta and para dichlorobenzenes.

In some cases authentic samples of the compounds listed in Tables 4.17 and 4.18 were not available. Therefore no retention time correlation times were obtained. In addition, compounds which afforded a reasonable match on the basis of an eight peak index search but for which no reference spectrum or authentic sample was available are not included among those listed in Tables 4.17 and 4.18.

A summary of compounds positively identified by mass spectrum and retention time appears in Table 4.19. For these compounds an estimate of concentration in sewage effluent was made on the basis of peak heights in the unnormalized total ion current traces of the samples. Linearity of the mass spectrometer was assumed along with a zero response for zero sample injected. Since no studies of recovery factors or concentration losses were made, changes in instrumental sensitivity may have occurred and resolution was not always good, these concentrations are stated as order of magnitude ranges. The lower number in the range is the average concentration in 120NB1,

Table 4.19 Compounds Positively Identified by Mass Spectrum
and Retention Time

Compound	Spec No	Spec No	Concentration Range in	
	CL1202	C-HALL	Primary Effluent (µg/l)	MEC
			GC - MS	
Tetrachloroethylene	11		5-50	1-10
p-Xylene	23		1-10	
o-Xylene	31		1-10	
Isopropylbenzene	44		2-20	
Tert-butylbenzene	62		10-100	
Chlorobenzene	19		10-100	1-10
m-Dichlorobenzene p-dichloro	61		10-100	0.4-4
p-Dichlorobenzene	69		3-30	1-10
α-Chlorotoluene	66		7-70**	0.4-4
Benzyl alcohol	77	51	10-100	
2-Phenylethanol	98	71	5-50	
Cresol (p?)	86	59	20-200	
Benzaldehyde	66	39	10-100	
Methyl Benzoate		69	0.4-4	
Methylsalicylate	117		7-70	
Benzophenone		178	1-10	
1-Methyl naphthalene and/or	133	111	5-50	
2-Methylnaphthalene	133			
Phenanthrene and/or		201	0.8-8	
Anthracene		201		
Glycerol triacetate		152	0.5-5	
Methyl stearate		260	0.7-7	
Dimethyl phthalate*		159	0.6-6	
Diethyl phthalate*	204	182	0.4-4	
Di-n-propyl phthalate*		209	0.3-3	
Di-n-butyl phthalate*		236	9-90	
Menthol	106	81	15-150	
Terpineol	110		20-200	
Camphor		89	1-10	
Bornylacetate		114	0.8-8	
Coumarin		164	2-20	

* Possibly from contamination during sampling and analysis.

** Estimate is probably high.

CL1202 and C-HALL if the compound was present in all three chromatograms. The actual concentration may be lower than this due to resolution problems. The higher number is one order of magnitude higher than the lower number and is an estimate of the maximum possible concentrations.

A list of those compounds whose spectra can be reasonably identified in the spectra from CL1202 and C-HALL but for which no authentic samples were available is compiled in Table 4.20. These compounds have been tentatively identified and in many cases several possible identifications were made for the individual spectra from CL1202 and C-HALL.

7. Correlations Among G.C. Chromatograms

In order to further study the compounds formed as a result of chlorination, a correlation among the GC chromatograms from the various GC instruments was attempted. While some information regarding these compounds can be obtained from the FID and EC detectors (e.g. Figures 4.24 and 4.10), the most significant information comes from the MEC and mass spectrometric detectors. Therefore correlations among retention time with the MEC detector, spectrum number in CL1202 and spectrum number in C-HALL were made. The MEC detector trace was first correlated with CL1202 through the use of three compounds and the zero point. CL1202 was then correlated to C-HALL on the basis of identical spectra from Tables 4.16, 4.17 and 4.18. The results of these correlations are displayed in Figure 4.34. It is interesting to note that both correlations are linear.

On the basis of Figure 4.34, the spectrum numbers of the halogen containing compounds were estimated. This data is summarized in Tables 4.21 and 4.22. From these tables it can be seen that seven to nine of the thirty-eight halogenated neutral or basic compounds detectable by MEC are also detectable by GC-MS, while none of the acidic compounds containing halogen are detectable by GC-MS. In the neutral and basic fraction only three of the

Table 4.20. Compounds Tentatively Identified by MS

Compound	Spectrum No	Spectrum No
	CL1202	C-HALL
Dihydroheptafulvene	98	225
2,3 Bis (4-methoxyphenyl) pent-2-ene		
1-Methyl,2-Ethylbenzene	56	
1-Methyl,3-Ethylbenzene	56	
1,3,5-Trimethyl-2-n-butylbenzene		127
1,3-Dimethylnapthalene		136
2,7-Dimethylnapthalene		136
1,4,5 Trimethylnapthalene		156
Dichlorocresol (4,6)	137	
2,4-Dimethylbenzylalcohol		99
2,5-Dimethylbenzylalcohol		99
2-n-Butoxyethanol	40	
p-t-Butylphenoxyethanol		211
Cedrol		168
α -Tetrahydrofurfurylalcohol*		176
Dihydrofuran (2,5)	8	
Benzofuran	145, 194	121
2-Methylazetidine	8	
2,2-Dimethylaziridine	8	
Indazole	145, 194	121
Benzemedazole	145, 194	121
Acetanilide	133	
3-Phenylpropylamine		99
Caffeine	See Figure 4.28	

* Retention time is very long and therefore suspect is some type of degradation product.

Figure 4.34 MEC - GC-MS Correlations.

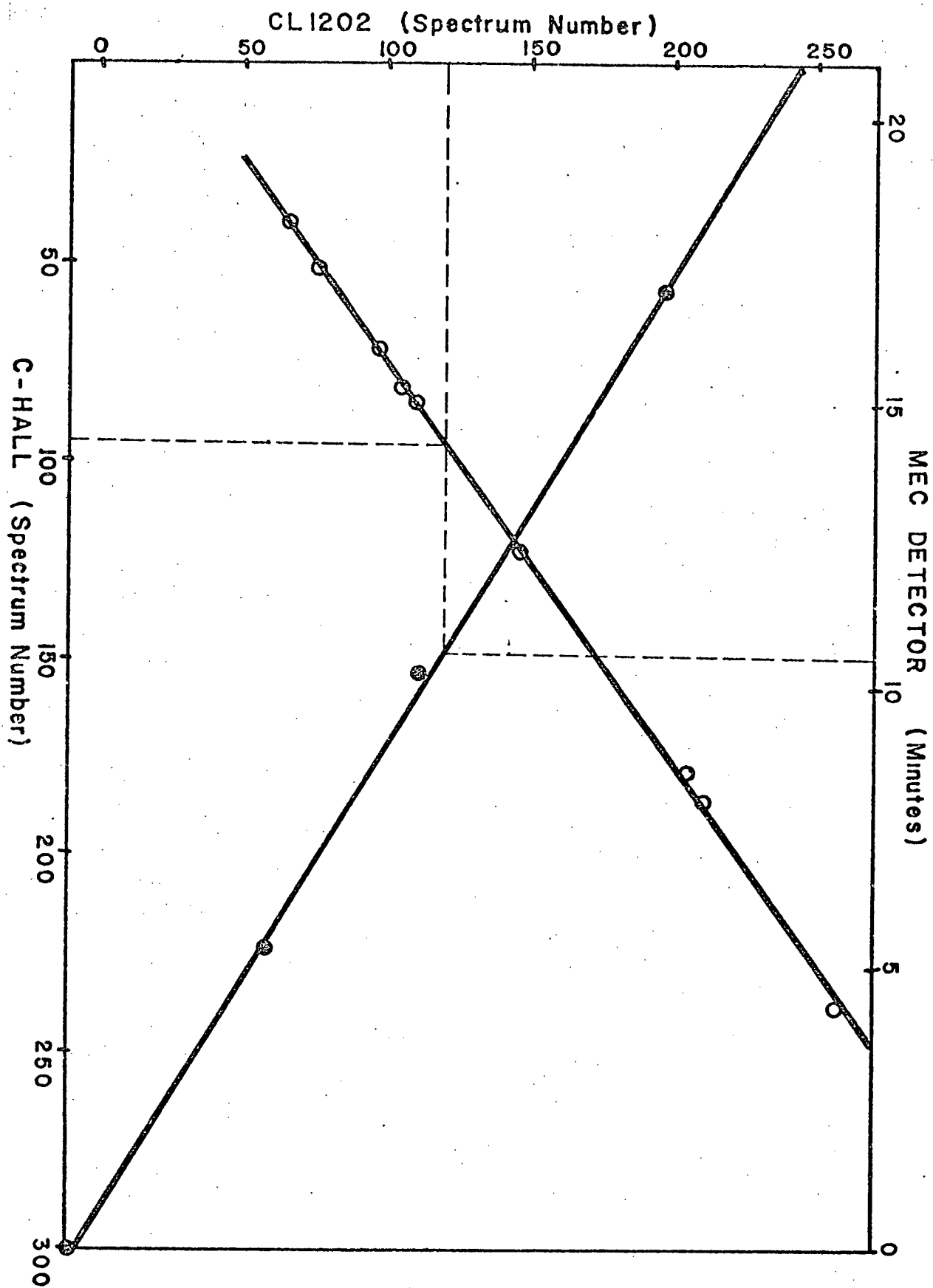


Table 4.21 - Spectrum Numbers of Halogenated Neutral and Basic Organics

Peak #	MEC Detector Retention Time (min)	Mass Spectrometer Spectrum Number		Spectrum Shows Chlorine	Compound Results from Chlorination
		CL1202	C-HALL		
1	1.2	5		No	No*
2	1.5	8		No	No*
3	1.8	12		Yes	No
4	2.3	19		Yes	Yes
5	3.0	25		Yes	Yes
6	3.7	36		No	Yes
6a	4.6	47		No	Yes
7	5.1	53		No	Yes
8	5.8	62	32	Yes	Yes
9	6.3	68	40	Yes	Yes
9a	7.6	83	56	No	Yes
9b	8.1	89	62	No	Yes
10	8.9	99	72	No	Yes
10a	9.6	107	80	No	No*
11	9.9	111	85	No	Yes
12	10.3	116	90	No	No
12a	10.9	124	98	No	No
13	11.2	127	101	Yes ^{aa}	No*
13a	11.6	131	106	No	No
14a	12.0	136	111	Yes	No*
14a	12.3	140	115	No	No*
15	12.6	142	117	No	No
16	12.9	147	122	No	No
17	13.4	153	128	No	No*
18	13.7	157	132	No	No
19	14.1	162	137	No	No
20	14.5	167	142	No	Yes
21	14.8	170	146	No	No
22	15.3	176	152	No	No
23	15.6	179	155	Yes ^a	No*
24	15.9	183	159	No	No
25	16.2	187	163	No	Yes
26	16.6	192	169	No	Yes*
27	16.9	196	173	No	Yes**
28	17.2	199	176	Yes ^a	No*
29a	17.6	203	180	No	No
29a	18.0	208	185	No	No
30	18.6	216	193	No	No
31	19.2	222	200	No	No
32	20.1	234	212	Yes	No

* Enhanced at 120 mg/l dosage only.

** Plant chlorinated and 120 mg/l only

a - unsat. HC spectrum

Table 4.22 Spectrum Numbers of Halogenated Acidic Compounds

Peak	MEC Detector Retention Time	Mass Spectrometer Spectrum Number CL120A	Spectrum Shows Chlorine	Compound Results from Chlorination
1	2.3	19	No	Yes ^a
2	10.2	112	No	Yes
3	11.7	133	No	No ^b
4	12.5	142	No	Yes ^c
5	12.9	149	No	No
6	13.3	152	No	Yes
7	13.8	158	No	No
8	14.5	166	No	Yes ^c
9	15.1	173	No	Yes ^b
10	15.4	177	No	No
11	16.7	193	No	No
12	19.1	222	No	Yes ^c
13	2.14	250	No	Yes

a - Appears only in plant chlorinated sample.

b - Appears only in plant sample chlorinated at 120 mg/l.

c - Appears only in sample chlorinated at 120 and 12 mg/l.

fifteen halogenated compounds formed as a result of chlorination could be identified. Peak 5 is an unidentifiable chloroalkyl compound while peak 9 is both p-dichlorobenzene and α -chloro toluene. Limited mass searches and spectral examinations of NBRAW1, CL12N1, NBPLCL and CL1202 show that p-dichlorobenzene is present in all of the extracts while the mass spectrum of peak 5, chlorobenzene, m-dichloro-benzene and α -chlorotoluene are present only in the chlorinated extracts. It was also found that the mass spectra corresponding to peaks 3, 13, 14, 23, 28 and 32 were present in all extracts. This indicates a good correlation among the peaks resulting from chlorination as monitored by the MEC detector and the mass spectrometer. It is also evident that as expected the MEC detector is much more sensitive than the mass spectrometer.

The fact that the two chlorophenols were used as calibrants allowed a more unequivocal search for chlorinated phenols. Limited mass searches of 128, 162, 142 and 176 were made in the acid and neutral plus basic fractions run under CL1202 GC conditions. Although the 128 and 162 LMRGC's showed peaks at spectrum 110 in all extracts including the unchlorinated ones and a peak at spectrum 59 only in the chlorinated samples, examination of the background subtracted spectra showed little more than tall grass. No isotopic clusters were evident in any of the spectra. It is also noteworthy that m/e 128 is a minor peak in the spectrum of α -terpineol which is the established identity of spectrum 110. On the other hand the MEC data shows that peak 2 in the acid fractions or peak 11 in the neutral and basic fractions or peak 11 in the neutral and basic fractions may be p-chlorophenol. The search for chlorinated cresols by LMRGC's yielded many peaks for m/e 142 or 176. Only spectrum 137 showed chlorine (m/e 176). In the region of spectra 80 - 140, no new peaks appeared in the LMRGC's (m/e 142) as a result of chlorination. Although peaks appeared at spectrum numbers 87, 91, 99, 110, 118, 125, 134

and 137, the peaks in the region 83 to 130 were so small that their presence was debatable in many extracts. Since peak 14 (Spectrum 137) is present in all extracts it appears as though the chlorination does not produce chlorinated phenols except possibly at chlorine dosages of 120 mg/l.

CHAPTER V

SUMMARY, IMPLICATIONS AND SUGGESTIONS FOR FURTHER STUDY.

1. Summary

The first part of this work dealt with the analytical methodology necessary to extract and separate the trace organic components of primary effluent. The work on extraction showed that while both methods gave adequate recoveries the continuous solvent extractor suffered from emulsion problems while the sorption method suffered from poor recovery of organics sorbed on particulates. The sorption method was chosen because of its compactness and ease of duplication. The separation studies indicated that the acid base solvent extraction provided useful preliminary separation but suffered from the high solubility of the organic solvent in water. Thin layer chromatography was valuable only for compounds with volatilities less than benzylalcohol or p-cresol. The GC studies indicated that all the low temperature silicone liquid phases provide good separation although it is evident that they do not give a separation of one component per peak even after optimizing the temperature programs.

The second part of this project centered upon the study of the effects of chlorination upon the volatile organic components of primary effluent and the identification of these components. It was found that with concentration factors of 5000-10,000 the effects of chlorination were only readily apparent with the microelectrolytic conductivity and electron capture GC detectors. The uptake of chlorine by the volatiles at dosage levels of around 12 mg/l was in the order of 0.01 percent of the applied dose. With a detection limit of 3 ng/l about 20 new halogenated compounds were formed as a result of chlorination and those compounds account for about 40 percent of the total organic halogen as chlorine, exclusive of the halogenated methanes

and ethanes, found in chlorinated primary effluent. The EC work showed that these effects were reproducible in different effluent samples.

In order to identify the organics in primary effluent a computerized GC-MS was essential. A large number of spectra could not be identified through file searches and the incomplete separation of compounds could be part of the reason for this. A total of 31 compounds were positively identified by both their mass spectra and GC retention times (Table 4.19), another 24 compounds were tentatively identified by their mass spectra (Table 4.20) and an additional 7 compounds were very tentatively identified on the basis of GC retention time (Table 4.12). Three of the chlorinated compounds formed by chlorination were positively identified (Tables 4.19 and 4.21).

2. Implications

The results of the second part of this study have some implications for the design of treatment plants and the effects of primary effluent upon the aquatic ecosystem. It is obvious that a large number of volatile organic compounds are present in $\mu\text{g/l}$ concentrations in primary effluent. If some of these compounds exhibited deleterious effects upon the receiving water or general ecosystem, treatment plants will have to be designed to reduce their concentrations to an acceptable level. Since biological oxidation rate is a function of substrate concentration this may necessitate the installation of physical-chemical rather than the biological treatment plants currently used.

In order to assess the possible environmental effects of the volatiles in primary effluent Table 5.1 was prepared. Before interpreting the table some general points should be made. The assignments of the possible principal sources were based upon an interpretation of the natural or industrial sources and major uses of a particular compound rather than a waste survey. Street surface runoff is included among the possible sources even though a separate

Table 5.1 - Guide to Environmental Effects of Identified Compounds

Compound	Possible Source ^b	Concen. ^c mg/l	Toxicity	
			Acute (mg/l)	Sub-acute ^a
Tetrachloroethylene	Co	0.005	1, F - (60) D	4, Met-Mu, Ca?
Orthoxylene	Co, SS, H	0.001	1, F - (50) L	2, N?
i-propylbenzene	Co, SS, H	0.002		3 N?
t-butyl benzene	Co, SS	0.01		
chlorobenzene	Co, H, Cl	0.01		3, Ca? / 2, CNS
m-dichlorobenzene	Cl	0.01		
p-dichlorobenzene	Co, H	0.003	1, F - (50) L	3, 1D
Benzyl alcohol	Co, H	0.01	1, Da - (360) TL _m 48	
2-phenyl ethanol		0.005		
α-chlorotoluene	Cl, Co	0.007	1, F - (10) D	3, Ir
Benzaldehyde	H	0.01	1, M - (16) D	
Methyl benzoate	H	0.0004		
Methyl salicylate	H	0.007		
Benzophenone	H	0.001		
Methyl naphthalene	Co, SS	0.005	1, F - (5) L _{1.0}	3, Ca?
Phenanthrene	Co, SS	0.0008	1, F - (5) L _{1.0}	3, Ca?
Anthracene	Co, SS	0.0008	1, F - (75) L ₂₄	3, Ca?
Glycerol triacetate	H	0.0005		
Methyl stearate	H	0.0007		
Dimethyl phthalate		0.0006		
Diethyl phthalate	Co, H	0.0004	1, F - (1) L _{0.5}	2, Ir
Di-n-propyl phthalate		0.0003		
Di-n-Butyl phthalate	Co, H	0.009		2, Ir
Menthol	H	0.015		
Camphor	H, Co	0.02	1, F - (75) D ₂₄	2, N
Terpineol	H	0.001		
Bornylacetate		0.0008		2, N?
Coumarin	H	0.002		

a - Effects upon mammals

b - References 2,3,5

c - Lower value

Table 5.1 Cont'd.

Symbols

Possible Sources - Co - Commercial/Industrial
 Cl - Chlorination of Primary Effluent
 H - Household
 SS - Street Surface Runoff

Toxicity

- Acute e.g. 1,F - (60)D
 1 - Reference Number
 F - Test Animal
 60 - Toxic Concentration
 D - Type of Toxic Effect
- Sub-acute 3,C? /2,CNS
 3 - Reference Number
 C - Effect
 / Next Reference
 2 Second Reference Number
 CNS - Effect

References

1. McKee and Wolf (1971)
2. Merck Index (1968)
3. Sax (1974)
4. Fishbein 1973B
5. Noller 1957

Symbols

Ca - Carcinogen or Cocarcinogen
 CNS - Affects Central Nervous System
 D - Deleterious but not lethal
 Da - Daphnia
 F - Fish
 ID - Internal Damage
 Ir - Irritant
 L - Lethal
 M - Minnows
 Met - Metabolic Products
 Mu - Mutagenic
 N - Narcotic

sewer system is employed in sewage collection area. This was done since groundwater infiltration does occur e.g. during wet weather although the sorption and leaching of organics on soils will affect the input of organics from this source. Regarding the toxicity data it is evident that there is little acute toxicity information available for fish let alone other aquatic organisms, moreover there is practically no data at all available on the subacute effects so those listed are primarily for non-aquatic mammals. From Table 5.1 it appears that no problems of acute toxicity to fish should result from the individual compounds of either unchlorinated or chlorinated/dechlorinated primary effluent, although the cumulative toxicity of all of the components and synergistic effects are difficult to predict. This conclusion is supported by Esvelt et al., (1973) who were able to correlate most of the toxicity of primary effluent to concentrations of MBAS and ammonia and Martens and Servizi (1975) who found that chlorination followed by dechlorination of primary effluent might even slightly reduce the toxicity of primary effluent to fish. On the other hand, the acute toxic effects upon aquatic insects, for example, may be important since dichlorobenzenes have been used as insecticides (Merck, 1968).

Although acute toxicity problems may not result from these compounds sub-lethal effects probably will. Possible effects (McKee and Wolf, 1971; Kemp et al., 1973; Gillet 1970; Walsh and Mitchell 1974) include central nervous system impairment - Brook Trout ~150 g 0.02 mg/l DDT, hyperactivity - tadpoles 0.5 μ g DDT residue, survival of fish from eggs exposed to a toxicant - 3% survival of steelhead 0.4 μ g/l DDT and taste in flesh - oysters 1 μ g/l chlorophenol. It should be pointed out that DDT is an extremely toxic substance and is certainly several orders of magnitude more toxic on a TL_m basis than most organic compounds. On the other hand if the mechanism of the sub-lethal toxicity is independent of that of the acute toxicity, it is

not possible to estimate what concentration of a particular compound will cause sub-lethal toxic effects. Furthermore, the previously stated harmful dosages of DDT and chlorophenol do not take into account bioaccumulation which has been shown to be 3 - 5 orders of magnitude with DDT and *Daphnia* (Kemp et al. 1973).

In summary, therefore, it is unlikely that the trace volatile organics identified as originally present in, or resulting from the chlorination and dechlorination of primary effluent will be acutely toxic to fish. It is possible however that these compounds, particularly those which are recalcitrant may be toxic to other organisms or have other deleterious effects upon the aquatic ecosystem. In view of the fact that 1 percent of the chlorine applied to primary effluent ends up as 'stable' non-volatile organo-chlorine compounds (Jolley 1973) while only 0.015 percent ends up as stable volatile organochlorine compounds, it is possible that the most serious effects of chlorination will be manifested in the non-volatile fraction.

3. Recommendations for Further Studies

i) Quantification of identified components: It is recommended that recovery studies be carried out using primary effluent as the solvent. Quantification of the 'identified' compounds can then be conveniently made by unnormalized LMRGC's.

ii) Further separation: Since the acidity separation did not prove highly effective it is recommended that fractionation on a HPLC instrument be made prior to final separation by GC.

iii) Identification of more constituents: Subsequent to the improvement in separation, more identifications can be made on the basis of mass spectrum and LC and GC retention time.

iv) Effects of chlorination: a) Distribution of chlorine uptake. It would be instructive to study the distribution of chlorine uptake in the

various molecular weight fractions. This could be done through the use of ^{36}Cl and gel permeation chromatography. b) It appears from this study that chlorine uptake is related to ammonia content of the sewage effluent. The formation of halogenated benzenes but not halogenated phenols suggests that the major mechanism of chlorine uptake may be other than electrophilic substitution. Further work on the mechanisms of chlorine uptake is therefore recommended.

v) Environmental Implications of the Resultant Chlorinated Organics.

a) Acute toxicity - Bioassays should be conducted to obtain the LC_{50} values for each of the compounds identified with a representative set of organisms.

b) Sublethal effects - Studies upon the inhibition of bacterial metabolic rates by these compounds can be easily carried out. Studies of the effects of these compounds on species diversity and predator/prey relationships and the sublethal effects are much more difficult to carry out but such investigations are warranted to identify those compounds requiring routine monitoring.

c) Persistence - Studies in this area should include degradation rates for acclimated bacteria, degradation times for non-acclimated bacteria, intake/metabolic/excretion/accumulation studies for some of the major biological species in the receiving waters and solubility/sorption/precipitation data for the effluent and receiving water to establish the availability of these compounds for biological uptake. If sewage sludge is to be used as fertilizer for agricultural crops studies on the fates of these compounds in this non-aquatic ecosystem are also warranted.

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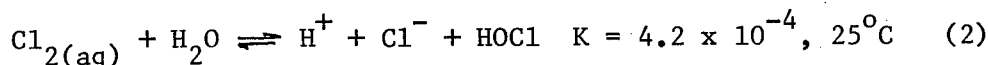
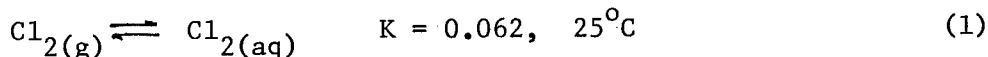
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APPENDIX I

REFINEMENTS TO THE AQUEOUS CHLORINE-AMMONIA MODEL

1. Reaction of Chlorine with Water

The following data is taken from Cotton and Wilkinson (1966) and Lister (1965). When a large amount of chlorine is added to a litre of water between 9.5°C and 100°C, the following equilibria are set up:



This means that a saturated aqueous solution of chlorine at 25°C will have the following composition at pH 4:

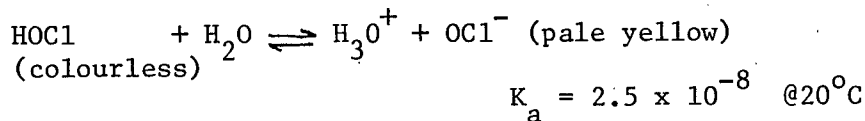
$$\text{Total Cl}_2 \quad 0.091 \text{ moles/l}$$

$$[\text{Cl}_{2(aq)}] = 0.001 \text{ M}$$

$$[\text{HOCl}], [\text{Cl}^-] = 0.090 \text{ M}$$

When less than one or two grams of Cl_2 is dissolved in a litre of water equilibrium (2) is reached in a few seconds. Thus it can be seen that if the total Cl_2 is less than 1.0 g/l and the pH is greater than 4 there is a negligible amount of $\text{Cl}_{2(aq)}$ present.

Hypochlorous acid is a weak acid and exists only in solution. It undergoes the following dissociation in aqueous solution.



Thus in the pH range 6.8 to 7.8 a dilute aqueous solution of HOCl contains 75% to 25% HOCl.

Below 9.5°C, $\text{Cl}_{2(g)}$ forms a crystalline hydrate with water. HOCl can exist at 0°C ($K_a = 1.5 \times 10^{-8}$) in aqueous solution.

Under ultraviolet light or at high temperatures, chlorine very slowly reacts with water according to the following equation.

in the pH ranges cited.

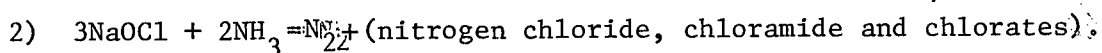
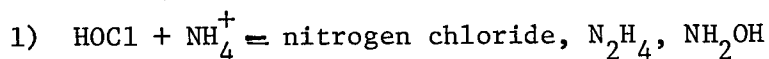
3. Reactions of HOCl and OCl⁻ with Ammonia

Reaction Products

The reaction of HOCl and OCl⁻ with aqueous solutions of ammonia gives rise to a complex set of equilibria dependent on pH, time, temperature, and concentration. They are compositely referred to as the chlorine break-point reaction. Before discussing this phenomenon, a few definitions are in order. Chlorine residual is divided into two general classifications, free and combined. Free residual chlorine is the amount of HOCl and OCl⁻ present expressed as mg/l Cl₂. Combined residual chlorine is the amount of chlorine in the +1 oxidation state which is chemically bound to nitrogen atoms. It is also expressed as mg/l Cl₂.

Griffin and Chamberlain (1941a,b) studied the fate of chlorine at various Cl₂/NH₃ ratios and produced what is called the breakpoint curve. The minimum residual chlorine at pH 7 was observed at a Cl₂/NH₃ - N ratio of 10:1 by weight or 2.0/1.0 on a mole basis. Subsequent work by Isomura (1967) determined more precisely the fate of Cl₂ in aqueous NH₃ systems. His results show that before the breakpoint, the residual chlorine is in the form of chloramines. After the breakpoint, chlorine is in the form of free chlorine and NCl₃.

The fate of the NH₃ - N during breakpoint chlorination has been a matter of controversy for some time. Mellor (1927, 1928) summarized the work prior to 1923 and presented the following equations:



Reaction (2) is second order overall and never complete in the conversion of NH₃ to N₂ at 15° - 25°C. It is accelerated by Cu, Hg, Pb, Fe (III), Co, Ni, Ti, Pt, Mn and Cr salts. The tentative identification of the gaseous product as N₂ became questionable when it was observed that trace amounts of

nitrites and nitrates were also produced.

Chapin (1931) when studying the effect of pH on chloramine in formation also found a gas produced at pH 5.0 which matched the 1898 description of N_2O , but found no N_2O at pH 9.0.

Following the recording of the UV absorption spectra of the chloramines by Metcalf (1942) and their confirmation by Czech et al. (1961), the development of the OTA, DPD and amperometric titration techniques for residual chlorine (APHA 1971) and the development of gas chromatographic techniques of gas analysis, great advances were made in the determination of the fate of $NH_3 - N$ during breakpoint chlorination. The reported nitrogenous products are NH_2Cl , $NHCl_2$ and NCl_3 (Chapin, 1931; Metcalf, 1942; Palin, 1950; Isomura, 1967; Pressley et al., 1972, 1973; Bauer and Snoeyink, 1973; Stasiuk et al., 1974), and $N_2, NO_3^- + NO_2^-$ (Palin, 1950; Pressley et al., 1972, 1973; Stasiuk et al., 1974). The relative amounts of chloramines, N_2 , $NO_2^- + NO_3^-$ and other possible products such as hydrazine depend upon many factors which are discussed below.

i) $Cl_2:N$ Ratio. If the NH_3 is in excess the products are dependent mainly upon pH. If the initial $Cl_2:NH_3 - N$ weight ratio is between 1 and 5, the major product is NH_2Cl . As the initial $Cl:NH_3 - N$ ratio is increased from 5 to 10 increasing quantities of $NHCl_2$, NCl_3 and free chlorine appear, (Palin, 1950; Pressley et al., 1972). Isomura (1967) also indicates that as the initial amount of NH_3 is increased the concentration of $HOCl$ at the breakpoint also increases.

ii) pH Effects. In the presence of excess NH_3 and with pH values greater than 8.5, monochloramine alone is present. At high pH's, formation of hydrazine by the Rachig synthesis is also expected:



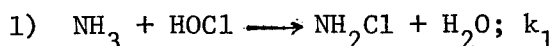
Dichloramine and monochloramine are present in equal quantities at pH 5. At

pH 4, NHCl_2 predominates while NCl_3 predominates below pH 2.8. The preceding pH values were taken from work by Palin (1950), Metcalf (1942), Chapin (1931) and Corbett et al. (1953).

Palin (1950) and Pressley et al. (1972) indicate that at Cl:N ratios large enough to produce free residual chlorine, the formation of $\text{NO}_3^- + \text{NO}_2^-$ is favoured by higher pH while the formation of NCl_3 is favoured by lower pH. The ratio of $\text{NCl}_3 - \text{N}$ to $\text{NO}_3^- + \text{NO}_2^- - \text{N}$ is 5.7 at pH 6.0, 1.0 at pH 6.4, 0.11 at pH 7.0, and 0.02 at pH 8.0. At pH 7, $\text{NH}_3 - \text{N}$ is 95-99% oxidized to N_2 .

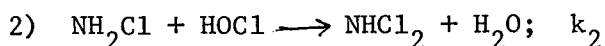
Reaction Rates

Kinetic studies of the various reactions involved in aqueous $\text{NH}_3 - \text{Cl}_2$ systems have been carried out by Weil and Morris (1949a,b), and reviewed by Morris (1965). The following data are presented:



reaction order overall is 2, first order in NH_3 and HOCl and pH dependent $k_{\text{obs}} = 8 \times 10^6$ at pH 8, 1×10^4 at pH 4 and pH 12

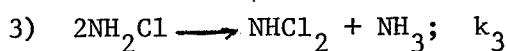
$$k_1 = 9.7 \times 10^8 \exp(-3000/RT) \text{ 1 mole}^{-1} \text{ sec}^{-1}$$



reaction order overall is 2, first order in NH_2Cl , HOCl ; it exhibits general acid catalysis and is also catalyzed by Cl^- .

$$k_2 = 7.6 \times 10^7 \exp(-7300/RT) \text{ 1 mol}^{-1} \text{ sec}^{-1}$$

$k_2^i = 3.4 \times 10^{22} (1 + 153 \times 10^4 [\text{H}^+] + 2 \times 10^2 [\text{HOAc}]) \text{ 1 mol}^{-1} \text{ sec}^{-1}$
at 25°C.



reaction order is 2, second order in NH_2Cl

$$k_3 = 80 \exp(-4300/RT) \text{ 1 mol}^{-1} \text{ sec}^{-1}$$

$$k_3^i = 5.6 \times 10^{-2} (1 + 1.3 \times 10^5 [\text{H}^+] + 35 [\text{HOAc}]) \text{ 1 mol}^{-1} \text{ sec}^{-1}$$



reaction order overall is 2, first order in NH_2Cl

$$k_{1a} = 8.7 \times 10^7 \exp(-17,000/RT) \text{ sec}^{-1}$$

Gupta et al. (1972) measured the rate of the breakpoint reaction at acid pH's. With equal 0.0125 M, Cl_2 and NH_3 concentrations the rate was first order in each reactant and second order overall. The k_{obs} ranged from 0.15 to 1.1 $\text{l mole}^{-1} \text{ sec}^{-1}$ between pH 3.5 and 4.5. The rate at $\text{pH} > 5$ was too fast to measure. They do not state whether residual ammonia was observed at pH 5 as was found by other investigators.

Mechanism Morris (1965) favours the nonionic mechanism for the reaction of chlorine and amines to form chloramines in aqueous solution while Soper (Mauger et al., 1946; Edmond et al., 1949; Hurst et al., 1949; Corbett et al., 1953) favours the ionic mechanism. Weil and Morris (1949a) found that ionic strength has no effect upon the reaction



at pH -1.9. Gupta et al. (1972) observed a negative effect of sulphate and acetate on the overall system at pH 3 - 4. Unfortunately the two mechanisms are not distinguishable since although increasing ionic strength should decrease only the rate of the ionic reaction, consideration of the effect of ionic strength on the hydrolysis of NH_3 and HOCl at any given pH will yield identical rate expressions. Both mechanisms are compatible with general acid catalysis.

While the formation of chloramines has been mechanistically described the reactions leading to the formation of N_2 and NO_3^- and NO_2^- have not. The most likely mechanism of N_2 formation would involve an hydrazine intermediate followed by oxidative degradation. The formation of $\text{NO}_3^- + \text{NO}_2^-$ probably involves the intermediate production of an hydroxylamine and/or NO or N_2O (Cahn and Powell, 1953; Audrieth and Rowe, 1955; Anbar and Yagil, 1962; Yagil and Anbar, 1962).

Chlorinated hydrazines, possibly due to their instability, have not been detected in aqueous $\text{NH}_3 - \text{Cl}_2$ systems. Therefore in considering the interactions of chlorine with sewage, only the interactions of chloramines will be considered.

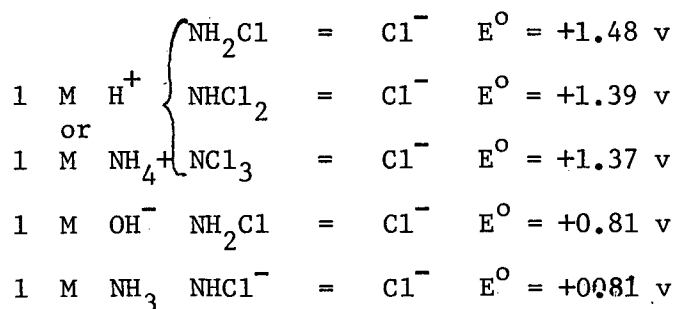
4. Thermodynamic Properties of Chloramines

Jolly (1956) has estimated the following acidity data from homologous series.

$$\text{pK}_a \text{ of } \text{NH}_2\text{Cl} \sim 14 \pm 2$$

$$\text{pK}_a \text{ of } \text{NHC1}_2 \sim 7 \pm 3$$

He measured the following oxidation potentials:



Chloramines are decomposed by activated carbon, (Bauer and Snoeyink, 1973), as well as by the common inorganic reducing agents.

Appendix II Summary of Chromatograms of Effluent Samples

Sample Date	Experiment & Extraction Method	Chlorine Dosages (mg/l)	Preliminary Separation		Total # of Peaks		# of New Peaks Due to Chlorination			GC-MS	MEC
			Method	Fraction	EC	FID	EC	FID	Total		
25/06/73	E-2; SE	0	---	---	33	---	---	---	---	---	---
03/07/73	E-2; SE	0	---	---	34	---	---	---	---	---	---
10/12/73	E-3-d; XAD	0	---	---	---	---	---	---	---	---	---
17/12/73	E-4; XAD	0	---	---	---	---	---	---	---	---	---
28/01/74	E-5; SE	0	F	P (M)	18	---	---	---	---	---	---
				So	50	---	---	---	---	---	---
	XAD	0	F	P (MC)	17	---	---	---	---	---	---
				So	50	---	---	---	---	---	---
	XAD	106	F	P (MAH)	15	---	---	---	---	---	---
				So	38	---	---	---	---	---	---
	S-1a SE, XAD	0,0,106	F,SG	1	42	---	---	---	---	---	---
				2	34	---	---	---	---	---	---
				3	20	---	---	---	---	---	---
18/03/74	S-1-6 XAD	0	F,ASB	N + B	52	51	17	5	17	---	---
	S-2	15		WA	38	36	} 3	} 2	} 5?	---	---
	C1-2	100		SA	21	8				---	---
		200									
29/04/74	C1-1 XAD	0	F,ASB	N + B	47	47	18	4	18		
	C1-4	12		WA	36	32	} 3	1	4?	MS-12	MS-12
	C1-2	103		SA	20	7					
08/07/74	C1-4 XAD	0	F,ASB	N + B	48	---	18	---			
	C1-2	25		WA	35	---	} 4	---			
				SA	20	---					
19/11/74	C1-5 XAD	0	F,AS	N + B	53	60	17	4	17	MS-12	
	C1-2	12		A	20	10	2	0	2		
18/12/74	C1-2 XAD	0	F,ASB	N + B	52	50	13	4	17		
		15		WA	37	31	12	4	2?		
		100		SA	20	7	1	0			
		200									
20/01/75	C1-7 XAD	0	F,AS	N + B	50	61	17	5	17	---	---
	C1-2	12		A	19	10	3	0	3	---	---
		120									

Appendix II cont'd.

8/03/75	C1-7	XAD	0	F,AS	N + B	53	63	18	5	18	F-3000
	C1-3		12		A	22	9	2	0	2	Yes
	C1-2		120								
			Plant								
	S-3		TEC								F-3000

Abbreviations

A - Acidic Fraction
 AS - Acidity Separation
 ASB - Acidity Separation with Bicarbonate Step
 F - Filtration
 M - Methanol, Soxhlet
 MC - Methanol, Chloroform Soxhlet
 MAH - Methanol, Acetone, Hexane Soxhlet
 N + B - Neutral and Basic Fraction
 P - Particulate Fraction
 SA - Strong Acid Fraction
 SE - Solvent Extraction
 SG - Silica Gel Column
 So - Soluble Fraction
 TLC - Thin Layer Chromatography
 XAD - XAD-2 Resin

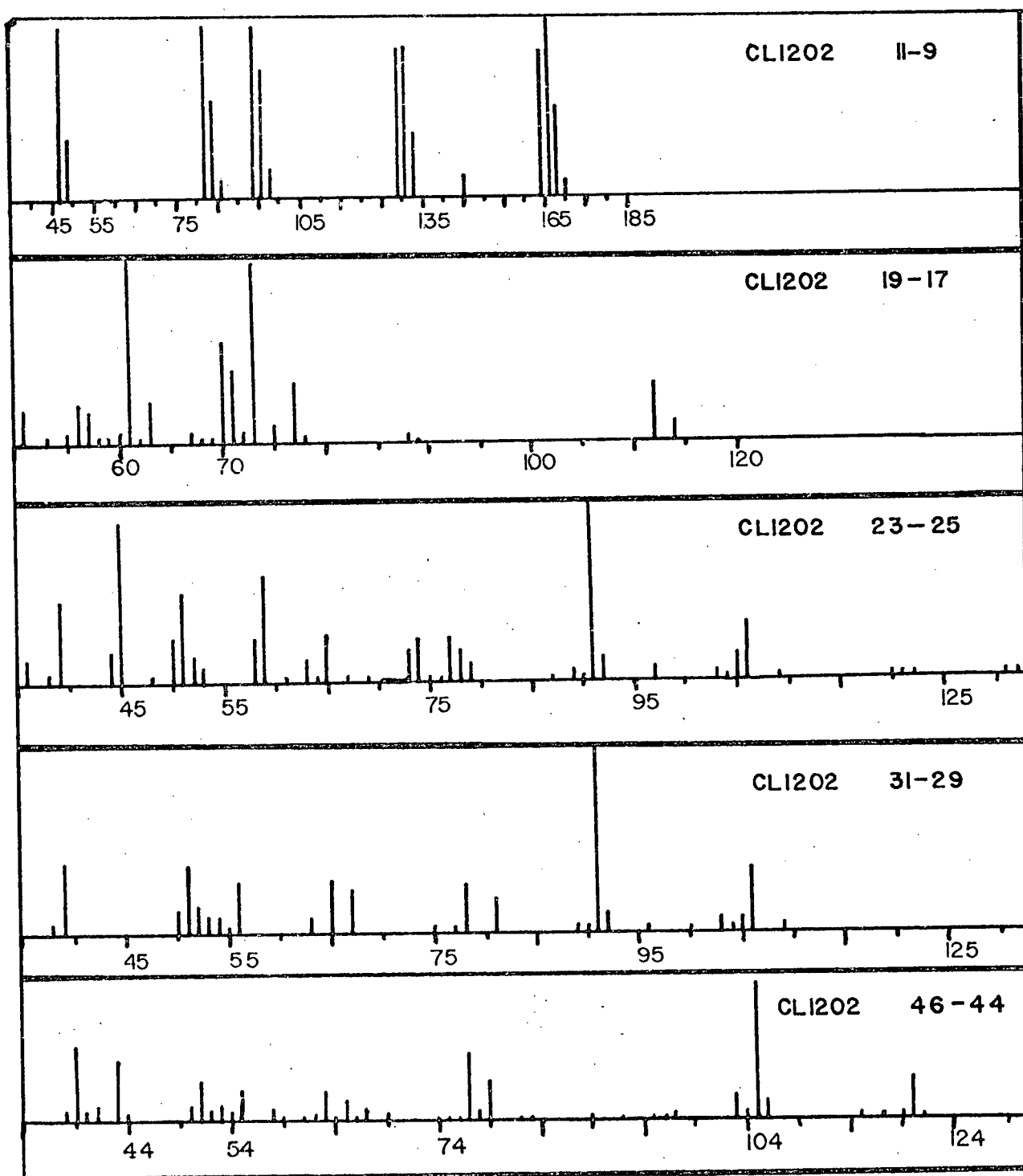
Appendix III CG Conditions for Figures

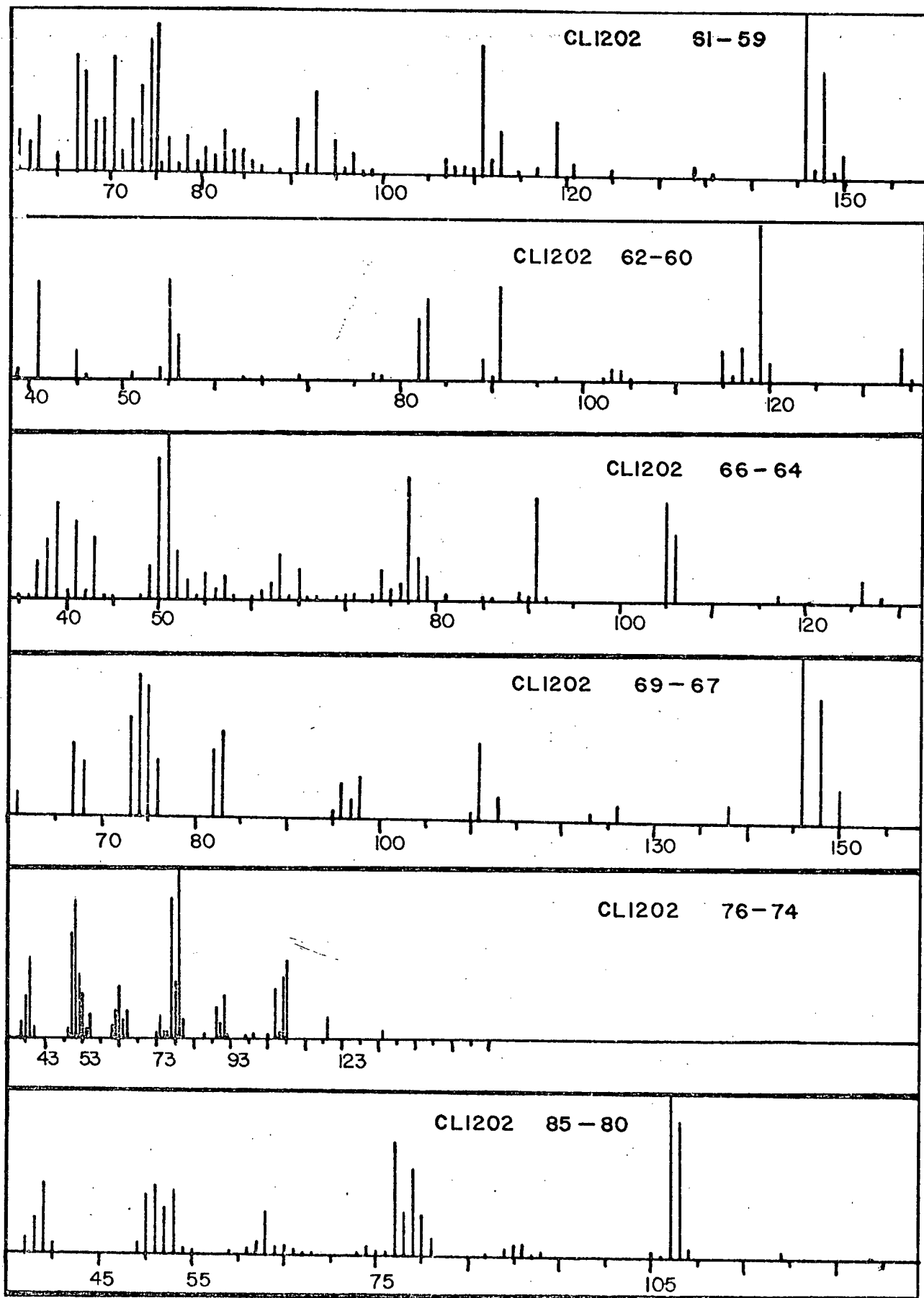
Figure	Instrument/Column	Detector/ Atten/Pulse (EC)	Temperature Program	Carrier Gas Flow
4.2	HP 5750 5% DC-11 on chromosorb W (HP) 80-100 mesh	EC; 64x10; 5 μ S	50°C/5 min, 100° min, 300°/30 min	65 ml/min
4.3	HP 5750 3% SE 30 on chrom W (HP) 80-100 mesh	EC; 32x10; 5 μ S	220°C isothermal	70 ml/min.
4.4		Identical to 4.2		
4.5	HP 5750 3% OV-101 on chrom W (HP) 80-100 mesh	EC; 64x10; 50 μ S	30°C/10 min 6%/min, 200°/ 20 min	65 ml/min
4.6	HP 5750 Various	As in 4.5	As in 4.5 except OV-1 100°C/20 min 6%/min, 260° /20 min	As in 4.5
4.7	HP 5750 Various	As in 4.5		
4.8	HP 5750 Various	FID; 32x10	As in 4.5	65 ml/min
4.9		As in 4.8		
4.10	HP 5750 6% SE-30, 4% OV-210 on Gas Chrom Q, 100-120 mesh	EC; 64x10; 50 μ S	48°C/10 min, 10°/min, 208° hold	70 ml/min
4.11	As in 4.10		48°C/6 min, 8°/ min, 208° hold	70 ml/min
4.13	HP 5750	As in 4.7		
4.14	3% OV-10/on Chrom W (HP), 80-100 mesh	As in 4.8		
4.15	As in 4.13			
4.16	As in 4.14			
4.17	As in 4.13			
4.18	As in 4.14			70 ml/min
4.19	HP 5750 3% OV-101 on Chrom W (HP) 80-100 mesh	EC; 64x10; 50 μ S	29°/10 min; 6° /min, 219°/20 min	75 ml/min
4.20	As in 4.19	FID 32x10	As in 4.19	
4.21	As in 4.19			
4.22	As in 4.20			
4.23	Microtek (Tracor 222)	Tracor 310 8x10	84°/4 min 10°/min, 200°/ 20 min	
4.24	As in 4.23			
4.25	As in 4.23	Tracor 310 Various	As in 4.23	

Appendix III Cont'd.

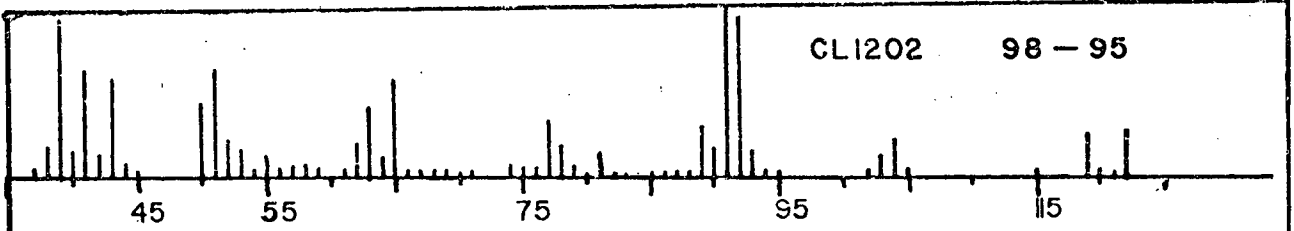
Figure	Instrument/Column	Detector/ Atten/Pulse (EC)	Temperature Program	Carrier Gas Flow
4.27	Pye 104	MS-12 3x15 ⁸ A full scale	As indicated	
4.29	As in 4.19			
4.30	Finn 3000, as in 4.10	F-3000	60°/2.5 min, 10°/min, 200°	32 psi
4.31	As in 4.30			
4.32	As in 4.30		80°/2.5 min, 10°/min, 200°	32 psi
4.33	As in 4.30			

APPENDIX IV

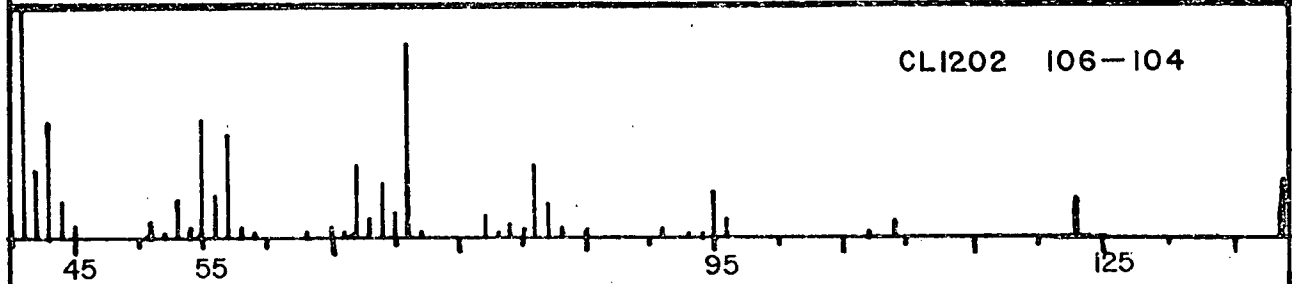
MASS SPECTRA OF COMPOUNDS POSITIVELY IDENTIFIED IN CHLORINATED PRIMARY
EFFLUENT



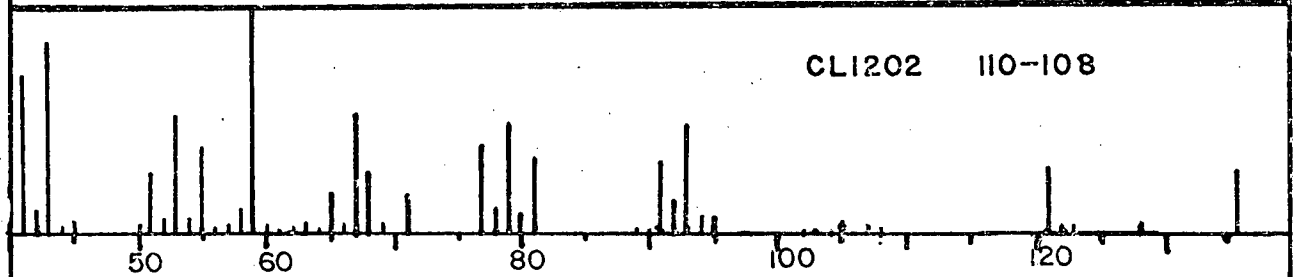
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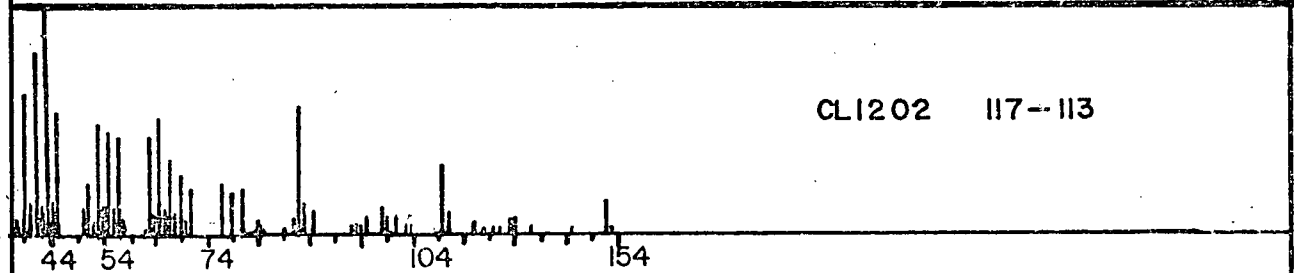
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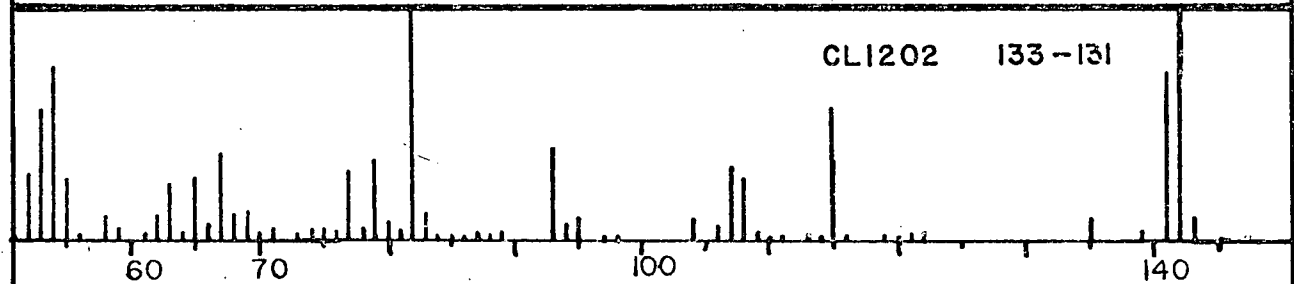
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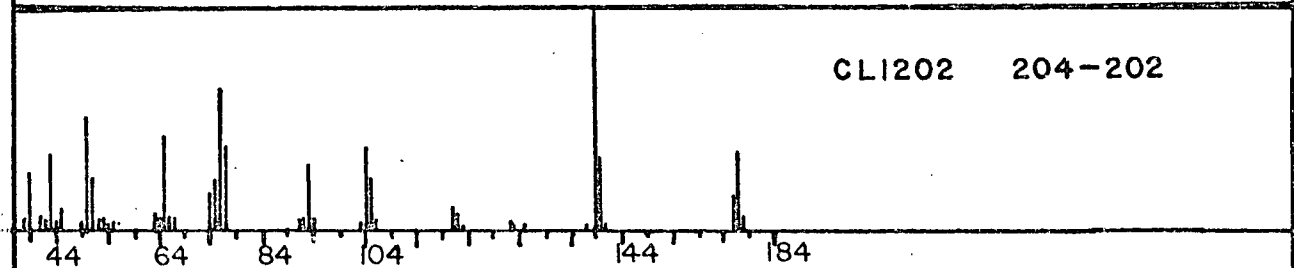
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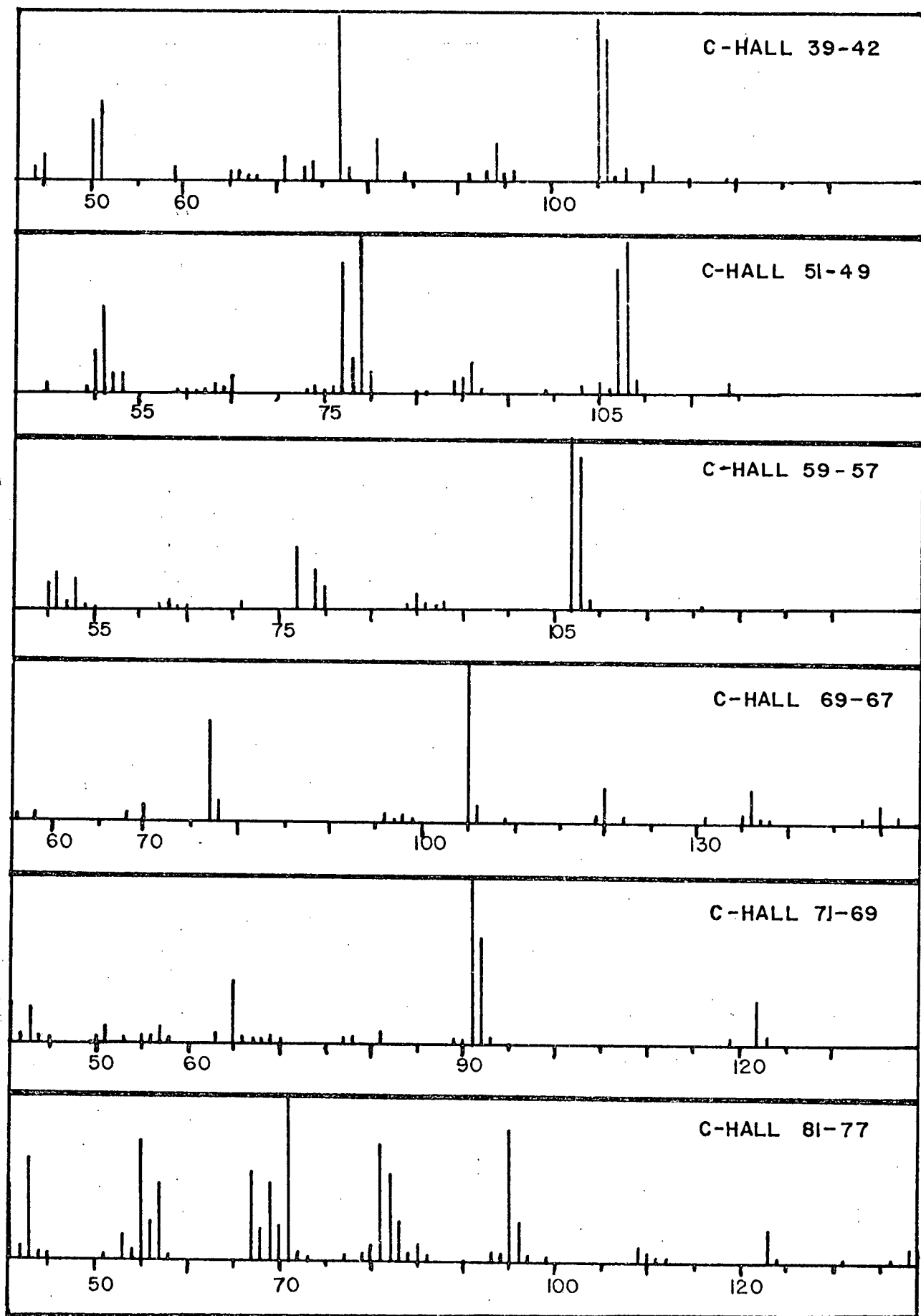


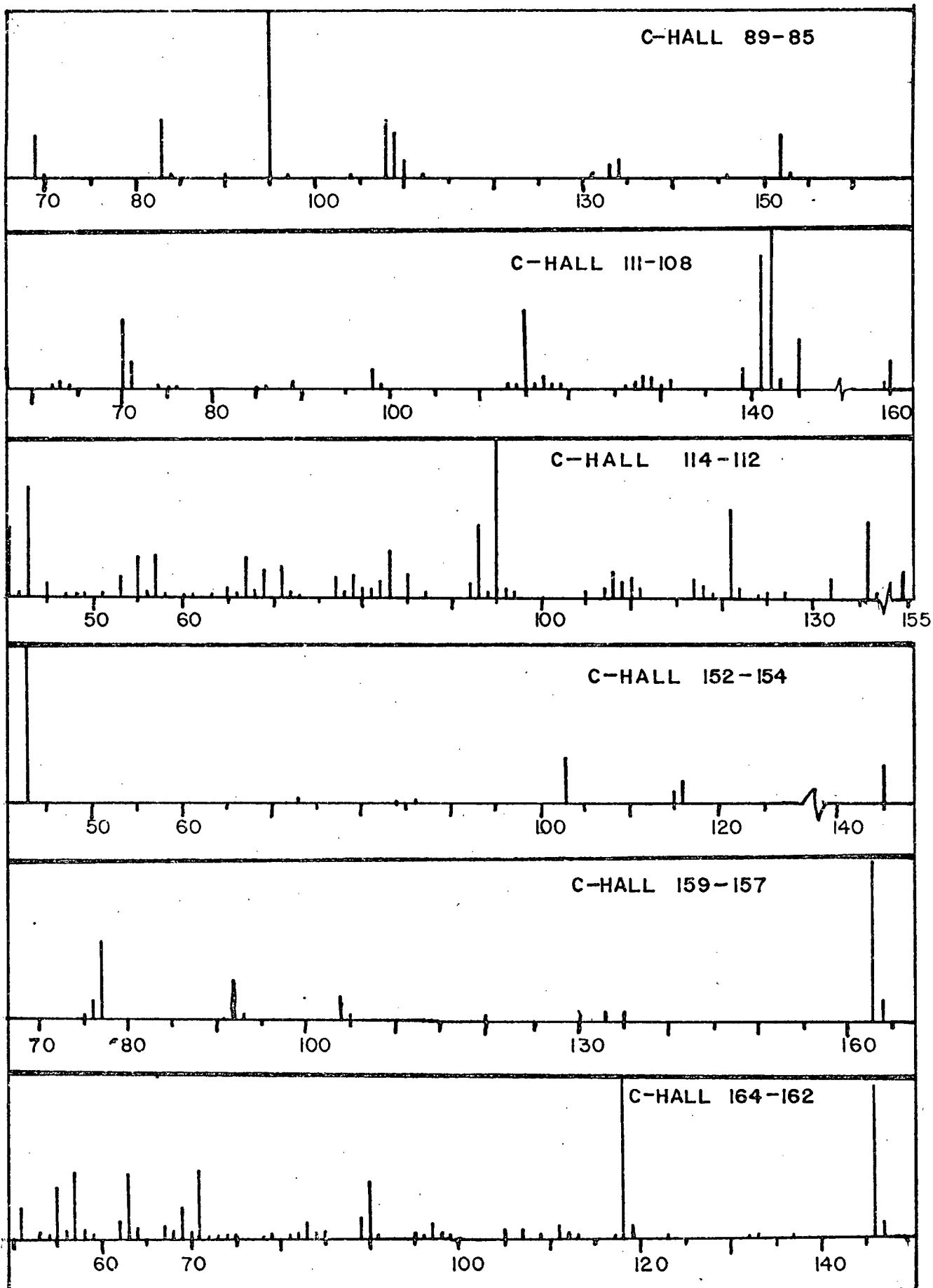
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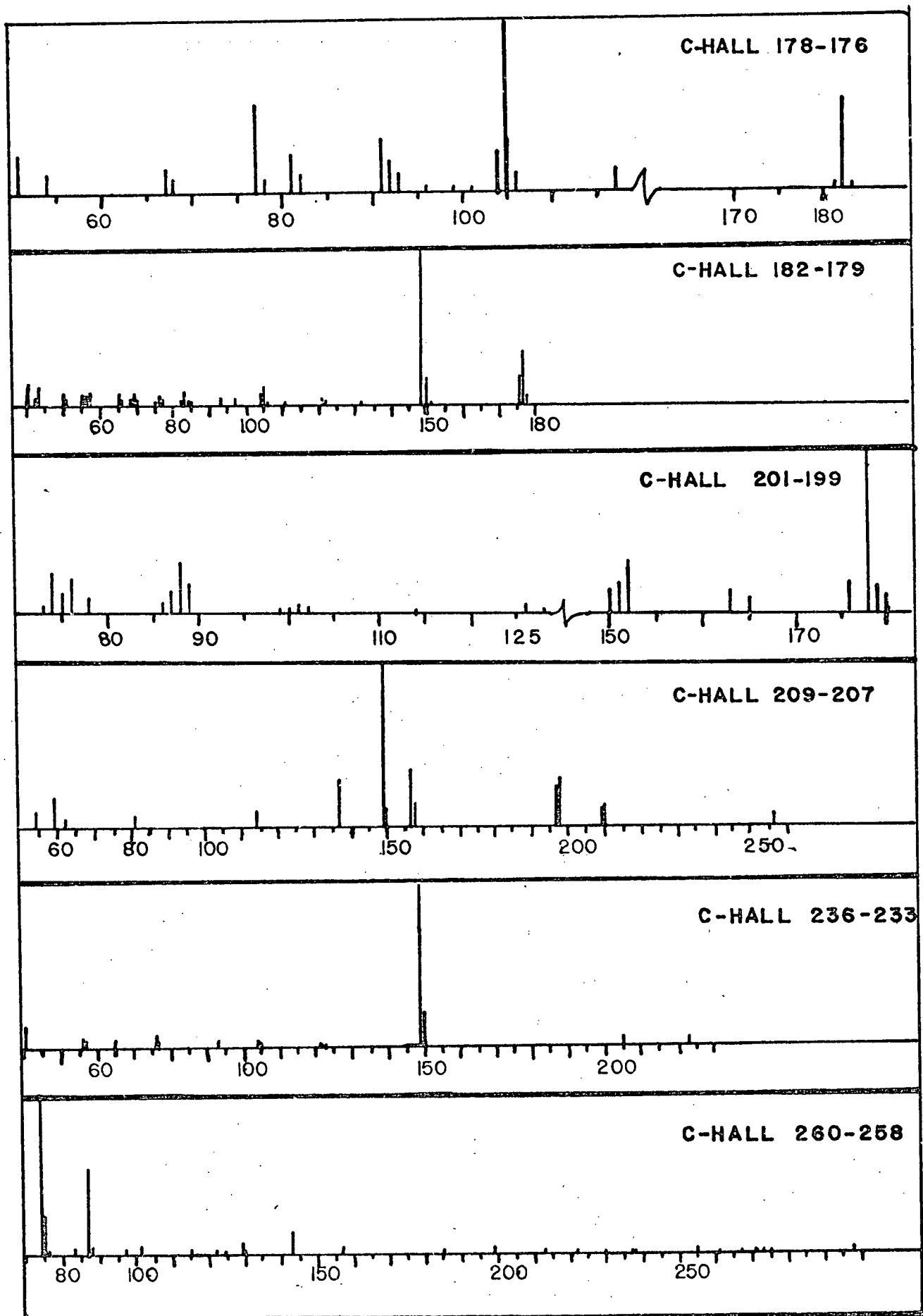


CL1202 204-202









APPENDIX V

MASS SPECTRA OF UNIDENTIFIED COMPONENTS OF CHLORINATED PRIMARY EFFLUENT

The spectra are organized by file names (see Table 4.14). They are presented in ascending order of spectrum number within a file. The interpretation of the structural features of each spectrum is according to McLafferty (1973) and his terminology is used.

Symbols and Abbreviations used are:

m/e - mass to charge ratio of a mass spectral peak

Int. - relative intensity of the specified peak

Str. Feat. - structural features of the compound suggested by its mass spectrum

File CL1202

Spectrum Number

Spectrum and Interpretation

8 - 5 m/e 92 91 74 73 71 70 69 58 57 56 55 54 53 51 50 46 45 44 43 42 41 40 39 38
Int. 3 7 10 4 72 100 87 45 92 96 99 72 98 52 42 92 98 99 92 96 87 99 93 85
Base 70; Parent 120; Str. Feat.- Cyclic amine, Methyl?.

14 - 15 m/e
14 - 15 m/e 100 89 87 85 79 71 70 69 59 58 57 56 55 45 43 42 41 39
Int. 3 1 1 8 1 1 1 9 1 15 29 8 9 61 100 26 62 44
Base 43; Parent ? ; Str. Feat.- Thiophene(dihydro), Methyl.

24 - 23 m/e 127 125 109 99 86 82 81 61 60 59 49 47 43 37 36 35
Int. 7 11 5 5 2 4 16 2 4 7 5 22 100 9 4 28
Base 43; Parent ? ; Str. Feat.- Propyl, Dichloro, Alkane.

26 - 24 m/e 123 121 113 88 86 85 84 77 71 70 69 57 56 55 45 43 42 41 40 39 38 37 36 35
Int. 1 1 1 1 1 6 2 2 5 6 16 28 51 37 8 71 41 100 10 32 1 1 2 3
Base 41; Parent ? ; Str. Feat.- Alkenyl, Chloroalkane.

40 - 38 m/e 87 85 75 72 71 58 57 56 55 45 43 42 41 40 39
Int. 11 1 5 2 3 3 100 11 9 85 19 18 10 97 33
Base 41; Parent 87? ; Str. Feat.- 2-nButoxyethanol; ONO ?.

56 - 51 m/e 121 120 119 106 105 104 103 91 79 78 77 65 63 57 51 50 41 39
Int. 2 32 8 8 100 4 9 20 13 11 22 11 12 8 24 11 28 49
Base 105; Parent 120; Str. Feat.- Methyl-ethylbenzene or n-Propylbenzene.

115 - 113 m/e 120 109 108 95 93 91 89 87 81 79 77 75 67 57 55 45 43 41 39
Int. 2 5 8 11 2 2 3 3 10 3 8 10 9 50 12 100 32 82 38
Base 45; Parent ? ; Str. Feat.- Alkyl, Alkenyl, EtO, Aromatic(weak).

124 - 122 m/e 133 131 123 119 118 103 97 95 94 91 85 83 79 77 69 68 67 66 65 55 48 45 43 41 39 35
Int. 2 4 2 11 12 4 8 10 27 20 21 50 15 21 32 14 28 16 25 25 22 20 47 100 76 3
Base 41; Parent ? ; Str. Feat.- Alkenyl, Aromatic(high, weak), Thiophene(weak).

137 - 135	m/e 180 178 177 176 175 160 148 145 143 141 133 121 119 117 105 95 93 91 79 77 59 57 55 53 51 Int. 2 7 3 11 3 3 2 4 8 18 10 12 6 9 17 20 14 17 12 32 23 15 18 16 25 m/e 50 45 43 41 39 Int. 8 28 100 55 25 Base 43(77); Parent 176; Str. Feat.- Aromatic(high), OH, PhCH ₂ , Dichloro.
145 - 142	m/e 160 145 139 130 129 128 124 119 118 115 104 93 91 90 81 79 78 77 76 75 68 67 66 65 64 63 Int. 2 8 13 8 6 7 8 10 86 5 5 8 71 14 8 6 7 6 6 6 16 58 18 30 33 37 m/e 53 52 51 50 43 41 40 39 38 37 Int. 49 45 35 26 95 68 30 100 37 20 Base 39(118); Parent 160? ; Str. Feat.- Indazole or Benzimidazole, Diene, Alkyne or Cyclo-alkene, Aromatic(high and low), Alkyl side chain.
155 - 153	m/e 159 156 155 141 128 115 95 91 89 84 81 79 77 71 69 68 67 59 55 53 51 43 42 41 39 Int. 3 12 5 13 7 7 7 6 4 7 9 8 8 28 12 10 13 51 36 12 11 100 20 64 47 Base 43; Parent 156? ; Str. Feat.- Alkenyl, Aromatic(weak), Exo-sulphur aromatic(weak), Methyl, Carbonyl?.
164 - 162	m/e 152 139 121 111 105 97 95 94 93 91 84 83 81 79 77 75 70 69 67 57 55 53 51 43 41 39 Int. 1 1 7 2 2 8 5 4 5 4 5 15 6 10 7 6 18 29 19 36 57 12 2 87 100 32 Base 41; Parent ? ; Str. Feat.- Alkenyl, Aromatic(weak).
169 - 167	m/e 123 117 109 101 95 89 87 85 79 77 75 73 71 59 58 57 56 55 45 44 43 41 39 Int. 1 1 2 2 2 7 5 5 2 2 8 3 3 16 7 32 8 8 100 17 45 49 15 Base 45; Parent ? ; Str. Feat.- Alkenyl, Alkyl(alcohol, ether, alkyl-silicon, thia-cycloalkane or substituted unsaturated sulphur compound).
173 - 171	m/e 170 169 155 142 141 129 128 115 105 95 93 91 81 79 77 71 69 67 65 63 59 57 55 53 51 50 43 441 Int. 10 5 7 3 8 3 7 15 8 7 5 15 11 12 18 10 13 15 12 12 17 19 30 18 19 10 100 56 Base 43; Parent 170; Str. Feat.- Alkyl, Aromatic, Aldehyde?.
177 - 174	m/e 170 156 145 135 1103 95 94 93 79 73 71 67 59 55 53 45 44 43 442441 39 Int. 1 1 2 1 6 2 2 2 2 1 3 2 8 4 3 1 4 100 8 10 7 Base 43; Parent ? ; Str. Feat.- Glycerol acetate like.

183 - 181 m/e 194 182 171 170 164 163 155 153 151 135 133 124 116 115 104 99 93 92 91 89 81 77 76 75 74
 Int. 1 2 1 2 8 78 9 13 33 9 9 6 11 7 16 16 8 18 16 31 12 47 30 16 21
 m/e 71 63 57 55 51 50 45 44 43 41 39
 Int. 21 27 20 18 22 40 10 20 100 35 40
 Base 43(163); Parent 163(164); Str. Feat.- Dimethyl Phthalate, Aromatic(low), Alkyl.

187 - 184 m/e 147 146 120 119 118 95 94 93 92 91 90 89 83 79 77 71 69 65 63 60 59 58 57 55 53 51 45 43 41
 Int. 1 7 3 3 17 77 6 5 5 7 9 8 3 6 3 11 14 10 6 12 51 13 12 24 10 6 16 100 58
 Base 43; Parent 146? ; Str. Feat.- Alkyl, Aromatic(weak), Thiophene(weak)?.

194 - 192 m/e 146 119 118 117 99 92 91 90 77 76 75 74 65 64 63 62 58 52 51 50 41 40 39 38 37
 Int. 6 8 100 9 6 7 82 25 4 8 10 4 18 48 40 15 10 27 16 18 22 12 46 32 20
 Base 118; Parent 118(146); Str. Feat.- Benzofuran, Benzimidazole, Indazole.

199 - 197 m/e 135 120 111 105 98 97 93 84 83 82 70 69 68 67 57 56 55 43 42 41 339
 Int. 2 7 2 2 2 12 3 8 20 7 20 31 12 7 31 30 67 42 22 100 22
 Base 41; Parent ? ; Str. Feat.- Alkenyl.

215 - 213 m/e 184 175 139 125 119 111 99 97 95 93 91 89 83 79 77 75 71 70 69 67 57 55 53 51 45 43 41 39
 Int. 3 2 1 1 2 2 16 8 7 7 7 7 13 4 2 3 13 10 20 8 38 45 8 3 48 98 100 23
 Base 41; Parent ? ; Str. Feat.- Alkenyl, Alkyl, Thiophene?.

219 - 216 m/e 185 171 157 143 112 115 105 97 87 85 83 77 74 73 71 69 61 60 59 57 55 45 43 41 39
 Int. 3 1 1 1 7 3 4 3 6 5 7 6 4 42 5 14 8 60 10 27 55 12 73 100 22
 Base 41(60); Parent 185; Str. Feat.- Alkenyl, Alkyl, 'Retro-Diels-Alder'.

230 - 228 m/e 180 179 149 135 134 125 119 117 115 107 97 93 83 77 71 70 69 57 56 55 45 43 41 39
 Int. 2 21 1 18 2 1 2 2 3 12 10 7 13 6 5 10 24 42 22 53 15 75 100 18
 Base 41; Parent 179(180); Str. Feat.- Alkenyl, Alkyl, OCO, or CS, CO or N₂.

236 - 233 m/e 221 220 219 218 184 183 182 181 166 165 155 154 153 152 142 140 115 114 113 112 102 101 99
 Int. 1 17 8 52 6 43 9 13 8 39 8 8 23 37 16 49 18 20 10 57 8 6 8
 m/e 91 89 78 77 76 75 74 73 65 63 58 52 51 50 39
 Int. 32 20 34 87 26 32 18 32 33 51 22 18 100 41 52
 Base 51; Parent 218(219); Str. Feat.- Aromatic(high and low), Ph, Monochloro, OH?, possibly
 is a Chlorophenyl-benzyl alcohol.

250 - 246 m/e 213 209 185 171 157 143 129 115 111 101 98 97 87 85 84 83 74 73 72 71 70 69 61 60 59 57 55
 Int. 2 1 1 1 1 1 8 4 2 3 4 8 11 10 6 13 8 77 8 22 8 32 20 100 12 63 83
 m/e 45 43 42 41
 Int. 28 71 33 72
 Base 60; Parent ? ; Str. Feat.- Alkenyl, Alkyl, Aliphatic acid or ester.

255 - 253 m/e 133 127 125 124 123 121 119 115 114 112 111 110 109 107 98 97 96 95 93 91 84 83 82 81 79 77
 Int. 1 1 1 1 2 1 1 1 2 1 3 3 3 1 5 12 8 10 2 2 8 22 10 22 12 5
 m/e 73 71 70 69 68 67 60 57 56 55 54 53 45 43 42 41 39
 Int. 12 8 12 42 18 41 27 27 23 100 32 15 22 79 23 93 29
 Base 55(41); Parent ? ; Str. Feat.- Alkenyl, Alkyl.

266 - 268 m/e 292 290 289 288 220 219 218 202 195 191 189 182 162 155 154 148 147 146 145 143 126 116 115
 Int. 23 62 15 54 31 15 92 23 15 23 15 38 23 23 15 38 15 46 38 38 15 23 85
 m/e 114 111 110 109 105 99 96 95 86 83 82 81 73 71 69 68 67 63 62 61 60 52 51 38
 Int. 46 38 23 85 38 22 23 38 77 15 23 46 46 61 100 31 31 77 31 31 46 15 84 15
 Base 69; Parent 288; Str. Feat.- Trichloro, Exo-sulphur aromatic, Diphenyl thio-ether?.

290 - 286 m/e 201 200 183 140 130 128 126 117 116 114 112 109 103 99 98 95 88 86 85 75 73 72 71 70 69 62
 Int. 1 9 4 1 1 1 1 1 9 2 3 1 26 5 12 3 3 11 27 2 3 7 5 11 6 12
 m/e 60 57 55 53 45 44 43 42 41 39
 Int. 30 25 45 3 23 30 82 28 100 20
 Base 41; Parent 200(201); Str. Feat.- Alkenyl, Alkyl, Acid.

326 - 322 m/e 237 160 149 143 141 139 131 126 114 105 104 99 98 96 95 89 88 85 83 77 75 74 71 70 69 67 59
 Int. 4 4 4 4 4 10 4 4 32 15 10 16 56 8 5 8 12 8 10 12 18 10 100 28 22 38 12 18
 m/e 57 56 55 45 44 43 42 41 39
 Int. 50 30 58 85 22 91 37 91 22
 Base 74; Parent ? ; Str. Feat.- Alkenyl, Alkyl, Methyl ester?.

342 - 335 m/e 268 267 237 215 208 198 190 189 175 161 159 151 147 137 135 133 131 119 117 114 107 103 92
 Int. 1 7 1 1 1 1 3 1 1 3 3 1 2 6 12 4 4 3 3 3 5 7 3
 m/e 89 87 78 77 73 71 59 57 45 43 41 39
 Int. 16 8 8 18 3 8 27 28 100 22 15 10
 Base 45; Parent ? ; Str. Feat.- Alkyl(Si, S or O), Aromatic(weak).

File CL1202

424 - 411 m/e 256 227 168 167 160 150 149 142 137 132 126 124 122 115 114 113 112 104 99 88 87 86 85 83 77
 Int. 1 1 1 10 1 7 69 2 3 2 2 1 2 1 16 3 4 16 4 5 3 4 3 6 5
 m/e 76 74 71 70 69 65 58 57 56 55 50 45 44 43 41 39
 Int. 7 100 16 26 12 3 5 59 30 45 2 14 16 83 94 17
 Base 74; Parent ? ; Str. Feat.- Alkyl, Alkenyl, Phthalate ester?.

File C-HALL

41 - 39 m/e 123 122 121 112 98 90 84 83 82 80 79 70 69 68 58 57 56 55 54 53 45 44 43 42 41
 Int. 2 41 18 1 1 1 1 1 1 1 4 18 2 1 2 100 20 12 1 1 1 2 10 7 46
 Base 57; Parent 122? ; Str. Feat.- Alkenyl, t-Butyl?.

64 - 61 m/e 144 143 142 140 136 134 125 123 121 120 119 111 95 91 85 84 83 82 81 80 73 72 69 67 57 43 41
 Int. 1 1 6 8 6 18 1 4 27 8 38 12 6 62 4 20 10 17 100 32 32 32 19 14 22 85 30
 Base 81; Parent ? ; Str. Feat.- Alkyl, Polyunsat or cyclic alcohol or ether?, Polychloro?.

94 - 91 m/e 135 134 133 120 119 118 117 116 105 104 103 91 90 89 85 82 79 78 77 71 65 63 57 51 50 43
 Int. 12 28 35 7 12 9 100 45 20 3 3 20065 38 10 8 7 10 18 12 12 24 28 30 18 36
 Base 117; Parent 135? ; Str. Feat.- Alkyl, Aromatic.

99 - 103 m/e 162 156 154 152 150 147 139 137 136 135 121 120 119 118 117 116 115 107 105 103 95 93 92 91
 Int. 1 2 5 4 3 1 6 14 31 8 40 8 72 92 57 10 14 22 9 12 10 22 10 100
 m/e 90 89 85 83 79 78 77 67 65 63 51 50 44
 Int. 9 10 20 31 31 9 32 15 30 20 23 12 18
 Base 91; Parent 156? ; Str. Feat.- Aromatic, OH, Methyl.

101 - 99 m/e 162 161 159 147 127 125 123 111 108 104 96 94 81 73 71 70 69 68 59 57 55 54 45 43 42 41
 Int. 7 4 7 10 2 4 4 11 13 2 22 2 7 18 42 8 77 12 7 18 20 7 44 65 7 100
 Base 41; Parent 162? ; Str. Feat.- Alkenyl, Alkyl(alcohol, ether or sulphur).

105 - 108 m/e 162 160 156 152 146 145 137 136 134* 133* 132 131 121* 118 117 111 99 97 86 85* 84 71* 70
 Int. 35 4 4 15 62 45 25 65 92 42 33 100 41 58 36 8 29 29 64 13 35 100 79

File C-HALL

105 - 108
(continued)
two
m/e 69* 57 56 55 51 44 43 41
Int. 31 80 90 35 40 35 70 7
Peaks marked with an asterisk (*) are not found in spectrum 105 - 103, relative intensities in the two spectra are similar.
Base 71(131) ; Parent 162? ; Str. Feat.- Alkyl.

109 - 107
m/e 160 142 141 118 115 108 106 104 95 93 91 82 80 79 77 65 58 54 53 41
Int. 10 32 29 6 8 23 9 21 26 40 50 100 3 5 4 10 17 72 18 22
Base 82; Parent 160; Str. Feat.- Cycloalkyl?, Cyclic ketone?, Alcohol?, Methyl.

116 - 113
m/e 163 160 147 145 135 131 119 118 117 112 109 97 87 85 83 82 79 73 71 59 58 57 55 44 43 41
Int. 8 28 13 33 13 20 24 40 30 10 7 10 10 100 93 20 10 28 22 28 50 21 30 10 32 40
Base 85; Parent 163? ; Str. Feat.- Cycloalkanol, Propyl, Sulphide?.

119 - 117
m/e 187 174 173 159 152 150 140 139 138 132 124 120 118 108 107 92 91 85 79 78 68 67 65 64 63
Int. 1 1 1 3 1 6 2 28 2 18 4 4 42 10 9 60 100 3 2 2 12 36 18 5 2
m/e 53 52 51 50 45
Int. 21 8 7 2 10
Base.91; Parent ? ; Str. Feat.- Cycloalkene, diene or alkyne, Alkyl-Ph.?.

121 - 119
m/e 174 173 159 132 130 125 120 119 118 104 91 90 78 76 75 71 64 63 62 52 50
Int. 2 1 4 2 1 1 3 4 100 6 20 8 1 2 1 10 18 10 2 8 2
Base 118; Parent ? ; Str. Feat.- Benzimidazole, Indazole or Benzofuran.

127 - 125
m/e 190 188 186 184 176 175 171 170 169 161 147 142 141 134 133 113 111 103 98 87 85 83 72 70
Int. 1 1 1 1 12 2 5 27 7 4 7 5 10 12 100 2 6 2 2 7 60 62 1 1
m/e 57 55 48
Int. 38 10 11
Base 133; Parent 176? ; Str. Feat.- Alkyl-trimethylbenzene, Dichlorocarbene?, Butyl?.

130 - 128
m/e 173 160 158 157 156 148 147 145 141 121 119 115 91 89 87 71 57 56 55 45 43 41
Int. 3 4 4 4 31 7 14 6 33 22 13 6 8 13 25 33 50 30 10 20 100 30
Base 43; Parent 156? ; Str. Feat.- Alkyl(alcohol, ether, Si or S).

136 - 132
m/e 159 157 156 155 153 152 142 141 128 115 85 77 76 75 64 63 58 57 51 50
Int. 9 12 100 32 13 11 10 83 12 14 20 6 11 6 5 6 5 8 4 1
Base 156: Parent 156? ; Str. Feat.- Bicyclo aromatic, Methyl, 1,3 or 2,7 Dimethylnapthalene.

File C-HALL

146 - 148 m/e 182 168 167 154 153 152 140 125 113 112 111 98 97 84 83 82 70 69 68 57 56 55 43 42 41
 Int. 1 13 8 2 4 5 3 2 2 5 10 10 26 25 47 20 57 73 22 49 73 95 100 32 95
 Base 43; Parent ? ; Str. Feat.- Alkenyl.

154 - 152 m/e 168 150 135 133 123 107 91 85 82 81 69 59 58 57 53 41
 Int. 33 24 42 11 9 21 11 100 10 10 8 11 10 20 8 18
 Base 85; Parent 168? ; Str. Feat.- Alkenyl, Thiophene?, Alcohol, Methyl, Carbonyl.

156 - 154 m/e 171 170 169 156 155 154 153 152 137 127 110 109 99 98 97 95 87 83 82 81 74 71 70 69 67 59
 Int. 7 50 8 3 41 4 10 8 5 3 8 7 9 100 15 18 10 28 14 16 18 13 25 220 27 28
 m/e 58 57 55 53 41
 Int. 13 16 30 8 60
 Base 98; Parent 170? ; Str. Feat.- Alkenyl, Cyclic ether or alcohol, contains spectrum of 1,4,5-Trimethylnaphthalene.

167 - 166 m/e 208 207 206 192 191 189 187 184 181 169 155 153 150 138 137 135 133 131 125 121 120 117 111
 Int. 9 9 13 13 88 13 18 56 13 22 32 20 20 37 28 23 23 37 22 45 100 28 22
 m/e 109 108 107 105 95 93 92 91 88 84 81 79 78 77 67 65 59 58 55 53 52 45 43 41
 Int. 22 13 28 28 33 23 63 27 45 12 12 37 19 12 38 37 22 31 40 37 10 5 19 100 72
 Base 43(120) ; Parent 206? ; Str. Feat.- Diene or cycloalkene, Aromatic(high), OH?.

168 - 167 m/e 209 207 204 189 184 169 161 155 151 150 149 138 135 121 119 111 109 107 95 93 91 85 81 79 78
 Int. 2 2 2 2 10 10 5 19 24 30 11 7 42 12 18 13 18 23 60 21 8 8 30 18 5
 m/e 77 71 69 67 65 57 55 53 45 43 41
 Int. 8 11 11 30 7 8 28 14 20 100 68
 Base 43; Parent ? ; Str. Feat.- similar to 167 - 166, contains spectrum of Cedrol.

169 - 168 m/e 224 209 196 181 161 159 151 150 149 138 135 122 119 109 108 107 99 96 95 91 81 73 72 69 67
 Int. 11 8 8 20 8 8 20 35 11 11 98 12 8 14 14 19 30 11 100 21 7 7 7 26 10
 m/e 57 55 41
 Int. 10 7 57
 Base 95; Parent 224? ; Str. Feat.- Diene or cycloalkene, Propyl, Cyclic ketone.

172 - 170 m/e 185 184 183 182 177 169 160 157 154 153 152 141 130 128 118 117 100 91 90 87 85 76 75 74 64
 Int. 6 40 6 40 6 70 4 6 8 16 3 6 2 3 52 3 3 13 3 5 100 7 3 10 13

File C-HALL

172 - 170 m/e 63 59 58 56 52 51
 (continued) Int. 8 28 36 10 3 7
 Base 85; Parent ? ; Str. Feat.- Cyclic ether or alcohol.

173 - 172 m/e 209 153 137 125 124 111 110 109 97 96 95 87 83 82 81 74 71 70 69 68 67 59 58 57 56 55 44 43 41
 Int. 3 8 8 1 5 3 3 4 10 20 11 7 20 31 18 11 38 13 23 22 21 27 38 51 17 41 22 100 52
 Base 43; Parent ? ; Str. Feat.- Cycloalkenyl(alcohol, Si or S), Alkyl, Carbonyl?.

176 - 174 m/e 169 155 120 111 98 83 73 72 71 69 56 55 43 41
 Int. 5 1 1 1 1 1 1 5 100 7 5 3 62 12
 Base 71; Parent ? ; Str. Feat.- Similar to 2-Hydroxy-3-methyltetrahydrofuran.

177 - 176 m/e 222 204 189 162 161 147 138 137 134 125 122 121 120 119 117 109 107 105 104 98 95 93 92 91 83
 Int. 23 17 17 17 35 23 78 30 41 35 23 36 36 23 30 41 60 41 23 41 39 60 23 23 35
 m/e 82 81 80 79 77 68 67 65 59 54 53 51 50
 Int. 35 100 23 48 30 18 71 30 60 23 12 6 42
 Base 81; Parent 222? ; Str. Feat.- Aromatic, Diene or cycloalkene, possibly Methyl ester of an aromatic acid with an ortho hydroxyl.

(177 - 176) - m/e 222 204 189 161 147 138 137 132 125 122 121 120 119 109 108 107 98 95 94 93 83 82 81 80 79 67
 (178 - 177) Int. 31 23 23 46 15 100 40 15 48 31 47 47 31 53 22 78 55 55 23 55 30 30 100 30 60 70
 m/e 65 57 53 50
 Int. 39 78 15 55
 Base 81(138); Parent 222? ; Str. Feat.- Similar to 177 - 176 except that m/e 77, 91, 92, 104 and 105 are missing.

187 - 185 m/e 293 237 220 219 216 215 198 195 184 183 180 179 169 165 159 138 137 109 107 82 81 78 77 59 54
 Int. 4 31 3 14 5 35 5 5 9 8 20 9 12 134 38 10 95 13 8 11 20 41 52 100 5
 Base 59; Parent ? ; Str. Feat.- Aromatic, Silicon, Septum bleed peak.

190 ± 189 m/e 196 146 124 111 110 99 98 97 96 95 84 83 82 80 74 71 69 68 67 57 56 55 44 43 41
 Int. 3 1 4 8 5 10 8 18 26 13 8 28 30 7 13 18 31 28 29 92 25 64 22 100 91
 Base 43; Parent 196? ; Str. Feat.- Cyclic alcohol or ether.

File C-HALL

192 - 190 m/e 253 244 230 229 197 196 195 181 175 173 155 135 131 119 107 99 92 91
 Int. 7 18 9 52 8 42 41 13 48 22 11 13 11 21 8 100 5 17
 Base 99; Parent ? ; Str. Feat.- Alkylsulphur.

195 - 193 m/e 237 221 219 215 210 198 187 186 185 184 183 179 168 159 153 147 145 139 138 137 117 109 104
 Int. 7 7 7 12 7 7 10 15 7 78 15 12 16 16 100 7 7 12 9 38 7 10 6
 m/e 92 91 77 67 59
 Int. 20 26 10 17 20
 Base 153; Parent ? ; Str. Feat.- Similar to 2-Methoxymethyl-3-methoxycarbonyl-5-methylfuran.

196 - 194 m/e 237 216 215 196 195 187 184 159 153 145 140 139 137 131 125 117 116 115 112 111 109 98 97 92
 Int. 2 3 3 10 5 5 23 9 32 8 5 9 18 6 7 10 10 9 10 30 8 11 38 10
 m/e 91 84 83 77 71 70 69 68 65 63 57 56 55 53 51 50 45 43 41
 Int. 65 24 57 15 73 33 57 22 8 2 50 40 66 5 5 2 20 100 60
 Base 43; Parent ? ; Str. Feat.- Alkyl, Alkenyl, Aromatic(weak), Alcohol or Fluoride?, iso-Propyl.

198 - 196 m/e 212 194 180 177 175 161 159 137 129 117 115 111 109 105 97 95 91 85 83 79 77 71 69 59 57 55
 Int. 5 6 2 3 3 2 2 10 6 4 6 21 8 45 11 5 23 14 25 5 15 30 32 22 35 53
 m/e 51 43 41
 Int. 5 100 63
 Base 43; Parent 212? ; Str. Feat.- Alkenyl, similar to 196 - 194 except m/e 105 and top end.

205 - 203 m/e 243 231 229 228 218 216 215 195 194 185 179 161 143 137 129 119 102 100 97 91 87 85 74 73 71
 Int. 6 1 3 7 3 5 2 3 7 5 8 8 3 3 8 3 19 3 5 7 18 49 23 12 12
 m/e 69 60 59 57 55 43 41
 Int. 16 30 15 28 28 100 37
 Base 43; Parent ? ; Str. Feat.- Alkenyl, Ester?, Amide?, Methyl?, Chloro?.

206 - 204 m/e 263 243 228 211 185 171 159 143 129 115 102 97 96 87 83 82 74 73 71 69 60 57 55 43 41
 Int. 2 10 3 1 2 1 1 1 6 2 13 6 4 9 7 6 12 11 14 13 30 32 23 100 40
 Base 43; Parent ? ; Str. Feat.- Similar to 205 - 203 except m/e 161, 179, 194, 195 and 216.

208 - 206 m/e 237 230 229 227 226 219 216 215 202 177 149 137 114 52
 Int. 7 100 28 13 21 7 10 62 10 7 38 24 13 10
 Base 230; Parent 230? ; Str. Feat.- Polycyclic aromatic hydrocarbon, Methyl?.

File C-HALL

209 - 208 m/e 256 210 209 198 197 158 157 150 149 137 114 81 62 59 54
 Int. 12 12 12 42 31 12 25 12 100 43 12 12 12 19 12
 Base 149; Parent ? ; Str. Feat.- Phthalate ester, possibly n-Propyl.

210 - 209 m/e 237 210 209 199 198 197 195 180 179 165 137 135 99
 Int. 12 30 12 12 75 50 32 12 100 20 17 50 17
 Base 179; Parent 237? ; Str. Feat.- Hydroxyl or carbonyl, Chloro?, Aromatic?.

211 - 210 m/e 250 219 210 198 196 180 179 159 137 136 135 119 111 107 97 95 91 83 78 77 71 59 57 55 45 43 41
 Int. 2 2 2 2 2 12 100 2 3 3 51 3 3 117 11 3 3 14 3 7 14 9 30 17 10 13 21
 Base 179; Parent ? ; Str. Feat.- Similar to p-t-Butylphenoxyethanol except no m/e 194.

213 - 211 m/e 137 125 117 112 111 104 97 85 84 83 82 78 77 70 69 57 56 55 43 41
 Int. 5 4 4 4 12 7 30 12 18 45 20 3 4 31 52 70 40 72 100 70
 Base 43; Parent ? ; Str. Feat.- Alkyl, Alkenyl, Aromatic(weak).

218 - 216 m/e 257 237 221 220 219 218 217 215 208 193 192 191 190 189 184 183 165 159 155 153 152 142 140
 Int. 7 15 7 18 21 46 9 37 10 9 30 18 9 12 18 52 24 37 25 12 15 27 78
 m/e 138 137 128 114 112 109 108 95 93 91 82 79 78 77 76 73 69 67 65 63 59 55 53 51 50 43 41
 Int. 15 100 12 9 37 33 12 12 12 40 16 38 19 62 91 24 18 33 10 25 80 10 12 40 15 12 10
 Base 137; Parent 257? ; Str. Feat.- Aromatic(high and low), Chloro, appears to be a mixture of spectrum 236 - 234 in CL1202 with those of some other compounds.

222 - 218 m/e 223 205 192 167 150 149 137 132 121 105 104 93 87 76 75 74 71 65 57 56 55 50 43 41
 Int. 2 1 1 1 9 100 1 1 2 2 6 2 3 5 2 8 5 3 33 7 2 2 10 23
 Base 149; Parent ? ; Str. Feat.- Phthalate ester, possibly t-Butyl.

225 - 223 m/e 297 283 282 268 253 242 237 212 211 170 163 160 159 147 141 137 133 130 128 127 117 115 91 58
 Int. 10 13 100 13 37 13 13 31 20 10 13 18 49 8 18 45 13 13 35 21 52 31 25 14
 Base 282; Parent 297? ; Str. Feat.- Cyclic or Aromatic, Methyl, Ketone or ester?.

226 - 225 m/e 268 254 253 240 237 220 218 179 178 161 159 146 145 141 137 136 135 128 127 120 117 115 109
 Int. 13 6 42 7 7 7 13 13 20 10 12 12 12 16 30 20 15 23 30 16 22 32 22
 m/e 108 105 103 92 91 81 79 78 77 69 67 65 58 53 52 51 45 43
 Int. 32 20 20 20052 30 31 26 70 100 30 22 32 30 12 30 12 55
 Base 69; Parent 268? ; Str. Feat.- Aromatic(high), Methyl, Carbonyl.

File C-HALL

229 - 227 m/e 280 257 237 223 215 212 205 185 150 149 137 104 87 76 59 51
 Int. 1 1 1 1 4 1 1 1 7 100 10 1 1 1 7 3
 Base 149; Parent ? ; Str. Feat.- Phthalate ester.

233 - 231 m/e 268 237 236 227 219 216 215 208 191 177 164 163 161 159 145 138 137 121 117 109 107 101 95 93
 Int. 7 13 11 7 7 7 29 7 7 7 28 7 7 21 10 13 100 18 23 18 10 13 28 13
 m/e 92 91 88 81 79 78 77 74 73 69 67 59 55 54 53 43 42 41
 Int. 13 70 23 49 22 28 35 18 25 31 28 60 46 10 10 48 31 22
 Base 137; Parent ? ; Str. Feat.- Aromatic(high), Nitro?, Methyl?.

238 - 236 m/e 256 237 219 215 159 150 148 137 122 121 105 104 93 87 85 84 77 76 65 60 59 57 56 55 50 43 41
 Int. 1 2 1 5 2 3 2 27 3 3 7 12 12 7 3 4 17 28 22 8 22 53 40 13 13 18 100
 Base 41; Parent ? ; Str. Feat.- Aromatic(low), Alkyl.

243 - 241 m/e 236 222 207 206 202 193 191 190 189 180 179 178 168 167 165 154 152 134 133 123 119 109 107
 Int. 47 10 12 36 10 20 30 12 16 40 17 40 30 32 32 17 17 10 10 10 13 22 30
 m/e 101 96 95 94 91 82 81 80 79 71 69 67 55 43
 Int. 10 16 80 22 26 35 88 26 40 42 100 55 65 45
 Base 69; Parent 236? ; Str. Feat.- Diene or cycloalkene, Diunsat. cyclic alcohol or ether, or Alkenyl carbonyl.

256 - 253 m/e 234 197 184 183 177 167 166 140 139 135 134 131 127 121 108 107 106 93 91 85 79 77 57 53 52 41
 Int. 8 1 1 2 4 10 15 2 12 2 100 2 7 3 3 31 3 4 6 12 22 3 22 7] 5
 Base 134; Parent ? ; Str. Feat.- contains spectrum of 2,4-Dimethyl-6-ethylpyridine (mw 135), t-Butyl, o-Methyl ester?.

269 - 265 m/e 354 250 247 228 209 175 167 151 150 149 98 93 83 76 70 69 67 65 55 41
 Int. 2 2 2 2 8 2 5 2 10 100 4 4 22 4 18 4 4 4 12 13
 Base 149; Parent ? ; Str. Feat.- Phthalate ester.

309 - 305 m/e 199 112 97 84 83 81 71 70 69 57 55 43 41
 Int. 50 25 17 18 25 18 58 50 33 100 50 50 32
 Base 57; Parent L? ; Str. Feat.- similar to Di-2-ethylhexylfumarate except for m/e 199.

File C-HALL

366 - 360 m/e 238 206 205 178 165 150 149 135 133 132 123 122 105 104 92 91 77 76 65 57 56 51 50 41
 Int. 1 15 2 2 1 11 100 4 2 12 12 8 10 15 5 71 5 10 18 4 5 2 4 15
 Base 149; Parent ? ; Str. Feat.- similar to Benzyl-butylphthalate.

506 - 498 m/e 299 279 253 243 231 229 222 220 217 203 198 191 188 186 178 168 167 150 149 113 112 104 83
 Int. 1 31 1 1 1 1 1 1 1 1 1 1 1 1 1 3 32 11 100 8 6 7 7
 m/e 76 71 70 57 55 43 41
 Int. 4 25 23 40 18 31 28
 Base 149; Parent ? ; Str. Feat.- Phthalate ester.

File APLCL1

83 - 88 m/e 109 108 107 91 90 89 80 79 78 77 63 62 55 53 52 51 50 39
 Int. 7 88 100 7 12 7 20 43 13 61 17 9 10 30 20 40 31 42
 Base 107; Parent 108? ; Str. Feat.- Methylphenol, probably p-Cresol.

114 - 111 m/e 187 115 101 87 85 84 74 73 69 61 60 555445443441339
 Int. 1 3 11 7 7 6 6 57 10 10 100 40 52 54 82 39
 Base 60; Parent ? ; Str. Feat.- Aliphatic acid.

152 - 145 m/e 129 115 104 101 97 91 87 83 73 71 69 61 60 57 55 45 43 41 39
 Int. 10 3 1 1 1 6 9 9 60 13 13 8 80 22 47 45 60 100 40
 Base 41; Parent ? ; Str. Feat.- Aliphatic acid.

187 - 182 m/e 185 171 158 157 143 130 129 115 111 101 99 98 97 87 85 83 73 71 69 60 57 55 45 43 41 39
 Int. 1 2 1 5 2 1 8 5 2 5 2 3 5 8 8 8 61 11 11 100 20 40 50 59 80 40
 Base 60; Parent ? ; Str. Feat.- Aliphatic acid.

243 - 240 m/e 129 123 115 111 110 109 101 98 97 96 95 87 84 83 81 79 77 73 69 67 60 57 56 55 54 53 45
 Int. 1 2 1 5 3 4 1 5 10 8 8 2 10 18 16 10 7 12 32 24 18 17 18 71 19 10 20
 m/e 43 41 39
 Int. 59 100430
 Base 41; Parent ? ; Str. Feat.- Aliphatic acid.

File APLCL1

274 m/e 137 125 123 111 109 97 95 83 82 81 79 77 73 69 68 67 60 57 55 54 45 43 41 39
(unsubtracted) Int. 2 1 2 3 3 9 10 17 10 21 12 8 8 30 13 33 21 16 69 22 18 51 100 24
Base 41; Parent ? ; Str. Feat.- Aliphatic acid.

File 35LBK1

146 - 143 m/e 241 239 237 215 201 195 161 160 159 141 137 109 81 79 78 77 59 51 39
Int. 7 7 33 40 8 8 8 8 40 7 33 10 21 6 51 96 100 18 80
Base 59; Parent ? ; Str. Feat.- Aromatic, similar to septum bleed.

193 - 189 m/e 237 219 215 167 159 155 154 139 137 113 112 99 883 82 78 77 65 59 57 55 43 41
Int. 1 1 1 1 1 2 1 7 4 5 10 100 3 3 2 4 1 5 28 7 25 50
Base 99; Parent ? ; Str. Feat.- Cyclic alcohol or ether.

211 - 205 m/e 297 295 294 293 277 273 # spectrum 146 - 143
also Int. 1 1 1 3 1 1
257 - 253 Base 59; Parent ? ; Str. Feat.- Aromatic, Septum bleed peaks.
330 - 320